A STUDY OF THE MAGNETIC BEHAVIOUR OF COMPLEXES CONTAINING THE PLATINUM METALS.

By D. P. MELLOR, M.Sc.

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Some years ago Van Vleck (1932) drew attention to the fact that complexes of the Pd and Pt transition series seemed, from the meagre data then available, to conform neither to the theory of free ions (with both spin and orbit contributing) so successful for compounds of the rare earths, nor to the Bose-Stoner "spin only" theory which satisfactorily described the behaviour of many compounds of elements of the iron series. The incomplete 4f sub-shell responsible for the paramagnetism of the rare earths lies buried deep within the atom beyond the influence of interatomic forces and for this reason the rare earths stand in a class apart. It is therefore not surprising that there is no close resemblance between the magnetic behaviour of rare earth compounds and those of elements of the Pd and Pt transition series. On the other hand, the similarities of the electronic configurations of corresponding elements of the Fe, Pd and Pt series, in all of which the incomplete sub-shell (3d, 4d or 5d) responsible for paramagnetism lies outermost, might be expected to produce similar magnetic behaviour. The fact that the platinum metals do not conform to the "spin only" theory is no longer considered anomalous because this theory is not universally successful in accounting for the behaviour of even the iron transition series. For example, the compounds [Fe(dipy)₃]Cl₂ and K₂[Ni(CN)₄] are diamagnetic (μ=0), whereas if the unmodified spin theory were applicable both compounds should be paramagnetic with susceptibilities corresponding to 5·9 and 2·8 Bohr magnetons respectively. It is obvious that, in addition to the quenching of orbital moment by asymmetrical electrostatic fields, other factors may come into play in determining the magnetic moment of an atom. A number of theories have been developed to account for moments lower than those required by the "spin only" theory for ions (Pauling, 1931; Van Vleck, 1932, 1935). Pauling, for example, has accounted for the fall in moment in terms of the effect of covalent bond formation on the number of unpaired electron spins. Thus he discriminates between complexes in which atoms or groups of atoms are attached to a metal by ion dipole or electrostatic bonds (ionic complexes) as in [FeF₆]³⁻ and [CoF₆]³⁻ and those in which atoms or groups are attached by covalent bonds as in [Co(CN)₆]³⁻ and [Fe(CN)₆]³⁻ (covalent complexes). Owing to the pairing of electrons which takes place in the formation of a covalent bond there is a profound difference in the magnetic moments of Fe³ and Co³ in each of the two types of complexes. In the course of developing

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1 In the iron series the magnetic effect of orbital angular momentum is blotted out by the action of asymmetric electric fields of surrounding atoms with the result that the magnetic moment is given by the formula μₙ = \sqrt{S(S+1)}, where S is the spin quantum number (Σs). A full discussion and the first satisfactory explanation of this quenching phenomenon has been given by Van Vleck (1932).

2 Explanations alternative to Pauling's are (1) the crystalline potential theory of Penny and Schiapp, (2) Mulliken's theory of molecular orbitals. Van Vleck (1935) has demonstrated "the similarity of the predictions with all three theories."
his theory of the nature of the chemical bond Pauling predicted the magnetic moments of atoms of the Fe, Pd and Pt transition series as set out in Table I.

\[ \text{Table I.} \]

\[ \text{Predicted Magnetic Moments of Complexes Containing Transition Elements.} \]

<table>
<thead>
<tr>
<th>The Iron Series</th>
<th>The Palladium Series</th>
<th>The Platinum Series</th>
<th>No. of electrons in d shell (3d, 4d or 5d)</th>
<th>For ionic or sp(^3) (tetrahedral) bonds.</th>
<th>For 4 dsp(^5) (square) bonds.</th>
<th>For 6 dsp(^6) (octahedral) bonds.</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClOsHsClHIV</td>
<td>RbJSrHsZrIVNbIVMoIV</td>
<td>CsBaH-IIIITaVWVI</td>
<td>0</td>
<td>0-0</td>
<td>0-0</td>
<td>0-0</td>
</tr>
<tr>
<td>VIV</td>
<td>NbIVMoV</td>
<td>WIV</td>
<td>1</td>
<td>1-73</td>
<td>1-73</td>
<td>1-73</td>
</tr>
<tr>
<td>VIIIIV</td>
<td>MoIVRuVI</td>
<td>WIV0sVI</td>
<td>2</td>
<td>2-83</td>
<td>2-83</td>
<td>2-83</td>
</tr>
<tr>
<td>VIIIIIV</td>
<td>MoIII</td>
<td>OaV</td>
<td>3</td>
<td>3-88</td>
<td>3-88</td>
<td>3-88</td>
</tr>
<tr>
<td>CrIVIII</td>
<td>MoIVRuIV</td>
<td>OaIV</td>
<td>4</td>
<td>4-90</td>
<td>4-90</td>
<td>2-83</td>
</tr>
<tr>
<td>MnIVFeIVCoIV</td>
<td>RuIII</td>
<td>OaIV0sRIV</td>
<td>5</td>
<td>5-91</td>
<td>3-88</td>
<td>1-73</td>
</tr>
<tr>
<td>FeCoIV</td>
<td>RuIRHsIPsIV</td>
<td>IrIIIIPsIV</td>
<td>6</td>
<td>4-90</td>
<td>2-83</td>
<td>0-00</td>
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<tr>
<td>CoIIIII</td>
<td>RhII</td>
<td>IrII</td>
<td>7</td>
<td>3-88</td>
<td>1-73</td>
<td></td>
</tr>
<tr>
<td>NiII</td>
<td>RhIPdIAsIII</td>
<td>PrIAsIII</td>
<td>8</td>
<td>2-83</td>
<td>0-00</td>
<td></td>
</tr>
</tbody>
</table>

This table is taken from the paper by L. Pauling and M. L. Huggins, *Zeit. für Krist.*, 87, 1934, 214.

