602. *The Magnetic Properties of Some* d^3-*Complexes.*

By B. N. Figgis, J. Lewis, and F. E. Mabbs.

The magnetic properties of twenty-one complexes of chromium, molybdenum, rhenium, osmium, and iridium have been measured between 80° and 300° K. The results are discussed with reference to the relation between the ligand fields, the interelectronic repulsions, and the spin–orbit coupling of the ions, and to the magnetic exchange between the ions. The results may be accounted for with reasonable values of the parameters after the fourth of these effects has been allowed for.

The rôle which ligand fields, spin–orbit coupling, and interelectronic repulsions play in determining the magnetic properties of transition-metal complexes was outlined in the preceding paper. For the d^4-complexes considered it appeared that consideration of these three quantities alone was sufficient. However, in the case of the d^3-configuration it is necessary to consider also the effects of magnetic exchange interaction.

It has long been known that in many first transition-series compounds where linear bond arrangements of the form M–L–M occur (L is a ligand atom, particularly oxygen or fluorine) the electron spins on the two metal atoms (M) may interact through the agency of L, and signs of magnetic interaction are found. These are usually antiferromagnetic in nature. However, it appears that in the second and third transition-series ions, where a greater degree of π-bonding occurs, accompanied by an increased chance of finding the magnetic electrons on the ligand atoms, antiferromagnetic coupling may be transmitted by bonding arrangements such as M–L–L–M.[1] Consequently, antiferromagnetic interactions have been detected in these series in compounds which would normally have been expected to be magnetically dilute. In particular, it is known that the interactions are possible between the metal atoms encased in an octahedron of halogen ligand atoms, as, for instance, in $[IrCl_6]^{2-}$. The possibility of magnetic exchange must, then, be borne in mind when considering the magnetic properties of complexes of the type which we have studied. The presence of magnetic interactions is found to be particularly prominent in the hexahalogen complexes of quadrivalent rhenium, and we have attempted to find the magnetic properties of this ion in the absence of the interactions.

Frequently, when dealing with compounds in which magnetic exchange occurs and which obey the Curie–Weiss law, the magnetic moment is calculated from the equation

$$\mu'_{\text{eff.}} = 2{\cdot}84[\chi_A(T + \theta)]^{\frac{1}{2}}. \qquad (1)$$

The use of this expression is based on the fact that many theories of antiferromagnetism predict that the Curie–Weiss law should hold at temperatures very much greater than the Curie temperature (T_c).[2] Although the Curie–Weiss law may hold for a limited range of temperature immediately above T_c it is not correct to employ in eqn. (1) the Weiss constant evaluated from such a range of temperature. Consequently, when dealing with temperature measurements extending from 80° to 300° K, the use of eqn. (1) is not justified if the Weiss constant exceeds, say, 30°, because the theories of antiferromagnetism predict that T_c should be of the order of θ.

The Magnetic Properties of the d^3*-Configuration.*—Provided that spin-orbit coupling can be regarded as a small perturbation of the ligand field or interelectronic repulsions, the magnetic properties of the d^3-configuration in a complex of octahedral stereochemistry is simple. A $^4A_2$ (t^3_{2g}) term lies lowest; the moment differs from the spin-only value for three unpaired electrons (3·88 B.M.) by the factor

$$(1 - 4\lambda''/10Dq)\,^{*} \qquad (2)$$

due to mixing in of the $^4T_1$ term into the $^4A_2$ through spin-orbit coupling.[3] The moment therefore is independent of temperature. The presence of a ligand-field component of symmetry lower than cubic can cause the moment to vary with temperature, as the spin degeneracy of the $^4A_1$ term is then lifted (zero field splitting), but this normally only occurs at very low temperatures.[4]

In the case of ions with large spin-orbit coupling it is necessary to consider an intermediate coupling scheme rather than the simple Russell–Saunders coupling scheme. As a result of the equivalence of the matrices for t^3_{2g} with those of p^3, it is possible to see the main features of the t^3_{2g} in intermediate coupling from the diagram given for p^3 by Condon and Shortley.[6] The lowest ($^4A_2$) level remains four-fold degenerate ($J = 3/2$) throughout the transition to $j\,.\,j$ coupling but interacts with a higher level, also with $J = 3/2$. The result of this, if the coupling is still largely of the Russell–Saunders type, is to " dilute " the $^4A_2$

---

* By λ'' we imply λ reduced by electron delocalisation in both the t_{2g}- and e_g-orbitals, as in the nomenclature of ref. 5 (cf. the footnote in the preceding paper). For the t^3_{2g} configuration $\lambda = \zeta/3$.

