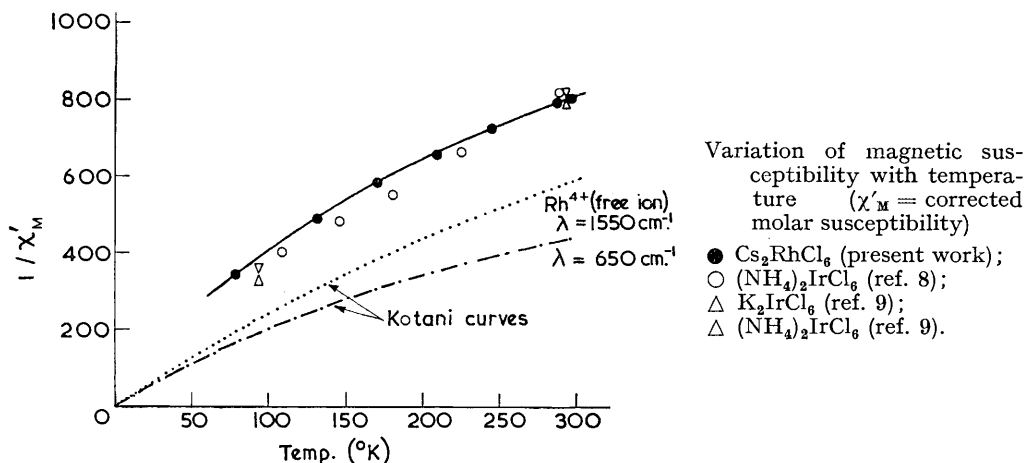


878. *The Magnetochemistry of the Hexachlororhodate(IV) Ion*

By I. FELDMAN, R. S. NYHOLM, and E. WATTON

The magnetic susceptibility of caesium hexachlororhodate has been measured over the temperature range 78–297°K. The effective magnetic moment varies from 1.7 B.M. at room temperature to 1.4 B.M. at 78°K. These data lead to a g value of 1.60, an electron-delocalisation factor, K' , of 0.7, and a spin-orbit coupling constant of 990 cm^{-1} . The susceptibility data are close to those observed earlier for the $[\text{IrCl}_6]^{2-}$ ion.

ALTHOUGH the hexachlororhodate(IV) anion was first reported as the blue-green caesium salt some years ago,^{1,2} its physical properties have been little studied, primarily because of the ease with which it undergoes decomposition. The caesium salt was shown² to be isomorphous with caesium hexachloroplatinate(IV), indicating an octahedrally co-ordinated rhodium(IV) atom. Jørgensen³ studied the reflectance spectrum, and by comparing this with the spectra of the isoelectronic $[\text{IrCl}_6]^{2-}$ and $[\text{RuCl}_6]^{3-}$ ions concluded that, as expected, the rhodium(IV) atom in Cs_2RhCl_6 has a spin-paired (d_e^5) configuration. It was also noted that Cs_2RhCl_6 has electron-transfer bonds at lower frequencies than any hexahalide complex of a transition metal so far studied; Jørgensen^{4,5} proposed that this indicates more



covalency in the $\text{Rh}^{\text{IV}}\text{-Cl}$ bond than in the corresponding hexahalide complexes of other transition metals. This conclusion is based on the correlation of a decreasing frequency of the electron-transfer bonds in hexahalogeno-transition-metal complexes with increasing oxidising power of the metal atom and reducing power of the halide ligand.^{4,5}

No previous magnetic susceptibility measurements on the $[\text{RhCl}_6]^{2-}$ ion have been reported, although the moments of several salts of the $[\text{RhF}_6]^{2-}$ anion have been measured at room temperature⁶ and between 90 and 295°K.⁷ All these values are between 1.7 and 2.0 B.M. We report here the results of the first studies of the magnetic susceptibility of the $[\text{RhCl}_6]^{2-}$ ion, measured over a range of temperatures; these support Jørgensen's general conclusions.

¹ F. P. Dwyer and R. S. Nyholm, *Nature*, 1947, **160**, 502.