It will be seen that the moments (given in Bohr magnetons) depend on

1. The valence or oxidation state of the metal atom.
2. The nature of the bonds linking other atoms or groups to the metal (ionic or covalent).
3. The number and configuration of these bonds (when they happen to be covalent).

The iron series has been extensively examined in the light of Table I (Pauling, 1940) and from the experimental results it is clear that when allowance is made for small orbital quenching due to incomplete quenching in atoms not in S states, there is reasonably good agreement between theory and experiment for both ionic and covalent complexes.

It is a matter of some interest to enquire how far the predictions embodied in Table I hold good for the heavier and more complex atoms of the two later transition series. So far as the author is aware, no systematic study, such as is attempted here, has yet been made for the purpose of testing the extent of the validity of Pauling's predictions for the Pd and Pt series. It is true that a good many measurements on compounds of the platinum metals have already been reported but there are inadequacies in the data in the sense that a number of valence states have not received attention and a number of investigations have been largely confined to the sometimes poorly defined anhydrous chlorides whose magnetic dilution is low and whose identity and purity may be in doubt since analytical data were in these instances, not always reported.

From the experimental data already available, more especially that of Bose and Bhar (1928), Guthrie and Bourland (1931), Christiansen and Asmussen (1934, 1935), Janes (1935) and Cabrera and Duperier (1939) and the present work it is clear that the platinum metals do not form ionic complexes,\(^2\) a fact which is

\(^2\) It is possible that fluorides like RhF\(_4\), PdF\(_4\) and PdF\(_6\), etc., may prove exceptions to this statement. The crystal structure of PdF\(_4\) (Ebert, 1931) does indeed strongly suggest that Pd-F bonds are ionic. The author's attempts to prepare PdF\(_5\) without the use of elementary fluorine were unsuccessful.
responsible for the diamagnetic or generally low paramagnetic susceptibilities of the compounds of these metals. Octahedral \((d^2sp^3)\) complexes of \(\text{Pt}^{\text{IV}}\), \(\text{Pd}^{\text{IV}}\), \(\text{Rh}^{\text{III}}\), \(\text{Ru}^{\text{II}}\) and \(\text{Ir}^{\text{II}}\) and square complexes of \(\text{Pt}^{\text{II}}\) and \(\text{Pd}^{\text{II}}\) are in point of fact all diamagnetic, which accords with Pauling's predictions for complexes of these types.

There are, however, instances where theory predicts paramagnetism as for example in the octahedral \((d^2sp^3)\) complexes of \(\text{Ru}^{\text{IV}}\), \(\text{Os}^{\text{IV}}\), \(\text{Ir}^{\text{IV}}\), \(\text{Ru}^{\text{II}}\), \(\text{Os}^{\text{II}}\), \(\text{Ir}^{\text{II}}\), and \(\text{Rh}^{\text{II}}\) (see Table I). It is the purpose of the present communication to report results of measurements on complexes containing metal atoms in the above valence states. As far as practicable, attention has been centred on well defined, magnetically dilute compounds whose structure is known from either physical or chemical investigations.

**Experimental.**

**Method of Measurement.**

Susceptibilities were measured by the Gouy method, full details of which have already been given by Sugden (1932). The small tube used was calibrated for fields ranging up to 6,000 gauss by means of \(\text{CuSO}_4\text{H}_2\text{O}\) whose relatively small paramagnetic susceptibility was in the neighbourhood of the susceptibilities of the compounds studied. The following values of the specific susceptibility \(\chi\) for \(\text{CuSO}_4\text{H}_2\text{O}\) have been reported:

<table>
<thead>
<tr>
<th>(\chi \times 10^6)</th>
<th>Temp. °C.</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.62</td>
<td>19.2</td>
<td>Rankie (1939).</td>
</tr>
<tr>
<td>5.95</td>
<td>17.0</td>
<td>de Haas and Gorter (1930).</td>
</tr>
<tr>
<td>5.92</td>
<td>18.9</td>
<td>Feytis (1911).</td>
</tr>
<tr>
<td>5.85</td>
<td>18.9</td>
<td>Honda and Ishiwara (1915).</td>
</tr>
</tbody>
</table>

The average value corrected to 19° C. is 5.92 \(\times 10^{-6}\), and this was the value adopted for the present work. Effective magnetic moments were calculated on the assumption that the compounds, being magnetically dilute, obey Curie's Law: \(\mu_{\text{eff}} = 2.839\sqrt{\chi T}\). This assumption is undoubtedly only an approximation, but it is sufficiently close to the truth to test the validity of the predictions of Table I. All compounds were made from the purest starting materials available and analysed for at least one constituent to check their purity and to ensure their correct identification. Some identifications were also checked by means of X-ray powder photographs.

**Substances Studied.**

**Compounds of Ruthenium.**

**Potassium pentachlorohydroxyruthenate (IV) \(\text{K}_4[\text{RuCl}_5\text{OH}]\).** Relatively few compounds of quadrivalent ruthenium have been described, and of these two at least have been the subject of a good deal of investigation and not a little controversy. As a result of the work of Aoyama (1924), Howe (1904, 1927) and Charonnat (1931), the constitution of the brown and black complex chloro salts of ruthenium have been established as \(\text{K}_4[\text{RuCl}_5\text{OH}]\) and \(\text{K}_4[\text{RuCl}_4]\) respectively. Of the two, \(\text{K}_4[\text{RuCl}_5\text{OH}]\) is the more easily prepared, and it forms a convenient starting material for the other chloro salts mentioned here. For the present work \(\text{K}_4[\text{RuCl}_5\text{OH}]\) was made by the

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4 It is possible that the deviations from Curie's law are considerable with the compounds \((\text{NH}_4)_2\text{OsCl}_4\) and \((\text{NH}_4)_2\text{OsBr}_4\). It is hoped to carry out low temperature measurements on these substances to check this point.