[1] Owen, Cooke, Lazenby, McKim, and Wolf, *Proc. Roy. Soc.*, 1959, *A*, **250**, 97.

[2] Cf. Liddiard, *Reports Progr. Phys.*, 1954, **17**, 201.

[3] Penney and Schlapp, *Phys. Rev.*, 1932, **42**, 666.

[4] Figgis, *Trans. Faraday Soc.*, 1960, **56**, 1553.

[5] Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.

[6] Condon and Shortley, " Theory of Atomic Spectra," Cambridge University Press, 1935.

ground level with an admixture of the $^2T_2$ term which also arises from the t^3_{2g} configuration. The magnetic behaviour of t^3_{2g} in intermediate coupling has been discussed; the g values for the $^4A_2$ term and the magnetic moment as a function of the parameter kT/ζ have been given.[7,8] For spin–orbit coupling constants large enough to require the intermediate coupling treatment, the effect of temperatures of 300° K or below is not important, and in Fig. 1 we have given μ_{eff} for the $^4A_2$ term at zero temperature, as a fraction of the spin-only moment ($\mu_{\text{s.o.}}$) in the Russell–Saunders coupling limit. The parameter against which μ_{eff} is plotted is $\eta = \zeta/(3B + C)$, which is a measure of the degree of $j\,.\,j$ coupling.

Of course, in the intermediate coupling scheme, the $^4A_2$ term is still subject to interaction with the higher ligand field $^4T_1$ term. A full treatment of the problem would require that the behaviour of the $^4A_2$ term be studied under simultaneous perturbation by interaction with the $^4T_1$ term and the influence of $j\,.\,j$ coupling. However, for the ions of importance to the present work, the degree of $j\,.\,j$ coupling is small and we have assumed that the two interactions affect the moment of the term independently. Thus, if $\mu_{\text{i.c.}}$ is written for the moment of t^3_{2g} set in the intermediate coupling scheme, then

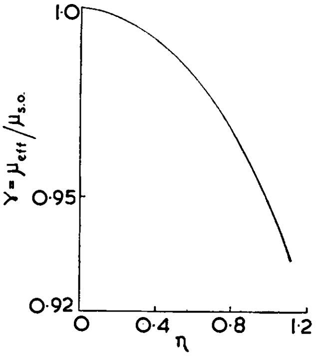


FIG. 1. *The magnetic moment of the t^3_{2g}-configuration in the intermediate coupling scheme.*

$$\begin{aligned}\mu_{\text{eff}} &= \mu_{\text{i.c.}}(1 - 4\lambda''/10Dq) \\ &= \gamma\mu_{\text{s.o.}}(1 - 4\lambda''/10Dq). \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The influence of asymmetry in the ligand field on the temperature-variation of the moment of the $^4A_2$ term is expected[4] to increase as ζ^2 and to decrease as $[10Dq]^2$. Since ζ' is very large in the complexes studied here it would be possible for a large asymmetry in the ligand field to affect appreciably the moment at temperatures as high as 80° K, in spite of the fact that $10Dq$ also is large. However, the complexes have six equivalent ligand atoms surrounding the central metal ion, and it is not expected that the asymmetry will be large. Thus it is unlikely that this effect could be entirely responsible for the great variation of the moment with temperature which occurs for the rhenium compounds. This is especially true when it is considered that such variations are not observed for the complexes of osmium and iridium where ζ' is greater than for rhenium. We have therefore not taken this effect into account. We have interpreted the variation of the moment of rhenium compounds with temperature and between solid and solution as reflecting magnetic interactions.

In order to compare our results with the theory outlined above, it is necessary to know the values of the parameters of spin–orbit coupling and interelectronic repulsion within the ions of the complexes. Such values are not available from direct measurement, nor are they available for the free ions from observation of the spectra, except for Mo^{3+}. Consequently, we have estimated the free-ion values of the parameters from a knowledge of those of the first-row and a few second-row transition-element ions, assuming that the

---

[7] Goodman, Fred, Moffitt, and Weinstock, *Mol. Phys.*, 1959, **2**, 109.

