A Study of Paramagnetic Transition Metal Carbonyls and Cyanides by Electron Spin Resonance Spectroscopy

by

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A Thesis submitted for the Degree of Doctor of Philosophy in the Faculty of Science at the University of Leicester

1983
Thesis
Dedicated to Dad, Mum,
Robert and Hannah
I wish to thank Professor Martyn Symons for all his help and encouragement during the course of this work, and for many interesting discussions. I am grateful to the members of the Physical Chemistry Department who have assisted me in many ways, to Vicky Orson-Wright for the typing of this thesis, Ann Crane who drew the diagrams, and the University of Leicester for financial support.

Finally, thanks are due to my parents for their love and total support throughout my education, and to my husband for being so understanding.
STATEMENT

The accompanying thesis submitted for the degree of Ph.D. entitled "A Study of Paramagnetic Transition Metal Carbonyls and Cyanides by Electron Spin Resonance Spectroscopy" is based on work conducted by the author in the Department of Chemistry of the University of Leicester mainly during the period between November 1978 and November 1982.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references.

None of the work has been submitted for another degree in this or any other university.

Signed: Jane Wyatt

Date: 20th June 1983.
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CHAPTER 1

BASIC PROCESS OF E.S.R.
TRANSITION METAL COMPLEXES
EFFECTS OF HIGH ENERGY RADIATION ON COMMON SOLVENTS
INTRODUCTION

The first electron spin resonance (ESR) experiment was performed more or less simultaneously just after the Second World War, by Zavoisky in Russia and Bleaney in Great Britain. Both studied transition metal complexes as these fulfilled the requirement for paramagnetism, although the higher transition groups, 4d, 5d, were little understood at the time.

The theory of e.s.r. spectroscopy is described in many standard texts. A definitive treatment of transition ions is given in a text by Abragam and Bleaney, transition metal complexes are described in articles by McGarvey, Goodman and Raynor and Orton. Inorganic radicals are discussed by Atkins and Symons.

Basic process of e.s.r.

The fundamental principle of e.s.r. is that an electron has a spin and an associated magnetic moment which may align itself either with or against the direction (z) of an external magnetic field. The presence of such a field lifts the degeneracy of the two spin orientations (±\(\frac{1}{2}\)), the lower energy being that where the electron is aligned with the applied field. If the system is irradiated with microwaves of a frequency corresponding to the energy separation, a transition occurs between the two electron spin energy states. This resonance condition is represented by:

\[ E = h\nu = g\beta B \]

where \(h\) is Planck's constant, \(\nu\) the microwave frequency, \(\beta\) the Bohr magneton and \(B\) the applied field at which resonance occurs (Fig. 1.1). The proportionality constant in the equation, \(g\), is a tensor quantity fundamentally important in the description of an e.s.r. spectrum. It is known as the "g-value" and is a unique property of any molecule under
FIG. 1.1
The e.s.r. experiment, showing transitions for X- and Q-band spectrometers.

FIG. 1.2
Transitions for a system where $S=\frac{1}{2}, I=\frac{1}{2}$ in high field approximation.
investigation.

Most e.s.r. spectrometers operate at X-band frequencies (ca. 9 GHz) and a magnetic field of the order of 3250 G. Other frequencies may occasionally be used however (Table 1.1).

<table>
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<tr>
<th>BAND</th>
<th>FREQUENCY (GHz)</th>
<th>APPROX. RESONANT FIELD</th>
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<tbody>
<tr>
<td>S</td>
<td>2.7</td>
<td>975</td>
</tr>
<tr>
<td>X</td>
<td>9</td>
<td>3250</td>
</tr>
<tr>
<td>K</td>
<td>21.5</td>
<td>7800</td>
</tr>
<tr>
<td>Q</td>
<td>34</td>
<td>12250</td>
</tr>
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The spin states of an unpaired electron are influenced by magnetic forces arising from the magnetic field generated by the motion of the electron relative to electronic charges ("spin-orbit" coupling) and from the direct magnetic interaction of nuclear magnetic moments ("hyperfine" coupling). This will now be described in more detail.

The $g$-value

The resonant position, referred to as the $g$-value, is directly determined by the separation of the $M_g = \pm \frac{1}{2}$ levels of the radical under investigation in a magnetic field. Variation of the $g$-value is interpreted in terms of the perturbation by the spin-orbit interactions and may be used to study changes in molecular structure.

For a free electron, i.e. possessing no orbital angular momentum, $g_e = 2.0023$. A first order approach suggests that $g_e = 2.00$, explained by the Dirac equation, but deviation from 2 is accounted for by the theory of quantum electrodynamics. However, an unpaired electron is seldom free, but bound within an atom or molecule. Deviation of the $g$-value from $g_e$ arises because of the interactions between the magnetic moments
due to the electron spin and the orbital motion. This is the "spin-orbit" coupling. When the unpaired electron is in an orbital far removed from other levels, \( g \) will be close to the "free spin" value of 2.0023. Any deviation in \( g \) depends on the type of orbital containing the electron, the energy separation between this orbital and others with which it can mix (\( \Delta \)) and the spin-orbit coupling constant (\( \lambda \)).

\[
\Delta g = \pm \frac{n\lambda}{\Delta}
\]

\( n \) is a small integer dependent on the nature of the mixing orbitals. \( n \) may be deduced from the pentagon:

Thus, for example:

For \( d^{1}_{x^2-y^2} \) \((d^9)\):

\[
\Delta g_{//} = \frac{8\lambda}{\Delta E(x^2-y^2 \leftrightarrow xy)}
\]

\[
\Delta g_{\perp} = \frac{2\lambda}{\Delta E(x^2-y^2 \leftrightarrow xz,yz)}
\]

resulting in \( g_{//} > g_{\perp} > 2 \).

For \( d^{1}_{z^2} \) \((d^7)\):

\( g_{//} = g_e \) as \( d^{1}_{z^2} \) does not mix with other orbitals in this direction.

\[
\Delta g_{\perp} = \frac{6\lambda}{\Delta E(z^2 \leftrightarrow xz,yz)}
\]

resulting in \( g_{\perp} > g_{//} = 2 \) for a \( d^7 \) case.

As \( \lambda \) increases rapidly with atomic number, the \( g \)-shift \( \Delta g \) may be large if there is sufficient spin-density in \( p \) or \( d \) orbitals on heavy atoms in a molecule. Positive deviations from \( g_e \) occur when the ground state mixes with a filled orbital, and negative deviations indicate mixing with empty
orbitals.

The $g$-value is generally anisotropic, having 3 principal values along 3 orthogonal axes, $g_x$, $g_y$ and $g_z$, since different levels are coupled by the magnetic field along these different directions. Powder spectra can give these $g$-values directly. Often the $g$-tensor is axial, and $g_{\parallel}$ and $g_{\perp}$ are obtained from the spectra.

The $g$-value is independent of any electron-nuclear hyperfine interactions that may be present, and provides information about magnetically coupled excited states, and the directional dependence of such coupling.

**Hyperfine coupling**

The hyperfine structure of e.s.r. is produced by the interaction of the electron spin magnetic moment with the magnetic moments of the nuclei contained by the molecular orbital of the unpaired electron.

If the nuclear spin is I, then each electronic level is split into $2I+1$ equally spaced levels corresponding to the $(2I+1)$ quantized orientations of the nucleus. For an electronic transition the selection rules are $M_s = \pm 1$, $M_I = 0$, where $M_I$ is the nuclear magnetic quantum number.

For a system where $S = \frac{1}{2}$, $I = \frac{1}{2}$, 2 lines will be detected in the e.s.r. spectrum at high field, corresponding to transitions between the $(M_s = -\frac{1}{2}, M_I = +\frac{1}{2})$ and $(M_s = +\frac{1}{2}, M_I = +\frac{1}{2})$, and $(M_s = -\frac{1}{2}, M_I = -\frac{1}{2})$ and $(M_s = +\frac{1}{2}, M_I = -\frac{1}{2})$ states (Fig. 1.2).

The hyperfine coupling constant, $A$, is measured as the separation between component peaks, and in the high field approximation, the equation;

$$h\nu = g \mu_B (B + M_I A)$$

is valid.

However, if the hyperfine interaction energy is comparable with the measuring frequency, the "zero-field splitting" must be taken into
account. This phenomenon arises because the electron and nuclear spins are already coupled before the application of an external field, their combined spins leading to apparent "triplet" and "singlet" states; (1, 0, -1) and 0 for a nucleus with $I = \frac{1}{2}$. In the presence of an applied magnetic field, the ±1 states diverge, but the 0 states are initially unaffected (Fig. 1.3). As the field is increased the 4 states merge with the high field states (Fig. 1.2).

The effect of this zero-field coupling is to move both absorption bands, for $I = \frac{1}{2}$, to low field, thus making the apparent hyperfine coupling and the $g$-value too large. In this case the high field approximation is no longer valid, and a correction must be made using the Breit-Rabi equation, which relates the field values for transitions to the real hyperfine and $g$-values. This is discussed later.

Like the $g$-value, the hyperfine coupling $A$ is also a tensor quantity. The interaction between the electron and the nucleus which gives rise to $A$ may occur in 3 ways. If the electron is largely confined to an $s$-orbital, with finite electron density at the nucleus, then the coupling constant will be large and independent of direction, due to the symmetry of $s$-orbitals. This is the "isotropic" coupling, $A_{iso}$.

Directionally dependent coupling arises if the electron resides in $p$ or $d$ orbitals, which have a node at the nucleus. The electron and the orbital then interact as 2 classical magnetic dipoles, giving rise to "anisotropic" coupling, $A_{aniso}$. This may be resolved into unique directions $(x, y, z)$ which average to zero:

$$A_x + A_y + A_z = 0.$$  

$s$, $p$ and $d$ orbitals may all contribute to the molecular orbital containing the unpaired electron, so the hyperfine coupling may consist of isotropic and anisotropic parts. In fluid solution, rapid molecular
tumbling averages the anisotropic part to zero, and only isotropic coupling is observed. In a frozen solution, powder or single crystal, the sum of the isotropic and anisotropic interactions is obtained. These can be separated, and yield estimates of \( s \) and \( p/d \) orbital populations. This can give a measure of the orbital hybridization and thus an indication of the radical structure.

**Isotropic coupling**

The isotropic hyperfine coupling may be composed of contributions from several effects, e.g. direct unpaired electron spin density at a nucleus occurs when the electron is in an \( s \)-orbital. Indirect contributions arise when the electron is in a \( p \)- or \( d \)-orbital. The Fermi contact term is concerned with \( s \)-electron density and is related to the magnetic moment of the nucleus, the relationship being:

\[
A_{iso} = \frac{8\pi}{3} g_e \beta_e g_N \beta_N \cdot \psi^2
\]

so the coupling is directly proportional to the nuclear moment and is positive. By knowledge of an accurate equation for the wavefunction, values for total \( s \)-orbital occupancy may be calculated. This enables the percentage \( s \)-character of a radical, \( \bar{a}_s^2 \), to be obtained using:

\[
\bar{a}_s^2 = \frac{A_{iso}(exp)}{A_{iso}(calc)} \times 100.
\]

**Spin polarization**

As \( A_{iso} \) is concerned with unpaired electron spin density at a nucleus, transition metals with an unpaired electron in a \( d \)-orbital would not be expected to exhibit any isotropic coupling. However, isotropic coupling is nearly always observed. This is due to an exchange interaction between the unpaired \( d \) and the paired \( s \) electrons in the core, and is dependent on spin orientation. As a consequence of Hund's rule, the \( d \)
electron attracts an s-electron of like spin, and repels that of opposite spin. The nucleus thus feels a preponderance of one spin over the other causing a net spin density at the nucleus, which manifests itself in $A_{iso}$.

Inner-shell polarization, involving polarization of 1s and 2s-electrons by 3d produces a large negative contribution to $A_{iso}$; whereas outer-shell spin polarization, i.e. 3s by 3d, results in a small positive contribution, the total effect is therefore negative (Fig. 1.4).

Electrons involved in bonding may also be slightly spin polarized so that, close to a given nucleus, one spin is preferred over another. Although most transition metal complexes possess largely "ionic" metal-ligand bonding, covalent bonding is appreciable for complexes with ligands such as -H, -CH₃, or to a lesser extent -NR₂, -O⁻ or -CN. In such cases spin polarization of σ-bonding electrons may be significant. If the outer s-orbital is involved in this covalency, this effect will make a positive contribution to $A_{iso}$ for the transition metal. Relatively small negative values for $A_{iso}$ in many covalent complexes are explicable in terms of this mechanism.

"Real" s-occupancy may occur in conjunction with spin-polarization, in which case the experimental isotropic coupling is less negative than spin-polarization alone would suggest. This arises when the unpaired electron is in an orbital of $A_1$ symmetry, e.g. $d_{z^2}$. A rough estimate of the s-admixture can be made by using "typical" values for spin-polarization.

**Anisotropic hyperfine coupling**

Experimentally, the hyperfine interaction of an unpaired electron in a p- or d-orbital is often found to be an axially symmetric tensor. Considering an electron in a pure p-orbital on an atom with $I = \frac{3}{2}$, an
\[ M_I = +\frac{1}{2}, M_S = +\frac{1}{2} \]
\[ M_I = -\frac{1}{2}, M_S = +\frac{1}{2} \]
\[ M_I = -\frac{1}{2}, M_S = -\frac{1}{2} \]
\[ M_I = +\frac{1}{2}, M_S = -\frac{1}{2} \]

**FIG. 1.3**
Energy levels for the same system as Diagram 1.2, showing how at low field, the zero field "triplet" and "singlet" arise

**FIG. 1.4**

*Inner Shell Polarization*  
*Outer Shell Polarization*
external field applied parallel to the axis of the p-orbital results in an interaction 2B. If the field is perpendicular to this axis, then the field from the nucleus at the electron is reversed and more dispersed, and reduced to -B (Fig. 1.5). The isotropic coupling, $A_{iso}$, must be added:

$$A_{\|} = A_{iso} + 2B$$

$$A_{\perp} = A_{iso} - B$$

The signs of $A_{\|}$ and $A_{\perp}$, measured from the spectrum, may be assigned by reference to the necessary requirements of the radicals concerned, and enable $A_{iso}$ and 2B to be calculated. Alternatively, if $|A_{iso}|$ is known from liquid phase studies, the relative signs of $A_{\|}$ and $A_{\perp}$ are fixed.

The situation for d-orbitals is similar to that for p-orbitals, but the change in orbital symmetry has the effect of changing the sign of the interaction, i.e. $A_{\|} = A_{iso} + 2B$, $A_{\perp} = A_{iso} + B$, except in the case of $d_{z^2}$, when the signs are unchanged.

An estimate of the orbital population for p- and d-orbitals may be made from the magnitude of the measured anisotropy and that calculated for unit occupancy:

$$a_{p/d}^2 = \frac{2B}{2B^0}$$

For d-orbitals, when the sign of the anisotropic coupling can often be deduced, it is possible to decide whether a $d_{z^2}$ or one of the remaining d-orbitals is involved.

As a fine powder or glassy solution contains radicals statistically distributed over all orientations, such spectra can give directly the 3 principal values of the g and A tensors, provided these share the same axes, but not the principal directions. It may be more difficult to interpret powder spectra when more than one magnetic nucleus contributes
FIG. 1.5  Field from a magnetic nucleus acting on a 2p-electron

\[ B_z (+2B) \]

Applied field \( B \) along the symmetry axis \( (2) \)

For a perpendicular field

\[ B_x (1)(-B) \]
hyperfine features, and different tensors may not share principal
directions. If possible, it is necessary to study the radicals in single
crystals.

** Corrections to hyperfine coupling constants **

**Breit-Rabi effect**

The Breit-Rabi equation must be used if the hyperfine coupling is
comparable in magnitude to the external field, when the zero-field
coupling between the electron and the nuclei must be taken into account,
as discussed earlier. This results in the hyperfine spacings being no
longer equal, the spacings generally increase from low to high field and
the position of the g-value is no longer obvious.

The combined electron and nuclear spins at zero-field, represented by
quantum number F (F=I ± ½), always give rise to 2 levels separated by the
zero-field splitting, (I ± ½)gβA (MHz). This is illustrated in Fig. 1.3
for I=½, and in Fig. 1.6 for I=½. It is apparent that, in both cases,
as the energy of the microwave field decreases, the lower field transition
moves rapidly to zero-field and then becomes unattainable. However, it
is replaced by an "n.m.r." transition, involving only a nuclear reorienta-
tion.

For isotropic systems, A_{iso} and g_{av} may be calculated from the field
values of the observed e.s.r. transitions using the Breit-Rabi equation.
For M_{I}=±I transitions for any value of I, the following equation is
satisfactory when the shifts involved are relatively small:

\[ A = \frac{2B_0(B_2-B_0)}{B_0(2I+1)-B_2} = \frac{2B_0(B_0-B_1)}{B_0(2I+1)-B_1} \]

B_0 is the resonance corresponding to the g-value, B_2 is the high field
transition and B_1 the low field transition.

For anisotropic systems, providing the anisotropy is small (2B<100 G
FIG. 1.6
Energy levels for a radical having $S = \frac{1}{2}$, $I = \frac{3}{2}$
for $A > 2000$ G), the simple Breit-Rabi equation can still be used. However, it is no longer applicable if the hyperfine anisotropy is large, equations for a case of axial symmetry and $I = \frac{1}{2}$ are given in Ref. 12. Byfleet et al. have developed a general method recommended if $I > \frac{1}{2}$ and the anisotropy relatively large.

**Orbital contributions**

When interpreting hyperfine coupling constants in terms of orbital populations it is important to correct for orbital magnetism which may cause $g$-values to be well removed from 2.0023. This results in a contribution to the hyperfine coupling constants, which must be adjusted to the values that would have been obtained at $g = 2.0023$. The measured coupling can thus be regarded as being comprised of the normal spin-only term and an orbital magnetic term. In order to allow for this contribution, adjustment in terms of $\lambda/\Delta E$ is made, where $\lambda$ is the spin orbital coupling constant and $\Delta E$ is the sum of the energies of separation between the half-filled level and those to which it is magnetically coupled. The correction may be conveniently expressed in terms of the experimental $g$-values as $\Delta g$ (if not too large) is also dependent on $\lambda/\Delta E$. The following equations may be used for $S = \frac{1}{2}$ systems;

For a $p$-orbital system; with $\Delta g \sim 0$ and $|\Delta g_x|$ large;

\[
A_\parallel = A_{\text{iso}} + 2B \\
A_\perp = A_{\text{iso}} - B (1 \pm \frac{9}{2} \Delta g_\perp)
\]

and for 3 $g$-values differing significantly from zero;

\[
A_x = A_{\text{iso}} + 2B (1 \pm \frac{5}{2} \Delta g_x) \\
A_y = A_{\text{iso}} - B (1 \pm \frac{5}{2} \Delta g_y) \\
A_z = A_{\text{iso}} - B (1 \pm \frac{5}{2} \Delta g_z)
\]

For $d$-orbitals;

\[
A_\parallel = A - 2B (1 \pm \frac{7}{4} \Delta g_\parallel) \\
A_\perp = A + B (1 \pm \frac{7}{2} \Delta g_\perp)
\]
For $d_{z^2}$, +B and -B are used.

**Transition Metal Complexes**

One of the most commonly encountered ligands in transition metal organometallic chemistry is carbon monoxide. The discovery of nickel tetracarbonyl in 1890 by Mond, Langer and Quincke\(^{14}\) led to the development of metal carbonyl chemistry, largely by Hieber and his co-workers from about 1920 to the present.

A simple molecular orbital treatment of the bonding in complexes containing a metal-carbonyl bond involves the sp orbital on the carbon atom containing the lone pair overlapping with a metal hybrid orbital of suitable symmetry to form a forward σ bond. Donation of the ligand lone pair results in increased electron density on the metal, and thus this bond is relatively weak. This excess electron density is effectively removed by a reverse π-bond, whereby a filled metal $d$-orbital containing an electron pair overlaps with an empty π* antibonding orbital of the CO group (Fig. 1.7). The extent of this retrodative π-bonding is quite

**FIG. 1.7**

variable in metal carbonyl derivatives, being dependent on the electron density at the metal. Thus it is affected by various factors such as other ligands attached to the metal, and the charge on the metal carbonyl species.
This "back-bonding" in metal carbonyl complexes places additional electron density into the antibonding $\pi^*$ orbitals of the CO ligand. This lowers the C-O bond order and therefore the C-O stretching force constant, an effect that can be measured from IR frequencies, e.g. $\nu$(CO) for gaseous CO occurs at 2143 cm$^{-1}$, and for a typical organic carbonyl compound at ca. 1700 cm$^{-1}$. In metal carbonyl compounds a terminal CO stretch usually occurs in the 1950-2050 cm$^{-1}$ region.

Many transition metal complexes contain other ligands in addition to CO, frequently these may be halogens or the $\pi$-cyclopentadienyl ligand. The chemistry of cyclopentadienyl containing compounds was stimulated by the discovery of ferrocene (bis-cyclopentadienyl iron) in 1951 by two different groups of workers, Kealy and Pauson in the United States and Miller, Tebboth and Tremaine in Great Britain. If the Cp-M fragment is considered separately, this has $C_5v$ local symmetry. The five $p_z$ atomic orbitals of the Cp ring combine to form five molecular orbitals, which fall into 3 symmetry groups; the $A_1$ bonding orbital, $E_1$ bonding orbitals, a degenerate pair, and $E_2$ antibonding orbitals, also a degenerate pair (Fig. 1.8). The metal $d$-orbitals are divided between 3 irreducible representations; $A_1 (d_{z^2})$, $E_1 (d_{xz}, d_{yz})$ and $E_2 (d_{xy}, d_{x^2-y^2})$, these are assumed to lie energetically between the $E_1$ and $E_2$ Cp orbitals. Although there is some disagreement over the extent of bonding overlaps and the order of energy levels, it is thought that $d_{z^2}$, $d_{xz}$ and $d_{yz}$ are bonding, and $d_{x^2-y^2}$, $d_{xy}$ are essentially antibonding. Other metal-ligand bonding will obviously modify any metal-Cp interaction, but by treating the Cp-M and M-CO bonding separately in terms of local symmetry, an overall bonding scheme may be proposed.

Other metal-ligand bonding will obviously modify any metal Cp interaction, but by treating the Cp-M and M-CO bonding separately in terms of
FIG. 1.8
Molecular orbitals of cyclopentadienyl group
local symmetry, an overall bonding scheme may be proposed.

**Effects of High Energy Radiation on common solvents**

Although the vast majority of carbonyl complexes are diamagnetic, Symons and co-workers have found that exposure of transition metal carbonyl derivatives to ionizing radiation produces low concentrations of electron-loss and electron-gain centres, which may be characterized by e.s.r. spectroscopy. When studying such compounds in frozen solutions, choice of the appropriate solvent may influence the species formed. Thus it is important to have a knowledge of the effects of high energy radiation on solvents commonly employed. It is proposed to briefly survey the mechanisms involved for a number of solvents after \( \gamma \)- or X- irradiation.

**Elementary Process**

The basic process involves absorption of the ionizing radiation by interaction with the electrons of the constituent molecules of the medium, resulting in electronically excited molecules. This leads to the formation of excited species, and subsequent ionization produces secondary electrons and positive ions. The ejected electron and the complementary positive hole (or positive ion formed from it) undergo a variety of reactions depending on the nature of the solvent, the extent of hydrogen-bonding in the solvent, and the nature of any solute present.

**Aqueous systems**

Absorption of the ionizing radiation involves the initial formation of an electronically excited water molecule;

\[
\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^* \quad \text{[1]}
\]

Subsequent to this, Weiss suggests that the active intermediate species can be represented as bound electron-hole pairs, from which the electrons
and/or holes can be scavenged by suitable solutes in the matrix. These electron-hole pairs can decay by a non-radiative process such as:

\[
[(H_2O)^+ \rightarrow (H_2O)^-] \rightarrow H + OH + H_2O
\]

.... [2]

Alternatively, the excited water molecule may form the cation and a solvated electron:

\[
H_2O^* \rightarrow e_{aq}^- + H_2O^+
\]

.... [3]

\[
H_2O^+ \rightarrow OH + H^+
\]

.... [4]

The process of solvation may be envisaged as the polarization of the solvent molecules owing to electron-dipole interactions, the electric field of the extra electron inducing a potential well which then traps and stabilizes the electron; \(e_{aq}^-\) is intensely coloured and mobile. It is very reactive, and may be scavenged by many reactive substrates:

\[
e_{aq}^- + S \rightarrow S^- \rightarrow \text{products}
\]

[S = substrate] .... [5]

It is interesting that trapped electron yields in glasses are invariably larger than in the corresponding crystalline phase. This is thought to be due to the fact that the electrons are trapped in existing potential wells resulting from the mean instantaneous distribution of molecular orientations which is frozen-in when glassy solids are made. When cooling produces crystallization, however, an ordered pattern of molecular orientations results, which seldom permits the occurrence of electron stabilization, except at defect sites.