MM—December 1, 1943.
method of Antony and Lucchesi (1899) starting with the C.P. metal. The dark brown relatively insoluble crystals were analysed for chlorine; found Cl, 47.1%, 47.05%: calculated for $K_2[RuCl_3OH]$ : Cl, 47.4%. As a rough check on the oxidation state of ruthenium in this compound, solutions were reduced with 0.0106N SnCl_2 (in excess) and then back titrated with standard iodine solution in the manner described by Howe (1927). For example, 26 ml of $K_2[RuCl_3OH]$ solution required 3.4 ml of 0.0106N SnCl_2 for its reduction to the trivalent state, whereas the amount required by theory was 3.5 ml. The reduction of $K_2[RuCl_3OH]$ with KI and Ti_2(SO_4)_3 has been studied by Crowell and Yost (1928) and there can be no doubt that in this compound the ruthenium is truly quadrivalent.

The valency of ruthenium in this compound is a matter of some interest in connection with later discussion of its magnetic behaviour which differs so radically from that of the closely related compound $K_2RuCl_4$.

Potassium Hexachlororuthenate (IV) $K_2[RuCl_4]$. The starting material used for the preparation of this compound was the red chloro salt, $K_2[RuCl_3H_2O]$, formed as a result of the reduction of $K_2[RuCl_3OH]$ by prolonged boiling with alcohol under the conditions given by Charonnat (1931). The red chloro salt was dissolved in a minimum of 10N HCl and the solution saturated with chlorine. The hexachloro salt separated as fine, jet black cubes and octahedra which when crushed on white paper gave a deep wine red smear very similar to that produced by $K_2[IrCl_4]$. The compound was analysed for chlorine; found : Cl, 54.2%; calculated for $K_2[RuCl_4]$ : Cl, 54.18%. The X-ray powder photograph of $K_2RuCl_4$ corresponded to a cubic lattice and was similar to the photographs produced by $K_2[IrCl_4]$ and $K_2[OsCl_6]$.

The hexachloro compound readily hydrolysed to the hydroxy compound, and several specimens of the hydroxy compound were prepared in this way. The extraordinary ease with which $K_2[RuCl_4]$ hydrolyses was noted by Charonnat, who states that even in 3N HCl the conversion to $K_2[RuCl_3OH]$ is almost complete.

Tervalent Ruthenium.

Potassium aquopentachlororuthenate (III) $K_2[RuCl_3H_2O]$. Since Ru^{III} complexes have already been extensively examined by Glen and Guntze (1938), one compound only was studied in the present work, and this mainly for the purpose of checking its constitution. $K_2[RuCl_3H_2O]$ was prepared following the method given by Charonnat (1931). When precipitated in a finely divided condition by means of alcohol, this substance possesses a light pinkish brown colour. The compound was analysed for chlorine; found : Cl, 47.3%. Calculated for $K_2[RuCl_3H_2O]$ : Cl, 47.3%. The anhydrous compound $K_2[RuCl_4]$ was prepared by heating the aquo compound to a temperature of 300°C in a stream of dry HCl. (Charonnat, 1931.)

Bivalent Rhodium.

As Rh^{III} complexes have been fully studied by Christiansen and Asmussen (1934), attention has been confined to Rh^{II}, the only other oxidation state in which well defined rhodium complexes appear to exist. Measurements were carried out on specimens described and analysed by Dwyer and Nyholm. They were as follows:

$\text{RhCl}_2\text{SnCl}_4(\text{AsMePh}_3)_3$. (Dwyer and Nyholm, 1942a.)
$\text{Rh(AsMePh}_2)\text{Cl}_2$. (Dwyer and Nyholm, 1941a.)
$\text{Rh(AsMePh}_3)_2\text{Br}_2$.
$[\text{Rh(AsMePh}_2)\text{Br}_2]$. (Dwyer and Nyholm, 1942b.)
$[\text{RhPy}_2\text{Br}]$.
$\text{Py}_2\text{H}[\text{RhBr}_2\text{Py}_2]$. (Dwyer and Nyholm, 1942c.)

The evidence for the state of oxidation of Rh in these complexes rests mainly on the analytical data but partly on their reducing action on silver nitrate solution. This reducing action was of course absent in the Rh^{III} analogues which have been described by Dwyer and Nyholm (1941b). From the analyses of numerous compounds there can be little doubt that, in the compounds under discussion, the Rh exists in the bivalent state. Work carried out recently in this laboratory on the polarography of Rh complexes clearly demonstrates the existence of Rh^{II} complexes at
Sexavalent Osmium.

Potassium osmylocyanitrite trihydrate $K_4[OsO_3(NO_2)_3]3H_2O$. This substance, first described by Wintrebert (1903) was prepared by the action of saturated $KNO_3$ solution on $OsO_4$. The dark olive green needle-shaped crystals were analysed for nitrogen. Found: N, 6·2%; calculated for $K_4[OsO_3(NO_2)_3]3H_2O$: N, 6·1%.

Quadrivalent Osmium.