[8] Kamimura, Koide, Sekiyama, and Sugano, *J. Phys. Soc. Japan*, 1960, **15**, 1264.

trends shown between the first and the second row, and between ions of increasing charge, are maintained. The estimates so obtained are set out in Table 1. The estimation procedure cannot be considered to be more reliable than about ±20% for each of the parameters. However, it is probable that the same type of error is present in the estimation of each of the parameters, so the ratio $\eta = \zeta/(3B + C)$ will also be reliable to about ±20%. A detailed account of the estimation of these parameters is to be published by Dr. T. M. Dunn. In order to compare the behaviour of the complexed ion, rather than the free ion, we have assumed that, in the complexed, the ratio of the spin–orbit coupling and the interelectronic repulsion parameters is unchanged, while the spin–orbit coupling parameter for use in $(1 - 4\lambda''/10Dq)$ is reduced from the free-ion value by the factor α^2k. On this approximation, η is independent of the ligand environment of the ion. Here α^2 allows for the delocalisation from the e_g orbitals connected with the $^4T_1$ term, while k allows for delocalisation from the t_{2g} orbitals. Thus $\lambda'' = \alpha^2k\zeta/3$.

TABLE 1. *Estimated values of the spin–orbit coupling and interelectronic repulsion parameters, and the ratio* $\eta = \zeta/(3B + C)$, *for the ions studied (free-ion values).*

	Ion	ζ (cm.$^{-1}$)	$3B + C$ ($3F_2 + 20F_4$) (cm.$^{-1}$)	η		Ion	ζ (cm.$^{-1}$)	$3B + C$ ($3F_2 + 20F_4$) (cm.$^{-1}$)	η
$3d^3$	Cr^{3+}	275 *	6200	0·04	$5d^3$	Re^{4+}	3300	3700	0·9
$4d^3$	Mo^{3+}	840 *	4300	0·2		Os^{5+}	4500	4200	1·1
						Ir^{6+}	6000	4700	1·3

B and C are Racah parameters of interelectronic repulsion; F_2 and F_4 are Condon–Shortley parameters.

* This value was obtained from the spectrum of the ion.

Results.—The results of the measurements of the magnetic susceptibility of twenty-one complexes of Cr^{III}, Mo^{III}, Re^{IV}, Os^{V}, and Ir^{VI} between 80° and 300° K, are set out in Table 2. μ_{eff} is plotted as a function of temperature in Figures 2—7. The results for only two of the complexes of chromium are given diagrammatically, because those for the other complexes are very similar. The results are summarised in Table 3. The mesasurements made in aqueous solution are included in Table 4.

TABLE 2. *Magnetic susceptibilities of the compounds studied. Temperatures in degrees* K, *susceptibilities in* 10^{-6} c.g.s./mole.

Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal
$K_3Cr(CN)_6$		$Cr(acac)_3$		$K_3Cr(CNS)_6,4H_2O$		$Cr\ en_3Cl_3,3H_2O$		$Cr\ en_3Br_3,3H_2O$		$Cr\ en_3I_3,H_2O$	
294·7°	6296	295·2°	6268	295·2°	6046	302·5°	6003	300·8°	6151	301·2°	6063
269·6	6923	270·3	6827	269·1	6634	278·9	6491	276·3	6673	277·2	6576
245·0	7536	245·5	7466	245·9	7275	253·2	7106	250·2	7334	251·1	7217
221·7	8331	222·0	8230	221·7	8035	229·2	7812	224·6	8119	226·1	7984
197·9	9287	198·1	9158	197·9	8949	204·4	8719	200·3	9103	201·0	8924
174·7	10,533	174·9	10,339	175·0	10,141	179·0	9915	174·7	10,390	173·8	10,270
151·4	12,083	152·0	11,819	151·7	11,611	151·1	11,710	143·5	12,630	147·4	12,080
129·2	14,183	130·0	13,789	129·4	13,601	124·7	14,160	124·7	14,440	123·8	14,330
105·6	17,190	106·5	16,630	105·4	16,880	106·2	16,590	103·6	17,410	103·6	17,150
81·2	22,350	82·1	21,470	82·1	21,110	85·0	20,800	84·6	21,340	79·7	22,140

Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal
K_3MoCl_6		$K_3Mo(CNS)_6,4H_2O$		K_2ReF_6		Cs_2ReF_6		K_2ReCl_6		Cs_2ReCl_6	
296·3°	6021	297·5°	5971	293·8°	4654	259·3°	4640	292·0°	4490	295·3°	4712
271·7	6537	273·0	6495	269·4	4843	270·6	5063	269·5	4770	271·0	5064
247·3	7144	248·6	7101	259·8	5075	246·0	5462	247·3	5074	246·6	5455
223·4	7880	222·4	7883	232·9	5561	222·3	6000	225·1	5450	223·0	5954
199·7	8762	193·1	9059	209·0	6147	198·5	6619	202·3	5903	199·2	6538
176·6	9847	168·8	10,321	191·7	6601	175·2	7412	178·5	6399	176·0	7210
152·7	11,265	143·0	12,231	168·5	7261	152·0	8378	155·6	6985	152·7	8045
131·3	12,990	117·7	14,820	151·0	7912	129·5	9619	132·9	7703	129·5	9170
109·3	15,370	104·6	16,610	127·4	8776	104·4	11,450	109·9	8563	104·0	10,730
86·2	18,960	79·8	21,500	116·0	9946	80·9	13,850	86·6	9560	80·0	12,870

TABLE 2. (*Continued.*)

Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal
$(PyH)_2ReCl_6$		$(QH)_2ReCl_6$		$(TH)_2ReCl_6$		Cs_2ReBr_6		K_2ReI_6		Cs_2ReI_6	
297·4°	5339	294·6°	5282	303·7°	4989	304·3°	4605	292·2°	4661	296·5°	4323
271·3	5803	271·1	5691	279·0	5393	279·8	4918	269·6	4922	270·6	4535
246·0	6330	246·8	6159	253·6	5830	254·4	5247	247·3	5262	245·6	4811
222·2	6952	220·7	6840	229·9	6346	232·8	5628	225·1	5665	221·0	5162
197·5	7759	192·1	7767	206·2	6941	206·0	6135	202·3	6117	196·3	5558
174·0	8703	169·0	8739	182·5	7703	183·3	6682	178·7	6624	172·1	5992
151·1	9987	146·0	10,030	160·0	8559	160·9	7293	155·5	7223	149·4	6454
130·2	11,500	118·5	12,140	138·1	9713	138·4	8076	132·7	7911	136·3	6702
106·7	13,830	104·5	13,724	119·7	10,840	121·5	8756	107·8	8800	128·4	6943
79·4	17,960	80·3	17,390	104·0	12,120	104·9	9525	86·6	9654	104·2	7635
				79·8	14,710	79·8	10,940			80·0	8465

Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal	Temp.	Metal
$KOsF_6$		$KOsF_6$		$CsOsF_6$		$CsOsF_6$		IrF_6		IrF_6	
295·2°	4613	182·7°	7401	293·7°	4393	190·0°	6798	293·6°	3725	172·6°	5784
273·2	4945	167·4	8380	269·7	4700	169·0	7565	265·1	3835	152·6	6442
252·7	5364	151·5	8891	253·0	5137	155·5	8251	243·6	4233	132·7	7182
219·3	6200	137·5	10,180	244·0	5345	133·7	9578	220·9	4647	112·1	8286
196·7	6892	115·0	11,430	224·7	5780	118·0	10,760	196·8	5165	90·1	9855
				205·7	6308						

TABLE 3. *Summary of magnetic moments at* 300°K *and the Weiss constants of the complexes studied.*

Compound	μ_{eff} (300°K)	θ	Compound	μ_{eff} (300°K)	θ	Compound	μ_{eff} (300°K)	θ
$K_3Cr(CN)_6$	3·87	1°	$K_3Mo(CNS)_6,4H_2O$	3·79	3°	$(TH)_2ReCl_6$ [e]	3·50	35°
$Cr(acac)_3$ [a]	3·86	7	K_2ReF_6	3·30	40	Cs_2ReBr_6	3·36	80
$K_3Cr(CNS)_6,4H_2O$	3·79	2	Cs_2ReF_6	3·32	24	K_2ReI_6	3·32	100
$Cr\ en_3Cl_3,3H_2O$ [b]	3·83	4	K_2ReCl_6	3·25	88	Cs_2ReI_6	3·22	135
$Cr\ en_3Br_3,3H_2O$	3·82	4	Cs_2ReCl_6	3·35	45	$KOsF_6$	3·34	0
$Cr\ en_3I_3,H_2O$	3·84	5	$(PyH)_2ReCl_6$ [c]	3·58	14	$CsOsF_6$	3·23	0
K_3MoCl_6	3·79	11	$(QH)_2ReCl_6$ [d]	3·54	13	IrF_6	(2·90) [f]	30

[a] acac = acetylacetone. [b] en = ethylenediamine. [c] PyH = pyridinium. [d] QH = quinolinium. [e] TH = *p*-toluidinium. [f] There is scatter in the experimental data for this compound at high temperatures, and the moment cannot be given accurately at 300° K.