In NaOH glasses at low temperatures, e.s.r. may be used to observe and characterize the trapped electron \(e_T^-\), the hydroxyl radical \((OH^+)\) and the oxygen radical anion \((O^-)\). It is thought that \(O^-\) is formed from \(OH^+\) by proton transfer to a neighbouring hydroxide ion, leaving solvated \(O^-\). The electron is trapped at the site vacated by the second hydroxide ion, the water molecule becoming part of the solvent shell. The solvated
electron may be regarded as an electron occupying a cavity within the solvent of the same size and structure as that which normally surrounds a monoatomic ion, e.g. I⁻. Solvent molecules such as water have no low-lying acceptor orbitals, so electrons in such media should meet with greater resistance to penetration outside the trapping cavity. This is confirmed by an e.s.r. experiment in which concentrated glassy solutions of salts in water show little or no width increment from cations or anions despite their close proximity. However, water protons do make a major contribution to the width because of the orientation polarization of cavity molecules. This is shown by experiments involving alcohols, γ-irradiation at 4.2 K results in a narrow e.s.r. singlet suggesting little width enhancement by OH protons. On warming to 77 K, the width is increased to its normal value, thus indicating strong OH coupling. Such an observation suggests that no orientational polarization exists initially, but at 77 K the electron charge breaks H-bonds and reorientates the solvent molecules.

In hydroxyl glasses, the species of main interest is the trapped electron, e⁻, which is produced by γ-irradiation of alkaline ices at 77 K. The immediate environment of the trapped electron is associated with several polarized O-H protons from the solvent. This phenomenon is closely linked to the "solvated" electron in fluid media, but the two are not necessarily identical as the extent of orientational polarization is likely to differ in solid and liquid states. The trapped electron is characterized by a sharp singlet at $g = 2.001$, and a broad intense absorption band, $\lambda_{\text{max}} = 585$ nm, which gives an intense blue colour to glasses. Scavenging experiments provide the most decisive evidence for the formation of a trapped electron; the addition of NO₃⁻, NO₂⁻ to alkaline solutions, and γ-irradiation at 77 K, results in the non appearance of the
singlet and blue colour. An e.s.r. pattern characteristic of interaction between the electron and the scavenger is seen, indicating that mobile electrons, which precede the formation of trapped electrons, have reacted with the scavenger.

Hydrogen atoms are not observed in ice at 77 K, and it is thought that they diffuse away, reacting to give diamagnetic products, although hydrogen atoms have been observed in γ-irradiated ice at 4 K using e.s.r. However, the presence of Bronsted acids, such as HSO₄⁻ and H₂PO₄⁻ do enable hydrogen atoms to be observed, presumably by scavenging the mobile electrons.

In aqueous glasses of H₂SO₄ at concentrations of up to 10M, the following overall reaction takes place:

\[
\begin{align*}
H_2O & \rightarrow H_2O^* & \text{[6]} \\
H_2O^* & \rightarrow H_2O^+ + e^- & \text{[7]} \\
e^- + HSO_4^- & \rightarrow HSO_4^{2-} \rightarrow H^+ + SO_4^{2-} & \text{[8]} \\
H_2O^+ + SO_4^{2-} & \rightarrow SO_4^{2-}.(H_2O) & \text{[9]}
\end{align*}
\]

The SO₄⁻ radical ion has a characteristic e.s.r. spectrum consisting of a single sharp line, width 4.1 G, centred at \( g = 2.003 \). It absorbs in the visible region, with an absorption maximum at 446 μm, and is responsible for the deep yellow colour of γ-irradiated H₂SO₄ solutions. This may be photochemically bleached with light which is absorbed by these coloured radical ions, causing an electron to be transferred from the hydration shell to the radical ions;

\[
SO_4^{2-}.(H_2O) + h\nu \rightarrow SO_4^{2-}.(H_2O)^+ \text{[10]}
\]

leading to the formation of a positive hole trapped in the hydration shell of the ions. If the sample is now annealed to approximately 120 K, the original colour is immediately restored by reaction [9].
Alcohols

The trapped products resulting from irradiation of methanol at 77 K are dependent on the physical state of the matrix. In an opaque, crystalline state, the matrix remains colourless and the characteristic singlet at $g = 2.001$ attributed to a solvated electron is absent. However, in methanolic glasses (CH$_3$OH + ~5% H$_2$O) the matrix appears intensely violet and two species are seen; CH$_2$OH and the solvated electron, trapped in almost stoichiometric amounts. The assignment of the solvated electron, trapped in the glassy matrix, has been confirmed by scavenging experiments.$^{25,29-31}$ Absorption spectroscopy provides supporting evidence for such an assignment; $\lambda_{\text{max}} = 533 \, \text{nm}$ for $e^-_t$, and a band in UV attributable to CH$_2$OH. The complementary positive ion, CH$_3$OH$^+$, has not been identified as being trapped in the matrix, but the fact that CH$_2$OH and $e^-_t$ are found in stoichiometric amounts suggests that their origin is closely related. It is feasible that they arise from an ion-molecule reaction involving an initially-formed "hot-ion", CH$_3$OH$^+$. The overall reaction scheme, applicable to all alcohols, may be summarized;

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{CH}_3\text{OH}^+ + e^-_m \\
 e^-_m & \rightarrow e^-_t \\
 \text{CH}_3\text{OH}^+ + \text{CH}_3\text{OH} & \rightarrow \text{CH}_3\text{OH}_2^+ + \cdot\text{CH}_2\text{OH}
\end{align*}
\]

MTHF

Another solvent commonly employed is methyltetrahydrofuran, a system involving no hydrogen-bonding, in contrast to the aqueous and alcoholic solvents already discussed. The radiation chemistry of MTHF is similar to that for water and alcohols in the respect that the primary products following excitation correspond to the mobile electron, $e^-_m$, which may be either trapped at a suitable site in the glassy matrix, or scavenged, and the complementary positive hole, MTHF$^+$. 
\[ \text{C}_5\text{H}_{10}\text{O} \quad \overset{\gamma}{\rightarrow} \quad \text{C}_5\text{H}_{10}\text{O}^+ + e_m^- \quad \text{.... [14]} \]
\[ \text{C}_5\text{H}_{10}\text{O}^+ + \text{C}_5\text{H}_{10}\text{O} \rightarrow \text{C}_5\text{H}_{11}\text{O}^+ + \text{C}_5\text{H}_9\text{O} \quad \text{.... [15]} \]
\[ e_m^- + \text{solute} \rightarrow \text{solute anion} \quad \text{.... [16]} \]

The electrons are produced in high yield, and move through the solvent to be scavenged by the solute [16], while the positive ions decompose by reaction [15]. It is thus a useful solvent for adding electrons to transition metal complexes.

The trapped electrons may be released by illumination with visible and UV light, i.e. bleaching, and they may then diffuse to positive ions and be captured. The e.s.r. spectrum of the trapped electron at 77 K in MTHF is very narrow (ca. 5 G) compared to that of the trapped electron in water and alcohols (ca. 15 G). It would appear that there is very little reorientation of the solvent, and very little solvent-electron interaction in non-H-bonding solvents.

**Alkyl halides**

In contrast to MTHF, alkyl halides provide a means of preparing solute cations, as these compounds act as electron scavengers. Their importance lies in the possible characterization of electron-loss centres in transition-metal complexes. The overall reaction scheme can be represented;

\[ \text{RX} \rightarrow \text{RX}^+ + e_m^- \quad \text{.... [17]} \]
\[ e_m^- + \text{RX} \rightarrow (\text{RX})^- \rightarrow \text{R}^- + \text{X}^- \quad \text{.... [18]} \]
\[ \text{RX}^+ + \text{solute} \rightarrow \text{RX} + \text{solute cation} \quad \text{.... [19]} \]

The positive charge in [17] and [19] conducts through the halide molecules until it is scavenged by a solute molecule doped at a site remote from the initial ionization. This ability to act as electron scavengers arises because of the empty low-lying orbitals of alkyl halides, thus...
yielding a thermodynamically feasible anion. However, the radical anion formed from RX (X=Cl, Br, I) has only a transitory existence at 77 K, and undergoes subsequent dissociation to more stable products, [18].

This is a simplified picture of the overall reaction however, as several metastable species are also trapped in the matrix, though in much smaller concentrations. Nevertheless, the most important reaction is the halogen-dissociating, thermal electron-attachment reaction. It should also be noted that alkyl radicals are formed in reaction [18].

The choice of alkyl halide matrix is somewhat limited however, because relatively few compounds form satisfactory glasses. CCl$_4$ is a very efficient electron scavenger in $\gamma$-irradiated organic glasses, sec-BuCl offers many of the same advantages but is a much better solvent and is glassy at 77 K. Another halogenic glassy matrix which may be used is an equivolume mixture of CCl$_3$F and CF$_2$BrCF$_2$Br, which forms transparent glasses at 77 K. On $\gamma$-irradiation, the electron ejected upon ionization of the freon mixture is scavenged by reaction [21];

$$\text{FM} + \gamma \rightarrow \text{FM}^+ + e^- \quad \text{[20]}$$
$$e^- + \text{CF}_2\text{BrCF}_2\text{Br} \rightarrow \text{CF}_2\text{BrCF}_2^- + \text{Br}^- \quad \text{[21]}$$

[FM = freon mixture]

The counterpart positive charge migrates by resonant charge transfer among the freon molecules until it encounters a solute molecule;

$$\text{FM}^+ + S \rightarrow \text{FM} + S^+ \quad \text{[22]}$$

[S = solute molecule].
REFERENCES FOR CHAPTER 1

EXPERIMENTAL ASPECTS

The Spectrometer

Detailed descriptions of the e.s.r. spectrometer are given in many standard texts.\textsuperscript{1-5} A typical spectrometer basically consists of a Klystron oscillator generating microwaves, and operating at X- or Q-band frequencies. The microwave power is transmitted through a rectangular waveguide which propagates and polarizes the radiation to a resonant cavity designed to produce the maximum microwave field at the position of the sample. This is achieved by a coating of a highly conductive metal such as gold or silver on the cavity and waveguide, and the cavity having interior dimensions comparable to the wavelength of the microwaves. A standing wave-pattern is set up within the cavity and so a high level of microwave power is concentrated within the vicinity of the sample.

The cavity is situated between the poles of a large electromagnet in an area of uniform magnetic field. At X-band, the poles of the electromagnet must be able to scan homogeneously from about 600 to 10,000 Gauss, as the frequency is held constant and the magnetic field is varied during the e.s.r. experiment. The usual arrangement (Fig. 2.1) incorporates a balanced microwave bridge with the Klystron attached to one arm, the sample cavity on another, the detector crystal on the third and a balanced termination stub on the fourth. The detector is usually a semi-conducting diode, at which an out-of-balance signal appears due to the absorption of power by the sample.

The resonance is converted to an alternating signal, which can be separated from random noise, by means of a modulating field. Application of an alternating current (~100 KHz) to a set of coils situated on either side of the cavity produces a variable field superimposed on the main magnetic field. Phase-sensitive detection produces a signal on a
FIG. 2.1
Block diagram of an e.s.r. spectrometer showing the essential elements.
pen recorder which approximates to the first derivative of the absorption spectrum. Appropriate choice of amplitude of the modulating field enables a good signal-to-noise ratio to be obtained, but care must be taken to avoid too large an amplitude as this will cause distortions if it exceeds the resonant linewidth. The spectrometer has a high sensitivity, and can be used to detect spin concentrations of less than $10^{12}$ spins mol$^{-1}$, such concentrations are not easily studied by other techniques.

The instruments used in this study were a Varian Associates E109 spectrometer, and a smaller E3 model, both operating at X-band frequencies and employing 100 KHz field modulation and phase-sensitive detection. Q-band spectra were obtained with a machine built in this Department by J. A. Brivati and described elsewhere.$^6$

Sample Preparation

Samples in this study were commonly prepared as either frozen solutions ("glasses") or powders. It is important that solutions are magnetically dilute, so that paramagnetic ions are separated from each other by a large number of diamagnetic molecules in order to prevent any magnetic exchange. Typical concentrations are $10^{-3}$ M. Frozen solutions were prepared in two ways, if removal of dissolved oxygen was not considered critical, small beads formed by pipetting the solution into a bath of liquid nitrogen were contained in small screw-topped bottles. Alternatively, the solution would be placed in an e.s.r. tube, and removal of oxygen effected by several freeze-thawing cycles on a vacuum line. Finally the tubes would be sealed in vacuo.

Quartz tubes are most commonly used, since Pyrex and other glasses contain small traces of paramagnetic impurities. Tubes used in this study for X-band e.s.r. work were 4mm O.D. "Heralux" standard (Heraeus
It is important that only a thin sample should be exposed to the microwave radiation, since all solvents absorb this to a certain extent. Too much absorption leads to "damping" and it is not possible to obtain resonance. Solvents causing the minimum of damping are characterized by having a low dielectric constant. Although the majority of organic solvents form glasses at liquid nitrogen temperatures, water is an exception owing to the presence of strong hydrogen-bonds making it unwilling to accommodate an impurity within the crystal structure. This results in local concentrations of paramagnetic ions, causing the spectrum to be broadened by dipolar and exchange interactions. Addition of an alcohol or phosphoric acid as diamagnetic impurities may help to sharpen up lines.

Powder samples were prepared by finely grinding in an agate pestle and mortar, and contained in screw-top bottles.

**Formation of Radicals**

γ-Irradiation was carried out by placing samples in a top-loading "Vickrad" source, thereby exposing them to ⁶⁰Co γ-rays at a nominal dose rate of ca. 1 MRad hr⁻¹. Irradiation periods were normally of up to 2 hours, during which time an adequate concentration of radicals was built up. Samples were placed in a Dewar filled with liquid nitrogen for irradiation at 77 K.

Photolysis experiments were performed either in situ or with the sample contained in a large quartz Dewar, using several lamps according to the type of radiation required. A tungsten source was employed for irradiation in the visible region, and a high-pressure mercury lamp with a Pyrex filter for unspecific UV radiation. Specific wavelength radiation at 253.7, 300 and 350 nm could be provided by a "Rayonet" photochemical reactor.
Recording the Spectrum

For studies at 77 K, the sample was immersed in liquid nitrogen in a quartz Dewar, with its tip in the sample cavity. By decanting the liquid nitrogen, samples could be annealed above this temperature whilst continuously monitoring the spectrum. If any significant changes were observed in the spectrum, the sample could be recooled to 77 K.

By passing a stream of nitrogen gas through a heat-exchanger and over the sample, the temperature could be varied between about 80 K and room temperature, using a Varian variable temperature accessory.

Occasionally, ambiguities arise in multiline spectra, for example, it may not be clear whether a line is a hyperfine component, or due to another species.

This can be resolved in a number of ways, one of which is isotopic dilution. Substituting a new isotope having a different magnetic moment or spin will result in a spectrum showing a different hyperfine interaction, in accord with these new parameters. If a spectrum is due to two species, it can be resolved by progressively increasing the microwave power. The two species will not usually have the same relaxation times, and so one will saturate before the other. This will be observed as a broadening and gradual disappearance of the line. Power saturation can be used to observe any features that may be obscured by solvent radicals, by saturating the latter.

Another technique, used to separate g-values (whether belonging to the same or different species) is to run a sample at both X- and Q-band. As the magnitude of the hyperfine interaction is independent of the external field, increasing the microwave frequency separates any g-values by a factor of approximately 3.75.

g-Values can be measured from the spectrum in either of two ways.
Provided the microwave frequency $\nu$ and the magnetic field $H$ can be measured accurately, $g$ may be calculated from the relationship $h\nu = g \beta H$.

As the majority of radicals studied here have $g$-values between 1.9 and 2.1, they are usually calibrated relative to 2,2'-diphenyl-1-picryl-hydrazyl (DPPH), a stable free radical with $g = 2.0036 \pm 0.0003$. This gives a single line e.s.r. spectrum, with a narrow linewidth of approximately 3 G. Another method of calibration utilizes a Hewlett-Packard 5246L frequency counter in conjunction with a Bruker B-H12E field probe.
REFERENCES FOR CHAPTER 2


CHAPTER 3

METAL CARBONYL COMPLEXES - A STUDY OF Fe(CO)₅
INTRODUCTION

The vast majority of carbonyl complexes have a low spin configuration owing to the strong ligand field characteristics of carbon monoxide. Only a few stable paramagnetic species exist, the most notable being V(CO)$_6$. Initial investigators suggested a dimeric formula for this complex, since no effects of paramagnetism were found in the n.m.r. spectrum even at high carbonyl concentrations. The compound was independently discovered by another group and formulated as monomeric, since it was found to be isomorphous with Cr(CO)$_6$. Exact magnetic measurements showed that the species was paramagnetic in both the solid and dissolved states.

In all investigations V(CO)$_6$ has been assumed to be octahedral, with zerovalent V having the electronic structure (Ar) 3d$^5$. Crystal field theory predicts a $^2T_{2g}$ ground state for low spin configuration in an octahedral field. However, according to the Jahn-Teller theorem, an octahedral complex in a $^2T_{2g}$ electronic state is unstable with respect to distortion. Group theoretical considerations show that either a trigonal (D$_{3d}$) or tetragonal (D$_{4h}$) distortion will remove the orbital degeneracy of the $^2T_{2g}$ state and satisfy the Jahn-Teller theorem. Such a distortion was identified by comparison of the IR spectra of V(CO)$_6$ and Cr(CO)$_6$, a dynamic distortion being preferred.

$g$-Values obtained from an e.s.r. study of V(CO)$_6$ at liquid helium temperatures are consistent with a small tetragonal distortion, yielding a $^2T_{2g}$ ground state. Although later work on V(CO)$_6$ in frozen cyclohexane glasses admits to axial distortion, no conclusions are drawn as to the nature of such a distortion.

IR and UV spectroscopy used to investigate the products of co-condensation of V atoms with CO at 10 K revealed that V(CO)$_6$ had D$_{4h}$ symmetry in
matrices at low temperatures. This technique also resulted in the formation of $V_2(CO)_{12}$.

Bernier and Kahn$^8$ studied the magnetic susceptibilities of $V(CO)_6$ in the temperature range 4.2-300 K and suggested that axial distortion was present below 66 K, together with a magnetic exchange interaction between pairs of molecules, making the solid essentially diamagnetic at 4.2 K.

An e.s.r. study of $V(CO)_6$ in cyclohexane by Perutz and co-workers$^9$ led to the conclusion that the unpaired electron resides in a $d_{xz}^2-y_z^2$ orbital, as opposed to $d_{xy}$, the transposition of axes facilitating making $d_{xz}$ and $d_{yz}$ inequivalent. The splitting between $d_{xz}$ and $d_{yz}$ arises through a movement of equatorial CO ligands towards the x-axis so $d_{xz}$ is higher in energy than $d_{yz}$. This results in an idealized $D_2h$ structure, preceded by a Jahn-Teller induced tetragonal distortion.

This chapter discusses the pentacoordinate carbonyl Fe(CO)$_5$, which is diamagnetic owing to its 18-electron closed-shell configuration. However, exposure to ionizing radiation results in paramagnetic species, detectable by e.s.r. Na$_2$Fe(CO)$_5$ is also studied for comparison.

Fe(CO)$_5$ and Na$_2$Fe(CO)$_5$: Description

The earliest electron diffraction study of Fe(CO)$_5$$^{10}$ favoured a trigonal bipyramidal structure, although O'Dwyer$^{11}$ claimed that the vibrational spectrum could best be interpreted assuming a square base pyramid. Further work on vibrational spectra$^{12}$ found the data consistent with the $D_{3h}$ model and not $C_{4v}$. Intramolecular exchange of axial and equatorial CO's was found to be fast on the n.m.r. timescale, so that the $^{13}C$ spectrum consisted of a single line only.

The crystal structure of Fe(CO)$_5$ was first investigated by Hanson,$^{13}$ and further refined by Donohue and Caron.$^{14}$ These studies have shown the
molecular structure to be trigonal bipyramidal, no significant difference between the axial and equatorial Fe-C bond lengths was found. Electron diffraction intensity data collected for gaseous Fe(CO)\textsubscript{5}\textsuperscript{15} confirmed the trigonal bipyramidal structure, the structural parameters are shown in Table 3.1:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O (mean)</td>
<td>1.145 ± 0.003</td>
</tr>
<tr>
<td>Fe-C (equatorial)</td>
<td>1.833 ± 0.004</td>
</tr>
<tr>
<td>Fe-C (axial)</td>
<td>1.806 ± 0.005</td>
</tr>
<tr>
<td>Fe-C (mean)</td>
<td>1.822 ± 0.003</td>
</tr>
</tbody>
</table>

There has been considerable interest in the fluxional behaviour of Fe(CO)\textsubscript{5}, exchange of all CO ligands occurs rapidly on the \textsuperscript{13}C n.m.r. timescale down to the lowest possible solution temperature.\textsuperscript{12} In a study of \textsuperscript{13}C n.m.r. of solid Fe(CO)\textsubscript{5}, Spiess and co-workers\textsuperscript{16} have concluded from both T\textsubscript{1} and lineshape measurements that down to at least 100 K Fe(CO)\textsubscript{5} is non-rigid, probably via an axial/equatorial exchange mechanism, and suggest that below about 30 K this motion will be frozen out. Preparation of a partially oriented sample of Fe(CO)\textsubscript{5} in solid CO at 20 K, and subsequent examination using visible/UV,\textsuperscript{17} led to the conclusion that rearrangements only occur within this matrix environment when energy is fed into the molecule, e.g. by photolysis. UV photolysis of matrix isolated Fe(CO)\textsubscript{5} in matrices other than CO, produces the Fe(CO)\textsubscript{4} fragment,\textsuperscript{18,19} which was thought to adopt a C\textsubscript{3v} structure due to Jahn-Teller distortion of the tetrahedron, but is now known to be C\textsubscript{2v}.\textsuperscript{20} Prolonged photolysis leads to [Fe(CO)\textsubscript{3}] and the lower carbonyls, the stepwise loss of CO eventually leading to Fe atoms.\textsuperscript{21} Fe(CO)\textsubscript{4} is not detected in solid CO because of its ready recombination with CO;
\[
\text{Fe(CO)}_5 \xrightarrow{\text{hv}} \text{Fe(CO)}_4 + \text{CO} \quad \text{recombination} \quad \text{Fe(CO)}_5
\]

E.s.r. has been employed to study radical anions produced by the alkali-metal reduction of Fe(CO)₅ in THF solution by Peake and workers.²² They identified a species at \( g = 2.041 \) as \( \text{Fe}_2(\text{CO})_6^{2-} \), subsequent exposure to air resulted in the formation of possibly an Fe(I) species at \( g = 2.053 \), the following scheme was postulated:

\[
\begin{align*}
\text{THF soln. of Fe(CO)}_5 &\xrightarrow{\text{Na mirror}} \text{Fe}_2(\text{CO})_6^{2-} \xrightarrow{\text{air}} \text{Fe(I) species + [Fe}_3(\text{CO})_{12}]^- \\
\text{Further aerial oxidation} &\quad \text{Fe}_3(\text{CO})_{12} \\
\text{No paramagnetic species}
\end{align*}
\]

Controversy exists as to the exact nature of the \( g = 2.053 \) species. Krusic's²³ alkali metal reduction of Fe(CO)₅ in THF produced e.s.r. spectra of up to 4 paramagnetic species, with \( g \)-values and their possible identities shown in Table 3.2.

**TABLE 3.2**

<table>
<thead>
<tr>
<th>Species</th>
<th>( g )-tensor components</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_2(\text{CO})_6^- )</td>
<td>( g_x )</td>
</tr>
<tr>
<td>( \text{Fe}<em>3(\text{CO})</em>{11}^- )</td>
<td>2.054</td>
</tr>
<tr>
<td>( \text{Fe}<em>3(\text{CO})</em>{12}^- )</td>
<td>2.0921</td>
</tr>
<tr>
<td>( \text{Fe}<em>3(\text{CO})</em>{13}^- )</td>
<td></td>
</tr>
</tbody>
</table>

Frozen solutions of \( \text{Fe}_2(\text{CO})_6^- \) exhibited a powder spectrum appropriate for an axially symmetric \( g \)-tensor; \( g_\parallel = 2.0540 \), \( g_{\perp} = 2.0092 \).
It seems that none of the species obtained were simple monomeric anions such as Fe(CO)$_5^-$ or Fe(CO)$_4^-$.

The aim of this work was to prepare these species. It is well established that radiolysis of rigid glassy solutions of substrates in various solvents including MTHF is a good method for adding one electron to these substrates under conditions which often lead to the stabilization of the parent anions, and which prevent the formation of dimer or oligomer species.\textsuperscript{24,25}

Reference will be made to a study of Fe$_3$(CO)$_{12}$ made previously by B. M. Peake in this laboratory.

**EXPERIMENTAL**

Fe(CO)$_5$ was purchased from Fluka Chemicals and used without further purification. Fe(CO)$_5$ enriched in $^{13}$CO (~80%) was kindly supplied by Dr. M. Poliakoff. Na$_2$Fe(CO)$_4$ was obtained from Lancaster Synthesis and used as a fine powder, without further purification. Solution samples were prepared as small glass beads, and in sealed e.s.r. tubes under vacuum when degassing was necessary.