² F. P. Dwyer, R. S. Nyholm, and L. E. Rogers, *Proc. Roy. Soc. New South Wales*, 1947, **81**, 267.

³ K. Jørgensen, *Mol. Phys.*, 1961, **4**, 231.

⁴ K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 518.

⁵ K. Jørgensen, *Mol. Phys.*, 1959, **2**, 309.

⁶ R. S. Nyholm and A. Sharpe, *J.*, 1952, 3579.

⁷ E. Weise and W. Klemm, *Z. anorg. Chem.*, 1953, **272**, 211.

The temperature variation of the magnetic susceptibility of Cs_2RhCl_6 over the range 78—297°K is shown in the Figure. The data agree well with those of Figgis⁸ for $(\text{NH}_4)_2\text{IrCl}_6$ over nearly the same temperature range, and with the data of Cooke *et al.*⁹ at 90 and 292°K.

The calculated magnetic moment, μ_{eff} , for each salt decreases almost linearly from about 1.7 B.M. at room temperature to about 1.4 B.M. at 78°K. These data suggest the presence of one unpaired spin, and hence a d_e^5 configuration. The temperature variation of the moment is probably attributable to the super-exchange type of antiferromagnetism believed by Griffiths *et al.*¹⁰ to be operative in $(\text{NH}_4)_2\text{IrCl}_6$ and K_2IrCl_6 . Their paramagnetic resonance spectra showed hyperfine structure due not only to the iridium nucleus but also to the nuclei of the six chlorine atoms. The Landé splitting factor, g , for the Ir^{IV} salts was 1.79. They concluded therefrom that there is spin transfer between nearest-neighbour pairs, *i.e.*, in the structure shown, by (formal) migration for 5% of the time of an unpaired electron from each Cl^- ion to the Ir^{4+} ion; thus, for 30% of the time there is cancellation of spin on the Ir atom and a transfer of the original electron hole from the Ir^{4+} ion to the Cl^- ions attached thereto. Westland and Bhiwandker concluded¹¹ that super-exchange is also responsible for the decrease of μ_{eff} with decreasing temperature for the hexahalide complexes of osmium(IV) and rhenium(IV).

Analysis of our data by use of the equation:

$$\chi_M = C/(T + \theta) + A_p + A_d \quad (1)$$

where A_p and A_d represent temperature-independent paramagnetism and diamagnetism, respectively, gives values of 0.205 for the Curie constant (C), 7.9°K for the Weiss constant (θ), and 570×10^{-6} c.g.s./mole for the temperature-independent paramagnetic susceptibility. The diamagnetic susceptibility, A_d , used for the calculation was 218×10^{-6} c.g.s./mole; this was calculated from Pascal's diamagnetic correction constants.

By inserting the Curie constant into the equation:⁹

$$C = Ng^2\beta^2S(S + 1)/3k \quad (2)$$

we obtain a splitting factor, g , equal to 1.45; hence, the effective orbital reduction, or delocalisation, factor,^{12,13} k' , calculated from:

$$g = (2/3)(2k' + 1) \quad (3)$$

was found to be 0.59. This is considerably less than the value (0.84) found¹⁴ for K_2IrCl_6 and $(\text{NH}_4)_2\text{IrCl}_6$.

From equation (1),

$$A_p = N(2 + g)^2\beta^2/6\zeta \quad (4)$$

we calculate an effective spin-orbit coupling constant, ζ , of 920 cm^{-1} for $\text{Rh}(\text{IV})$ in $[\text{RhCl}_6]^{2-}$ after inserting our experimentally determined values for A_p and g . This value

⁸ B. N. Figgis, Rome Conference on Coordination Compounds, 1957, supplement to *J. Inorg. Nuclear Chem.*, 1958, 476.

⁹ A. H. Cooke, R. Lazenby, F. R. McKim, J. Owen, and W. P. Wolf, *Proc. Roy. Soc.*, 1959, *A*, **250**, 97.

¹⁰ J. H. E. Griffiths, J. Owen, J. G. Park, and M. F. Partridge, *Proc. Roy. Soc.*, 1959, *A*, **250**, 84.