TABLE 4. *Magnetic susceptibilities of compounds of molybdenum and rhenium in solution.*

Compound	Solvent	Concn. (M)	Temp. (K)	$10^6\chi_A$	μ_{eff}
K_3MoCl_6	4N-HCl	0·080	293°	5906	3·74
K_2ReF_6	H_2O	0·040	293	4979	3·43
K_2ReCl_6	4N-HCl	0·050	293	5382	3·55
K_2ReBr_6	8N-HBr	0·040	295	5346	3·56
K_2ReI_6	9N-HI	0·050	295	5313	3·55

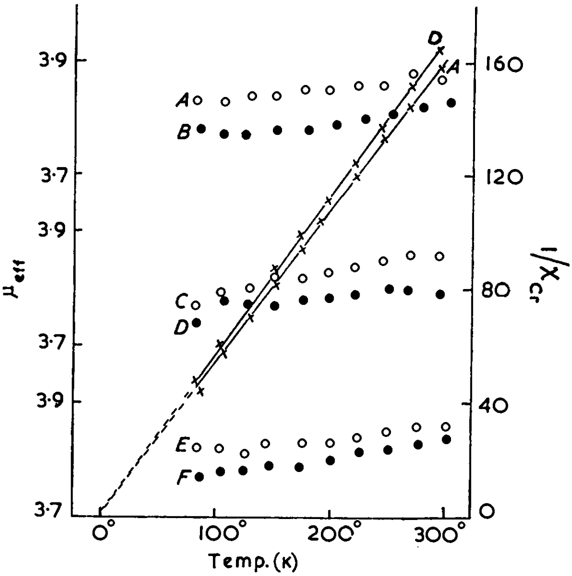
DISCUSSION

Chromium.—With $\lambda = 91$ cm.$^{-1}$ and $10Dq \approx 20,000$ cm.$^{-1}$, the moments of Cr^{III} complexes are reduced below the spin-only value through operation of eqn. (2) by only some 2%, or less if λ'' is lower than λ. Such a reduction is not far outside the experimental error of the measurements. The moments of the chromium complexes studied fall in the range 3·74—3·87 B.M., which is centered around the 3·81 B.M. expected. The spin–orbit coupling constant is so small that application of the intermediate coupling results have no effect on the moment which is predicted. In agreement with the theory the moments vary very little with temperature.

Molybdenum.—For tervalent molybdenum, with $\lambda = 280$ cm.$^{-1}$ and $10Dq \approx 20,000$ cm.$^{-1}$, applcation of eqn. (2) leads to a moment as much as 5·6% below the spin-only value. Although the spin-orbit coupling constant is a good deal larger than for chromium, effects of intermediate

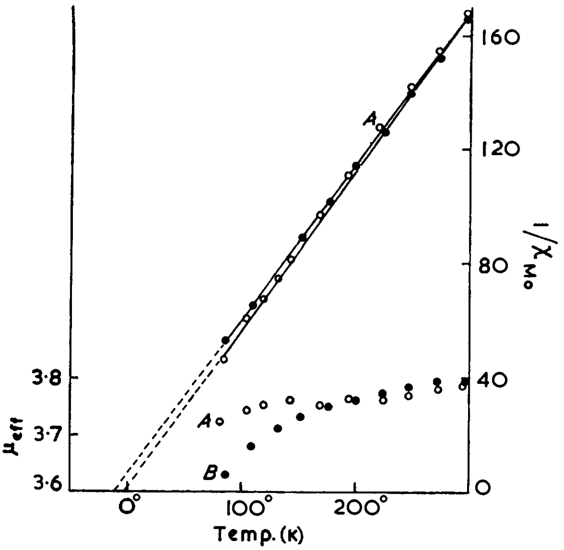
FIGS. 2—7. *Plots of* μ_{eff} *and* $1/\chi_{Metal}$ *against temperature.*