**RESULTS**

No detectable paramagnetic species were observed after exposure of the pure carbonyl Fe(CO)$_5$ to $^{60}$Co $\gamma$-rays at 77 K after degassing. However, when dilute solutions ($\leq 5 \times 10^{-3}$ mol dm$^{-3}$) of Fe(CO)$_5$ in MTHF were used, well-defined features attributable to iron carbonyl derivatives were observed (Fig. 3.1a).

The major species formed at 77 K (A) was well-defined with a perpendicular feature at $g=2.071$ and a parallel feature at $g=2.0015$. The latter was concealed by solvent features but was detectable at high powers such that the solvent features were strongly saturated.
FIG. 3.1
X-band e.s.r. spectra for Fe(CO)$_5$ in MTHF after $\gamma$-irradiation at 77 K and anneal showing species A

a) Normal Fe(CO)$_5$

b) Fe(CO)$_5$ enriched in $^{13}$CO (c.a. 80%)
FIG. 3.2
X-band e.s.r. spectra for Fe(CO)$_5$ in MIHF after γ-irradiation at 77 K and anneal, showing species B

a) Normal Fe(CO)$_5$

\[ 3200 \, \text{G} \]

\[ \begin{array}{c}
g_x \\
g_y \\
\end{array} \]

b) Fe(CO)$_5$ enriched in $^{13}$CO (c.a. 80%)

\[ \begin{array}{c}
g_x \\
g_y \\
g_z \\
\end{array} \]

\[ \begin{array}{c}
^{13}_C \\
^{13}_C \\
\end{array} \]
FIG. 3.3
X-band e.s.r. spectrum of pure Na$_2$Fe(CO)$_5$.1·5$ dioxane, showing the perpendicular feature assigned to species B.
Alternatively, very careful annealing caused much of the signal from solvent radicals to be removed before A was lost.

Further annealing resulted in the decay of species A, and the appearance of new features assigned to species B, with $g$-tensor components $g_x = 2.055$, $g_y = 2.049$ and $g_z = 2.008$ (Fig. 3.2a). It was interesting to observe satellite lines assigned to $^{13}$C in natural abundance on the parallel feature for B. B decayed on further annealing to the softening point of the glass, and no other features were observed growing in.

Exposure of powdered Na$_2$Fe(CO)$_4$ to $^{60}$Co $\gamma$-rays at 77 K produced only one well-defined paramagnetic species. The features were identical with those for B, the $g$-tensor components being $g_x = 2.055$, $g_y = 2.055$ and $g_z = ca. 2.008$ (Fig. 3.3).

The experiment using $^{13}$C enriched Fe(CO)$_5$ was disappointing in that no extra resolved features could be detected. However, there was a definite broadening of all features, the form of which precludes the presence of 1 strongly coupled $^{13}$C and favours the presence of 2 equivalent $^{13}$C nuclei strongly coupled (Figs. 3.1b and 3.2b).

**DISCUSSION**

Centre A must be attributable to an electron gain species, as judged from the suppression of the normal blue-black colour characteristic of trapped electrons in MTHF. The most obvious candidates for the species formed must be Fe(CO)$_5^-$ or Fe(CO)$_4^-$.

Since the Fe(CO)$_4^{2-}$ ion gave species B after $\gamma$-irradiation at 77 K, it seems most probable that B is Fe(CO)$_4^-$. If species B is attributed to Fe(CO)$_4^-$, species A may be assigned to Fe(CO)$_5^-$. If such an assignment is correct, it is quite conceivable that there should be efficient loss of CO from the 19-electron Fe(CO)$_5^-$ moiety, such species being normally
unstable even at low temperatures. However, the possibility that Fe(CO)$_5^-$ may decompose spontaneously at any temperature must not be discounted. In such a case, both A and B must be Fe(CO)$_4^-$. It should be noted that the e.s.r. parameters for B are quite close to those assigned by Krusic et al. to Fe$_2$(CO)$_6^-$, except that their $g$-tensor was accurately axial, whilst in this study it is quite clearly non-axial. If the possibility of dimerization is considered;

$$Fe(CO)_4^- + Fe(CO)_5 \rightarrow Fe_2(CO)_6^- + CO$$

it seems most improbable that such a reaction should occur at ca. 120 K in rigid MTHF. Such bimolecular processes are found by experience to be completely prevented in this glass at this temperature. There seems to be no reason why Fe(CO)$_4^-$ should be an exception, and the process is far more likely to be unimolecular. The bimolecular process also seems unlikely when behaviour in extremely dilute solutions is considered. In this situation, conversion to the electron adducts must be extensive, and complete conversion A$\rightarrow$B is observed. This would be unlikely if the dimerization reaction was occurring.

It should be noted that, in all cases, the form of the $g$-tensor components for these formally $d^9$ species requires that the unpaired electron be in a $3d_{x^2}$ orbital on iron. It was hoped that study of the $^{13}$C enriched Fe(CO)$_5$ would show definitive $^{13}$C splittings, and thus provide conclusive evidence for the identification of species A and B. Although no well-defined splittings were observed, the broadening allows certain structural assignments to be made. There would appear to be two reasonable alternatives concerning the structures of A and B; (i) that A is Fe(CO)$_5^-$ and B is Fe(CO)$_4^-$ as already postulated, (ii) the possibility that both A and B are Fe(CO)$_4^-$ must not be discounted. If this were the case, it is suggested that A has
the $C_{3v}$ structure (I) (Fig. 3.4) observed by Turner and co-workers, and B has the alternative $D_{2d}$ symmetry (III).

Considering case (i), it is suggested that Fe(CO)$_5^-$ probably has the trigonal bipyramidal structure of the parent molecule (II), this would be in accord with the observed axial symmetry. The $^{13}$C evidence, which requires the presence of at least 2 strongly coupled $^{13}$C nuclei having their maximum coupling along the major parallel axis, would also be accommodated by such a structure. The infrared data of Turner, who prepared Fe(CO)$_4^-$ in inert matrices at 10 K by co-condensation of Na atoms and Fe(CO)$_5$ with UV photolysis, and by electron bombardment, are consistent with a $C_{3v}$ structure (I). It is noteworthy that the iso-electronic molecule, Co(CO)$_4$, is also thought to be $C_{3v}$ from IR spectra. An e.s.r. study of Co(CO)$_4$ by Symons and co-workers gave unambiguous information about the orbital of the unpaired electron. The electronic configuration was deduced to be $(d^5)^5$, $(d_{x^2-y^2})^2$, $(d_{z^2})^1$, the molecule having $C_{3v}$ symmetry. This was confirmed by Hanlan et al. who studied Co(CO)$_4$ in a CO matrix in the temperature range 6-15 K. They found that a consistent explanation of the $g$-values which showed axial symmetry, $(g_{\parallel}=2.007, g_{\perp}=2.128)$, required the assumption of a $C_{3v}$ distortion, placing the unpaired electron in a $d_{z^2}$ orbital. A $^{13}$C study revealed only 1 of the 4 carbon atoms showing a significant hyperfine interaction, as expected for $d_{z^2}$ in $C_{3v}$. It should be mentioned that their results assigned to Co(CO)$_4$ in argon matrices are quite different and seem contradictory, and consequently will not be discussed further.

Thus it is feasible that loss of CO from Fe(CO)$_5^-$ on anneal could give rise to the $C_{3v}$ structure. Alternatively, it is also reasonable that the parent structure (II) of Fe(CO)$_5^-$ could give rise to the $D_{2d}$ structure shown in (III), in which all 4 CO ligands would be made equivalent by the
Proposed structures of species A and B, Fe(CO)$_5^-$ and Fe(CO)$_5^+$. 

I. Fe(CO)$_4^-$ (C$_{3v}$)

III. Fe(CO)$_4^-$ (D$_{2d}$)

IV. Fe(CO)$_5^+$
improper 4-fold symmetry axis of $D_{2d}$. However, the $C_{3v}$ structure for B should still give axial symmetry to the $g$-tensor and it would be expected to show one $^{13}\text{C}$ coupling on the $z$-axis to be very much greater than the other three, partly because these will lie quite close to a nodal surface and also because the coupling will be closer to the minimum ($\mu$) values than to the maximum ($\nu$) values. In the absence of such a coupling, the $D_{2d}$ structure for B is considered more likely than the $C_{3v}$.

The results are not quite as easily explained in case (ii). The observed axial symmetry of A is in accord with the $C_{3v}$ structure, but as in case (i) for B, some evidence of doublet splitting from the single axial $^{13}\text{C}$ would have been expected.

Thus case (i) is favoured, in which A is Fe(CO)$_5^-$ having the trigonal bipyramidal structure (II) of the parent molecule, loss of CO on anneal giving Fe(CO)$_4^-$ with a $D_{2d}$ structure (III). Incorporating the results of Turner, it is suggested that loss of CO at ca. 4 K in a rare-gas matrix gives the $C_{3v}$ structure (I) initially, but this rearranges to $D_{2d}$ at temperatures below 120 K. Thus it would appear that $C_{3v}$ is kinetically favoured whilst $D_{2d}$ is thermodynamically favoured. The retention of CO in the initial formation of Fe(CO)$_5^-$ in MTHF may reflect the rigidity of this matrix compared to the rare-gas matrix.

Although these conclusions seem acceptable on the basis of this study, it is recognised that the postulate of a stable 19-electron species at 77 K may be unacceptable to many. However, it is possible for species such as this, which are intrinsically unstable with respect to dissociation, to achieve stability at low temperatures via distortions that do not lead directly to dissociation. Although such a situation has not been established for transition metal carbonyls, $\cdot$PL$_4^-$ may be taken as an example. This radical anion may be unstable with respect to dissociation
into \( \cdot \text{PL}_3 \) and \( \text{L}^- \), but initial electron capture causes \( \text{PL}_4^- \) to undergo a bending distortion which confers some stability on \( \cdot \text{PL}_4^- \). Dissociation occurs at higher temperatures, caused by a stretching distortion.

It is surprising that both \( 3d^3 \) species favour a \( d_{x^2-y^2}^2 d_{z^2}^1 \) configuration, especially when compared with the \( 3d^7 \) species \( \text{Fe} (\text{CO})_5^+ \) and \( \text{Mn} (\text{CO})_5 \).

Lionel et al.\(^{31}\) studied the e.s.r. spectra of single crystals of \( \text{Cr} (\text{CO})_6 \) doped with \( \text{Fe} (\text{CO})_5 \) after radiolysis at 77 K, and identified the species formed as \( \text{Fe} (\text{CO})_5^+ \). When \(^{13}\text{C}\)-enriched \( \text{Fe} (\text{CO})_5 \) was used, there was evidence of \(^{13}\text{C}\) hyperfine coupling to one unique carbon atom and four equivalent carbon atoms, strongly suggesting \( C_{\text{iv}} \) symmetry. It was deduced from the e.s.r. parameters that the unpaired electron occupied a SOMO comprised of 55% \( \text{Fe} (3d_{z^2}) \) character. The isoelectronic \( \text{Mn} (\text{CO})_5 \)\(^{32,33}\) has similarly been found to favour a \( d_{z^2} \) configuration and \( C_{\text{iv}} \) symmetry.

\( \text{Fe} (\text{CO})_5 \) in Freon

Following the work of Lionel et al.\(^{31}\) as discussed above, it seemed of interest to attempt to prepare the same species using a freon solvent such as \( \text{CCl}_3\text{F} \). As discussed in Chapter 1, these alkyl halide solvents may be used for the formation of cation radicals of neutral molecules, a process which has been shown to be remarkably effective.\(^{34-36}\) There has not been any previous record of transition metal complexes being studied in these solvents.

It was found that a species was formed having the same form of \( g \)-tensor components as those previously published (Table 3.3), but there is a rather large difference in values (\( g_\parallel = 2.057 \), as opposed to ca. 2.080 reported previously). No explanation can be offered to account for such a discrepancy. As far as is known, only radical cations or their
reaction products have been formed in experiments using freon solvents. However, the evidence for the species formed in Fe(CO)₅ doped Cr(CO)₆ and H₂SO₄ being Fe(CO)₅⁺ is very strong. It is conceivable that a CO ligand has been lost in the freon solvent, also the possibility of a significant medium effect must not be discounted. However, the close similarity of the Cr(CO)₆ and H₂SO₄ results make the latter unlikely.

Fe₃(CO)₁₂

Another iron carbonyl complex has previously been studied in this laboratory by B. M. Peake, and it seems appropriate to mention the results here. Comparison may be made with the work of Krusic et al., who investigated the reaction of Fe(CO)₅ in THF solution with alkali metals. Four paramagnetic species were observed, each characterized by a single e.s.r. absorption and a unique g-factor (Table 3.2).

Peake studied the solution spectra of the trimer Fe₃(CO)₁₂ and observed a major species exhibiting non-axial symmetry, with gₓ = 2.0094, gᵧ = 2.0045, and gᵣ = 1.990, giving gₑᵥₑ = 2.0010 (Fig. 3.5). The species identified as Fe₃(CO)₁₂⁺ by Krusic has gₑᵥₑ = 2.0016, so there can be little doubt that these are the same species. The low gᵣ value is indicative of magnetic coupling to a low-lying empty orbital, which is unusual for complexes derived from monomers having d⁸ or d⁹ configurations.

At least two other species were detected in low concentrations at 77 K, one having g₁ = 2.0914 which is very similar to the maximum g-value for Fe₃(CO)₁₁⁻ identified by Krusic. CO loss could be a minor pathway on electron addition at 77 K although the other two g-features were not detected. The other species, having g₁ ~ 2.0785 (very weak) and g₁ = 2.071 (weak) have not been identified. The latter could conceivably be A [Fe(CO)₅⁻], but if so, it is probably formed from Fe(CO)₅ impurity rather
FIG. 3.5
X-band e.s.r. spectrum for \( \text{Pe}_3(\text{CO})_3 \) in MnF after \( \gamma \)-irradiation at 77 K.
than from the trimer.

TABLE 3.3

$g$-values for various iron carbonyl species

<table>
<thead>
<tr>
<th>Species</th>
<th>Medium</th>
<th>$g$-tensor components</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$g_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe(CO)}_5^-$</td>
<td>MTHF</td>
<td></td>
<td>2.071</td>
<td>2.071</td>
<td>2.0015</td>
<td>2.048</td>
</tr>
<tr>
<td>$\text{Fe(CO)}_4^-$</td>
<td>MTHF</td>
<td>$\text{Na}_2\text{Fe(CO)}_4$</td>
<td>2.055</td>
<td>2.049</td>
<td>2.008</td>
<td>2.037</td>
</tr>
<tr>
<td>$\text{Fe(CO)}_5^+$</td>
<td>$\text{Cr(CO)}_6$</td>
<td>CFCI$_3$</td>
<td>2.0833</td>
<td>2.0797</td>
<td>2.0008</td>
<td>2.0546</td>
</tr>
<tr>
<td>$\text{Fe}<em>3(\text{CO})</em>{12}^-$</td>
<td></td>
<td></td>
<td>2.0094</td>
<td>2.0045</td>
<td>1.990</td>
<td>2.0013</td>
</tr>
</tbody>
</table>

$^a$ $^{13}$C parameters deduced fine line broadening gave $A(\text{for } 1 ^{13}\text{C}) \sim 13$ G, $A_1(\text{for } 1 ^{13}\text{C}) \text{ca. } 7$ G.

$^b$ $^{13}$C parameters deduced fine line broadening gave $A( ^{13}\text{C} > 2) \sim 10$ G, $A_1( ^{13}\text{C} > 2) < 10$ G.

REFERENCES FOR CHAPTER 3

24. M. C. R. Symons, Radiation Research, 1979, 6, 238.


CHAPTER 4

COMPLEXES CONTAINING METAL-METAL BONDS
INTRODUCTION

Decacarbonyl di-manganese, Mn₂(CO)₁₀, and decacarbonyl di-rhenium, Re₂(CO)₁₀, were the first polynuclear metal carbonyls known to be held together by direct metal-metal bonds. Although Re₂(CO)₁₀ was known,¹ Mn₂(CO)₁₀ was not isolated and characterized until 1954.² Infra-red spectra suggested that dimerization did not occur through CO bridges, but through the formation of metal-metal bonds.

Structural studies³,⁴ of Mn₂(CO)₁₀ have shown that each Mn atom is octahedrally coordinated to 5 CO groups and the other Mn atom in such a way that the equatorial CO groups are arranged in a staggered conformation, resulting in a distorted D₄h symmetry (Fig. 4.1).

The metal-metal bond enables each Mn atom to attain a "closed shell" electronic configuration, in accord with the observed diamagnetism of the compound; a fact which suggests that Mn₂(CO)₁₀ does not lend itself to e.s.r. study. However, a M.O. approach⁵ assigns an electronic absorption band at 24,900 cm⁻¹ to → σ* transition, and photolysis of Mn₂(CO)₁₀ in solution at energies close to this transition results in homolytic cleavage of the M-M bond.⁶,⁷ The importance of clean rupture of metal-metal bonds lies in the possible characterization of paramagnetic organometallic complexes, cleavage of M-M should potentially lead to two paramagnetic centres. Mn(CO)₅⁺ has been found to have a very short lifetime (~msecs),⁶,⁸ and has been much sought by e.s.r. spectroscopists. A species originally thought to be Mn(CO)₅⁺ has been identified as Mn(CO)₅O₂,⁶,⁹ a paramagnetic adduct formed by abstraction of traces of dissolved O₂ from hydrocarbon solvents, in which O₂ coordinates to the sixth axial position in the coordinatively unsaturated Mn(CO)₅⁺. However, Mn(CO)₅⁺ is thought to be formed by the reaction between Na or Ag atoms and Mn(CO)₅Cl or Mn(CO)₅Br on a rotating cryostat, and has been
FIG. 4.1
Molecular configuration, bond distances, and bond angles of Mn₂(CO)₁₀.
characterized by e.s.r.\textsuperscript{10} Homolysis of Mn\textsubscript{2}(CO)\textsubscript{10} has been studied by techniques such as mass spectrometry,\textsuperscript{11} flash photolysis\textsuperscript{8} and kinetics.\textsuperscript{12} Mn(CO)\textsubscript{5}\textsuperscript{*} has been detected using a spin trapping technique.\textsuperscript{6,13} Symons and workers\textsuperscript{14} exposed Mn\textsubscript{2}(CO)\textsubscript{10} and Re\textsubscript{2}(CO)\textsubscript{10} to \textsuperscript{60}Co γ-rays, and from subsequent e.s.r. study identified a $g=2$ centre for Mn\textsubscript{2}(CO)\textsubscript{10} as the primary anion [Mn\textsubscript{2}(CO)\textsubscript{10}]\textsuperscript{-}, the results suggesting that the unpaired electron resides in a metal-metal $σ^*$ anti-bonding orbital. A $g=6$ species was thought to be an electron loss centre, in which one Mn atom has acquired an $S=\frac{5}{2}$ configuration. Re\textsubscript{2}(CO)\textsubscript{10} showed a similar anionic centre, but no electron loss centre was detected.

Thus exposure of metal-metal bonded complexes to ionizing radiation is a powerful method for preparing paramagnetic derivatives whose structure can frequently be probed by e.s.r. spectroscopy. This chapter describes such a study of disubstituted derivatives of Mn\textsubscript{2}(CO)\textsubscript{10}, (PR\textsubscript{3})\textsubscript{2}Mn\textsubscript{2}(CO)\textsubscript{8}, a group of M-Hg-M complexes and their halide derivatives, Br-Hg-M complexes.

**PART I Mn\textsubscript{2}(CO)\textsubscript{8}(PR\textsubscript{3})\textsubscript{2}**

**DESCRIPTION**

Several substituted derivatives of type Mn\textsubscript{2}(CO)\textsubscript{8}(PR\textsubscript{3})\textsubscript{2} are known. This series of compounds is closely related to Mn\textsubscript{2}(CO)\textsubscript{10}, the two axial CO groups having been replaced by phosphine or phosphite ligands. It was originally thought that they existed as paramagnetic monomers;\textsuperscript{15}

\[
\text{Mn}_2(\text{CO})_{10} + 2\text{PR}_3 \underset{\text{heat in xylene}}{\overset{16 \text{ hours}}{\longrightarrow}} 2\text{Mn}(\text{CO})_4\text{PR}_3 + 2\text{CO} \quad \text{paramagnetic solid}
\]

suggesting that Mn\textsubscript{2}(CO)\textsubscript{10} underwent homolytic cleavage during the reaction. Further study\textsuperscript{16} gave rise to the hypothesis that photochemical
initiation led to the dimeric diamagnetic product, with retention of the metal-metal bond during substitution.

However, the true dimeric nature of the complexes was revealed in further work\textsuperscript{17-20} which established that the observed paramagnetism reached a peak only after 8 hours heating at 120°C. Osborne and Stiddard\textsuperscript{16} heated the reaction mixture for only 4 hrs. and so no paramagnetic product was observed. The paramagnetic species could not be isolated, and it was not possible to determine whether it was due to a genuine Mn\textsuperscript{0} species or impurities. Miller and Myers\textsuperscript{20} dismissed photochemical initiation being responsible for dimer formation.

The strengths of metal-metal bonds of these complexes have been defined and inferred in a number of ways. Jackson and Poë\textsuperscript{21} investigated the kinetics of some reactions of these compounds, the activation enthalpies assigned to homolytic fission of Mn-Mn providing a kinetic measure of the strengths of these bonds, varying with L in the order;

\[ L = \text{CO} \sim P(O\text{Me})_3 \sim P(O\text{Ph})_3 > \text{PET}_3 > \text{PBu}_3 > \text{PPh}_3 \]

the sequence being closely related to the size of the substituents.

From electronic spectra,\textsuperscript{22} assignment of \( h\nu(\sigma \rightarrow \pi^*) \) for \([\text{M(CO)}_4L]\textsubscript{2}\) with varying L provides another measure of the \( \sigma \) interaction between the two metal atoms. Data for \([\text{Co(CO)}_4L]\textsubscript{2}\) complexes show exactly the same form of dependence of \( h\nu(\sigma \rightarrow \pi^*) \) on L as do \([\text{Mn(CO)}_4L]\textsubscript{2}\) and are shown in Table 4.1 for comparison.

It is found that the bonding interaction energies are substantially greater than the energies needed for the complex to undergo homolytic fission because of favourable changes in L-L and M-L interactions as the Mn-Mn bond is stretched. The interaction energies increase as the axial substituents increase in \( \sigma \)-basicity and \( \pi \)-acidity.

\([\text{Mn(CO)}_4\text{PR}_3]\textsubscript{2}\) complexes are well suited to e.s.r. study as both Mn and
P have isotopes with non-zero nuclear spin, and the nature of P–Mn–Mn–P can be investigated. This work makes an interesting comparison with the previous e.s.r. study of [(CO)$_5$Mn$^-$Mn(CO)$_5$]$^-$ and [(CO)$_5$Re$^-$Re(CO)$_5$]$^-$, in which the electrons are added into the metal-metal bond, and [(CO)$_5$Mn$^-$X]$^-$, in which the excess electron is accommodated in the metal-halogen σ* orbitals. One problem concerning all these complexes is the role of the axial ligands; are the excess electrons delocalized on them, or are they lost on electron addition? It was hoped that the two axial $^{31}$P nuclei would give resolved hyperfine coupling, and thus provide information regarding the axial ligands. Reference is also made to a study of $^{13}$CO enriched Mn$_2$(CO)$_{10}$, from which it was hoped that direct information might be gained from $^{13}$C hyperfine coupling.

A similar compound, [Co(CO)$_5$PBU$_3$]$^2$, has recently been studied by Hayashida et al.,$^{24}$ γ-irradiation in MTHF at 77 K produced the anion radical, with the odd electrons occupying the Co-Co σ* orbital together with the Co-P σ* orbital.

**EXPERIMENTAL**

Mn$_2$(CO)$_8$(PBU$_3$)$_2$ and Mn$_2$(CO)$_8$[P(OMe)$_3$]$_2$ were kindly provided by Dr. B. M. Peake, University of Otago, New Zealand. Samples were γ-irradiated.
as pure compounds, and as dilute solutions in MTHF. Degassed solutions
were frozen in liquid nitrogen as small glassy beads, and then γ-
irradiated at 77 K with doses up to 2 MRad.

RESULTS

Of the two complexes studied, Mn₂(CO)₈[P(Bu₃)]₂ gave the best results.
The spectrum showed 11 parallel features as expected for two equivalent
⁵⁵Mn nuclei (⁵⁵Mn has I = ⁵/₂), the outer parallel features comprising
well-defined 1:2:1 triplets assigned to hyperfine coupling to two
equivalent ³¹P nuclei (³¹P has I = ¹/₂) (Fig. 4.2).