¹¹ A. D. Westland and N. C. Bhiwandker, *Canad. J. Chem.*, 1961, **39**, 1284, 2353.

¹² B. R. Judd, *Proc. Roy. Soc.*, 1959, *A*, **250**, 110.

¹³ K. W. H. Stevens, *Proc. Roy. Soc.*, 1953, *A*, **219**, 542.

¹⁴ J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc.*, 1954, *A*, **226**, 96.

is in good agreement with the observation¹⁵ that $\zeta_{5d} \sim 2\zeta_{4d}$, since Ir(IV) in $[\text{IrCl}_6]^{2-}$ has a ζ value¹⁶ of 2100 cm^{-1} .

The value of g , however, varies according to the method of calculation, and if it be computed by assuming that the slope of the experimentally determined susceptibility curves is proportional to g^2 , then $g = 1.60$. This value of g leads to a value of $k' = 0.7$, and a spin-orbit coupling constant $\lambda = 990 \text{ cm}^{-1}$. The sensitivity of the value of g and λ to the method of calculation is noteworthy. We consider the values $g = 1.60$, $k' = 0.7$, and $\lambda = 990 \text{ cm}^{-1}$ to be the more acceptable.

DISCUSSION

The delocalisation factor, k' , has been interpreted¹⁷ as the probability of finding the unpaired electron in orbitals near the central metal nucleus of complexes, so that the departure of k' from unity measures the percentage of magnetic electron in molecular orbitals, mainly involving π -bonds. The lower k' value in $[\text{RhCl}_6]^{2-}$ as compared with that in $[\text{IrCl}_6]^{2-}$ accordingly indicates that there is considerably more π -bonding, and hence more covalent character, in the $[\text{RhCl}_6]^{2-}$ complex. This conclusion is in agreement with Jorgensen's interpretation of the absorption spectra,³⁻⁵ *i.e.*, that electron-transfer bonds with lowest frequency are due to π -electrons from ligands which have been transferred to holes in the metal d -shell, and that the lower the frequency the smaller the energy required originally to produce this transfer. Some chemical evidence for this interpretation concerning the hexahalide complexes under discussion lies in the fact that rhodium(IV) oxidises an attached Cl^- readily when Cs_2RhCl_6 dissolves in water, and that K^+ and NH_4^+ salts of $[\text{RhCl}_6]^-$ cannot be prepared except as a mixed crystal with a $[\text{PtCl}_6]^{2-}$ salt. On the other hand, both K_2IrCl_6 and $(\text{NH}_4)_2\text{IrCl}_6$ are easily prepared, and $[\text{IrCl}_6]^{2-}$ is stable in hydrochloric acid solution.

Although one might expect, therefore, significantly more super-exchange in Cs_2RhCl_6 than in $(\text{NH}_4)_2\text{IrCl}_6$, μ_{eff} for the two salts is almost the same from 78 to 290°. This apparent contradiction is presumably due to a cancellation of opposite effects. The decrease in the first term of equation (1), as measured by the lower C for $[\text{RhCl}_6]^{2-}$, due to more π -bonding in this ion, is nearly equal to the increase in the second term, A_p , because of the lower spin-orbit coupling constant ζ_{4d} relative to ζ_{5d} . It is probably only coincidence that these opposing effects are so close in magnitude.

The comparison of $[\text{RhCl}_6]^{2-}$ and $[\text{IrCl}_6]^{2-}$ salts of different cations, Cs^+ and NH_4^+ , respectively, might be questionable. However, since the super-exchange involves only neighbouring pairs of complex ions, the cation should have little specific effect on the anti-ferromagnetism so long as distortion of this particular unit does not occur. In fact, the two salts are isomorphous.

One might also question the calculation of the g value of Cs_2RhCl_6 from magnetic measurements on the pure crystals. Evidence that g is approximately the same in both magnetically dilute and pure crystals of $(\text{NH}_4)_2\text{IrCl}_6$ was given by Cooke *et al.*⁹ We assume that this is true also for Cs_2RhCl_6 .

