

Paramagnetic Resonance in Platinum Group Compounds

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During the past few years there has been an increasing interest in the magnetic properties of palladium and platinum group compounds. In these the magnetism arises from electrons in an unfilled 4d (Pd group) or 5d (Pt group) shell. The main difference in magnetic behaviour of ions of these groups compared with that of the more commonly investigated ions of the iron group which have an unfilled 3d shell, arises from the stronger covalent bonds which are formed between the ion and its immediate diamagnetic neighbours. The effects of bonding on magnetic properties in general are consequently easier to investigate in the higher transition groups, especially the platinum group, and it is the purpose of this article to give a brief account of some paramagnetic resonance investigations of such effects.

The measurements have been made by a group at Oxford on salts provided by the Johnson Matthey Research Laboratories.

First will be given a short description of the paramagnetic resonance technique, and then an outline of two of the most interesting results. These are (i) a method of measuring the unpaired electron distribution over the paramagnetic complex, and (ii) a method of measuring the antiferromagnetic exchange interactions between neighbouring magnetic ions in the crystal.

Experimental Technique

The paramagnetic specimen is placed in a waveguide or cavity resonator in an external magnetic field H . Each magnetic ion then has an associated set of Zeeman energy levels corresponding to the allowed orientations of

the magnetic moment in H . Microwave radiation of frequency ν in the waveguide is absorbed when the spacing between adjacent Zeeman levels equals the quantum of microwave energy $h\nu$. The resonance condition is then $h\nu = g \beta H$, where β is the Bohr magneton and g is the spectroscopic splitting factor which is often close to 2 for ions in crystals and is 2.0023 for a free electron.

Typical operating conditions might be $\nu = 10000$ Mcps (corresponding to a wavelength of 3 cm) and $H = 3500$ gauss at resonance. Two of the most important quantities measured are (i) the g -value which is effectively a direct measure of the spin and orbital magnetic moment of the ion; and (ii) shifts or splittings of the absorption line arising from internal fields in the specimen. Such internal fields may be present, for example, if there is hyperfine interaction between the electron and a nucleus of spin I , which splits the absorption line into $2I + 1$ hyperfine components. A second kind of internal field may result from the interaction of the magnetic electrons with the electron magnetic moments of neighbouring paramagnetic ions.

Bonds and Electron Distribution

The measurement of electron distribution will be illustrated by reference to the mixed compound $(\text{NH}_4)_2\text{Ir}_2\text{PtCl}_6$ with $\text{Ir}:\text{Pt} \sim 1:100$. Here the Ir(IV) ion has configuration $5d^5$, and only one of these five electrons is unpaired and this electron is responsible for the paramagnetism. The Pt(IV) ions, $5d^6$, have all their electrons paired off and are diamagnetic; they merely serve as a diluent to keep the magnetic Ir ions well separated. The para-

magnetic resonance spectrum shows a hyperfine structure due to interaction of the Ir unpaired electron both with the Ir nucleus and with the surrounding octahedron of Cl nuclei in the $(\text{IrCl}_6)^{2-}$ complex, as is shown in the figure below.

The spectrum can be accurately interpreted by assuming that this unpaired electron is distributed over the $(\text{IrCl}_6)^{2-}$ complex in π -antibonding molecular orbitals. The size of the Cl hyperfine structure is simply proportional to the probability p of finding the unpaired electron in a p_π -orbital on a Cl multiplied by the size of the hyperfine structure in a free Cl atom. The results give $p=5$ per cent, so that the unpaired spin is approximately 70 per cent on the Ir ion and 30 per cent on the six Cl ions.

This result is also confirmed independently by the g -value, which on the molecular orbital theory is $g=2-4p$, as was first shown by Stevens. The observed g is 1.8 which again gives an electron transfer of $p=5$ per cent.

These measurements of hyperfine structures and g -values provide two of the most direct methods available for investigating electron distribution and bonding in paramagnetic complexes. Since the initial work on iridium salts, they have been applied to other systems including iron group salts. A

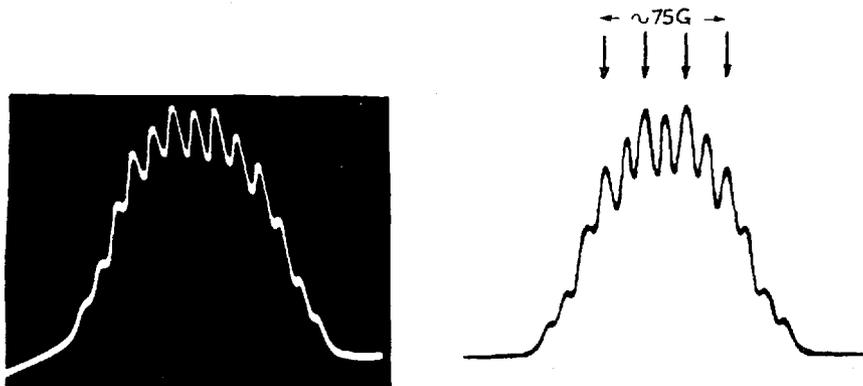
Complex	Con-figuration	Bond type	Per cent transfer, p
$(\text{MnF}_6)^{4-}$	$3d^5$	$\sigma (\pi)$	~ 2
$(\text{Ni}(\text{H}_2\text{O})_6)^{2+}$	$3d^8$	σ	~ 3
$(\text{RuCl}_6)^{3-}$	$4d^5$	π	2
$(\text{IrCl}_6)^{2-}$	$5d^5$	π	5
$(\text{IrBr}_6)^{2-}$	$5d^5$	π	5