FIG. 2. *Tervalent chromium.*



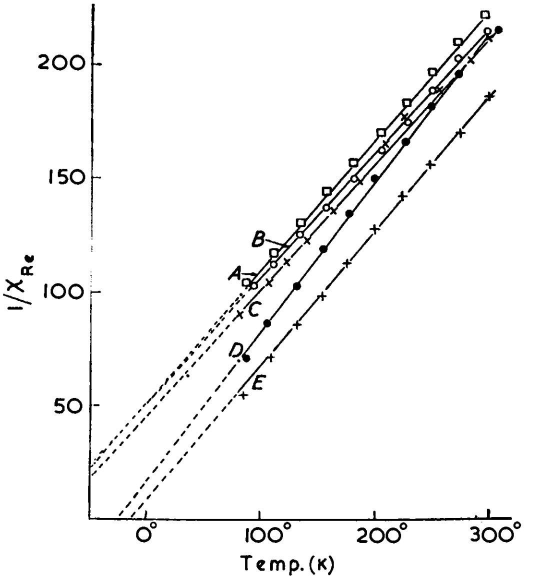
A, $K_3Cr(CN)_6$; *B*, $Cr(en)_3Cl_3,3H_2O$; *C*, $Cr(acac)_3$; *D*, $K_3Cr(CNS)_6,4H_2O$; *E*, $Cr(en)_3I_3,H_2O$; *F*, $Cr(en)_3Br_3,3H_2O$. × refers to $1/\chi_{Cr}$ and the right-hand ordinate.

FIG. 3. *Tervalent molybdenum.*



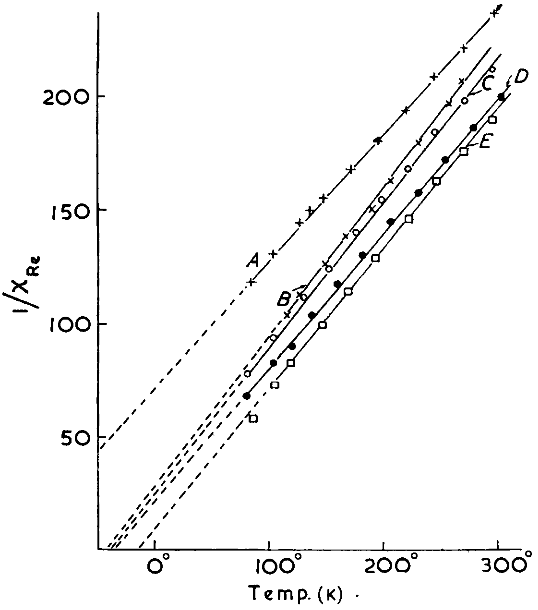
A, $K_3Mo(CNS)_6,4H_2O$ ○; *B*, K_3MoCl_6, ●.

FIG. 4. *Quadrivalent rhenium.*



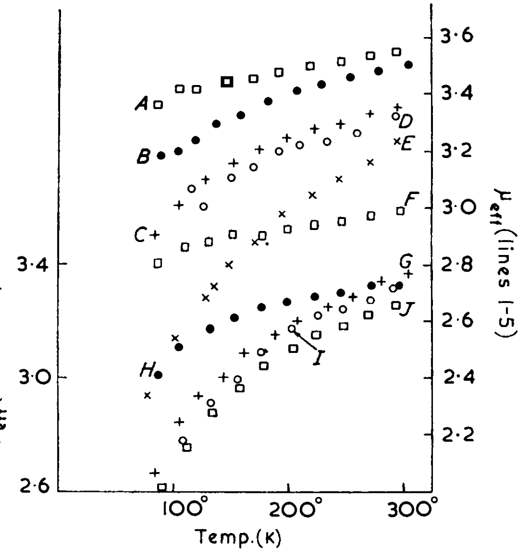
A, K_2ReCl_6; *B*, K_2ReI_6; *C*, Cs_2ReBr_6; *D*, Cs_2ReF_6; *E*, $(PyH)_2ReCl_6$.