It is more difficult to extract the ⁵⁵Mn and ³¹P perpendicular (x and
y) coupling constants, but the best fit is shown using a stick diagram
in Fig. 4.2, although other interpretations are possible. The locations
of the first I = ±5 (⁵⁵Mn) perpendicular features were fixed unambiguously
from the spectrum. It can be seen that the (0) line is almost isotropic
thus fixing the (0) components. The (±1) lines can also be located
unambiguously. Using these field values, it is possible to estimate the
positions of the remaining features. The outer perpendicular features
are broad and not well defined, as is frequently the case with such
spectra, and are concealed under the relatively sharp parallel lines.
It is concluded that the ³¹P splitting on the perpendicular features is
in the range 6 ± 1 G, from the form of the central components.

The high- and low-field features are of comparable intensity, and
analysis of the g-values (g₁ = 2.002 ± 0.001 and gₓ = 2.000 ± 0.001)
indicates almost no g-anisotropy. The e.s.r. parameters for this complex
and other related complexes are shown in Table 4.2.

Solutions of Mn₂(CO)₈[P(OMe)₃]₂ in MTHF after γ-irradiation at 77 K
gave e.s.r. spectra almost indistinguishable from those for the
FIG. 4.2

X-band e.s.r. spectrum for $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ in MIHF after $\gamma$-irradiation at 77 K and anneal

$3250 \text{ G (9.1310 GHz)}$

$50 \text{ G}$

Gain $\times 100$

$M_1^{(55\text{Mn})_\perp}$

$M_1^{(31\text{P})_\parallel}$

$M_1^{(55\text{Mn})_\parallel}$
### TABLE 4.2

E.s.r. parameters for \([\text{Mn}_2(\text{CO})_8(\text{PBU}_3)_2]^\top\) and related complexes

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>(g#)</th>
<th>(g_\perp)</th>
<th>HYPERFINE COUPLING CONSTANTS/G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Metal Nuclei</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(A#)</td>
</tr>
<tr>
<td>([\text{Mn}_2(\text{CO})_8(\text{PBU}_3)_2]^\top)</td>
<td>2.000</td>
<td>2.002</td>
<td>39.5</td>
</tr>
<tr>
<td>([\text{Mn}<em>2(\text{CO})</em>{10}]^\top)\footnote{a}</td>
<td>1.999</td>
<td>1.998</td>
<td>34.9</td>
</tr>
<tr>
<td>([\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2]^\top)\footnote{b,c}</td>
<td>2.009</td>
<td>2.047</td>
<td>41.2</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3)_2]^+)\footnote{d}</td>
<td>1.994</td>
<td>2.157</td>
<td>14.7</td>
</tr>
</tbody>
</table>

\footnote{a} Ref. (J.C.S. Dalton Trans., 1977, 1314)  \footnote{b} Ref. (Chem. Lett., 1980, 517)  \footnote{c} Data reported as: \(A\# = 38.5 \times 10^{-4} \text{ cm}^{-1}\) \(59\text{Co}\) \(A_\perp = 29.4 \times 10^{-4} \text{ cm}^{-1}\) \(31\text{p}\) \(A\# = 85.5 \times 10^{-4} \text{ cm}^{-1}\) \(59\text{Co}\) \(A_\perp = 48.4 \times 10^{-4} \text{ cm}^{-1}\) \(31\text{p}\)  \footnote{d} Ref. (J.C.S. Chem. Comm., 1979, 945)
\([\text{Mn}_2(\text{CO})_{10}]^-\) anion,\(^\text{14}\) so it is not possible to state categorically that
they are due to the \(\text{P}(*\text{Me})_3\) derivative. However, the lines are broad
and could conceivably conceal weak \(^{31}\text{P}\) coupling.

**DISCUSSION**

\(\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2\)

As the species is formed in high yield in MTHF, a solvent well known
for its electron donating properties, it must be the parent anion,
\([\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2]^-\). Consideration of the \(g\)-values, both very close to
free spin, suggests that the unpaired electron must be very isolated from
neighbouring coupled levels. This was also observed previously for
\([\text{Mn}_2(\text{CO})_{10}]^-\) anions.

Assuming that the \(^{31}\text{P}\) hyperfine coupling constants have like signs,
by comparison with studies of similar complexes, then these coupling
constants should be the principal values, and the \(3s\) and \(3p\) orbital
populations obtained from the \(A\) and \(2B\) values. However, because of the
very high spin density on Mn and very low spin density on P, allowance
must be made for indirect dipolar coupling between the metal and ligand
nuclei. This results in a coupling for \(^{31}\text{P}\) of \(\text{ca.}\ 1\ \text{G}\).

The fact that \(A_1 < A_2\) is consistent with a \(\sigma^*\) structure, involving an
anti-bonding combination of \(s-p\) hybridized P lone-pair orbitals, and Mn
\(d_{z^2}\) orbital. It is interesting to compare these results with those for
\([\text{Mn}_2(\text{CO})_{10}]^-\). The \(^{55}\text{Mn}\) hyperfine coupling constants for the two anions
are almost equal, suggesting that the extent of delocalisation of spin
density onto the ligands hardly changed on replacing CO by PR\(_3\), which is
surprising. However, the \(^{31}\text{P}\) hyperfine coupling corresponds to a formal
delocalisation of \(\sim 1\%\) on each ligand. This is no larger than expected
for spin-polarization of \(\sigma\) electrons,\(^\text{25}\) so that delocalisation is
effectively zero.

It is possible that electron addition causes the metal-metal bond to stretch, reducing the $\sigma^*$ orbital energy, and thus the unpaired electron is strongly confined to the metal-metal bond (Fig. 4.3).

![Diagram of metal-metal bond stretching](image)

**FIG. 4.3**
Metal-metal bond stretches to lower $\sigma^*$ orbital and accommodate the electron.

It is interesting to compare this with the results obtained from a study of $^{13}$CO labelled $\text{Mn}_2(\text{CO})_{10}$. The spectra seemed identical with those for the $^{12}$CO anion, and no $^{13}$C coupling was resolved. However, a coupling to $^{13}$C $< 4$ G could have been concealed beneath the quite broad features. Loss of one axial ligand would make the two Mn atoms inequivalent, which was not observed, and although it is possible that both axial ligands were lost, it seems unlikely. In view of the results for the diphosphine substituted anion, delocalisation onto the axial ligands would be expected to be small. If spin-polarization is the major source of coupling, an upper limit of ca. 5 G would be expected. Thus it is tempting to argue that in this case the Mn-Mn bond stretches to accommodate the excess electron.

However, comparing the data for $[\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2]^+$ and $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]^+$, the latter having a $\sigma^*$ structure, as indicated by e.s.r. parameters, but more delocalisation onto the PR$_3$ ligands, a
reasonable alternative to the stretching being confined to the metal-metal bond seems to be slight stretching of all three of the localized bond components. This would equally well stabilize the orbital $\sigma_4$ involved (Fig. 4.4). The estimated total spin-density on $^{31}\text{P}$ decreases from $\sim23\%$ in the di-cobalt derivative to $\sim1\%$ in the case of di-manganese. This trend is expected for a $\sigma^*$ antibonding orbital; i.e. as the electronegativity of the metal increases, relative to $\text{P}$ in this case, so the unpaired electron shifts towards the more electronegative $\text{P}$. (Fig. 4.5); but such a redistribution of spin density is remarkable, being far greater than the trends observed for $\sigma^*$ radicals involving only one localized bond.\textsuperscript{25,26} For example, although the spin density in various $V_k$ centres such as $(\text{ClX}^-)$ is found to shift increasingly from Cl towards X in the order of decreasing electronegativity, i.e. $F > Cl > Br > OH > I$,\textsuperscript{29} the changes in spin distribution are much less drastic than those observed on
going from the cobalt derivative to the manganese derivative.

This greatly increased sensitivity to changes in metal electronegativity is probably due to the fact that there is a choice in the mode of deformation such that the electron is excluded from the metal-ligand region if elongation is confined to the metal-metal bond. It is valid to argue that electron addition could conceivably cause metal-metal bond breakage as opposed to loss of an axial ligand.

Kawamura et al. have studied the cation radical of \( \text{Rh}_2(\text{O}_2\text{CCH})_4(\text{PPh}_3)_4 \) and found a large electron density on the \(^{31}\text{P}\) atoms (a total of 53%). Although the perpendicular feature for \(^{103}\text{Rh}\) was not resolved, and so good hyperfine coupling constants were not obtained for these nuclei, they suggested that the unpaired electron was excluded from the Rh-Rh bond and largely confined to the outer Rh-P bonds. \([\text{Rh}_2(\text{O}_2\text{CCH})_4(\text{PPh}_3)_4]^+\) is thought to have a \(\text{---}\sigma_1^1\) structure [Fig. 4.4] and the results seem to reflect that this orbital is bonding in the Rh-Rh region, but antibonding in Rh-P.

Hyperfine coupling constants obtained from \(^{31}\text{P}\) enable 3s and 3p orbital populations to be estimated (Table 4.3), and the ratio 3p:3s can lead to calculation of the C-P-C bond angles in R₃P ligands. The p:3s ratio will obviously fall if there is a greater s-admixture, illustrated by the fact that in σ* centres such as \([\text{R}_3\text{P}\_\perp\text{PR}_3]^+\), \(^{32}\text{P}_Z(\sigma)\) is not com-
TABLE 4.3

Estimated orbital populations

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>METAL (^a)</th>
<th>PHOSPHINE LIGANDS (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>([\text{Mn}_2(\text{CO})_8(\text{PBU}_3)_2]) (^\ddagger)</td>
<td>80</td>
<td>ca. 6 (^d)</td>
</tr>
<tr>
<td>([\text{Mn}<em>2(\text{CO})</em>{10}] (^e)</td>
<td>78</td>
<td>ca. 6</td>
</tr>
<tr>
<td>([\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2]) (^f)</td>
<td>62</td>
<td>ca. 2</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{O}_2\text{C}t)_4(\text{PPh}_3)_2]) (^g)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Total on both metal atoms;

\(^b\) Total on both phosphorus atoms;

\(^c\) After correction for indirect dipolar coupling, probably entirely due to spin-polarization;

\(^d\) Estimated from isotropic coupling on assumption that spin-polarization of inner \(s\)-orbitals could give ca. -80 G for unit spin density;

\(^e\) Ref. 14 (J.C.S. Dalton, 1977, 1314);

\(^f\) Ref. 24 (Chem. Lett., 1980, 577);

\(^g\) Ref. 27 (J.C.S. Chem. Comm., 1979, 945).
pletely available, provided the $R_3P$ local configuration remains pyramidal, hence there is a degree of $s$-admixture dependent on the pyramidal character: $p:s$ for such centres is ca. 3.4.

The $p:s$ ratio for $[Mn_2(CO)_8(PBu_3)_2]^*$ is ca. 3±1, which is close to the values for the dimer $\sigma^*$ cations $[R_3P-PR_3]^+$. The larger value of 4.7 for $[Rh_2(O_2CMe)_3(PPh_3)_2]^+$ suggests a slight flattening of $R_3P$, with a C-P-C bond angle of 112°, which is between that of PPh$_3$ (103°) and those of cation radicals of phosphines (ca. 115°). Raynor$^{30}$ has calculated the bond angle for Co-PL$_3$ complexes, the surprisingly small $p:s$ ratio of 2.0 reflected the small bond angles (102°-104° region) of most phosphine ligands in these complexes.

Finally, a mention must be made of the $p:s$ ratio for $[Co_2(CO)_6(PBu_3)_2]^*$, which was found to be 7. This seems anomalously high for PR$_3$ ligands, although why this should be so is not understood.

$Mn_2(CO)_8[P(OMe)_3]_2$

Despite the fact that the e.s.r. spectra for $Mn_2(CO)_8[P(OMe)_3]_2$ were almost indistinguishable from those for the $[Mn_2(CO)]^-$ anion, the great similarity between $g$ and $^{55}Mn$ data for the $[Mn_2(CO)]^-$ and $[Mn_2(CO)_8(PBu_3)_2]^-$ and the very small $^{31}P$ couplings suggest that possibly the $[Mn_2(CO)_8[P(OMe)_3]_2]^-$ anion was prepared.

**PART II** Hg[CpM(CO)$_n$]$_2$ and derivatives

**DESCRIPTION**

This group of M-Hg-M complexes were also initially thought to contain bridging carbonyl groups, but spectroscopic$^{31}$ and X-ray crystallographic$^{32}$ studies have revealed linear, unsupported metal-mercury-metal covalent bonds. The mercury atom has little or no tendency to be 4-coordinate in
these symmetrical trimetallic complexes, and in this respect they resemble organo-mercury compounds. They can be compared to dialkyls and diaryls of mercury, \( \text{R}_2\text{Hg} \), which contain linear \( \text{C-Hg-C} \) covalent bonds.

The complexes\(^{33-36} \) may be prepared by standard procedures given in the literature, the method involving the reaction of a metal cyclopentadienide and the corresponding metal carbonyl to form \([\text{MCp(CO)}_n]\), and subsequent precipitation by \( \text{Hg(CN)}_2 \).

Infra-red studies of these complexes assign bands in the low frequency region to mercury-metal stretching modes.\(^{37} \) The spectra are quite similar in the CO stretching region. Fischer and Noake\(^{38} \) postulate a single isomer with a skew configuration of \( \text{M(CO)}_3\text{C}_5\text{H}_5 \) groups about a linear \( \text{M-Hg-M} \) system. Consideration of the \( \nu(\text{CO}) \) stretching frequencies for \( \text{Hg[FeCp(CO)}_2]_2 \)\(^{39} \) shows the spectra to be consistent with a structure of \( \text{C}_2 \), symmetry containing a linear arrangement of metal atoms.

\( \text{Hg[MCp(CO)}_n]_2 \) is well suited to e.s.r. study because mercury has two naturally occurring isotopes with non-zero nuclear spin. In the cases where \( \text{M=} \text{Mo, Cr} \), analysis is simplified as these metals also have isotopes with non-zero nuclear spin. The mercury hyperfine coupling is very large compared to Cr, Mo so the hyperfine interactions with these metals should be easily separated.

Exposure of \( \text{Hg[Co(CO)}_4]_2 \) in MeTHF to ionizing radiation at 77 K, and subsequent e.s.r. study,\(^{40} \) revealed the formation of an electron capture centre, \( \text{Hg[Co(CO)}_4]_{2}^- \). The unpaired electron was interpreted as occupying a \( d_{z^2}/p_{z^2} \) orbital on Co, with 34% orbital occupancy on each atom, and 28% s-occupancy on Hg. The structural analogies between this and the \( \text{M-Hg-M} \) complexes studied in this chapter are obvious, and the results will be discussed and compared.
EXPERIMENTAL

The trinuclear complexes, Hg\[MCp(CO)\_n\]\_2 and their bromo-derivatives, BrHgMCp(CO)\_n, were supplied by Dr. S. Bratt. They were studied as powders and in solutions of dried, degassed MTHF, frozen in liquid nitrogen as small beads, and \(\gamma\)-irradiated at 77 K for periods of up to 2 hours.

RESULTS

Solutions of the complexes in MTHF after \(\gamma\)-irradiation at 77 K showed the high field lines (\(B_2\)) for \(^{199}\text{Hg}\) (16.8% natural abundance, \(I = \frac{1}{2}\)) and \(^{201}\text{Hg}\) (13.2%, \(I = \frac{3}{2}\)) in all cases. This analysis of the mercury coupling was aided by the fact that \(^{199}\text{Hg}\) and \(^{201}\text{Hg}\) occur at about the same abundance, and so the \(^{199}\text{Hg}\) features should have twice the intensity of the \(^{201}\text{Hg}\) because of the ratio of their nuclear spins. The low field lines for \(^{201}\text{Hg}\) were also present for all the complexes studied, but the low field line for \(^{199}\text{Hg}\) was not observed except in the case of Hg[FeCp(CO)]\_2. The non-magnetic mercury feature in the centre region of the spectrum is taken as \(B_0\).

The spectrum obtained from Hg[MoCp(CO)]\_2 in MTHF (Fig. 4.6a and b) showed some anisotropy on the high field \(^{199}\text{Hg}\) line, but this was not apparent on the \(^{201}\text{Hg}\) features. There was no evidence of any molybdenum satellites (\(^{95}\text{Mo}\), 15.8% natural abundance, \(I = \frac{5}{2}\); \(^{97}\text{Mo}\), 9.6%, \(I = \frac{5}{2}\)) on either the \(^{199}\text{Hg}\) or \(^{201}\text{Hg}\) features, although a consideration of the natural abundance of Mo suggests that features due to two equivalent Mo atoms should be visible. Presumably such features are hidden under the wings of the central part of the spectrum. If this were the case, taking the width of the central lines as 160 G suggests that the hyperfine coupling to Mo must be less than, or equal to, 32 G, which is an acceptable
FIG. 4.6a
X-band e.s.r. spectrum of Hg[MoCp(CO)$_3$]$_2$ in MTHF after γ-irradiation at 77 K

Gain x 10
FIG. 4.6b
X-band e.s.r. spectrum for Hg[MoCp(CO)₃]₂ in MTHF after γ-irradiation at 77 K

2200G

200G

H

^{201}\text{Hg}\begin{array}{c}
-\frac{3}{2} \\
-\frac{1}{2} \\
+\frac{1}{2}
\end{array}
figure for Mo.

Hg[CrCp(CO)$_3$]$_2$ in MTHF showed no anisotropy on the $^{199}$Hg or $^{201}$Hg features, and no chromium satellites were observed ($^{53}$Cr has natural abundance 9.5%, $I = \frac{3}{2}$) (Fig. 4.7a and b).

The only complex to show the $^{199}$Hg low field component was Hg[FeCp(CO)$_2$]$_2$ (Fig. 4.8). The mercury experimental e.s.r. parameters are shown in Table 4.4.

The bromo-derivatives also showed the high field $^{199}$Hg and $^{201}$Hg components, but the low field features were not present. In the spectrum of BrHgMoCp(CO)$_3$ (Fig. 4.9a and b) bromine hyperfine coupling was evident both in the central region and on the high field $^{199}$Hg feature ($^{79}$Br has 50.5% natural abundance, $I = \frac{5}{2}$; $^{81}$Br 49.5%, $I = \frac{3}{2}$) with $A_\parallel(\text{Br}) = 125$ G, $A_\perp(\text{Br}) = 60$ G. Unexpectedly, $g_\parallel$ was less than free spin ($= 1.943$) indicating coupling to empty orbitals. No hyperfine structure attributable to Mo was observed, this would be expected to be the case. The spectrum of BrHgCrCp(CO)$_3$ was very similar to that of BrHgMoCp(CO)$_3$ (Fig. 4.10), showing almost the same bromine couplings. Bromine hyperfine coupling was clearly seen in the central region of the spectrum of BrHgFeCp(CO)$_2$ (Fig. 4.11a and b), with $A_\parallel(\text{Br}) = 117$ G. The bromine perpendicular components were not so well defined, but $A_\perp(\text{Br})$ could be estimated to be between 50 and 70 G. An approximate value of $\sim 60$ G is taken. In all the bromo-derivatives, $g_\parallel$ is found to be below free spin. The experimental e.s.r. parameters for the bromo-derivatives are shown in Table 4.5.

DISCUSSION

It is concluded that electron capture has occurred with all the complexes studied in MTHF, the solvent being a good effective electron donor.

Because of the large coupling constants involved, the Breit-Rabi
FIG. 4.8

X-band e.s.r. spectrum of Hg[FeCp(CO)₂]₂ in MTHF after γ-irradiation at 77 K
FIG. 4.9a

X-band e.s.r. spectrum for BrHgMoCp(CO)$_3$ in THF after $\gamma$-irradiation at 77 K
FIG. 4.9b

X-band e.s.r. spectrum of BrHgMoCp(CO)$_3$ in MeHF after $\gamma$-irradiation at 77 K
FIG. 4.10
X-band e.s.r. spectrum of BrHgCrCp(CO)$_3$ in MTHF after $\gamma$-irradiation at 77 K
FIG. 4.11a
X-band e.s.r. spectrum of BrHgFeCp(CO)$_2$
in MIHF after γ-irradiation at 77 K
FIG. 4.11b
X-band e.s.r. spectrum of BrHgFeCp(CO)$_2$ in MIHF after γ-irradiation at 77 K
TABLE 4.4

Experimental ESR and derived parameters for irradiated Hg[MCP(CO)₃]₂ complexes and BrHgMCP(CO)₃ derivatives

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>B₀</th>
<th>B₁⁽¹⁹⁹Hg⁾ (exp)</th>
<th>B₁⁽¹⁹⁹Hg⁾ (calc)</th>
<th>B₂⁽¹⁹⁹Hg⁾ (exp)</th>
<th>A⁽¹⁹⁹Hg⁾ (corr)</th>
<th>B₁⁽²⁰¹Hg⁾ (exp)</th>
<th>B₁⁽²⁰¹Hg⁾ (calc)</th>
<th>B₂⁽²⁰¹Hg⁾ (exp)</th>
<th>A⁽²⁰¹Hg⁾ (predicted)</th>
<th>g₁₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg[MoCp(CO)₃]₂</td>
<td>3290</td>
<td>-</td>
<td>-319</td>
<td>4420</td>
<td>3442</td>
<td>970</td>
<td>966</td>
<td>4870</td>
<td>1254</td>
<td>1268</td>
</tr>
<tr>
<td>Hg[CrCp(CO)₃]₂</td>
<td>3320</td>
<td>-</td>
<td>+60</td>
<td>4420</td>
<td>3290</td>
<td>1090</td>
<td>1091</td>
<td>4860</td>
<td>1214</td>
<td>1212</td>
</tr>
<tr>
<td>Hg[FeCp(CO)₂]₂</td>
<td>3290</td>
<td>1640</td>
<td>1694</td>
<td>4100</td>
<td>2149</td>
<td>1924</td>
<td>1924</td>
<td>4360</td>
<td>800</td>
<td>792</td>
</tr>
<tr>
<td>BrHgMoCp(CO)₃</td>
<td>3310</td>
<td>-</td>
<td>-926</td>
<td>4500</td>
<td>3716</td>
<td>-</td>
<td>659</td>
<td>5038</td>
<td>1395</td>
<td>1369</td>
</tr>
<tr>
<td>BrHgCrCp(CO)₃</td>
<td>3300</td>
<td>-</td>
<td>-494</td>
<td>4450</td>
<td>3530</td>
<td>-</td>
<td>916</td>
<td>4910</td>
<td>1281</td>
<td>1301</td>
</tr>
<tr>
<td>BrHgFeCp(CO)₂</td>
<td>3290</td>
<td>-</td>
<td>1253</td>
<td>4200</td>
<td>2516</td>
<td>-</td>
<td>902</td>
<td>4480</td>
<td>902</td>
<td>927</td>
</tr>
</tbody>
</table>
### TABLE 4.5
Experimental ESR parameters for bromo-derivatives

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$A_{\parallel}$(Br)</th>
<th>$A_{\perp}$(Br)</th>
<th>$g_{\parallel}$</th>
<th>$g_{\perp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrHgMoCp(CO)$_3^-$</td>
<td>125</td>
<td>60</td>
<td>1.943</td>
<td>1.990</td>
</tr>
<tr>
<td>BrHgCrCp(CO)$_3^-$</td>
<td>125</td>
<td>60</td>
<td>1.999</td>
<td>1.997</td>
</tr>
<tr>
<td>BrHgFeCp(CO)$_2^-$</td>
<td>117</td>
<td>~60</td>
<td>1.990</td>
<td>1.982</td>
</tr>
</tbody>
</table>

### TABLE 4.6
Approximate orbital populations

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$^{199}$Hg %s$^a$</th>
<th>$^{81}$Br %p$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg[MoCp(CO)$_3$]$_2^-$</td>
<td>27</td>
<td>-</td>
</tr>
<tr>
<td>Hg[CrCp(CO)$_3$]$_2^-$</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td>Hg[FeCp(CO)$_2$]$_2^-$</td>
<td>17</td>
<td>-</td>
</tr>
<tr>
<td>BrHgMoCp(CO)$_3^-$</td>
<td>29</td>
<td>9</td>
</tr>
<tr>
<td>BrHgCrCp(CO)$_3^-$</td>
<td>28</td>
<td>8</td>
</tr>
<tr>
<td>BrHgFeCp(CO)$_2^-$</td>
<td>20</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$ Estimated using the "experimental" result for Hg$^+$ ions (reference 41);

$^b$ Estimated using data from reference 25.
formula must be applied to obtain the corrected isotropic coupling:

\[
A = \frac{2B_0(B_2 - B_0)}{B_0(2I+1) - B_2} = \frac{2B_0(B_0 - B_1)}{B_0(2I+1) - B_1}
\]

Resubstitution into the equation enables \(B_1\), the low field component, to be predicted. These values are shown in Table 4.4, the negative values may clearly be disregarded. The same procedure may be applied to both \(^{199}\text{Hg}\) and \(^{201}\text{Hg}\), and \(A(^{201}\text{Hg})\) may be predicted from \(A(^{199}\text{Hg})\) and the \(2B^0\) values for each isotope;

\[
A(^{201}\text{Hg}) = A(^{199}\text{Hg}) \times \frac{105}{285}
\]

It is seen that the isotropic coupling to mercury increases in the order Fe < Cr < Mo in both the trinuclear complexes and their bromo-derivatives. The isotropic coupling to \(^{199}\text{Hg}\) can be used in a rough estimate of the percentage \(s\)-character on the mercury atom by dividing by \(A^o\). In this case, the "experimental" result for \(\text{Hg}^+\) ions is used as a rough guide. Approximate orbital populations are given in Table 4.6.