Ammonium hexachloro-osmate (IV) $(NH_4)_2[OsCl_6]$. Among the most readily prepared and well defined compounds of Os$^{IV}$ are the hexachloro and hexabromo salts, both of which have been deemed sufficiently stable for atomic weight determinations (Gilchrist, 1932). $(NH_4)_2[OsCl_6]$ and $(NH_4)_2[OsBr_6]$ were both prepared by Gilchrist's method, viz. digestion of $OsO_4$ with HCl (or HBr) and subsequent addition of $NH_4Cl$ (or $NH_4Br$), except that recrystallization from weakly acid solutions was avoided owing to the possibility of hydrolysis to hydroxy compounds. Analyses: (I) Found: N, 6·4%; Os, 42·8%; Calculated for $(NH_4)_2[OsCl_6]$: N, 6·4%; Os, 43·3%. (II) Found: Os, 26·9%; Calculated for $(NH_4)_2[OsBr_6]$: Os, 26·9·5%. Osmium in each case was determined by igniting the salt in a stream of pure hydrogen. The identity of $(NH_4)_2[OsCl_6]$ was checked by means of an X-ray powder photograph. $K_4[OsCl_6]$ was prepared in a similar manner and also by treating $K_2[OsO_3(NO_2)_3]$ with concentrated HCl (Wintrebert, 1903). No analysis of the potassium salt was made.

Tervalent Osmium.

Potassium pentanitro-osmate (III) $K_2[Os(NO_2)_3]$. Attempts to prepare this salt by Wintrebert's (1903) method were not very successful owing mainly to the fact that $K_2[Os(NO_2)_3]$ was invariably accompanied by large amounts of $K_2[OsO_3(NO_2)_2]3H_2O$. However, approximately 50 mg. of a substance corresponding to Wintrebert's description of the pentanitro complex were isolated. The amber yellow crystals were very soluble and quite stable in water. They were analysed for nitrogen. Found: N, 13·8%. Calculated for $K_2[Os(NO_2)_3]$: N, 14·0%. The pentanitro complex would seem to be the only$^7$ stable $Os^{III}$ complex so far described. Crowell, Brinton and Evenson (1938) studied $K_4[OsCl_6]$ in solution but succeeded in isolating only impure specimens of the solid.

Bivalent Osmium.

Potassium hexacyano-osmate (II) trihydrate $K_4[Os(CN)_6]3H_2O$. This compound was prepared according to the method given by Krauss and Schrader (1928), viz. by the interaction of $K_4OsO_4$ and KCN. The colourless crystals (isomorphous with $K_4[Fe(CN)_6]3H_2O$, Dufet, 1895) were analysed for nitrogen. Found: N, 15·2%. Calculated for $K_4[Os(CN)_6]3H_2O$: N, 15·1%.

A NOTE ON THE ATOMIC WEIGHT OF OSMIUM.

There exists at the present a curious discrepancy between the atomic weight of Os as determined chemically by Gilchrist (1932) and that determined physically by Nier (1937). Although the former's value of 191·6 was accepted from 1935 to 1938, Nier's value of 190·2 is the one now adopted by the International Committee on Atomic Weights and the one used in the present work. In the past, when chemical and physical measurements have disagreed, subsequent chemical work has harmonized the values. (Cf. Be, B, Sb, etc., Aston, 1942.) This may well prove true with...
regard to osmium. There are remarkably close analogies between the chemistry of osmium and that of ruthenium (Wintrebert, 1903). As already mentioned, K₄[RuCl₄] shows an extraordinary tendency to undergo hydrolysis to K₄[RuCl₃OH] (Charonnat, 1931) which occurs even in 3N HCl. It seems very probable that Gilchrist's high value of 191.6 may be due to the contamination of the hexachloro (and hexabromo) salts with the corresponding hydroxy compounds, especially when it is recalled that the salts were purified by recrystallization from solutions containing as little as 7% HCl (or HBr). The author has noted subtle differences in the colour of various specimens of K₄OsCl₆ which did not seem to depend on the state of subdivision of the specimen but which may well have been due to the presence of the hydroxy salt, in amounts too small to be easily detected by analysis.

**Compounds of Iridium.**

**Quadrivalent Iridium.**

*Ammonium hexachloro-iridate* (IV) (NH₄)₄[IrCl₆]. Very few, if any, complex cations containing Ir⁴⁺ are reported in the literature; on the other hand complex anions are well known and easily prepared in the form of the hexachloro salts. The ammonium salt was prepared simply by adding NH₄Cl to H₂IrCl₆, the latter having been prepared from iridium which had been purified according to hydrolytic method of Gilchrist (1932). Ammonium chloro-iridate (IV) crystallizes in jet black octahedra. Analysis for the metal was made by simply igniting the salt. Found: Ir, 43.77%. Calculated for (NH₄)₄IrCl₆: Ir, 43.70%. The identity of the salt was also checked by an X-ray powder photograph.

In preparing the potassium salt, the more direct method of passing chlorine over a heated mixture of Ir and KCl was employed. Since C.P. Ir and KCl were used for this preparation, no analysis of K₄[IrCl₄] was made.

**Bivalent Iridium.**

From a search of the literature it would seem that with the possible exception of IrCl₂ (Wohler and Streicher, 1913), no compounds of bivalent iridium have been described. The very early work of Skoobolikoff (1853) dealing with alleged Ir⁷⁺ ammines could not be confirmed by Palma (1895), who after a very extensive investigation stated that he was unable to prepare the ammines of either Ir⁴⁺ or Ir⁷⁺. The complex measured (Ir[AsMePh₂]₂Br₂) was prepared and described by Dwyer and Nyholm (1943). The results of the susceptibility measurements are set out in Tables IIa and IIb.