FIG. 5. *Quadrivalent rhenium.*



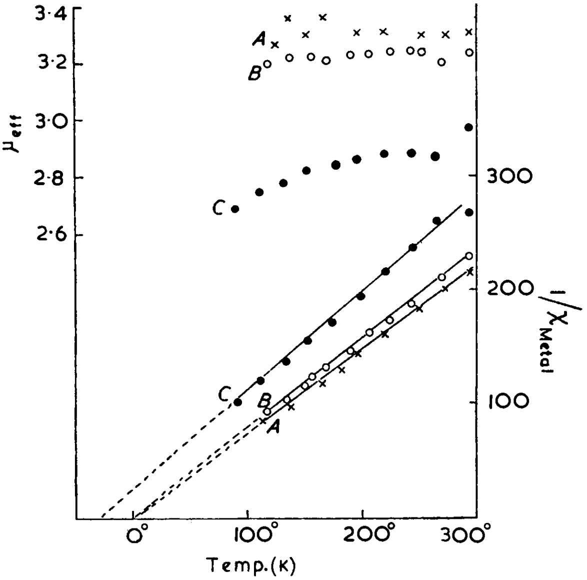
A, Cs_2ReI_6; *B*, K_2ReF_6; *C*, Cs_2ReCl_6; *D*, $(TH)_2ReCl_6$; *E*, $(QH)_2ReCl_6$.

FIG. 6. *Quadrivalent rhenium.*



A, $(QH)_2ReCl_6$; *B*, $(TH)_2ReCl_6$; *C*, Cs_2ReCl_6; *D*, K_2ReF_6; *E*, Cs_2ReI_6; *F*, $(PyH)_2ReCl_6$; *G*, Cs_2ReF_6; *H*, Cs_2ReBr_6; *I*, K_2ReI_6; *J*, K_2ReCl_6.

FIG. 7. *Quinquevalent osmium and sexivalent iridium.*



A, $KOsF_6$; *B*, $CsOsF_6$; *C*, IrF_6.

coupling are negligible: for $\eta = 0{\cdot}2$ the moment is reduced by only 0·2%. The moment observed for the hexachloromolybdate(III) ion varies appreciably with temperature: $\theta = 11°$. Rather than correct the moment with the aid of eqn. (1), we accepted the value of μ_{eff} for this ion in solution. The two complexes of molybdenum(III) studied then yield moments about 3% below the spin-only value. The reduction in moment is too small to allow an accurate evaluation of λ'', but it seems that it is about $0{\cdot}5\,\lambda$, *i.e.*, $\alpha^2 k \approx 0{\cdot}5$. A 50% reduction in the effective spin–orbit coupling parameter by delocalisation effects is not unreasonable for the hexachloro- and hexathiocyanato-molybdate(III) ions.

Rhenium.—For quadrivalent rhenium the effect of the intermediate coupling scheme becomes of some importance. For $\eta = 0{\cdot}9$ the moment is reduced by the factor $\gamma = 0{\cdot}96$. Under the influence of eqn. (2), with $\lambda = 1100$ cm.$^{-1}$ and $10Dq \approx 27{,}000$ cm.$^{-1}$, the moment could be reduced by 16%. The magnetic moment exhibited by the rhenium atom in the hexahalogenorhenate(IV) complexes studied here is not known with the certainty which is desirable. The moments vary with temperature in a manner which suggests magnetic exchange interactions are present. However, even though Weiss constants as high as 135° have been found, our measurements give no indication of the existence of a Curie temperature. Consequently, it seems that the substances cannot be regarded as well-behaved antiferromagnetics. For this reason we have not attempted to use moments calculated on the basis of eqn. (1) for comparison with the theory.

In order to obtain data not subject to uncertainty from magnetic exchange effects, we studied hexahalogenorhenates(IV) with large organic cations, in the hope that these would provide adequate magnetic dilution. While the magnetic exchange appears to be less in such compounds, it is by no means absent. The magnetic exchange in these systems will depend critically on (*a*) the tendency of the electron to be transferred to the ligand and (*b*) the halogen–halogen separation between ions in the solid. We therefore expect that the interaction may vary radically on changing the nature of both the co-ordinating anion and the cation. This effect is illustrated by the value of θ for the hexachlororhenate ion when the cation is varied. The value of θ is low for the pyridinium and quinolinium salts, but relatively high for the potassium and *p*-toluidinium salts. We have found the latter pair of salts to be isomorphous; the former pair have different structures. The compounds K_2ReF_6, K_2ReCl_6, and K_2ReBr_6

are reported to be isomorphous with K_2PtCl_6 and cubic,[9] whilst K_2ReI_6 is reported to be orthorhombic,[10] and in this series it appears that the antiferromagnetic interaction increases in the order $F < Cl < Br < I$. We therefore used the results obtained on the ions in solution, though the accuracy is not high, as the solubilities of the ions are low, and measurement over reasonable temperature range is not possible.