The results for the trinuclear complexes may be compared with those obtained for \(\text{Hg}[\text{Co}(\text{CO})_4]_2^-\) in a previous study. In this case, the isotropic coupling to \(^{199}\text{Hg}\) was found to be 3350 G, which is in good agreement with that for the molybdenum-mercury and chromium-mercury complexes. Hyperfine coupling to cobalt was also observed \([A_\parallel(\text{Co}) = 39.3 \text{ G, } A_\perp(\text{Co}) = 39.3 \text{ G}]\), but the mercury-metal complexes studied here showed no evidence of metal coupling. However, this is probably because of the low abundance and low magnetic moments of molybdenum and chromium \((^{95}\text{Mo has 15.72% natural abundance, } \mu = -0.9133; \quad ^{97}\text{Mo has 9.46% natural abundance, } \mu = -0.9325; \quad ^{53}\text{Cr has 9.55% natural abundance, } \mu = -0.4744)\), compared to those of cobalt (100% natural abundance, \(\mu = +4.649\)). However, the metal atoms must still be present in order to affect the mercury coupling in the manner observed.
Taking into account the electronegativities of the metal atoms attached to Hg in both the tri-nuclear and bromo-derivatives, one would expect to observe a trend for such $\sigma^*$ complexes, i.e. the higher the electronegativity of the metal, the greater the $\%s$ orbital population on Hg (Fig. 4.12);

![Diagram](image)

The results for the $\%s$ orbital population on Hg on going from the Cr to the Mo anions show only a very slight increase, however there is a substantial decrease in the case of the Fe anions, (Table 4.6) which is unexpected. This discrepancy may be due to the fact that the Cr and Mo anions are formally $d^5$ and the Fe derivatives are $d^7$. The effect of these extra electrons could reduce the effective electronegativity of the metal, resulting in a decreased Hg coupling. Such an effect is also observed in complexes containing metal-halogen bonds, discussed in chapter 5.

The bromo-derivatives all show evidence of coupling to bromine of the same form as $\text{Mn(CO)}_5\text{Br}$, in that $A_{g} \approx 2A_{l}$. An interesting comparison may be made with $\text{XHgCo(CO)}_4$ complexes, where $X=\text{Cl, Br, SCN}$. It was thought that, in this case, $\gamma$-irradiation of the compounds in MTHF resulted in loss of the ligand $X$ as no halogen or pseudo-halogen coupling was observed. Bromine has obviously been retained in the complexes studied here.
REFERENCES FOR CHAPTER 4

CHAPTER 5

COMPLEXES CONTAINING METAL-HALOGEN BONDS
INTRODUCTION

It is well established that a binuclear metal carbonyl compound containing a metal-metal bond may be cleaved by halogens to form the corresponding halogeno-metal carbonyl derivative. Examples include [Cr(CO)₅I]⁻, M(CO)₅X (where M = Mn, Tc, Re; X = Cl, Br, I), Mo(π-C₅H₅)(CO)₃I, and M(π-C₅H₅)(CO)₅X, formed by the direct halogenation of [Cr₂(CO)₁₀]²⁻,¹ M₂(CO)₁₀², [Mo(π-C₅H₅)(CO)₃]³⁻, and [M(π-C₅H₅)(CO)₂]⁴⁻ (M = Fe, Ru, Os).

Carbonyl complexes containing metal-halogen bonds have been studied by e.s.r. after exposure to ionizing radiation at 77 K.⁵ The manganese pentacarbonyl halides [Mn(CO)₅X] (X = Cl, Br, I) produced an S = ½ centre having a g-value ca. 2 and a large hyperfine coupling to ⁵⁵Mn and halogen nuclei. The results were interpreted in terms of electron addition into a σ* orbital involving mainly the metal d₅z² and halide p₂ orbitals. All three complexes also exhibited a second centre, concluded to be cations formed by loss of an electron and one or more CO groups, with unpairing of the remaining electrons to give S = ⁵/₂.

The isostructural Cr, Mo and W derivatives have similarly been studied⁶ in this laboratory. The tetraalkylammonium salts of (CO)₅M⁺ all gave electron addition products when γ-irradiated in MTHF at 77 K. The captured excess electron was interpreted as being accommodated in the metal-halogen σ* orbital, comprised, as in the case of [Mn(CO)₅X], of primarily (d₅z²-p₂).

This chapter deals with such a study of Re(CO)₅X, where X = Br, I, the aim being to prepare the (CO)₅Re-X⁻ anion to compare with other members of the isostructural series. The second part of the chapter discusses complexes containing metal-halogen bonds in which a cyclopentadienyl ring is bonded to the metal. (C₅H₅)Mo(CO)₅Mo(C₅H₅) and (C₅H₅)W(CO)₅W(C₅H₅) were the first examples of compounds with only one cyclopentadienyl ring
bonded to a transition metal atom to be described.\(^7\) A binuclear "triple-decker sandwich" structure was initially proposed for these compounds, in which all the CO groups were located between the metal atoms in a 5- or 6-membered ring for Mo and W respectively. However, a 3-dimensional X-ray diffraction study of the molybdenum complex\(^8\) suggested a non-linear arrangement with a metal-metal bond and non-bridging independently coordinated CO groups that form no ring. This provides for a completed 18-electron shell for the metal atom in accord with the observed diamagnetism of the compound.

The cyclopentadienyl ring in mono- and binuclear cyclopentadienyl-carbon monoxide and associated compounds is bonded to the metal atom in a manner similar to that in bis-cyclopentadienyl compounds.\(^9,10\) However, the symmetries of compounds with only one \(C_5H_5\) ring per metal atom are different from the highly symmetrical bis-cyclopentadienyl compounds. It is difficult to construct a complete bonding scheme for these low symmetry compounds, but by splitting the molecule into two parts of relatively high local symmetry, and considering each separately, an overall bonding scheme may be proposed by combination of the two.

**PART I**

**DESCRIPTION**

Re\((CO)\_5X\) (where \(X = \text{Cl, Br or I}\)) may be prepared by the direct halogenation of the parent binuclear complex,\(^11\) or carbonylation of the complex \(K_2\text{ReX}_6;\(^12,13\)

\[
K_2\text{ReX}_6 + CO + Cu \rightarrow \text{Re(CO)}_5X
\]

These rhenium halogenopentacarbonyls possess \(C_{4v}\) symmetry\(^14\) by analogy with \(\text{HMn(CO)}_5\) which has been studied by X-ray diffraction\(^15\) and shown to
have this symmetry. Infra-red and Raman data have been shown to be consistent with this assignment.\textsuperscript{14,16}

Cleavage of the metal-metal bond in the parent \( \text{Re}_2(\text{CO})_{10} \) has been the subject of photochemical study.\textsuperscript{17} Photo-excitation of the binuclear complex in \( \text{CCl}_4 \) results in rupture of Re-Re bond and two molecules of the halogenopentacarbonyl complex are formed:

\[
\text{Re}_2(\text{CO})_{10} \xrightarrow{\text{313 nm} \ \text{CCl}_4} 2 \text{Re}(\text{CO})_5\text{Cl}
\]

supporting the concept of symmetrical metal-metal bond cleavage. Irradiation at 313 nm or 366 nm promotes a \( \sigma_b + \sigma^* \) excitation which results in a significantly weakened Re-Re bonding interaction.

**EXPERIMENTAL**

Purified samples of the rhenium pentacarbonyl halides were kindly supplied by Dr. John Holloway. Solutions of the compounds in degassed MTHF were cooled to 77 K, and exposed to \( ^{60}\text{Co} \gamma\)-rays for periods of up to 2 hours.

**RESULTS**

The spectrum for \( \text{Re(CO)}_5\text{Br} \) in MTHF after \( \gamma \)-irradiation at 77 K is shown in Fig. 5.1. Rhenium has two magnetic isotopes, \(^{185}\text{Re} \) (37.1\% natural abundance) and \(^{187}\text{Re} \) (62.9\% natural abundance), both with \( I = \frac{5}{2} \), having such similar magnetic moments that transitions from each are normally coincident. The parallel features, which exhibit very small second order shifts, are clearly visible, the outer features showing evidence of coupling to \(^{81}\text{Br} \) (49\% natural abundance, \( I = \frac{5}{2} \)) and \(^{79}\text{Br} \).

\( \text{Re(CO)}_5\text{I} \) in MTHF showed equally well defined parallel features (Fig. 5.2), with clear evidence of coupling to \(^{127}\text{I} \) (100\% natural abundance,
FIG. 5.1
X-band e.s.r. spectrum for (CO)$_3$ReBr in MTHF after γ-irradiation at 77 K
FIG. 5.2
X-band e.s.r. spectrum of (CO)₅ReI in MTHF, after γ-irradiation at 77 K.
I = 9/2). In both cases, it was more difficult to assign the perpendicular components, which exhibit larger shifts than the parallel features. However, the best fit is shown in both Figs. 5.1 and 5.2. The central features in both spectra are due to solvent radicals.

The e.s.r. parameters are summarized in Table 5.1, alongside results for other metal-halogen complexes for comparison.

DISCUSSION

By analogy with the previous e.s.r. study of \( \gamma \)-irradiated \([\text{Mn(CO)}_5\text{X}]\), it would be expected that in the case of \([\text{Re(CO)}_5\text{X}]\), the excess electron would occupy a \( \sigma^* \) orbital involving mainly the metal \( d_{z^2} \) and halide \( p_z \) orbitals. The experimental e.s.r. parameters are summarized in Table 5.1, the results for the Cr, Mo, W and Mn derivatives are presented alongside for comparison. The similarity between the results for Re and Mn appear to confirm this assumption.

Approximate orbital populations have been estimated in the usual way, using calculated unit populations (Table 5.2). In deriving these data, it is assumed that the halogen hyperfine components \( A_\parallel \) and \( A_\perp \) (\(^{127}\)I and \(^{79/81}\)Br) are both positive, in common with other \( \sigma^* \) halogen complexes.

However, when considering the metal hyperfine tensor components for \((\text{CO})_5\text{Mn}^-\text{hal}^- \) anions, the results required that \( A_\parallel \) be positive and \( A_\perp \) negative. So, although this is not necessarily the case for the Re complexes, special attention must be paid to the sign of \( A_\perp \). It was found that by using negative values of \( A_\perp \), higher anisotropic values (2B) were obtained. The higher value is clearly preferable in the case of \((\text{CO})_5\text{ReBr}^-\), but for \((\text{CO})_5\text{ReI}^- \) a \( d \)-orbital population of 92% is probably too high, so a positive value for \( A_\perp \) is favoured. Calculated orbital populations are shown in Table 5.3.
### TABLE 5.1
Experimental ESR parameters for metal-halogen complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>g-values</th>
<th>Hyperfine Coupling/G</th>
<th>Halogen</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{</td>
<td></td>
<td>}$</td>
<td>$g_{\perp}$</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{ReBr}^-$</td>
<td>1.999</td>
<td>2.002</td>
<td>320</td>
<td>160</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{ReI}^-$</td>
<td>2.002</td>
<td>2.003</td>
<td>425</td>
<td>223</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{CrI}^2^-$</td>
<td>2.000</td>
<td>1.997</td>
<td>145</td>
<td>93</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{MoI}^2^-$</td>
<td>1.999</td>
<td>2.000</td>
<td>235</td>
<td>153</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{WI}^2^-$</td>
<td>1.999</td>
<td>2.001</td>
<td>256</td>
<td>164</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{MnCl}^- \text{a}$</td>
<td>2.000</td>
<td>2.001</td>
<td>38.8</td>
<td>19.4</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{MnBr}^- \text{a}$</td>
<td>2.003</td>
<td>2.003</td>
<td>240</td>
<td>119</td>
</tr>
<tr>
<td>$(\text{CO})_3\text{MnI}^- \text{a}$</td>
<td>2.000</td>
<td>2.004</td>
<td>292</td>
<td>155</td>
</tr>
</tbody>
</table>

\text{a} Taken from ref. 5.
### TABLE 5.2

Derived ESR parameters + calculated orbital populations for halogen atoms

<table>
<thead>
<tr>
<th>Complex</th>
<th>$A_{iso}/G$</th>
<th>$2B/G$</th>
<th>$% s^2$</th>
<th>$% p^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO)$_5$ReBr$^-$</td>
<td>213</td>
<td>107</td>
<td>1.7</td>
<td>22</td>
</tr>
<tr>
<td>(CO)$_5$ReI$^-$</td>
<td>290</td>
<td>134.5</td>
<td>2.0</td>
<td>28</td>
</tr>
<tr>
<td>(CO)$_5$CrI$^{2-}$</td>
<td>110</td>
<td>45</td>
<td>0.7</td>
<td>9.9</td>
</tr>
<tr>
<td>(CO)$_5$MoI$^{2-}$</td>
<td>180</td>
<td>55</td>
<td>1.2</td>
<td>12.1</td>
</tr>
<tr>
<td>(CO)$<em>5$W$</em>{2}^-$</td>
<td>195</td>
<td>61</td>
<td>1.3</td>
<td>13.5</td>
</tr>
<tr>
<td>(CO)$_5$MnCl$^-$</td>
<td>26</td>
<td>13</td>
<td>1.2</td>
<td>13.0</td>
</tr>
<tr>
<td>(CO)$_5$MnBr$^-$</td>
<td>159</td>
<td>81</td>
<td>1.3</td>
<td>16.0</td>
</tr>
<tr>
<td>(CO)$_5$MnI$^-$</td>
<td>201</td>
<td>91</td>
<td>1.5</td>
<td>20.0</td>
</tr>
</tbody>
</table>

$^a$ Estimated from data in Ref. 30

$^b$ Estimated from data in Ref. 31
TABLE 5.3
Derived ESR parameters + calculated orbital populations
for metal atoms

<table>
<thead>
<tr>
<th>Complex</th>
<th>α</th>
<th>A_{iso}/G</th>
<th>2B/G</th>
<th>s^2/δ^b</th>
<th>d^2/ε^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO)_5ReBr^-</td>
<td>α</td>
<td>+113</td>
<td>+67</td>
<td>5.3</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>+6.7</td>
<td>+173</td>
<td>4.7</td>
<td>87</td>
</tr>
<tr>
<td>(CO)_5ReI^-</td>
<td>α</td>
<td>+108</td>
<td>+117</td>
<td>5.5</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>+42</td>
<td>+183</td>
<td>5.1</td>
<td>92</td>
</tr>
<tr>
<td>(CO)_5CrI_2^-</td>
<td>α</td>
<td>+12.5</td>
<td>+2.7</td>
<td>8.2</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>-2.3</td>
<td>+17.3</td>
<td>4.0</td>
<td>86</td>
</tr>
<tr>
<td>(CO)_5MoI_2^-</td>
<td>α</td>
<td>+10.7</td>
<td>+7.3</td>
<td>6.2</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>+1.3</td>
<td>+16.7</td>
<td>5.0</td>
<td>60</td>
</tr>
<tr>
<td>(CO)_5W_2^-</td>
<td>α</td>
<td>+12</td>
<td>+24</td>
<td>5.6</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>-17</td>
<td>+69</td>
<td>1.3</td>
<td>63</td>
</tr>
<tr>
<td>(CO)_5MnCl^-</td>
<td>β</td>
<td>-17</td>
<td>+65</td>
<td>1.3</td>
<td>59</td>
</tr>
<tr>
<td>(CO)_5MnBr^-</td>
<td>β</td>
<td>-15</td>
<td>+66</td>
<td>1.2</td>
<td>60</td>
</tr>
</tbody>
</table>

α signifies A// and A_4 of like signs
β " " " opposite signs
b Estimated from data in Ref. 30
c " " " Ref. 31
The $g$-characters ($a_s^2$) derived from the metal hyperfine parameters were calculated by subtracting the normal spin polarization values from the experimental isotropic coupling constants, giving the positive contributions assigned to admixtures of outer $g$-orbitals. In all cases, there appears to be a relatively high outer $g$-orbital admixture.

The spin densities on the metal ions estimated from the metal hyperfine coupling constants confirm that the excess electron is remarkably confined to the metal-halogen $\sigma$ bonding region, although these values can only be considered as a rough indication of the true values. Delocalization onto axial or equatorial CO groups must be small.

Certain trends in the halogen hyperfine coupling appear in the results. As illustrated in Fig. 5.3, the higher the electronegativity of the metal, for a given halogen, the higher the spin density on the halogen;

![Image](image.png)

**FIG. 5.3**

The upward trend in $\pi$-orbital population for the I atom observed on going from Cr to W implies an increase in effective electronegativity for these metals. Electronegativity values increase across a period, and this is observed in an increase of $\pi$-orbital spin density on passing from Cr to Mn. A similar trend is observed from Mn to Re.

The sharp fall in halogen spin density on going from I $\rightarrow$ Br $\rightarrow$ Cl again follows the expected behaviour for a $\sigma^*$ electron, i.e. the higher the electronegativity of the halogen, for a given metal, the lower the spin density on the halogen (Fig. 5.4);
This is well illustrated by the Mn and Re results. Conversely, the higher the electronegativity of the halogen, the higher the spin-density on the metal. This is evident from the Re results, but there is a lack of trend in the case of Mn. There may be a compensatory shift between the different ligands, leaving the metal relatively unaffected.

Absence of any good electronegativity parameters for heavy elements precludes any attempt to quantify these results.

In general, as the p-character increases on the halogen, so does the estimated s-character. A previous e.s.r. study of σ* radical anions derived from halogen derivatives of perfluorobenzene also showed the spin-density on the halogen atom to increase in the order Cl < Br < I, as already mentioned. A plot of %s vs. %p for a range of these complexes showed a p:s ratio of ca. 15. A similar plot for the σ* anions studied in this work shows a reasonably good correlation, with a slope of 13.8 (Fig. 5.5). Thus it would appear that the degree of s-p admixture for the halogens is almost constant in such radicals and is independent of the group to which the halogen is bound.

Special mention must be made of the axial CO ligand. In all the complexes studied, it is quite possible that the axial carbonyl ligand may be lost on electron addition. This possibility has been investigated by using 13C-enriched Mn(CO)5Cl, but no extra 13C hyperfine features
FIG. 5.5
Link between the estimated s-character and p-character for a range of (CO)₅M-hal σ* complexes
were detected. This indicates that either coupling to the axial CO is very small, or that the CO ligand has been lost.

On annealing, the $\sigma^*$ anions, Re(CO)$_5X^-$, decayed uniformly without giving any new detectable paramagnetic products. This was also the case for the other anions, except (CO)$_5$WI$^{2-}$, which displayed a well-defined doublet splitting on all features after anneal. This was assigned to hyperfine coupling due to a single proton, although in the absence of a proton donor, the source of hydrogen was not clear. It may be that one of the CO ligands has been replaced by H, as a descent in symmetry was observed, indicating that one of the equatorial ligands had been modified or replaced. Curiously, this only occurred for the tungsten complex; why this should be so is not clear.

PART II

DESCRIPTION

Part I of this chapter discussed electron addition to [Cr(CO)$_5$I]$^-$, [Mo(CO)$_5$I]$^-$, [W(CO)$_5$I]$^-$, [Re(CO)$_5$Br] and [Re(CO)$_5$I], giving the corresponding anions. This section deals with complexes containing a $\eta^5$-cyclopentadienyl ligand in addition to a metal-halogen bond. In this case, an added electron has the choice between being strongly associated with the organic ligand or with the halogen, e.s.r. spectroscopy should be able to distinguish between these alternatives. The only paramagnetic mononuclear metal carbonyl containing a $\eta^5$-cyclopentadienyl ligand previously studied in this way is CoCp(CO)$_2^-$, formed by electron addition to the neutral complex in MTHF at 77 K. Mention will also be made in this section of an attempt to prepare the anion of MnCp(CO)$_3$, previously studied in this laboratory.
The mixed ligand complexes to be discussed are \([\text{FeCp(CO)}_2\text{I}]\), \([\text{FeCp(CO)}_2\text{Cl}]\), \([\text{MoCp(CO)}_3\text{I}]\) and \([\text{WCp(CO)}_3\text{I}]\).

Halogenation of the binuclear complex \([\text{CpFe(CO)}_2]_2\) results in the formation of \(\text{FeCp(CO)}_2\text{X}\), where \(X = \text{Cl}, \text{Br}, \text{I}\). The molecule has at most \(C_8\) symmetry, and although a \(C_{2v}\) local symmetry for the \(\text{M(CO)}_2\) group may be assumed, it is probable that this is perturbed to a limited extent by the other halide ligand. \(\text{FeCp(CO)}_2\text{X}\) derives from a binuclear parent molecule containing bridging CO groups (Fig. 5.6);

![FIG. 5.6](image)

Study of the infra-red spectra of such complexes indicates an \(\text{OC-M-CO}\) angle of \(\text{ca. } 90^\circ\). Formally, iron in \(\text{CpFe(CO)}_2\text{X}\) is in the oxidation state +2, since the halide ligand and the \(\pi\)-cyclopentadienyl ring act as uninegative ligands.

Similarly, the metal-metal bond in bis(tricarbonyl-\(\pi\)-cyclopentadienyl molybdenum) is immediately cleaved by iodine in solution, to form the metal halogen complex\(^3\) (Fig. 5.7);

![FIG. 5.7](image)
The molybdenum atom in \([\text{MoCp}(\text{CO})_3]\) may be regarded as being in a formal oxidation state of +2. The crystal structure of the complex has not been reported but is assumed to be very similar, if not identical, to that of \([\text{MoCp}(\text{CO})_3\text{Cl}]\). The six bonding orbitals of Mo to the Cp ring and CO ligands are thought to form a distorted octahedron.

The corresponding tungsten complex, \([\text{WCp}(\text{CO})_3]\), may be prepared by the iodination of the hydride, \([\text{WCp}(\text{CO})_3\text{H}]\), in ether.

**EXPERIMENTAL**

The iron complexes \([\text{FeCp}(\text{CO})_2]\) and \([\text{FeCp}(\text{CO})_2\text{Cl}]\) were prepared by S. Bratt, by the halogenation of \([\text{FeCp}(\text{CO})_2]\)_2 purchased from Alfa Inorganics, Mass. The Mo and W complexes were also previously prepared in this laboratory. \([\text{MoCp}(\text{CO})_3]\) was prepared in quantitative yield by refluxing \([\text{MoCp}(\text{CO})_3]\)_2 (Strem Chemicals Inc., Danvers, Mass.) with iodine in an inert solvent. \([\text{WCp}(\text{CO})_3]\) was prepared by the iodination of the hydride, \([\text{WCp}(\text{CO})_3\text{H}]\).

Samples were studied as powders and in solution in MTHF and CD₃OD.

**RESULTS**

\([\text{FeCp}(\text{CO})_2]\)_2

The powder spectrum was poorly defined, but the spectra of a solution in MTHF gave reasonably clear features (Fig. 5.8), thought to be due to an e⁻ capture centre, as expected in MTHF. The six parallel and perpendicular features assignable to \(^{127}\text{I}\) (\(^{127}\text{I}\) has \(I = \frac{5}{2}\) and is 100\% abundant) were visible. On annealing the sample, these features and those attributable to the solvent were lost, and two new iron complexes were seen to grow in, I and II (Fig. 5.9). I exhibited axial symmetry, with \(g_1 \gg g_\parallel \approx 2.0023\), as is normal for a \(-d_{z^2}\) configuration. Species II also showed
FIG. 5.8
X-band e.s.r. spectrum for FeCp(CO)₂I in MIFP after γ-irradiation at 77 K.
FIG. 5.9
X-band e.s.r. spectrum for FeCp(CO)$_2$I in MTHF after anneal, showing species I and II.

3250G (9.0100GHz)

H

50G

+\frac{1}{2} -\frac{1}{2} +\frac{1}{2} -\frac{1}{2}
a similar form of $g$-tensor, but the $g_\perp$ shift was much smaller, and both
the parallel and perpendicular features showed a well-defined doublet
splitting. Repeating the experiment using CD$_3$OD as the solvent resulted
in the appearance of a triplet centred on the same $g_\perp$, having a splitting
exactly equal to that calculated for D, establishing that species II
must be a protonated species (Fig. 5.10).

$[\text{FeCp(COD)}_2\text{Cl}]$

As in the case of the iodide derivative, the powder spectra were
poorly defined. However, solutions in MTHF showed two features to low
field of the central solvent features, having the form of parallel lines
and relative intensities correct for $^{35}\text{Cl}$ and $^{37}\text{Cl}$ features. Assuming
that the separation between these features is normal, this may be used
together with the magnetic moments of the isotopes to calculate an
approximate value for $A_\parallel$, yielding $A_\parallel(\text{CD}) = 55$ G, giving $g_\parallel \approx 2.008$.
Unfortunately, the high field ($-\frac{3}{2}$) line was too weak to be resolved in
the tail of the spectrum due to organic radicals. On anneal, this centre
was lost and species I was formed as for the iodide discussed above.