**Table IIa.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight</th>
<th>Specific Susceptibility, $x \times 10^6$</th>
<th>Temperature, °C</th>
<th>$\psi_M$</th>
<th>Diamagnetic Correction</th>
<th>Atomic Susceptibility, $\psi_A$</th>
<th>$\mu$ Bohr Magneton</th>
<th>Number of Unpaired Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₄[IrCl₄]</td>
<td>442</td>
<td>2.30</td>
<td>293</td>
<td>1.017</td>
<td>167</td>
<td>1.184</td>
<td>1.67</td>
<td>1</td>
</tr>
<tr>
<td>K₄[IrCl₄]</td>
<td>484</td>
<td>2.02</td>
<td>295</td>
<td>0.978</td>
<td>171</td>
<td>1.149</td>
<td>1.65</td>
<td>1</td>
</tr>
<tr>
<td>K₄[OsCl₄]</td>
<td>481</td>
<td>1.47</td>
<td>294</td>
<td>0.707</td>
<td>171</td>
<td>878</td>
<td>1.44</td>
<td>—</td>
</tr>
<tr>
<td>(NH₄)₂[OsCl₄]</td>
<td>439</td>
<td>1.63</td>
<td>290</td>
<td>0.716</td>
<td>167</td>
<td>883</td>
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<tr>
<td>(NH₄)₂[OsBr₄]</td>
<td>706</td>
<td>1.01</td>
<td>291</td>
<td>0.713</td>
<td>238</td>
<td>958</td>
<td>1.49</td>
<td>—</td>
</tr>
<tr>
<td>K₄[RuCl₄H₂O]</td>
<td>375</td>
<td>4.31</td>
<td>293</td>
<td>1.616</td>
<td>160</td>
<td>1.776</td>
<td>2.04</td>
<td>1</td>
</tr>
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</table>

* The diamagnetic corrections applied are those of Trew (1941), which are the means of the most reliable results in the literature.
† For K₄[RuCl₄], $\mu = 1.8$ B.M.
procedure proved beyond doubt that \( \text{K}_2[\text{EuCl}_5\text{OH}] \) was not contaminated with any paramagnetic (or ferromagnetic) impurity, the diamagnetism of \( \text{K}_2[\text{EuCl}_5\text{OH}] \) was a quite unexpected phenomenon.

Several compounds exhibited effective magnetic moments corresponding to the presence of one unpaired electron spin. To this class belong \( \text{K}_2[\text{IrCl}_6] \) and \((\text{NH}_4)_2[\text{IrCl}_6]\), the moments for both of which correspond fairly closely to the theoretical value (1.73). In this respect the hexachloro-iridates are different from \( \text{K}_2[\text{BuCl}_6] \), whose moment (3.07 Bohr magnetons) is somewhat greater than the theoretical value for two unpaired spins owing, no doubt, to some unquenched orbital contribution. This difference is interesting in view of the practically identical atomic environment of the iridium and ruthenium atoms in the potassium salts, a point which will be referred to again in the discussion of the hexaehloro-osmates. One unpaired electron spin is found for \( \text{Eu}^{3+} \) in \( \text{K}_2[\text{EuCl}_5\text{H}_2\text{O}] \), although here again the moment (2.04 Bohr magnetons) is larger than the theoretical value owing to unquenched orbital contribution. The effective moment agrees reasonably well with that found by Gleu et al. (1936) for trivalent ruthenium ammines and also with the values reported by Malatesta (1938) and Guthrie and Bourland (1931) for other \( \text{Eu}^{3+} \) complexes. The main interest of the present measurement is that it confirms the constitution proposed by Howe (1927) and Charonnat (1931) for the red chloro salt, viz. \( \text{K}_2[\text{EuCl}_5\text{H}_2\text{O}] \). The moment of the anhydrous salt \( \text{K}_2[\text{EuCl}_5] \) can be taken to mean that in preserving its coordination number of six, \( \text{Eu}^{3+} \) does not form a \( \text{Eu-Eu} \) bond in this complex but instead forms a halogen bridge:

### Paramagnetic Compounds.

A moment in the neighbourhood of 2.8 to 0 Bohr magnetons was anticipated for \( \text{K}_2[\text{OsCl}_6] \) and related compounds but the measured value is far short of this and is in fact even less than the value required for one unpaired electron spin. To determine the extent of the deviation from theory it is obvious that low temperature measurements are required for the hexachloro and hexabromo-osmates. One point is, however, worthy of comment. Since these osmium compounds form part of the isomorphous series \( \text{K}_2[\text{PtCl}_6], \text{K}_2[\text{IrCl}_6], \text{K}_2[\text{EuCl}_6], \) etc., it would seem that departure from theory is not closely related to the effects produced by interatomic forces since, except for a small variation in the lattice constant, the environment of the platinum metal atoms is the same throughout the series.

### Diamagnetic Compounds.

Among the elements of iron transition series, manganese has been examined in the widest range of oxidation states (from +2 to +7) and even in such a high oxidation state as +6 (in \( \text{K}_2\text{MnO}_4 \)) conformity with Pauling's theory has been found (Goldenberg, 1940). It was therefore a matter of interest to see whether this was true of a heavy metal atom like osmium in a high oxidation state as in \( \text{K}_2[\text{Os}_3(\text{NO}_2)_2] \) for which should be in the neighbourhood of 2.8 Bohr magnetons. The observed value of zero would seem to show that Hund's rule requiring a maximum number of unpaired electrons (in the 5d sub-shell) breaks down for osmium.

**Compounds which Conform to Theory.**

Diamagnetic Compounds.

It will be seen that Pauling's theory of magnetic moments accounts for the behaviour of a fairly wide range of platinum metal compounds, both para- and diamagnetic. Previous workers have shown that octahedral complexes of \( \text{Pt}^{IV}, \text{Pd}^{IV}, \text{Rh}^{III}, \text{Ir}^{III}, \text{Ru}^{II} \) and square complexes of \( \text{Pt}^{II} \) and \( \text{Pd}^{II} \) are all diamagnetic, which is to be expected (see Table I). To this list must now be added octahedrally coordinated Os\(^{IV} \), whose complexes are also diamagnetic.