The postulated greater π -bonding in the $[\text{RhCl}_6]^{2-}$ complexes relative to that in the $[\text{IrCl}_6]^{2-}$ derivatives calls for comment. Discontinuities in the sequence 1st \rightarrow 2nd \rightarrow 3rd transition series are, however, quite common. Thus, the first ionisation energies for copper, silver, and gold are 7.72, 7.57, and 9.22 eV; similarly, the ionisation potentials for the $d^{10} \rightarrow d^9$ transition for Ni⁰, Pd⁰, and Pt⁰ are, respectively, 5.87, 8.32, and 8.20 eV. This indicates that the order of electron release or attraction when comparing the 1st, 2nd, and 3rd transition series is very sensitive to the charge on the metal atom.

¹⁵ T. M. Dunn, in "Modern Coordination Chemistry," ed. J. Lewis and R. Wilkins, Interscience, New York, 1960, p. 292.

¹⁶ J. Owen, *Discuss. Faraday Soc.*, 1958, **26**, 174.

¹⁷ J. Owen, *Proc. Roy. Soc.*, 1955, **A**, **227**, 183.

EXPERIMENTAL

Cæsium hexachlororhodate(IV) was prepared by a method which involved several small improvements on the original² procedure. Rhodium trichloride trihydrate (1.0 g.) was dissolved in 8M-hydrochloric acid (30 ml.) by heating, and the solution was immediately placed in an ice-bath, saturated with chlorine, and the vigorously stirred solution treated with cæsium chloride (2.0 g.) dissolved in ice-cold 8M-hydrochloric acid (8 ml.) previously saturated with chlorine. The pink precipitate was separated quickly by centrifugation. To this precipitate were added successively cæsium chloride (0.1 g.) and ice-cold 0.1M-ammonium hexanitratocerate(IV) in nitric acid (1M) saturated with chlorine, and the resulting mixture was centrifuged. The process of treatment of the precipitate with cæsium chloride and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was repeated twice. A blue-green precipitate was obtained; this was washed by centrifuge treatment with ice-cold 1M-nitric acid and finally with dry acetone (twice). After removal of the acetone by vacuum the compound was left for 24 hr. *in vacuo* over phosphorus pentoxide, and for 6 hr. at $\sim 60^\circ\text{C}$ (again *in vacuo*) over phosphorus pentoxide. Magnetic measurements were then made on such a preparation. Analytical values, however, include a correction for loss of weight at 120°C in the oven. This loss in weight varied from 0.25 to 2.5%.

Chloride was determined (Volhard) on the filtrate obtained after dissolving a sample in excess of ferrous sulphate solution (powered zinc was added to effect reduction), acidification with sulphuric acid, and filtration. Rhodium was weighed as the metal after treatment of another sample with zinc and sulphuric acid, and drying the filtered metal at 150°C (Found: Rh, 17.5; Cl, 37.0. Calc. for K_2RhCl_6 : Rh, 17.85; Cl, 36.56).

In accordance with the conclusion of Dwyer *et al.*,^{1,2} that the Rh(IV) is reduced by chloride ions when Cs_2RhCl_6 dissolves in water, 85–88% of the theoretical amount of chlorine only was found from samples dissolved in water. Magnetic susceptibilities were measured as described previously.¹⁸

The authors are indebted to Mr. Peter Woolliams for helpful discussions and assistance with experimental work.

One of us (I. F.) was supported by a Fellowship from the Division of General Medical Sciences, U.S. Public Health Service, and by the U.S. Atomic Energy Commission through contract with the University of Rochester Atomic Energy Project, Rochester, New York.

[*Note added in Proof.*—We are indebted to Dr. J. Owen¹⁹ for the comment that the unusually small value for the exchange interaction is perhaps due to the fact that the lattice is larger with the cæsium ion than with the other alkali metals. He had observed a similar effect with the corresponding iridium salt.²⁰]

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE,
GOWER STREET, LONDON W.C.1.

[Received, February 24th, 1965.]

¹⁸ B. N. Figgis and R. S. Nyholm, *J.*, 1959, 331.

¹⁹ J. Owen, 1965, personal communication.

²⁰ J. Owen, *J. Appl. Phys.*, 1962, 33, 355.