$[\text{MoCp(CO)}_3\text{I}]$

The major species formed in irradiated MTHF solutions of $[\text{MoCp(CO)}_3\text{I}]$
was identified as an electron gain centre, $[\text{MoCp(CO)}_3\text{I}^-]$ (Fig. 5.11).
The same species was seen in the powder spectrum, although the lines were
much narrower. Extra features in the powder spectrum may be due to
electron loss centres, the intense central lines may possibly be associated
with radicals derived from cyclopentadiene (Fig. 5.12).

Both spectra exhibit an anisotropic sextet arising from $^{127}\text{I}$, together
with some extra features due to Mo satellites in the powder spectrum
($^{95}\text{Mo}$, 15.78% abundant and $^{97}\text{Mo}$, 9.60% abundant, both have $I = \frac{5}{2}$, and
such similar magnetic moments that these features are superimposed). The
FIG. 5.10
X-band e.s.r. spectrum for FeCp(CO)$_2$I in CD$_3$OD, showing species II and the protonated species.
FIG. 5.11
X-band e.s.r. spectrum for MoO₃(CO)₃I in MTHF after γ-irradiation at 77 K

\[ {^{127}I(M_I)Z} \]
\[ +{5/2} \]
\[ +{3/2} \]
\[ +{1/2} \]
\[ -{1/2} \]
\[ -{3/2} \]
\[ -{5/2} \]
FIG. 5.12
X-band e.s.r. spectrum of powdered MoO(OC)₃, I after γ-irradiation
presence of further features which are unaccounted for suggests a possibility of the existence of two isomers having identical parallel (z) couplings, but slightly different x and y coupling and g-values.

A single crystal study made previously in this laboratory\textsuperscript{19} can be used to check these assignments and the possibility of major deviations of the three tensors from common axes (Fig. 5.13). This revealed two magnetically distinct radicals per unit cell. A wide range of orientations were studied, in many cases all the Mo hyperfine coupling was resolved. As expected for a σ* structure, the three tensors were found to be nearly coaxial. Several spectra showed quite intense features, thought to be due to electron loss centres, as they were not readily assignable to forbidden transitions made prominent by quadrupole effects. However, owing to the poor definition it was not possible to make a complete analysis as in the case of the powder spectrum.

On annealing \([\text{MoCp(CO)}_3\text{I}]^-\) in MTHF, a new species III, still showing hyperfine coupling to \(^{127}\text{I}\) was formed. The spectrum was not well defined, but suggested that \(^{127}\text{I}\) and g were no longer coaxial. It is thought that this new species is still \([\text{MoCp(CO)}_3\text{I}]^-\), but having a different electronic structure from that of the primary species (Fig. 5.14).

\([\text{WCp(CO)}_3\text{I}]\)

The powder spectrum of \([\text{WCp(CO)}_3\text{I}]\) showed broader features than the Mo case, but no W satellites were detected (Fig. 5.15). In MTHF, the \(M_I(^{127}\text{I}) = +\frac{1}{2}\) line was well-defined, but all other features were too broad to detect. This is due to the fact that the +\(\frac{1}{2}\) line is almost isotropic. Had only the solution spectrum been available, this may have been erroneously analysed.
FIG. 5.13
X-band e.s.r. spectrum for a single crystal of MoCp(CO)$_3$I in an arbitrary orientation after γ-irradiation at 77 K
FIG. 5.14
X-band e.s.r. spectrum for powdered MoO$_2$(CO)$_3$I after γ-irradiation and anneal (α probably due to another species)

$^{127}$I($M_I$)$_z$

$+\frac{5}{2}$ $+\frac{3}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$ $-\frac{3}{2}$ $-\frac{5}{2}$

$\alpha$

3300 G (9.0700 GHz)

100 G

x, y range
FIG. 5.15

X-band e.s.r. spectrum for W(CO)₃I after γ-irradiation at 77 K (α due to Cp ligands)

Gain x 10
DISCUSSION

In all cases electron addition occurred, as could be judged by the fact that the blue/violet colour characteristic of trapped electrons in irradiated MTHF was absent. The form and magnitude of the $^{127}\text{I}$ hyperfine coupling was characteristic of $\sigma^*$ complexes. No information was present in the spectrum pertaining to whether or not CO ligands had been lost, but it is assumed that all are retained. However, loss of CO is a possibility that should be borne in mind. The dissociative $e^-$ capture and thermal loss of halide ion from the iron complexes is important, as this has not been previously detected in such $\sigma^*$ complexes. If CO had been lost, no strong driving force would be present for the additional loss of $X^-$. 

The hyperfine coupling data for all the complexes can be used to give insight into the electron distribution in the SOMO. The results for the halogens are fairly unambiguous in that both $A_\parallel$ and $A_\perp$ are positive. Approximate orbital populations may be derived in the usual way from the isotropic and dipolar coupling constants. The results show the $s$-population to be low, and the $p$-orbital population is as expected for $\sigma^*$ complexes. The form of the $g$-tensor components is compatible with a $d^2$ configuration in all cases, however metal hyperfine coupling was only detected in the case of the Mo complex. The usual ambiguity in the signs of $A_\parallel$ and $A_\perp$ is present, taking both as negative results in a $d^2$ population of 24% which is too low. The best arrangement is for $A_\parallel$ to be positive and $A_\perp$ negative, this gives a $d^2$ population of 53% which is more acceptable.

Trends in halogen hyperfine coupling

The results can be compared with those for the Cr, Mo and W iodides discussed in the preceding part of this chapter, in which it was stated
that as the electronegativity of the metal atom increases, so the p-orbital population of the halogens increases in the case of a σ* complex. Similarly, as the electronegativity of the halogen increases, so the spin density falls on the halogen. The former trend is observed in the cyclopentadienyl complexes on going from Mo → W, but is not followed on going from these to [FeCp(CO)₂I]⁻, as might be expected. Instead, there is a clear decrease in the p-orbital population of the iodide ligand. However, this may be explained by the fact that the extra electrons in the formally d⁷ Fe complex, compared with the d⁵ Mo and W anions reduce the effective electronegativity of the metal. This is supported by the observation that the iodine spin density falls on replacing the Cp ligand with two CO groups in the anions [MoCp(CO)₃I]⁻ and [Mo(CO)₅I]²⁻, i.e. going from a d⁵ to d⁷ complex. The same decrease is seen for the W complexes to a greater extent. The increase predicted on electronegativity grounds is seen clearly on going from Mo(CO)₅I²⁻ to FeCp(CO)₂I⁻. Both are d⁷ complexes but the electronegativity of the metal increases Mo → Fe.

Secondary species

The new species I formed on annealing [FeCp(CO)₂I] in MTHF, showed no hyperfine coupling from the ligands, and so limited information is available from the spectrum. However, it is clear that the iodide ligand has been lost, and the resulting spectrum is probably due to [FeCp(CO)₂]. The results suggest that the SOMO is largely d⁵₂ on iron.

Comparison may be made with the manganese carbonyl complex, [MnCp(CO)₃], which gave a well-defined anion [MnCp(CO)₃]⁻ after γ-irradiation at 77 K in MTHF.¹⁹ Unfortunately, on annealing the primary anion, the secondary product [MnCp(CO)₂]⁻ was not detected, which is isoelectronic with the corresponding iron derivatives. That CO loss has not occurred from the manganese complex is supported by the observation that there is a
significant difference in $g$-values which would not be expected on going from $[\text{FeCp(CO)}_2]$ to the isoelectronic $[\text{MnCp(CO)}_2]^{-}$ (Table 5.5).

The results for $[\text{MnCp(CO)}_3]^{-}$ may be compared with those for $\text{Mn(CO)}_5$. If $A_1^{(55\text{Mn})}$ is assumed to be negative, the $d_{z^2}$ population increases from 58% for $\text{Mn(CO)}_5$ to 69% for $[\text{MnCp(CO)}_3]^{-}$, indicating that the SOMO is more confined to Mn in the cyclopentadienyl complex. This suggests that delocalization from $d_{z^2}$ into the Cp ring is small, which in turn implies that donation from Cp$^-$ into $d_{z^2}$ is small. This is in accord with expectation which suggests that bonding involving the $\pi$-levels ($E_1 : d_{xz}, d_{yz}$) is strong, but that for the $\sigma$-level ($A_1 : d_{z^2}$) is weak.

Hofmann $^{29}$ has performed extended Hückel type M.O. calculations on $\text{MnCp(CO)}_2$, which is isoelectronic with $\text{FeCp(CO)}_2^+$. He found that the HOMO and LUMO in the planar form of this 16-electron species are very close in energy, the HOMO comprising largely a non-bonding electron pair at the metal (Fig. 5.16), whilst the LUMO is mainly $3d_{xz}$ on the metal, having a large $\pi^*$ CO component. On going from a planar to a pyramidal configuration there is an increase in the HOMO/LUMO separation.

$[\text{FeCp(CO)}_2]$ is isoelectronic with $[\text{MnCp(CO)}_2]^{-}$, which should have its unpaired electron in $3d_{xz}$ according to Hofmann's calculations. However, the $g$-values for $[\text{FeCp(CO)}_2]$ are not consistent with such a configuration ($g_\perp = 2.144, g_\parallel = 2.003$ strongly suggests a $d_{z^2}$ configuration). It is suggested that the two frontier orbitals in the Fe complex are inverted ($3d_{xz}^2, 3d_{xz}^1$), in which case the complex has probably relaxed to a near planar configuration since such an inversion seems improbable for a strongly pyramidal complex. If this is correct, it is still surprising that it should have an exactly axial $g$-tensor.

The radical $[\text{CoCp(CO)}_2]^-$ $^{20}$ possesses two extra electrons relative to the Fe complex. A previous e.s.r. study suggested a $3d_{xy}^1$ structure,
FIG. 5.16 Axes selected for MnCp(00)$_2$
using the axes selected in Fig. 5.16. It is concluded that the order for the metal orbitals in [FeCp(CO)] is $d_{xz}(\pi^*) < d_{z^2}(\text{weakly } \sigma^*) < d_{xy}$, where the $\pi$ and $\sigma$ bonding relate to the ligands.

The secondary species, III, formed on annealing [MoCp(CO)$_3$I] in MTHF and still exhibiting hyperfine coupling to $^{127}$I, is thought to be the thermodynamically favoured $\pi^*$ complex. This is based on the observation that the Mo and W complexes initially react with electrons to give $\sigma^*$ ($d_{x^2}$) complexes, when it might be expected that one of the orbitals with greater $\pi^*$ character would have been selected. It is interesting that electron capture is occurring into the same type of orbital as that selected for the $d^6$ complexes Mo(CO)$_5$ and W(CO)$_5$. It is suggested that this is a kinetically controlled process and the relaxation required to capture an electron in $\sigma^*$ occurs more readily than that required for capture into $\pi^*$. Such behaviour is often observed in electron capture processes in rigid matrices. Unfortunately, full interpretation was not possible as the spectra were not well enough defined, although it can be deduced that the maximum coupling to $^{127}$I is less than ca. 100 G, and there is a large position $g$-shift associated with these components. If there is a component having a $g$-value close to 2.00, the hyperfine coupling for this feature cannot be greater than ca. 40 G. These approximate data can reasonably be associated with a low symmetry $\pi$ radical of the type envisaged, and are clearly quite different from those characteristic of $\sigma^*$.

Finally, species II, formed after annealing [FeCp(CO)$_2$I] in MTHF, is clearly a proton adduct, as evidenced by the well-defined doublet splitting on the parallel and perpendicular features. It may have been formed by hydrogen atom attack. Protonation of the parent anion prior to loss of halide ion is thought to be responsible for the formation of
the species in CD$_3$OD. The $^1$H hyperfine coupling is large as is also the anisotropy (Table 5.5). It is probable that an Fe-H bond has been formed; however, the evidence is not definitive.
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>SOLVENT</th>
<th>g-VALUES</th>
<th>HYPERFINE COUPLING/G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>g_x</td>
<td>g_y</td>
</tr>
<tr>
<td>[FeCp(CO)_2I]^-</td>
<td>MTHF</td>
<td>2.008</td>
<td>2.008</td>
</tr>
<tr>
<td>[FeCp(CO)_2Cl]^-</td>
<td>MTHF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MoCp(CO)_3I]^-</td>
<td>MTHF</td>
<td>2.004</td>
<td>1.995</td>
</tr>
<tr>
<td>[WCp(CO)_3I]^-</td>
<td>MTHF</td>
<td>2.031</td>
<td>1.997</td>
</tr>
<tr>
<td>[Mo(CO)_5I]^-</td>
<td>MTHF</td>
<td>2.000</td>
<td>2.000</td>
</tr>
<tr>
<td>[W(CO)_5I]^-</td>
<td>MTHF</td>
<td>2.001</td>
<td>2.001</td>
</tr>
</tbody>
</table>

a In MTHF, only the M_I = +\(\frac{1}{2}\) feature was detected;
b From Part I of this chapter;
c Only the M_I = +\(\frac{3}{2}\) features (^35Cl, ^37Cl) were detected.
### TABLE 5.5

Experimental ESR parameters for other carbonyl (η⁵-cyclopentadienyl) metal complexes

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>SOLVENT</th>
<th>g-VALUES</th>
<th>HYPERFINE COUPLING/G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>g∥</td>
<td>g⊥</td>
</tr>
<tr>
<td>FeCp(CO)₂</td>
<td>MTHF or CD₃OD</td>
<td>2.003</td>
<td>2.144</td>
</tr>
<tr>
<td>HFe(Cp)(CO)₂</td>
<td>MTHF</td>
<td>2.000</td>
<td>2.045</td>
</tr>
<tr>
<td>DFeCp(CO)₂</td>
<td>CD₃OD</td>
<td>a</td>
<td>2.045</td>
</tr>
<tr>
<td>[MnCp(CO)₃]⁻ b</td>
<td>MTHF</td>
<td>2.004</td>
<td>1.99</td>
</tr>
<tr>
<td>[CoCp(CO)₂]⁻ c</td>
<td>MTHF</td>
<td>2.005</td>
<td>2.004</td>
</tr>
<tr>
<td>Mn(CO)₅ d</td>
<td>Ar</td>
<td>2.004</td>
<td>2.043</td>
</tr>
</tbody>
</table>

a Features obscured by solvent radical signals;
b From Ref. 19;
c From Ref. 20;
d From Ref. 27.
TABLE 5.6

Derived ESR parameters and calculated orbital populations for halogen ligands

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$A_{iso}/G$</th>
<th>$2B/G$</th>
<th>$\bar{a}_S^2/%$</th>
<th>$\bar{a}_P^2/%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{FeCp(CO)}_2\text{I}]^-$</td>
<td>119</td>
<td>73</td>
<td>0.8</td>
<td>16.2</td>
</tr>
<tr>
<td>$[\text{MoCp(CO)}_3\text{I}]^- c$</td>
<td>193</td>
<td>97</td>
<td>1.3</td>
<td>21.5</td>
</tr>
<tr>
<td>$[\text{WCp(CO)}_3\text{I}]^-$</td>
<td>208</td>
<td>127</td>
<td>1.4</td>
<td>28.1</td>
</tr>
<tr>
<td>$[\text{Mo(CO)}_5\text{I}]^{2-} d$</td>
<td>180</td>
<td>55</td>
<td>1.2</td>
<td>12.1</td>
</tr>
<tr>
<td>$[\text{W(CO)}_5\text{I}]^{2-}$</td>
<td>195</td>
<td>61</td>
<td>1.3</td>
<td>13.5</td>
</tr>
</tbody>
</table>

$^a$ Estimated from data in Ref. 30;
$^b$ Estimated from data in Ref. 31;
$^c$ $^{95/97}\text{Mo } A_{iso} = -8.7, 2B = +14.7, \bar{a}_S^2 = 53\%$;
$^d$ $^{95/97}\text{Mo } A_{iso} = +1.8, 2B = +16.6, \bar{a}_S^2 = 60\%$. 
REFERENCES FOR CHAPTER 5

CHAPTER 6

THE TRANSITION METAL - HYDROGEN ATOM BOND
INTRODUCTION

The first example of a molecular complex containing a transition metal-hydrogen bond was reported in 1931 by Hieber and Leutert, who formed iron tetracarbonylhydride, Fe(CO)$_4$H$_2$, by the reaction of Fe(CO)$_5$ with alkali. Since then, hydride complexes have been isolated and characterized for all the transition metals in Groups IV to VIII of the Periodic Table. Such complexes are discussed in a comprehensive text by Muetterties and a volume edited by Bau.

A distinguishing property of many transition metals rich in d-electrons is their ability to activate hydrogen, hence the extensive use of Pt, Pd, Ni and others for catalytic hydrogenations. For this reason, transition metal hydride complexes have attracted much research as the metal-hydrogen bond is a key element in many kinds of homogeneous catalytic reactions. It can interact reversibly with a number of organic substrates, and many aspects of laboratory synthesis and industrial processes have felt the impact of transition metal hydride chemistry.

The two most useful and reliable techniques used for the spectroscopic characterization of the metal-hydrogen bond are infra red and proton magnetic resonance spectroscopy. In addition, structural analysis has been greatly facilitated by diffraction studies.

The stretching vibration of a terminal M-H bond may be observed in the 1700-2300 cm$^{-1}$ region in the IR or Raman spectra. The most reliable spectroscopic evidence for the presence of a metal-hydrogen bond is the observation of a resonance to high field from tetramethylsilane (TMS) in the proton magnetic resonance spectrum. The number of hydride ligands present may also be inferred from the proton spectrum by comparing the integrated area of a ligand resonance with that of the hydride.
E.S.R. may be used in the characterization of paramagnetic hydride complexes, and can detect both the presence and number of hydride ligands, e.g. the e.s.r. spectrum of $[\text{H}_2\text{Ti}(\pi-\text{C}_5\text{H}_5)_2]$ anion clearly shows the unpaired electron coupling with two hydride ligands ($A \approx 7-8$ G) and ten $\pi$-cyclopentadienyl protons ($A \approx 0.4$ G).\(^4,^5\) There has been some controversy concerning the orbital occupied by the unpaired electron in these type of complexes,\(^6\) but e.s.r. results obtained by Kenworthy et al.\(^7\) suggest that the orbital largely involved is $d_{z^2}$. The complex is thought to have an approximately tetrahedral arrangement of the 2 cyclopentadiene and 2 hydride ligands, with the $d_{z^2}$ orbital lying along the symmetry axis between the cyclopentadiene rings and bisecting the H-Ti-H angle (Fig. 6.1).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6_1.png}
\caption{FIG. 6.1}
\end{figure}

\textbf{DESCRIPTION}

The electronic configuration of Pt in oxidation state +2 is particularly suited to producing square planar complexes when influenced by strong field ligands such as CN\(^-\), CO, NO\(^+\) and (C\(_2\)O\(_4\))\(^2^-\). These ligands are favourable in regard to size, electron withdrawing tendency, and capacity to cause orbital splitting in producing such square planar configurations. Fig. 6.2 shows a square planar complex in a coordinate system with the central atom at the origin, and the 4 ligands along the $x$ and $y$ axes.
FIG. 6.2
Molecular orbital co-ordinate system for a square planar metal complex.
The metal orbitals involved in σ-bonding in square planar complexes are the \( nd_{z^2}, nd_{x^2-y^2}, (n+1)s, (n+1)p_x \) and \( (n+1)p_y \). The \( nd_{x^2-y^2}, (n+1)s, (n+1)p_x \) and \( (n+1)p_y \) orbitals account for most of the σ-bonding, the empty \( dx_{2-y^2} \) orbital is favourably directed towards the ligands and shares their bonding electrons. The \( nd_{z^2} \) orbital makes only a minor contribution to σ-bonding. A stable π-bonding orbital ("ring π") is formed by combination of the metal \( p_z \) and the four ligand π-orbitals.

There have been two main points of disagreement in describing the electronic structure of the Pt(CN)₄²⁻ ion, based on its electronic absorption and MCD spectra. Controversy concerns the ordering of the occupied metal \( d \) molecular orbitals and their participation in bonding, and the extent to which the several empty, low-lying \( \pi^* \) CN⁻ molecular orbitals are involved in electronic transitions. Gray and Ballhausen interpreted the 3 lowest energy absorption bands in the solution electronic spectra as \( M \rightarrow L \) transitions from the occupied \( d \)-orbitals to a single \( \pi^* \) CN⁻ orbital, \( a_{2u}(\pi^*) \). Their ordering of excited states implied the ordering of the \( d \)-levels as \( d_{xy} > d_{xz}, d_{yz} > d_{z^2} \), assuming negligible electronic repulsion differences. Piepho et al. analysed the MCD spectra of the Pt(CN)₄²⁻ ion, their interpretation also involved \( M \rightarrow L \) transitions to the \( a_{2u}(\pi^*) \) level, but included spin-orbit coupling in excited states. As a consequence of this, formally spin-forbidden transitions were assumed to gain considerable intensity. The implied ordering of the \( d \)-levels was \( d_{z^2} \approx d_{xz}, d_{yz} > d_{xy} \). Isci and Mason studied the solution electronic absorption and MCD spectra for Pt(CN)₄²⁻, and proposed the order of occupied \( d \)-levels as \( d_{z^2} > d_{xz}, d_{yz} > d_{xy} \), obtained from the order of the excited states.

There have been very few studies of such complexes involving their exposure to ionizing radiation and subsequent investigation by e.s.r.
Amano and Fujiwara\textsuperscript{11} produced electron gain centres by exposure of a range of bivalent nickel complexes to $\gamma$-radiation, and by the photo-ionization with $NNN'N'$-tetramethylphenylenediamine. X-irradiation of a tetracyanonickelate complex in a NaCl lattice by Reddy and co-workers\textsuperscript{12} produced two paramagnetic species, characterized as low spin $d^7$ and $d^9$ complexes, represented as $[\text{Ni(CN)}_4\text{Cl}_2]^{3-}$ and $[\text{Ni(CN)}_4\text{Cl}_2]^{5-}$ respectively. These centres were also produced in a similar study by Danon \textit{et al.}\textsuperscript{13} in a KCl lattice.

When studying the effect of ionizing radiation on complexes containing cyanide ligands, various structural changes may also occur in addition to the formation of electron gain and loss centres. For example, one or more of the CN ligands may bend away from the metal-ligand axis, in which case slight electron delocalization onto the nitrogen atoms will be detected.\textsuperscript{14-16} Such possibilities must be borne in mind when interpreting the spectra of such complexes.

An interesting centre was formed in a study of tetracyanonickelate(II) ions by Symons and co-workers.\textsuperscript{17} Exposure of salts and aqueous glasses to $^{60}$Co $\gamma$-rays at 77 K resulted in both electron loss and gain centres, $[\text{Ni(CN)}_4]^{-}(d^7)$ and $[\text{Ni(CN)}_4]^3-$ ($d^9$) respectively. However, in certain cases, especially for Ba[\text{Ni(CN)}_4].H$_2$O, a novel species exhibiting large hyperfine coupling (ca. 150 G) to a single proton was detected. This was identified as $\text{H}^+\text{Ni(CN)}_4^{2-}$, in which the hydrogen atom occupies the axial position and the unpaired electron resides in a $\sigma^*$ orbital with a spin-density of ca. 0.3 on hydrogen. The alternative, which would involve hydrogen atom addition to one of the CN ligands to give a $\text{CH(=N)}$ ligand could not give rise to such a large proton coupling and still retain considerable nickel character since the coupling in $\text{HCON}^-$ radicals is only ca. 130 G.\textsuperscript{18} Unfortunately, it was not possible to obtain any direct
information about the metal contribution, as $^{61}\text{Ni}$ has a very low natural abundance ($1.19\%, I = \frac{3}{2}$).

As a continuation of this work, it seemed of interest to find other systems in which such bonding occurs, and in particular, to obtain information about the metal contribution from its hyperfine coupling constants. The square planar complex $\text{K}_2\text{Pt(CN)}_4$ was studied and the results discussed in this chapter. It is worth noting that the first hydride complex of Pt to be reported was trans-$[(\text{PEt}_3)_2\text{PtHCl}]$ in 1957.\(^{19}\)

All the known hydride complexes of Pt(II) are square planar, the majority having a trans-configuration. The hydride complexes of divalent Pt and Pd are discussed in a text by Hartley.\(^{20}\)

**EXPERIMENTAL**

$\text{K}_2\text{Pt(CN)}_4$ was obtained from Strem Chemicals, Fluorochem Ltd., and used without further purification. Solution samples were prepared as glass beads, and in sealed e.s.r. tubes under vacuum when degassing of the solvent was necessary.