### Paramagnetic Compounds.

Notwithstanding the fact that some paramagnetic platinum metal compounds have been previously reported and the fact that the present work adds several more to the list, compounds in this category form a minority group among the platinum metals. One of the most interesting cases brought to light is that of \( \text{K}_2[\text{RuCl}_4] \), the effective moment (3.07 Bohr magnetons) of which shows that \( \text{Ru}^{IV} \) contains two unpaired electrons. This compound is notable as being the most strongly paramagnetic compound of the platinum metals described to date. Indeed so pronounced is its paramagnetism that the first preparation of the compound was mistakenly set aside as accidentally contaminated. On repeating the work there was no doubt about the high paramagnetic susceptibility which proved to be independent of field strength. To make sure that no accidental contamination had occurred, the \( \text{K}_2[\text{RuCl}_4] \) was hydrolysed to \( \text{K}_2[\text{RuCl}_5\text{OH}] \) and the susceptibility again measured. It was then found that the paramagnetism had entirely disappeared. Although this

![PtCl4](image)

If this is so, the diamagnetism of \( \text{Pt}^{IV} \) accords with Table I.

---

* I am indebted to Mr. W. A. Rawlinson of the Walter and Eliza Hall Institute of Research, Melbourne, for this measurement, which was made on 13.9 mgm. in water solution. The measurement was made by means of a Curie-Cheneveau Balance.

**Discussion.**

**Table III.**

### Diamagnetic Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Specific Susceptibility, ( \chi \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{K}_2[\text{RuCl}_4\text{OH}] )</td>
<td>-0.49</td>
</tr>
<tr>
<td>( \text{K}_2[\text{OSeCN}_3\text{H}_3\text{O}] )</td>
<td>-0.10</td>
</tr>
<tr>
<td>( \text{K}_2[\text{Os(NO}_3)_6] )</td>
<td>-0.55</td>
</tr>
<tr>
<td>( \text{[Rh(Ph}_3\text{MeAs})_3\text{Br}_2] )</td>
<td>-0.4</td>
</tr>
<tr>
<td>( \text{[Rh(Ph}_3\text{MeAs})_3\text{Cl}_2] )</td>
<td>-0.5</td>
</tr>
<tr>
<td>( \text{[RhPy}_3\text{Br}_3\text{Br}] )</td>
<td>-0.31</td>
</tr>
<tr>
<td>( \text{Py}_3\text{H}_4(\text{RhBr}_3\text{Py}) )</td>
<td>-0.12</td>
</tr>
<tr>
<td>( \text{[Rh(Ph}_3\text{MeAs})_3\text{Br}_2] )</td>
<td>-0.38</td>
</tr>
<tr>
<td>( \text{Ir(Ph}_3\text{MeAs})_3\text{Br}_2 )</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

* From Table I it appears that a substance like \( \text{PtL}_4 \) should have a moment of 4.9 Bohr magnetons, if the platinum is quadricovalent. Actually the substance is diamagnetic. (Unpublished work with J. B. Willis.) It is almost certain that the configuration of the platinum is not tetrahedral but octahedral:
Perhaps the most interesting complexes in this group are those in which the metal atoms should have an odd electron and a moment corresponding to one unpaired spin. Complexes of Rh\textsubscript{11} and Ir\textsubscript{11} fall into this group. A wide search was made for paramagnetic bivalent rhodium complexes, but entirely without success. The evidence for state of oxidation of Rh\textsubscript{TI} in the complexes studied has already been reviewed and there seems little doubt that one is here really dealing with Rh\textsubscript{11}. In the polynuclear compounds there is the possibility that Rh-Rh bonds are formed by means of which the odd electron on each metal atom becomes paired as it does in Hg\textsubscript{2}Cl\textsubscript{2}. X-ray crystal analysis (Wells, 1938) has shown that the bridge in the arsine complexes of palladium consists of two halogen (bromine) atoms: \[\text{Br}, \text{Br}\] and in all probability the same kind of bridge functions in the Rh\textsubscript{TI} complexes. Since it is theoretically possible to formulate the binuclear Rh\textsubscript{2}I complexes in terms of Rh-Rh bonds, at the same time retaining octahedral coordination for the metal atom, efforts were made to secure compounds in which the possibility of metal to metal bonds was ruled out. Two such compounds, [RhPy\textsubscript{5}Br]\textsubscript{Br} and [Rh(AsMe\textsubscript{2}Ph)\textsubscript{4}Br\textsubscript{2}], were examined and found to be diamagnetic. It appears therefore that we have in the Rh\textsubscript{n} complexes an instance of the quenching of spin moment, the mechanism of quenching being similar to that responsible for the disappearance of orbital moment in the transition elements other than the rare earths. A similar quenching of spin moment was observed in the one Ir\textsubscript{XI} compound measured. In regard to the quenching of spin, the electronic configuration of the two atoms (Rh\textsubscript{11} and Ir\textsubscript{TI}) in d\textsubscript{2}sp\textsubscript{3} complexes may possess some special significance; in each instance the odd electron must occupy an outer unstable orbital (cf. Co\textsuperscript{11}, Pauling, 1940) and in this situation it may be peculiarly liable to the quenching effect.