few examples are given in the table above. Here, p denotes the probability of finding the unpaired electrons on any one of the attached ions of the complex and only the bonding responsible for this transfer is quoted.

In general, the results show that with a given type of bond and complex, the electron transfer and bond strength increase as the unpaired electrons are changed from $3d$ to $4d$ to $5d$, or from $4f$ to $5f$. This is not unexpected because of the increasing radius of the electron orbits. Similarly, for a given type of central ion the bonds to different ligands can be directly compared. For example, almost exactly the same charge transfer is found in $(\text{IrCl}_6)^{2-}$ and $(\text{IrBr}_6)^{2-}$.

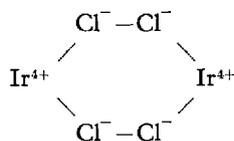
Exchange Interactions

The measurement of exchange interactions will also be illustrated by $(\text{NH}_4)_2\text{Ir}_2\text{PtCl}_6$ with $\text{Ir}:\text{Pt}\sim 1:10$. With this concentration there is an appreciable chance of two $(\text{IrCl}_6)^{2-}$

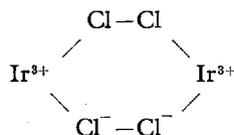


Photograph and reconstruction of paramagnetic resonance spectrum from $(\text{IrCl}_6)^{2-}$ complex. The magnetic field H is increasing from left to right. The reconstruction assumes a Cl-Ir-Cl hyperfine structure arising from a 5 per cent transfer of the unpaired electron spin from Ir to Cl

complexes occupying nearest neighbour positions in the crystal lattice, which has face-centred cubic structure. The pair could be represented diagrammatically by the structure



if the two unpaired spins were localised on their respective iridium ions. However, the measurements described above show that there is an 0.5 per cent chance of finding these spins on adjacent Cl atoms giving a possible structure of the form



There can then be an exchange interaction between the two unpaired electrons rather like that which occurs in a Cl_2 molecule.

The lowest energy levels of this system are a ground state singlet (spins anti-parallel) and a triplet (spins parallel) higher in energy by the antiferromagnetic exchange interaction J .

The paramagnetic resonance spectrum from the triplet and the temperature dependence of its intensity gives a direct measure of this exchange interaction, $J = 5 \text{ cm}^{-1}$. In the concentrated salt, $(\text{NH}_4)_2\text{IrCl}_6$, it is found that the magnetic susceptibility obeys a

Curie-Weiss law with Weiss constant $\theta = 20^\circ\text{K}$. This value is in good agreement with that predicted from the directly measured $J = 5 \text{ cm}^{-1}$ in semidilute crystals. It is also found that the salt goes antiferromagnetic at 2.1°K , and a direct knowledge of J is very helpful in the interpretation of this transition.

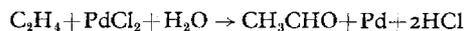
This method of studying the mechanism and the magnitude of exchange interactions, which is perhaps the only direct method available, is applicable to any antiferromagnetic which can be diluted by replacing the magnetic ions by diamagnetic ions. Work is at present in progress on other platinum group compounds, and also on the well-known antiferromagnetic oxides of the iron group.

In conclusion, it may be said that the paramagnetic resonance investigation of platinum group compounds has so far been a very interesting problem, because it has contributed not only to a better understanding of these compounds, but also to the understanding of the magnetic properties of transition group salts in general. It seems likely that further magnetic resonance research on the platinum group may also lead to new results of fundamental interest.

This work has been carried out by a group at the Clarendon Laboratory, Oxford. It is a pleasure for us to thank the Research Laboratories of Johnson, Matthey & Co., Limited, for their help and co-operation, and particularly to thank Dr. F. M. Lever and Mr. A. R. Powell.

A New Route to Acetaldehyde

A process for the direct oxidation of ethylene to acetaldehyde announced by the Consortium für Elektrochemische Industrie of München involves reacting a rising stream of ethylene-containing gas in a tower with a descending 0.1 M aqueous solution of palladium chloride:



Liquid from the tower is passed to a still, where crude acetaldehyde is stripped off,

while the spent palladium chloride is regenerated by air oxidation in another tower:



The advantages claimed for this process, which gives a 90 per cent yield, include low initial investment and the use of cheap raw materials. The same route could, it is thought, be employed economically to produce acetone from propylene and methyl ethyl ketone from normal butylene.