**RESULTS**

Solutions of $\text{K}_2\text{Pt(CN)}_4$ in $\text{CH}_3\text{OH}$ gave a variety of paramagnetic species after exposure to $\gamma$-irradiation at 77 K. Initially, it was thought that one species was a $d^9$ centre from the form of the $g$-values ($g_y > g_\perp > 2.000$) with $g_y = 2.147$ and $g_\perp = 2.091$. In addition to this species there appeared to be two other major species, both resembling $d^7$ with $g$-tensors of the form $g_\perp > g_y \approx 2.000$, this being characteristic of complexes with a $d_{z^2}$ configuration. Each of these species were seen to exhibit large proton hyperfine couplings (ca. 175 G) (Fig. 6.3).

A variable temperature experiment was performed on a methanolic
FIG. 6.3
First derivative X-band e.s.r. spectrum for a dilute solution of K₂Pt(CN)₄ in CH₃OH, showing features assigned to the \([H⁻Pt(CN)₄]^{2-}\) complex, and the "g₉" species.
solution of $\text{K}_2\text{Pt(CN)}_4$, and it was found that both the "d$^7$-type" species decayed together at -125°C. This seemed an interesting and important observation (Figs. 6.4a and b).

Repeating the experiment using CD$_3$OD resulted in 2 sets of triplets being obtained (Fig. 6.5). The change in the splittings for the doublets and triplets was exactly that predicted for $^1\text{H}$ and $^2\text{H}$ hyperfine coupling [CH$_3$OH $A(\text{H}) = 175$ G; CD$_3$OD $A(\text{D}) = 27$ G supporting $A(\text{H}) = 6.5 \times A(\text{H})$]. The low field triplet set were seen to exhibit exhibit perpendicular and parallel components. The parallel sets were not completely resolved, but their high field components were well defined. Approximate $g_\parallel$ values were obtained on the assumption that, as with the Ni complex, the $^1\text{H}$ and $^2\text{H}$ coupling was almost isotropic.

When solutions of 6M H$_2$SO$_4$ and 6M D$_2$SO$_4$ were used, the same hydrido species were obtained as in the methanolic case, i.e. doublets in the former and triplets in the latter were observed (Figs. 6.6 and 6.7). There was one difference, however, between the methanolic case and the acidic solutions. Whilst the low field set of doublets or triplets exhibited parallel and perpendicular components in methanol, they were seen to be almost isotropic in the acidic case.

To test whether electron addition was responsible for any of the species observed, frozen methanolic solutions containing NNN'$\text{N}'$-tetramethylphenylenediamine (TMPD), a photosensitive electron source, were photolysed with 253 nm light to give the TMPD$^+$ cation and electrons (Fig. 6.8). It was significant that the results obtained were very similar to those from the $\gamma$-irradiation of the methanolic and acidic solutions, suggesting that these centres were due to electron addition.

In an experiment using a 4:1 mixture of CD$_3$OD/CH$_3$OH and K$_2$Pt(CN)$_4$, the proportion of H-adduct and D-adduct were seen to be equal in the spectra,
FIG. 6.4(a)
First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in CH$_3$OH, recorded at $-160^\circ$C.
FIG. 6.4(b)
First derivative X-band e.s.r. spectrum for a dilute solution of K$_2$Pt(CN)$_4$ in CH$_3$OH, recorded at -130°C, showing decay of [H$^-$-Pt(CN)$_4$]$^{2-}$ complex.
First derivative e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in CD$_3$OD/D$_2$O, showing features assigned to the $[D^2Pt(CN)_4]^{2-}$ complex.
FIG. 6.6
First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in 6M $H_2SO_4$ after annealing, showing features assigned to the $[H-Pt(CN)_4]^2-$ complex.
First derivative X-band e.s.r. spectrum for a dilute solution of $\text{K}_2\text{Pt}(\text{CN})_4$ in $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ showing features assigned to the $\text{D}_{\text{Pt}}(\text{CN})_4^{2-}$ complex. [a is due to $\text{H}^-\text{Pt}(\text{CN})_4^{2-}$ in low yield.]
**FIG. 6.8**
First derivative X-band e.s.r. spectrum for a dilute solution of K₂Pt(CN)₄ in CD₃OD/D₂O + TMPD after 253 nm photolysis for 2½ hours, showing features assigned to the [D⁻Pt(CN)₄]²⁻ species.
FIG. 6.9
First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in $CD_3OD/CH_3OH + TMPD$ after 253 nm photolysis.
FIG. 6.10
First derivative X-band e.s.r. spectrum for a dilute solution of K₂Pt(CN)₄ in CD₃OD/D₂O + CH₃I, illustrating suppression of features assigned to [D-Pt(CN)₄]²⁻ complex.
suggesting that protonation is faster than deuteration, as would be expected (Fig. 6.9).

Further evidence supporting the concept of electron addition is gained from the observation that the presence of CH₃I in a CD₃OD/D₂O solution causes suppression of the triplet features (Fig. 6.10). Alkyl halides act as electron scavengers (see Chapter 1), and it is postulated that in methanolic solutions the species arise from electron addition followed by protonation.

DISCUSSION

It was initially thought that the doublets and triplets observed in the acidic and methanolic solutions arose from two different species. In this case it was necessary to formulate two different structures for species each containing one strongly coupled hydrogen ligand, formed indirectly by electron addition and subsequent protonation, or directly by hydrogen atom addition. Both species are obviously formed in equal concentration and have the same hyperfine splitting.

One possibility considered was that an extra sixth ligand was incorporated into the adduct, such as CH₃OH or H₂O, but this does not account for the equal yields observed. Another alternative is that the ²H-triplet is split by a doublet, but it cannot be ¹⁹⁵Pt as one would expect to see a central line attributable to ¹⁹⁵Pt [¹⁹⁴Pt is non-magnetic and is 32.9% abundant; ¹⁹⁵Pt is 33.8% abundant and has I = ½]. Other possibilities included the presence of an impurity of higher electron affinity, or that one -CN ligand had inverted and become -NC.

The low field triplet exhibits extra features at the base of the peaks, these were initially thought to be the ¹⁹⁵Pt perpendicular +½ satellites, the ¹⁹⁵Pt -½ component not being observed as it was thought to be very
weak. This assumption was based on the observation that these features disappeared together with the $^2\!H$ lines. However, if this were the case, this results in a small negative coupling for $A_1$(Pt) of -20 G, and $A_\parallel ^{195}$ Pt = 400 G. This produces a $2B$ value that is unreasonably large however.

Thus it was not possible to formulate two different structures. It was puzzling that no $^{195}$Pt satellites were detected flanking the perpendicular components, assuming that the above assignment can be discounted. However, if a completely different approach is taken, then both these difficulties are overcome. It is possible that there is only one type of complex present, and that the low field doublet or triplet set is due to complexes containing $^{195}$Pt. At first, this seems unlikely when the intensities of the two sets of features are considered. The intensity of the $^{195}$Pt set is about equal to that of the features due to complexes containing non-magnetic Pt, which is not in accord with the natural abundance of the two isotopes. However, if $A_\parallel ^{195}$ Pt $\gg A_1 ^{195}$ Pt then this is overcome. The $M_s = -1/2$ ($^{195}$Pt) component associated with the parallel features was observed at high field on increasing the gain of the instrument. The features confirm the isotropic character of the $^2\!H$ hyperfine coupling. Thus the disproportionately high intensity of the low field set of features arises because the $M_s = +1/2$ parallel and perpendicular features almost coincide. Calculation using the appropriate spin Hamiltonian shows that the $M_s = +1/2$ component associated with the parallel features should indeed appear close to the low field set.

In order to understand this spectrum it should be appreciated that the parallel and perpendicular components for the $M_s = +1/2$ set cover a very small field range (ca. 20 G), the central non-magnetic components cover a large field range (ca. 180 G) whilst the $M_s = -1/2$ components cover a very large range (ca. 330 G). Since the intensities of the turning point
features of the first derivative powder spectra are directly proportional to the field range spanned by each component, the \(+\frac{1}{2}\) set are very intense and the \(-\frac{1}{2}\) set very weak.

On slight annealing, the supposed \(d^9\) complex \([\text{Pt(CN)}_4]^{3-}\) in methanol was lost, and the features assigned to the \([\text{H}^-\text{Pt(CN)}_4]^{2-}\) complex grew proportionately, suggesting therefore, that these anions must be strongly basic relative to methanol. In fact, in a later stage of the work, this was found to be an erroneous assignment, and the parallel and perpendicular features attributed to such a \(d^9\) species were found to be due to some other species. This is discussed in detail in chapter 7. It is interesting to note that the \([\text{Ni(CN)}_4]^{3-}\) ions were not protonated under these conditions, the signals from these \(d^9\) complexes were broadened reversibly on anneal.

The results obtained from the TMPD photolysis support the assignment in that very similar spectra were produced. Irradiation of glassy solutions of \(K_2\text{Pt(CN)}_4\) in 6M \(H_2SO_4/H_2O\) or \(D_2SO_4/D_2O\) gave the hydrido complex in high yield, with suppression of the normal H* or D* yield. This establishes that the hydrido complex can be formed either (i) directly by hydrogen atom addition or (ii) indirectly, by electron addition and protonation. The experimental e.s.r. parameters for the hydrogen atom adduct are shown in Table 6.1.

Prior to the conversion of the hyperfine coupling constants into orbital populations in order to determine the nature of the Pt-H bond, allowance must be made for the contribution of the induced orbital motion, arising because of the deviation of the g-values from free spin (see chapter 1). This results in the data presented in Table 6.2. The form of the g-tensor establishes that the electron is in a \(5d_{z^2}\) orbital on Pt, so the anisotropic coupling must be positive. This results in a large
TABLE 6.1

Experimental ESR parameters for \([\text{H}^-\text{Pt(CN)}_4]^{2-}\) and \([\text{D}^-\text{Pt(CN)}_4]^{2-}\) in various media

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>(g) VALUES</th>
<th>HYPERFINE COUPLING</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g_{</td>
<td></td>
</tr>
<tr>
<td>(\text{CD}_3\text{OD/D}_2\text{O})</td>
<td>1.987</td>
<td>2.107</td>
</tr>
<tr>
<td>6M (\text{D}_2\text{SO}_4)</td>
<td>1.986</td>
<td>2.102</td>
</tr>
<tr>
<td>(\text{CD}_3\text{OD/D}_2\text{O} \text{TMPD})</td>
<td>1.986</td>
<td>2.106</td>
</tr>
<tr>
<td>6M (\text{H}_2\text{SO}_4)</td>
<td>1.985</td>
<td>2.102</td>
</tr>
<tr>
<td>(\text{CH}_3\text{OH})</td>
<td>1.985</td>
<td>2.104</td>
</tr>
<tr>
<td>6M (\text{H}_3\text{PO}_4)</td>
<td>1.986</td>
<td>2.103</td>
</tr>
</tbody>
</table>
TABLE 6.2

Derived ESR parameters and calculated orbital populations for $[\text{H—Pt(CN)₄}]^{2-}$ and $[\text{D—Pt(CN)₄}]^{2-}$ after correction for orbital contributions

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>$A_{150}/G$</th>
<th>2B/G</th>
<th>$\bar{a}_s^2$ (H)(D) $%$</th>
<th>$\bar{a}_d^2$ (Pt) $%$ a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD₃OD/D₂O</td>
<td>209</td>
<td>233</td>
<td>35</td>
<td>84</td>
</tr>
<tr>
<td>6M D₂SO₄</td>
<td>230</td>
<td>230</td>
<td>35</td>
<td>83</td>
</tr>
<tr>
<td>CD₃OD/D₂O TMPD</td>
<td>210</td>
<td>231</td>
<td>35</td>
<td>83</td>
</tr>
<tr>
<td>6M H₂SO₄</td>
<td>230</td>
<td>234</td>
<td>35</td>
<td>84</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>206</td>
<td>233</td>
<td>34</td>
<td>84</td>
</tr>
<tr>
<td>6M-H₃PO₄</td>
<td>228</td>
<td>231</td>
<td>36</td>
<td>83</td>
</tr>
</tbody>
</table>

a Calculated using the wave functions of Froese
positive value for $A_{1s0}$, indicating considerable admixture of the Pt 6$s$ orbital overbalancing the normal negative coupling caused by spin polarization of inner s-electrons. This is as expected for a $\sigma^*$ orbital.

Using the wavefunctions of Froese, the spin densities on Pt estimated from the $5d_{z^2}$ coupling is ca. 0.83. The alternative wavefunctions of Herman and Skillman yield a value of ca. 0.77. The spin density on H is estimated at ca. 0.35. Allowing for the inaccuracies involved for elements of high atomic number, the agreement with the more accurate results derived from the $^1H$ coupling is reasonable.

It may be concluded, therefore, that the unpaired electron is closely confined to hydrogen and platinum, the hydrogen ligand occupying an axial position as in the case of the [HNi(CN)$_4$]$^{2-}$ ion. The $^1H$ proton coupling corresponds to a spin density in the 1$s$ orbital of ca. 0.35, this compares favourably with the nickel complex for which a value of ca. 0.33 was obtained. Information concerning the metal contribution was obtainable in the Pt case as opposed to Ni, and shows that the unpaired electron has a slight preference for Pt. It can therefore be deduced that the bonding $\sigma$ electron pair must have a comparable preference for hydrogen, thus indicating that this has definite hydride ion character.
REFERENCES FOR CHAPTER 6


CHAPTER 7

QUEST FOR THE METAL-ALKYL BOND
INTRODUCTION

The main aim of the work was to form a paramagnetic species in which the unpaired electron resides in a metal-alkyl bond, the alkyl group being situated in the axial position above the square plane of the \([Pt(CN)_4]^{2−}\) group, analogous to the \((CN)_4 Pt\cdot H\) adduct discussed in the preceding chapter. It was hoped that by using solvents known to produce an abundance of mobile alkyl radicals on radiolysis or photolysis, such a species might be formed.

Solvents used in the study

An obvious initial choice was CH\(_3\)CN, which is known to have two crystalline phases, I and II, with a transition temperature of 216.9 K.\(^1\) Sudden freezing of liquid CH\(_3\)CN at 77 K results in the formation of crystal I. \(\gamma\)-Irradiation at 77 K produces dimer radical anions \((CH_3CN)_2^−\) in crystal I, and monomer radical anions, CH\(_3CN^−\), in crystal II. On photobleaching, both species yield methyl radicals adjacent to cyanide ions, with which they may recombine in the reverse of the photobleaching process.

\[
\begin{align*}
\text{In crystal I:} & \quad (CH_3CN)_2^- & \xrightarrow{\Delta} & \quad CH_3^- + CN^- + CH_3CN \\
\text{In crystal II:} & \quad CH_3CN^- & \xrightarrow{\Delta} & \quad CH_3^- + CN^-
\end{align*}
\]

There has been found to be a slight difference between CH\(_3\)\(\cdot\) radicals produced by \(\gamma\)-radiolysis and subsequent photobleaching, and those produced by 185 nm photolysis of CH\(_3\)CN.\(^2\) The CH\(_3\)\(\cdot\) radical of the CH\(_3\)----CN\(^−\) pair produced by the former process decays via hydrogen abstraction at 77 K, and the e.s.r. spectrum exhibits a proton hyperfine coupling of 22 G;

\[
\dot{CH}_3 + CH_3CN \rightarrow CH_4 + \dot{CH}_2CN
\]

The "free" \(\dot{CH}_3\) radicals produced by photolysis are quite stable at 77 K, and exhibit a proton hyperfine coupling of 23 G. This difference
is thought to be due to a slight pyramidal deformation of planar CH₃· in CH₃—CN⁻. Delocalization of the unpaired electron and the influence of the negative charge in CH₃—CN⁻ could also affect the coupling.

Symons et al.³ have studied CH₃Br in CH₃CN, alkyl halides normally being expected to act as electron scavengers, undergoing dissociative electron capture to give CH₃· radicals and halide ions after exposure to ⁶⁰Co γ-rays at 77 K. From their study, CH₃· radicals loosely associated with bromide ions were formed. The Br hyperfine tensor components showed transfer of spin to Br to be small, and possibly spin density is acquired mainly by spin polarization.

Similar results were obtained from CH₃I and C₂H₅Br. The same compounds in CH₃OH gave only the corresponding alkyl radicals with no halide interaction, this is explained in terms of the far greater anion solvating power of the alcohol. Sprague and Williams⁴ also studied CH₃Br in CH₃CN after γ-irradiation at 77 K, their results showed clear features from Br, and 1:3:3:1 quartets with a proton coupling of 20.6 G. This reduced value was assigned to the protons of CH₃· radicals undergoing a weak interaction with Br.

Other possible sources of alkyl radicals are the dimethyl and diethyl carbonates. γ-Irradiation of these compounds at 77 K show quite complex e.s.r. spectra which change markedly on warming.⁵ Dimethyl carbonate showed narrow features assigned to CH₃· radicals, which disappeared on warming to about 120 K. Another species was detected which gave broader features characteristic of two rapidly interchanging protons. This is thought to be due to CH₂·O·CO·OCH₃ formed by the reaction;

\[
\text{CH}_3\text{O·CO·OCH}_3 \rightarrow \text{CH}_3· + \hat{\text{O·}}\text{CO·OCH}_3
\]

\[
\hat{\text{O·}}\text{CO·OCH}_3 + (\text{CH}_3)_2\text{CO}_3 \rightarrow \hat{\text{CH}_2\text{O·CO·OCH}_3}
\]

i.e. the CH₃-O bond is thought to break to give CH₃· radicals and the
methoxycarbonyl radicals \( \cdot \text{CO} \cdot \text{OCH}_3 \).

Also worthy of consideration is methane sulphonylic acid, \( \text{CH}_3\text{SO}_3\text{H} \). Erikson and co-workers\(^6\) made e.s.r. measurements on \( \gamma \)-irradiated single crystals of the acid and showed that two radicals are formed, \( \cdot \text{CH}_2\text{SO}_2\text{(OH)} \) and \( \cdot \text{CH}_3\text{SO}_2\text{(OH)}^- \). The former gives rise to a triplet in the central part of the spectrum, with \( A = 24.9 \text{ G} \), whilst four quintets attributed to the anion radical are seen with \( A^{(33)\text{S}} = 93.6 \text{ G} \), \( A^{(1\text{H})} = 13 \text{ G} \). It is thought that the unpaired electron probably occupies a 3-centre orbital along the O-S-C bond (Fig. 7.1).

Trimethyl phosphate, \( (\text{CH}_3)_3\text{PO}_4 \), is known to produce methyl radicals after \( \gamma \)-radiolysis at 77 K,\(^7\) easily visible in the central part of the spectrum, together with \( \text{H}_2\text{COPO(OCH}_3)_2 \) radicals. In addition to these, Ginns et al. observed weak, broad doublets attributed to \( (\text{CH}_3\text{O})_3\text{PO}^- \) and \( (\text{CH}_3\text{O})_2\text{PO}^- \). On annealing, the former rearranges to the latter:

\[
(\text{CH}_3\text{O})_3\text{PO}^- \rightarrow \text{CH}_3\text{O}^- + (\text{CH}_3\text{O})_2\text{PO}^- 
\]

Dimethylsulphoxide (DMSO) has been studied by Williams and co-workers\(^8\) in the solid state, and been shown to exhibit interesting behaviour. Electron capture leads to the formation of methyl radicals, which in the case of \( \cdot \text{CD} \), from \( (\text{CD}_3)_2\text{SO} \) are weakly complexed with the anion, \( (\text{CD}_3)_3\text{SO}^- \);

\[
(\text{CD}_3)_2\text{SO} + e^- \rightarrow \text{D}_3\text{C}---\text{S(O)CD}_3^- 
\]

However, \( (\text{CH}_3)_2\text{SO} \) irradiated at 77 K does not contain trapped methyl radicals, so that the reaction;

\[
\cdot \text{CH}_3 + (\text{CH}_3)_2\text{SO} \rightarrow \text{CH}_4 + \text{H}_2\text{C}---\text{S(O)CH}_3 
\]

must have occurred for the protonated compound. Thus an unusual phenomenon exists whereby the deuterated anion pair (I) is stable at 77 K, but the protonated form (II) is not.

It has been shown previously\(^3,^9\) that both \( \cdot \text{CH}_3 \) and \( \cdot \text{CD}_3 \) form adducts, so the significant difference between I and II may lie in the difference...
FIG. 7.1
3-centre orbital of $\text{CH}_3\text{SO}_2\text{(OH)}^-$ radical
between the anions. Symons\textsuperscript{10} has suggested that loss of \( \cdot \text{CH}_3 \) in (\( \text{CH}_3 \))\textsubscript{2}SO is largely due to the greater reactivity of the C-H over the C-D bond.

The weakness of the bond between the methyl radical and the methane sulphonate group is illustrated on anneal when, just prior to irreversible loss of \( \cdot \text{CD}_3 \), the hyperfine coupling increases from 2.95 G for the adduct, to that of the free species, 3.5 G. This behaviour is analogous to that observed for halide ion adducts.

The behaviour of alkyl bromides is paralleled by solutions of (\( \text{CH}_3 \))\textsubscript{2}SO or (\( \text{CD}_3 \))\textsubscript{2}SO in CD\textsubscript{3}OD, when "normal" \( \cdot \text{CH}_3 \) and \( \cdot \text{CD}_3 \) radicals are formed. This effect is thought to be due to the increased solvation of ejected anions.

**EXPERIMENTAL**

Solutions of \( \text{K}_2\text{Pt(CN)}_4 \) in the various solvents were frozen as small beads in liquid nitrogen, or where necessary, deoxygenated and contained in sealed tubes. Irradiations were carried out for periods of up to 2 hours.

\(^{13}\text{C}-\text{enriched } \text{K}_2\text{Pt(CN)}_4 \) was prepared by a standard literature method\textsuperscript{11} using \( \text{K}_2[\text{PtCl}_4] \), purchased from Johnson Matthey, and \( \text{K}^{13}\text{CN} \), obtained from Merck, Sharp & Dohme.

**RESULTS**

A major product at 77 K in several solvents was a feature with properties expected for a d\textsuperscript{7} centre, with \( g_\perp = 2.050, g_\parallel = \text{FS} \) (known hereafter as species 'C'). However, this species must be formed by an
electron addition process, in view of the solvent types. Figs. 7.2 to 7.6 show the species in CH$_3$OH/H$_2$O, dimethylformamide (DMF), CH$_3$CN/CH$_3$OH, CH$_3$CN/H$_2$O and (CH$_3$O)$_2$CO/CH$_3$OH.

In order to prove whether or not the feature is due to an electron addition species, photolysis of K$_2$Pt(CN)$_4$ in CD$_3$OD/D$_2$O containing a trace of TMPD was carried out. Irradiation for 2$\frac{1}{2}$ hours with 253 nm light resulted in the spectrum shown in Fig. 7.7. Plenty of the Pt-D adduct can be seen to have been formed, but not much of the species under investigation is visible. It is certainly not in the same abundance as it is normally seen in methanol matrices.

To determine whether C is, in fact, destroyed by photolysis, a methanolic solution of K$_2$Pt(CN)$_4$ was $\gamma$-irradiated and then photolysed with 253 nm light. A significant decay of C was observed after 1$\frac{1}{2}$ hours illumination.

It was not possible to assign any features in the X-band spectra to $^{195}$Pt satellites of this species. In order to ascertain whether any such features are present, a Q-band spectrum of K$_2$Pt(CN)$_4$ in CD$_3$OD/D$_2$O was recorded (Fig. 7.8). This revealed two quite broad peaks, one at the position expected for C. If this is assumed to be the $^{194}$Pt line, with the adjacent peak the $^{195}$Pt + $\frac{1}{2}$ satellite, the following parameters are obtained: $A_\perp(^{195}$Pt$) = 126$ G, $A_\parallel(^{195}$Pt$) = 520-620$ G. The position of the $^{195}$Pt parallel features is not clear, and only a range can be proposed at this stage.

Such an interpretation means that the $^{195}$Pt$_\perp + \frac{1}{2}$ feature is in the position of the "$d_{\perp}^{9}$" line at X-band (previously mentioned in chapter 6). This is not present as a pure g-feature at Q-band, and so may be favoured as a $^{195}$Pt satellite.

In an attempt to determine whether or not this species is possibly a
First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in CH$_3$OH/H$_2$O, showing species "C".
FIG. 7.3
First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in dimethylformamide (DMF), showing species "C".
FIG. 7.4
First derivative X-band e.s.r. spectrum for a dilute solution of K₂Pt(CN)₄ in CH₃CN/CH₃OH, showing species "C".
FIG. 7.5
First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in $CH_3CN/H_2O$, showing species "C".
First derivative-X band e.s.r. spectrum for a dilute solution of K$_2$Pt(CN)$_4$ in dimethylcarbone, (CH$_3$O)$_2$, showing species "C".
First derivative X-band e.s.r. spectrum for a solution of $\text{K}_2\text{Pt(CN)}_4$ in $\text{CD}_3\text{OD}/\text{D}_2\text{O} + \text{TMPD}$ after 253 nm photolysis.
FIG. 7.8

Q-band spectrum for K₂Pt(CN)₄ in CD₃OD/D₂O, showing features assigned to $^{195}\text{Pt}_\perp (+\frac{1}{2})$ and $^{194}\text{Pt}_\perp ("C")$, and proposed range of parallel features.
Pt-alkyl centre, a study was made of K₂Pt(CN)₄ in ¹³CH₃OH/H₂O, and compared with a simultaneous run using ¹²CH₃OH/H₂O. No ¹³C broadening or splitting of any features was observed. After several anneals, when all the (CN)₄Pt⁻⁻H adduct had decayed, the two lines assigned to ¹⁹⁴Pt₁ and ¹⁹⁵Pt₁ +½ remained (Fig. 7.9), further substantiating the theory that these features are due to the same species. Further annealing caused the two lines to decay simultaneously.