It is doubtful whether these are the only circumstances in which the electron spin is quenched because Osm compounds which should behave similarly to those of Rum and have moments in the neighbourhood of 1.73 Bohr magnetons are in fact diamagnetic (\(\mu=0\)). It must be admitted that the number of cases so far examined is very small owing to the fact that very few compounds of tervalent osmium have been described. One only, namely K\textsubscript{2}[Os(N\textsubscript{2})\textsubscript{5}], was studied in the present work and for this (\(\mu=0\), an observation in agreement with the data for Co\textsubscript{11} are none too clear on this point; K\textsubscript{4}[Co(CN)\textsubscript{6}] has been reported to be diamagnetic, but the substance is so unstable that its empirical composition cannot be regarded as established with any great certainty. There is evidence that in solution the cobaltocyanide ion has the composition [Co(CN)\textsubscript{5}]\textsuperscript{-} (or Co\textsubscript{2}(CN\textsubscript{10}) (Glasstone and Speakman, 1930). The diamagnetism of the cobaltocyanide ion may be explained in terms of a structure such as:

\[
\begin{array}{c}
\text{CN} \\
\text{Co} \\
\text{CN}
\end{array}
\]

This formulation finds some support from the measurements of Cambi and Ferrari (1935) on K\textsubscript{2}Ca[Co(N\textsubscript{2})\textsubscript{6}] and closely related compounds whose moments show that Co\textsubscript{11} has one unpaired spin. On the other hand, if we accept the results of Cambi and Ferrari it must mean that there is no quenching of the spin of the electron occupying the unstable 4p orbital. The unpaired electron in Os\textsubscript{11} and Ru\textsubscript{11} occupies a stable orbital, viz. one of the 5d.

\[
\begin{array}{c}
\text{Ru} \\
\text{Cl} \\
\text{Ru} \\
\text{Cl}
\end{array}
\]

**COMPOUNDS WHICH DO NOT CONFORM TO THEORY.**

**Paramagnetic Compounds.**

A moment in the neighbourhood of 2.8-3.0 Bohr magnetons was anticipated for K\textsubscript{2}[OsCl\textsubscript{6}] and related compounds but the measured value is far short of this and is in fact even less than the value required for one unpaired electron spin. To determine the extent of the deviation from theory it is obvious that low temperature measurements are required for the hexachloro and hexabromo-osmates. One point is, however, worthy of comment. Since these osmium compounds form part of the isomorphous series K\textsubscript{2}[PtCl\textsubscript{6}], K\textsubscript{2}[IrCl\textsubscript{6}], K\textsubscript{2}[RuCl\textsubscript{6}], etc., it would seem that departure from theory is not closely related to the effects produced by interatomic forces since, except for a small variation in the lattice constant, the environment of the platinum metal atoms is the same throughout the series.

**Diamagnetic Compounds.**

Among the elements of iron transition series, manganese has been examined in the widest range of oxidation states (from +2 to +7) and even in such a high oxidation state as +6 (in K\textsubscript{2}MnO\textsubscript{4}) conformity with Pauling's theory has been found (Goldenberg, 1940). It was therefore a matter of interest to see whether this was true of a heavy metal atom like osmium in a high oxidation state as in K\textsubscript{2}[OsO\textsubscript{3}(NO\textsubscript{2})\textsubscript{2}] for which \(\mu\) should be in the neighbourhood of 2.83 Bohr magnetons. The observed value of zero would seem to show that Hund's rule requiring a maximum number of unpaired electrons (in the 5d sub-shell) breaks down for osmium.

\[\text{The values given by Gleu and Rehm (1936) range from 2.00 to 2.07 Bohr magnetons.}\]
Perhaps the most interesting complexes in this group are those in which the metal atoms should have an odd electron and a moment corresponding to one unpaired spin. Complexes of Rh\textsuperscript{II} and Ir\textsuperscript{II} fall into this group. A wide search was made for paramagnetic bivalent rhodium complexes, but entirely without success. The evidence for state of oxidation of Rh\textsuperscript{II} in the complexes studied has already been reviewed and there seems little doubt that one is here really dealing with Rh\textsuperscript{II}. In the polymeric compounds there is the possibility that Rh-Rh bonds are formed by means of which the odd electron on each metal atom becomes paired as it does in Hg\textsubscript{2}Cl\textsubscript{2}. X-ray crystal analysis (Wells, 1938) has shown that the bridge in the arsine complexes of palladium consists of two halogen (bromine) atoms:

\[
\begin{array}{c}
Pd \\
\text{Br} \\
\text{Pd}
\end{array}
\]

and in all probability the same kind of bridge functions in the Rh\textsuperscript{II} complexes. Since it is theoretically possible to formulate the binuclear Rh\textsuperscript{II} complexes in terms of Rh-Rh bonds, at the same time retaining octahedral coordination for the metal atom, efforts were made to secure compounds in which the possibility of metal to metal bonds was ruled out. Two such compounds, [RhPy\textsubscript{6}Br]Br and [Rh(AsMe\textsubscript{2}Ph\textsubscript{4}Br\textsubscript{2}], were examined and found to be diamagnetic.

It appears therefore that we have in the Rh\textsuperscript{II} complexes an instance of the quenching of spin moment, the mechanism of quenching being similar to that responsible for the disappearance of orbital moment in the transition elements other than the rare earths. A similar quenching of spin moment was observed in the one Ir\textsuperscript{II} compound measured. In regard to the quenching of spin, the electronic configuration of the two atoms (Rh\textsuperscript{II} and Ir\textsuperscript{II}) in \textit{d}^{2}\textit{s}\textit{p}\textsubscript{3} complexes may possess some special significance; in each instance the odd electron must occupy an outer unstable orbital (cf. Co\textsuperscript{II},\textsuperscript{10} Pauling, 1940) and in this situation it may be peculiarly liable to the quenching effect.