The solution measurements lead to the conclusion that $\mu_{eff} = 0{\cdot}915\,\mu_{s.o.}$. If η is taken to be the estimated 0·9, the delocalisation factor α^2k has to be 0·3, a rather improbably small value. However, if ζ is reduced to 2600 cm.$^{-1}$, which is within the range of the accuracy we have allowed for, the estimated value of η is reduced to 0·7, $\gamma = 0{\cdot}975$, and α^2k becomes 0·5. Such a value of the delocalisation parameter is reasonable. As comparison between theory and experiment is only approximate we do not consider the results for the individual compounds of each ion. We are attempting to obtain more results for the ions in order to be able to correlate the delocalisation factor with the halogen ligand atom.

Osmium.—Our studies on quinquevalent osmium include two hexafluoro-complexes. Their moments do not vary with temperature. Since they involve the same hexafluoro-osmate(V) ions with rather similar cations, and the moments do not differ much, we will compare the mean of the two values (3·29 B.M. $= 0{\cdot}85\,\mu_{s.o.}$) with theory. The estimated value of η (1·1) leads to $\gamma = 0{\cdot}91$. With $\lambda = 1500$ cm.$^{-1}$, a delocalisation factor of 0·4 is required to account for the rest of the reduction in moment. A small reduction in ζ enables a larger value of α^2k to be employed, and that may be considered more suitable for a fluoro-complex.

Iridium.—We have results only for iridium hexafluoride. Its moment varies with temperature ($\theta = 30°$), and we could not make measurements on it in a more magnetically dilute form. Since the use of eqn. (2) in connection with the compounds of rhenium leads to moments higher than those obtained from the measurements on solutions, we have hesitated to apply it to the IrF_6 result. μ_{eff} for the compound is $\sim$2·90 B.M. at 300° K (there is a little uncertainty about the results at high temperature); when corrected by the use of eqn. (1) this becomes 3·05 B.M. With η estimated as 1·3 for Ir^{6+}, γ is 0·91. If α^2k is taken to be 0·5, λ'' is 1000 cm.$^{-1}$, and if $10Dq$ is estimated to be 30,000 cm.$^{-1}$ this leads to a calculated moment of 3·05 B.M. In view of the uncertainty in the moment and the approximations involved in the theory, for which each of $3B + C$ and $10Dq$ are available only as estimates, it does not seem worthwhile pursuing the details of this agreement.

From the preceding discussion it may be concluded that the magnetic properties of the t^3_{2g} compounds studied are in accord with the theory for the configuration if reasonable values of the parameters which govern the theory are employed. However, the results are too limited, and their significance is reduced too much by magnetic exchange, for comparison between theory and experiment to be more than semiquantitative. Since it is unlikely that further complexes of quinquevalent osmium or sexivalent iridium will become available, it appears that future work on elucidating the magnetic behaviour of the configuration will depend on obtaining hexahalogenorhenates(IV), or other quadrivalent rhenium complexes, in higher magnetic dilution. The main feature of the application of the intermediate coupling scheme is that it allows a considerable amount of electron delocalisation to be assumed; without this scheme, the use of eqn. (2) would indicate that no delocalisation takes place.

Experimental.—The compounds employed were prepared and analysed by standard methods. The authors are indebted to Dr. R. D. Peacock for the loan of the fluoride complexes and to Dr. A. Earnshaw for the measurement of the magnetic susceptibilities of these. The accuracy of the measurement of the absolute magnetic susceptibilities was 2—3%, that of the relative susceptibility of the same compound at different temperatures was about 0·5%,[11] except that for iridium hexafluoride, which is volatile, the results at about room temperature show scatter.

William Ramsay and Ralph Forster Laboratories,
University College, Gower Street,
London, W.C.1.

[*Received, March* 3*rd*, 1961.]

---

[9] Ruff and Kwasnik, *Z. anorg. Chem.*, 1954, **219**, 78.

[10] Temple and Dauben, *J. Amer. Chem. Soc.*, 1951, **73**, 4492.

[11] Figgis and Nyholm, *J.*, 1959, 331.