Finally, ~90% ¹³C-enriched K₂Pt(CN)₄ was prepared and investigated. Simultaneous experiments were carried out using this and the ¹²C-K₂Pt(CN)₄ in CD₃OD/D₂O solvent. Although no well-defined ¹³C splittings were evident on any of the features, it was apparent that the ¹⁹⁴Pt₁ line was broadened in the ¹³C-enriched case. The width of the peak, measured at half-height, was found to be 17 G for the ¹³C case, and 11 G for the ¹²C. The broadening appeared to be repeated on the ¹⁹⁵Pt₁ +½ feature, but this was more difficult to quantify (Figs. 7.10 and 7.11).

Encouraged by this evidence of some ¹³C structure, it seemed important to locate the parallel features more precisely. A broad feature at high field, present in all these systems studied but as yet unidentified, seemed a possible candidate. Unfortunately, the position of this line coincides with the (Pt⁻⁻H)⁻½ parallel triplet features in CD₃OD/D₂O, so the experiment was repeated using the ¹³C- and ¹²C- samples in CH₃OH/H₂O. In this case, the doublet ¹⁹⁵Pt⁻½ features from the (Pt⁻⁻H) adduct did not coincide with the suspected parallel feature, and ¹³C-broadening was revealed in the ¹³C-enriched sample (Figs. 7.12 and 7.13). Thus the position of the ¹⁹⁵Pt⁻½ parallel feature can now be fixed.

**DISCUSSION**

It was initially thought that this major centre might possibly be due
FIG. 7.9
First derivative X-band e.s.r. spectrum for a solution of
K₂Pt(CN)₄ in CH₃OH/H₂O, after annealing to remove [H₂Pt(CN)₄]²⁻,
showing features assigned to ⁵₁₉Pt (±½) and ⁴₁₉Pt⊥.
FIG. 7.10

First derivative X-band e.s.r. spectrum for a dilute solution of ~90\% $^{13}$C-enriched $K_2Pt(CN)_4$ in $CD_3OD/D_2O$, showing broadening of $^{193}Pt_1$ feature.
FIG. 7.11
First derivative X-band e.s.r. spectrum for a dilute solution of K₂Pt(CN)₆ in CD₃OD/D₂O, showing ¹⁹⁵Pt₁ feature.
FIG. 7.12
First derivative X-band e.s.r. spectrum for ~90% $^{13}$C-enriched K$_2$Pt(CN)$_4$ in CH$_3$OH/H$_2$O, showing broadening of the $^{195}$Pt ($-\frac{1}{2}$) feature.
First derivative X-band e.s.r. spectrum for K$_2$Pt(CN)$_6$ in CH$_3$OH/H$_2$O, showing the $^{195}$Pt ($\pm \frac{1}{2}$) feature.
to a Pt-alkyl adduct. The solvents in which it was found to be present could all conceivably give rise to alkyl radicals, and the species was certainly not present in the sulphuric acid experiments. The Q-band experiment, which suggests the probable position of the $^{195}\text{Pt}_\perp (+\frac{1}{2})$ satellite, gives rise to parameters which are quite compatible with those expected for a (Pt–R) species. They may be compared with those for the (Pt–H) adduct, $A_\perp(^{195}\text{Pt}) = 130$ G, $A_\parallel(^{195}\text{Pt}) = 450$ G, with an unusually small $\Delta g$ value ($g_\perp - g_\parallel$).

If it were the case that this centre was a Pt–R adduct, then using $^{13}\text{CH}_3\text{OH/H}_2\text{O}$ would be expected to show $^{13}\text{C}$ splitting, or at least some broadening, of the features. However, this experiment was disappointing in that nothing of this nature was observed on this or any other feature. Thus it seemed that the possibility of this species being a Pt–R adduct could be ruled out. However, should the species have been proved to be a (Pt–R) centre, it would have been somewhat surprising when its intensity is considered. It is always present in far greater abundance than the (Pt–H) adduct, except in the case of the TMPD photolysis, and such a centre would not be expected to form quite so readily. However, the results show that it is an electron addition species, as the solvents in which it was formed all possess electron-donating properties, despite the fact that it has a distinct "d$^7"-type appearance, in that $g_\perp > g_\parallel = FS$.

The problem remained, therefore, to try and identify the exact nature of this centre. It was puzzling that a d$^9$ centre should have the appearance of a d$^7$-type species, and it was hoped to resolve this by using $^{13}\text{C}$-enriched $\text{K}_2\text{Pt(CN)}_4$.

At this stage, the position of the parallel features was still not clear. The main perpendicular feature at $g = 2.050$ was established as the $^{194}\text{Pt}_\perp$ line, and the $^{195}\text{Pt}_\perp (+\frac{1}{2})$ feature was thought to coincide with the
"d₉" line, first discussed in context with the (Pt-H) adduct. But suppose that this d⁹ species was not actually observed at all, but that it all immediately protonated. Indeed, this seems more likely, as it seems unusual to observe the intermediate d⁹ species and its product, the (Pt-H) adduct, together. This leaves available the previously-named "d⁹", which could conceivably be assigned to the ¹⁹⁵Pt// (+½) feature.

If the other ¹⁹⁵Pt// (-½) feature is taken to be the broad signal at high field, which exhibits ¹³C-broadening when ¹³C-enriched K₂Pt(CN)₄ is used, the following parameters are obtained: A₁(¹⁹⁵Pt) = 460 G, A₁(¹⁹⁵Pt) = 110 G, g₀ = 1.996, g₁ = 2.050. Such an assignment is further verified on annealing, when all the (Pt-D) species has decayed, and the ¹⁹⁵Pt// (+½), ¹⁹⁵Pt₁ (+½) and ¹⁹⁵Pt₁ features remain (Fig. 7.9). At this stage, the ¹⁹⁵Pt₁ (+½) line is approximately 17% of the intensity of the ¹⁹⁵Pt₁ feature which is equal to that predicted from natural abundance. This is not observed until all of the (Pt-D) species has decayed, as the ¹⁹⁵Pt₁ (+½) line coincides with one of the components of the (¹⁹⁵Pt-D) triplet.

A more detailed study of the spectrum reveals two shoulders in the ¹³C-enriched K₂Pt(CN)₄ case on either side of the 1 feature. It is conceivable that this broadening is due to two equivalent ¹³C nuclei, giving A(¹³C) ≈ 5 G (Fig. 7.14).

As a result of this study, a possible structure for this species may be proposed. It is thought that by a process of distortion, the expected d⁹ (dₓ²−y²) species is changed into a (d₁²) species. It is suggested that it is formed by electron addition, followed by loss of cyanide ion in solution;

\[
\text{Pt(CN)}₄^{2-} + e^- \xrightarrow{77K} \text{Pt(CN)}₄^{3-} \rightarrow \text{d}¹_{x²−y²} \text{Pt(CN)}₃^{2-} \text{d}¹_{z²} + \text{CN}⁻
\]
First derivative X-band e.s.r. spectrum for ~90% $^{13}$C-enriched $\text{K}_2\text{Pt(CN)}_4$ in CD$_3$OD/D$_2$O, showing $^{13}$C broadening of $^{194}\text{Pt}_1$ feature.
this process occurring in competition with protonation of the \( \text{d}^9 \) species;

\[
\text{Pt(NC)}_4^{3-} + \text{H}^+ \rightarrow \text{HPT(CN)}_4^{2-}
\]

Although \( \text{Pt(CN)}_3^{2-} \) might be expected to have a \( \text{d}^2 \) \( \text{z}_y^2 \) structure, it is suggested that this distorts and switches its axis to \( \text{d}^2 \) (Fig. 7.15).

If this were the case, we would expect to observe two \( ^{13} \text{C} \) couplings from the ligands situated at each end of the \( \text{d}^2 \) orbital. In the experiment using \( ^{13} \text{C} \)-enriched \( \text{K}_2\text{Pt(CN)}_4 \), this is in fact observed on the \( ^{195} \text{Pt} \) feature.

At the limit of distortion to a linear T-structure, the \( \text{d}^2 \) orbital will lie directly along the NC-Pt-CN axis, with a consequent high spin density on the C nuclei (Fig. 7.16). However, it would seem more likely that linearity is not achieved, resulting in a relatively low spin density on the ligands, as suggested by the magnitude of the \( ^{13} \text{C} \) coupling observed. Such a structure is favoured, and the possibility of solvent molecules also being attached to Pt is not ruled out (Fig. 7.17).

The \( ^{195} \text{Pt} \) hyperfine coupling may be analysed in the usual way, preceded by subtraction of the orbital magnetic contribution. If it is assumed that the unpaired electron occupies a \( 5\text{d}_{z^2} \) orbital on platinum as described above, the anisotropic coupling must be positive, and therefore the isotropic coupling is positive. The values obtained are \( 2B = 237 \text{ G} \), and \( A_{\text{iso}} = 214 \text{ G} \). Thus there is a considerable admixture of \( 6\text{g} \) (Pt) character, as is usually the case for \( \sigma^* \) species. Using the wavefunctions of Froese, the spin density on Pt estimated from the \( 5\text{d}_{z^2} \) coupling is \( \text{ca.} 0.85 \). This is very close to the value obtained for the \( [\text{H—Pt(CN)}_4]^2- \) species (\( \text{ca.} 0.83 \)).

An interesting phenomenon occurs in the methanolic solutions which should be mentioned. After annealing to a point where all the \( [\text{H—Pt(CN)}_4]^2- \) adduct and electron addition features have decayed, signals
FIG. 7.15
Suggested distortion of cyanide ligands in Pt(CN)$_3^{2-}$. 
FIG. 7.16
The $d_{z^2}$ orbital at the limit of distortion to a linear T-structure in Pt(CN)$_3^{2-}$.

FIG. 7.17
Non linear alignment of $d_{z^2}$ in Pt(CN)$_3^{2-}$. 
attributable to \( \cdot \text{CH}_3 \) radicals appear in the centre of the spectrum. This is a curious observation, suggesting that these radicals are somehow trapped, although no explanation can be offered as to why this occurs. The fact that it does however, makes the likelihood of platinum-alkyl adduct formation even more remote.

Other platinum centres present in these systems

Two solvents containing \( \text{K}_2 \text{Pt(CN)}_4 \) gave rise to features which could possibly be due to a platinum-alkyl species after \( \gamma \)-irradiation at 77 K. One was methane sulphonic acid, the other dimethylsulphoxide (DMSO). These are discussed separately.

\( \text{CH}_3\text{SO}_3\text{H}/\text{D}_2\text{O} \) system

\( \gamma \)-Irradiation at 77 K of \( \text{K}_2 \text{Pt(CN)}_4 \) in this solvent results in the formation of a substantial amount of the \([\text{D}^\cdot \text{Pt(CN)}_4]^2^-\) species initially, together with a small amount of the hydrogen atom adduct. It is significant that \( \text{C} \) was not detected. In terms of our theory for \( \text{C} \), this means that protonation in this solvent is fast compared with loss of \( \text{CN}^-\).

A 1:3:3:1 quartet in the centre of the spectrum, with \( A(\text{H}) = 23 \text{ G} \) confirms the presence of \( \cdot \text{CH}_3 \) radicals. Also present is a triplet due to the \( \cdot \text{CH}_2\text{SO}_2(\text{OH}) \) radical, with \( A(\text{H}) = 25 \text{ G} \), centred on free spin (Fig. 7.18).

Annealing the sample to the point where all the \([\text{D}^\cdot \text{Pt(CN)}_4]^2^-\) species had decayed resulted in the appearance of a strong perpendicular feature at \( g_\parallel = 2.11 \) (Fig. 7.19). A possible parallel feature is seen at \( g_\parallel = 1.978 \). It is conceivable that these are \( ^{195}\text{Pt} \) lines, if so, the \( ^{195}\text{Pt} \) satellites could be present at either side, as shown in Fig. 7.20. This gives rise to the parameters; \( A_\parallel = 370 \text{ G}, A_\perp = 100 \text{ G}, g_\parallel = 1.978, g_\perp = 2.111 \). These features have not been observed in any other solvent system.

If it is assumed that a platinum-alkyl species would have parameters
First derivative X-band e.s.r. spectrum for a dilute solution of K₂Pt(CN)₄ in CH₃SO₃H/D₂O (2:1 v/v), showing features assigned to the [D~Pt(CN)₄]²⁻ complex. Central features are due to CH₂SO₂(OH) and CH₃ radicals.
FIG. 7.19
First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Pt(CN)_4$ in $\text{CH}_3\text{SO}_3\text{H}/\text{D}_2\text{O}$ (2:1 $\nu/\nu$), after annealing.
of the same form as the [H—Pt(CN)]\(^{2—}\) adduct, then these features could conceivably be due to such a species. It was thought possible that a CH\(_2\)SO\(_2\)(OH) radical might have become attached to the platinum, particularly as the appearance of these lines coincided with the decay of the solvent radicals. However, careful study of the potential platinum-alkyl features, including a second derivative spectrum, revealed no suggestion of any hyperfine structure which could be attributed to proton coupling. The slight broadening of the \(^{195}\text{Pt}_\perp (\pm \frac{1}{2})\) feature is attributed to some [H—Pt(CN)]\(^{2—}\) still being present, the coincident \(^{195}\text{Pt}_\perp, \:^1\text{H}(\pm \frac{1}{2})\) line resulting in the misshapen appearance. There is evidence of some residual [H—Pt(CN)]\(^{2—}\) being present in that the \(^{195}\text{Pt}_\perp\) feature for this species is visible.

In the absence of any definitive proton coupling, it is concluded that the species observed on anneal is a d\(^7\) electron loss species, [Pt(CN)]\(^{—}\).

Calculation of \(A_{\text{iso}}\) and \(2B\), after correction for the orbital magnetic contribution, results in a spin density on Pt estimated from the 5d\(^2\) coupling of ca. 0.65.

**DMSO system**

DMSO acts as an electron scavenger, consequently very little of the [H—Pt(CN)]\(^{2—}\) species is formed after \(\gamma\)-irradiation of a DMSO solution of K\(_2\)Pt(CN)\(_4\).

However, two new features are observed, both having features characteristic of d\(^7\) complexes, and it is conceivable that one is a \(^{195}\text{Pt}_\perp (\pm \frac{1}{2})\) satellite on \(^{196}\text{Pt}_\perp\) (Fig. 7.20). This gives rise to \(g_\perp = 2.068\). When H\(_6\)DMSO is used, the feature assigned to \(^{196}\text{Pt}_\perp\) is not very well defined. However, it is interesting that when d\(_6\)-DMSO is used, both features are seen to sharpen up (Fig. 7.21). If the peak width at half-height is measured for the \(^{195}\text{Pt}_\perp (\pm \frac{1}{2})\) satellite, then this is 25 G in the
FIG. 7.20

First derivative X-band e.s.r. spectrum for a dilute solution of K₂Pt(CN)₅ in dimethylsulphoxide (DMSO).
First derivative X-band e.s.r. spectrum for a dilute solution of \( K_2Pt(CN)_4 \) in d$_6$-DMSO.
protonated case, and 17 G in the deuterated solvent. Further investigation of the protonated case suggests possible structure on this feature of ca. 7 G.

Consideration of the intensities of these features suggests that the $^{195}\text{Pt}_{\parallel} (+\frac{1}{2})$ feature must lie below the $^{195}\text{Pt}_{\perp} (+\frac{1}{2})$ line, making the intensity of this greater than would be expected. Although the $^{195}\text{Pt} (-\frac{1}{2})$ features are not observed, it is possible to estimate the experimental e.s.r. parameters, assuming $g_{\parallel} = FS$. This gives $A_{\parallel} = 280$ G, $A_{\perp} = 114$ G, $g_{\parallel} = FS$, $g_{\perp} = 2.068$.

It should be noted that the $^{194}\text{Pt}_{\perp}$ feature is a different shape from its $^{195}\text{Pt}_{\perp} (+\frac{1}{2})$ satellite; this is due to the $^{194}\text{Pt}_{\perp}, H(-\frac{1}{2})$ feature coinciding with the $^{194}\text{Pt}_{\perp}$ line.

This species seems to be the most promising candidate for a platinum-alkyl adduct, but, as in the case of CH$_3$SO$_3$H, lack of any definitive structure makes any conclusive statement impossible. The possibility of it simply being a d$^7$ electron-loss centre should not be ruled out.

K$_2$Ni(CN)$_4$.H$_2$O

It seemed a worthwhile experiment to attempt to prepare a nickel-alkyl adduct by analogous methods to those used for the platinum salt, bearing in mind that both tetracyano-complexes formed the protonated species, the H atom occupying the axial position.

RESULTS AND DISCUSSION

Exposure of K$_2$Ni(CN)$_4$.H$_2$O in methanolic solution to $^{60}$Co $\gamma$-rays at 77 K resulted in the formation of electron-loss and electron-gain centres previously reported by Symons and co-workers.$^{12}$ Fig. 7.22 shows these centres.

The electron-gain centre was recognised as a d$^9$ complex by the
FIG. 7.22
First derivative X-band e.s.r. spectrum for a dilute solution of K$_2$Ni(CN)$_4$ in CD$_3$OD/D$_2$O, showing electron-loss and electron-gain species.

Gain $\times$ 10

$\uparrow$ d$^9$ $\uparrow$ d$^7$ $\uparrow$ d$^7$ $\uparrow$ d$^7$ $\uparrow$ d$^9$
characteristic form of the \( g \)-tensor components, i.e. \( g_z > g_x > 2.00 \), with the unpaired electron occupying a \( d_{x^2-y^2} \) orbital on the metal. Both the parallel and perpendicular features are unusually broad and it is thought that the width arises primarily from small variations in the environment, bearing in mind that the complex exhibits a high \( g \) value, and \( \Delta g \) is strongly dependent on the environment of the \( d^9 \) complex. The shifts are thought to be controlled primarily by interaction between the medium and the nitrogen atoms of the cyanide ions. The stronger this interaction the weaker the \( \sigma \) bonding to nickel. This lowers the \( \sigma^* (d_{x^2-y^2}) \) orbital containing the unpaired electron, moving it closer to the \( \pi \)-orbitals with which it couples, thereby increasing \( \Delta g \).

The electron-loss complexes show much sharper features than the \( d^9 \) complex, and are identified as \( d^7 \) complexes, exhibiting the characteristic form of \( g \)-tensor components, i.e. \( g_z > g_x > 2.00 \).

On annealing solutions of \( K_2Ni(CN)_4 \cdot H_2O \) in various solvents to the point where most of the \( d^9 \) and \( d^7 \) centres had decayed, a new species ("D") could clearly be seen, not previously observed by Symons et al., exhibiting the \( g \)-tensor components \( g_z = 2.08 \), \( g_x = 2.007 \). This strongly suggests a \( d^7 \) configuration, the unpaired electron occupying a \( d_{x^2} \) orbital on nickel. This feature is shown in Figs. 7.23 to 7.26 for the various solvents. It was thought to be a possible candidate for a nickel-alkyl species, especially since all the solvents used [\( CH_3OH \), \( CD_3CN/D_2O \), \( Na_2MePO_3/CH_3OH/H_2O \) and \( (CH_3)_3PO_4/H_2O \)] could conceivably give rise to alkyl radicals after radiolysis.

Further investigation of the parallel and perpendicular features revealed possible \( ^{61}Ni \) satellites on the perpendicular feature (Fig. 7.26), taking into account the relative intensities of the lines [\( ^{61}Ni \) has 1.19% natural abundance, \( I = \frac{3}{2} \)]. Moreover, the parallel feature is
FIG. 7.23

First derivative X-band e.s.r. spectrum for a dilute solution of $K_2Ni(CN)_4$ in $CH_3OH$ after annealing to show species D.
FIG. 7.24
First derivative X-band e.s.r. spectrum for a dilute solution of $^{55}$K$_2$Ni(CN)$_4$ in CD$_3$CN/D$_2$O (1:1 V/V) showing species D and accompanying $^{61}$Ni satellites, and $^{14}$N hyperfine coupling.
FIG. 7.25
First derivative X-band e.s.r. spectrum for a dilute solution of K$_2$Ni(CN)$_4$ in Na$_2$MePO$_3$/CH$_3$OH/H$_2$O after annealing to show species D together with residual electron-gain and electron-loss centres.
FIG. 7.26
First derivative X-band e.s.r. spectrum for a dilute solution of K$_2$Ni(CN)$_4$ in (CH$_3$)$_3$PO$_4$/$\text{H}_2\text{O}$ after annealing to show species D.
seen to exhibit hyperfine structure in CD₃CN/D₂O and (CH₃)₃PO/ H₂O systems of ca. 5 G. The fact that identical structure is observed in both these precludes any possibility of it being due to either proton or deuterium coupling, and thus rules out the suggestion of a nickel-alkyl adduct. It is therefore concluded to be attributable to ¹⁴N coupling and comprises probably 5 lines. This suggests two coupled nuclei. It is tentatively suggested that on annealing the sample, the [CN]⁻ ligands undergo some kind of distortion whereby coupling to two equivalent ¹⁴N nuclei can occur along the z-axis. The coupling of ca. 5 G is considered too small for an N-bonded group, if the ligand had turned through 180° to form an isocyanide linkage,¹³ but is close to values obtained for "bent" ligands.¹⁴⁻¹⁶ The hyperfine coupling to ¹⁴N will increase on twisting since ¹⁴N coupling via the σ-orbital of [CN]⁻, which is all that can occur for the linear configuration, is extremely small. On twisting off axis, interaction with ¹⁴N becomes more direct. It is thus suggested that two of the [CN]⁻ ligands bend out of the xy square plane on warming to a position whereby coupling can occur in the z-direction.
REFERENCES FOR CHAPTER 7

APPENDIX

Hyperfine coupling constants for unit population of atomic orbitals

<table>
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<tr>
<th>ISOTOPE</th>
<th>NUCLEAR SPIN I</th>
<th>NATURAL ABUNDANCE</th>
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<th>NUCLEAR MAGNETIC MOMENT μ</th>
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a Calculated from the Hermann-Skillman wave-function

b Calculated from Hartree-Fock atomic wave-functions
A STUDY OF PARAMAGNETIC TRANSITION METAL CARBONYLS AND CYANIDES BY ELECTRON SPIN RESONANCE SPECTROSCOPY

by Jane L. Wyatt

Abstract

Exposure of diamagnetic transition metal carbonyls and cyanides either as the pure compounds or as dilute solutions to ionizing radiation at 77 K results in the formation of electron-loss and electron-capture centres. Working at low temperatures enables unstable complexes to be studied that are not detectable by conventional procedures. The low concentrations produced are ideal for e.s.r. studied since spin-spin broadening is avoided.

Four types of complex are studied, each involving a different transition metal-ligand bond. Exposure of dilute solutions of Fe(CO)$_5$ in 2-methyltetrahydrofuran to $^{60}$Co $\gamma$-rays at 77 K resulted in electron addition to give a 3$d^{3}$ species, tentatively identified as Fe(CO)$_5$$. The form of the g-tensor components requires a 3$d^{2}_{x^2}$ assignment for the unpaired electron on Fe.

A similar study of Mn$_2$(CO)$_8$(PR$_3$)$_2$ and M(CO)$_5$X (M = Cr, Mo, W, Re; X = Br, I) shows the excess electron to be accommodated in the metal-metal and metal-halogen $\sigma^*$ orbitals respectively. Resolved hyperfine coupling from the 2 axial $^{31}$P nuclei in Mn$_2$(CO)$_8$(PR$_3$)$_2$ reveals information regarding the delocalisation of the excess electron upon the axial ligands.

Electron addition to mixed ligand complexes, MCp(CO)$_n$X, (M = Mo, W, Fe; X = Cl, I) results in electron capture into the metal-halogen $\sigma^*$ orbitals, suggesting this is preferred to association with the organic ligand.

The transition metal-hydrogen atom bond was probed in the same way. $\gamma$-Radiolysis of Pt(CN)$_4^{2-}$ ions in aqueous sulphuric acid matrices at 77 K results in the formation of [H$^-$Pt(CN)$_4$]$^{2-}$, the unpaired electron being in a $\sigma^*$ orbital confined to hydrogen and platinum. Finally, it was hoped to form a transition metal-alkyl bond in the same way, using Pt(CN)$_4^{2-}$ and Ni(CN)$_4^{2-}$ ions in a variety of solvents known to produce alkyl radicals on radiolysis, but these experiments have so far been inconclusive.