It is doubtful whether these are the only circumstances in which the electron spin is quenched because Os\textsuperscript{III} compounds\textsuperscript{11} which should behave similarly to those of Ru\textsuperscript{III} and have moments in the neighbourhood of 1.73 Bohr magnetons are in point of fact diamagnetic (\(\mu = 0\)). It must be admitted that the number of cases so far examined is very small owing to the fact that very few compounds of tervalent osmium have been described. One only, namely K\textsubscript{3}[Os(NO\textsubscript{2})\textsubscript{5}], was studied in the present work and for this \(\mu = 0\), an observation in agreement

\textsuperscript{10} Unfortunately the data for Co\textsuperscript{II} are none too clear on this point: K\textsubscript{4}[Co(CN)\textsubscript{6}] has been reported to be diamagnetic, but the substance is so unstable that its empirical composition cannot be regarded as established with any great certainty. There is evidence that in solution the cobaltocyanide ion has the composition [Co(CN)\textsubscript{3}]\textsuperscript{3-} (or Co\textsubscript{3}(CN)\textsubscript{5}) (Glasstone and Speakman, 1930). The diamagnetism of the cobaltocyanide ion may be explained in terms of a structure such as:

\[
\begin{array}{c}
\text{CN} \\
/ \\
\text{CN}
\end{array}
\]

\[
\begin{array}{c}
\text{CN} \\
/ \\
\text{CN}
\end{array}
\]

\[
\begin{array}{c}
\text{CN} \\
/ \\
\text{CN}
\end{array}
\]

\[
\begin{array}{c}
\text{CN} \\
/ \\
\text{CN}
\end{array}
\]

\[
\begin{array}{c}
\text{CN} \\
/ \\
\text{CN}
\end{array}
\]

This formulation finds some support from the measurements of Cambi and Ferrari (1935) on K\textsubscript{4}Ca[Co(NO\textsubscript{2})\textsubscript{6}] and closely related compounds whose moments show that Co\textsuperscript{II} has one unpaired spin. On the other hand, if we accept the results of Cambi and Ferrari it must mean that there is no quenching of the spin of the electron occupying the unstable \textit{4p} orbital.

\textsuperscript{11} The unpaired electron in Os\textsuperscript{III} and Ru\textsuperscript{III} occupies a stable orbital, viz. one of the \textit{5d}.
with Bose and Bhar's value of OsCl₅. With K₂[Os(NO₂)₅] it is difficult to be sure whether we have a real departure from theory or not. The probability is that Os is not penta-coordinated here and that the complex is [Os₂(NO₂)₁₀]. In that event, there are two possible alternative structures, one involving a metal-metal bond, the other a bridge formed by two nitro groups:

\[
\begin{align*}
\text{Os} & \quad \text{N} \quad \text{O} \\
\text{N} & \quad \text{O} \\
\text{Os} & \quad \text{O}
\end{align*}
\]

That the nitro group can so bridge has been demonstrated by Mann and Purdie (1936), and it would seem that such a bridge is the more probable explanation of the structure of K₂[Os(NO₂)₅]. On the other hand, if the complex should contain the Os-Os bond its diamagnetism is not inconsistent with theory. Apart from crystal structure analysis there appears to be little prospect of distinguishing between these alternatives unless it can be shown that Os^{III} complexes which are definitely mononuclear have a moment of 1.73 Bohr magnetons.

One further curious anomaly remains to be noted, namely the difference between the magnetic moment of Ru^{IV} in K₂[RuCl₄] (\(\mu = 3.07\) Bohr magnetons) and the moment of Ru^{IV} in K₂[RuCl₅OH] (\(\mu = 0\)). The quenching of the moment to be expected from two unpaired electron spins in the latter compound is extremely puzzling and the only circumstance of significance seems to be the difference in the symmetry of the crystalline field about the ruthenium atom in the two compounds. X-ray powder photographs of K₂[RuCl₅OH] show that its symmetry is lower than cubic and it follows that there must be a correspondingly lower symmetry in the distribution of interatomic forces about the ruthenium atom; indeed the very nature of the complex ion itself suggests this. If this is the correct explanation of the phenomenon, it is not clear why the quenching of spin moment does not occur in K₂[RuCl₅H₂O] (\(\mu = 2.04\) Bohr magnetons). Investigations of compounds of the type [Ir^{IV}A₆]X₂, [Rh^{IV}A₆]X₂ and K₂[IrX₂Y] may throw more light on this question. There seems to be little doubt that covalent bond formation alone does not explain the abnormally low magnetism of complexes of the palladium and platinum metals since the moments found in certain instances are lower than those required by Pauling's theory.

In concluding his chapter on the palladium and platinum transition groups, Van Vleck (1932) wrote: "Further experimental data on the different salts of the Pd and Pt groups are greatly to be desired. Without them further discussion would be too speculative." The main purpose of this investigation has been to supply some of the previously missing data for the purpose of testing as far as possible the existing theories, with the hope that the discrepancies between theory and experiment which have been brought to light may lead to further theoretical investigation.

ACKNOWLEDGMENTS.

The author is indebted to Messrs. F. P. Dwyer and R. S. Nyholm for their generous cooperation in making available compounds of rhodium and iridium; for their assistance in micro-analyses for chlorine and for the loan of ruthenium; to Mr. J. L. Sullivan for taking powder photographs of some of the materials used in this investigation; to Mrs. L. Buckley for micro-analyses for

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12 In discussing the moment of Os^{III} (in OsCl₅) Van Vleck (1932) has considered the possibility that strong internal magnetic coupling leading to quenching of both spin and orbital moment is responsible for the abnormally low magnetism, but he points out that a possibly insuperable objection to this explanation is the fact that Os^{III} is in a 4S state.
nitrilege; and finally to the Commonwealth Research Fund for a grant to purchase osmium and iridium.

SUMMARY.

Complexes of the platinum metals in different valence states have been systematically examined with the object of testing the table of magnetic moments drawn up by Pauling for the transition elements. Over a wide range the predictions have been verified, but instances of breakdown have been observed, notably for OsVI, OsIV, OsII, RuIV, RhII and IrII. Interesting examples of the quenching of spin moment have been noted among the complexes of RhII, IrII and RuIV.

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