

601. *The Magnetic Properties of Some d^4 -Complexes.*

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The magnetic susceptibilities of a number of complexes of rhenium, ruthenium, osmium, and iridium of the d^4 -electronic configuration 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 constants of the ions concerned. It is found that the free-ion values of those parameters account for the results.

RECENTLY a better understanding of the reasons for the difference between the magnetic behaviour of the first transition-series ions on the one hand, and the second- and third-series ions on the other, has been achieved.¹⁻⁵ It has been realised that both the ligand fields and the spin-orbit coupling are greater in the later transition series, and that this invalidates the assumptions which simplify the magnetic properties of most of the complexes of the first transition-series elements. The larger ligand fields lead to complexes that are always of the spin-paired type. In the presence of large spin-orbit coupling the theory which describes the magnetic properties of $4d^4$ - and $5d^4$ -ions cannot be simplified as it can for $3d^4$ -configuration, and magnetic behaviour has to be considered separately for each ion, or perhaps even for each complex.

The present paper presents measurements of the variation of the magnetic susceptibility with temperature for a number of second and third transition-series complexes. The results obtained for d^4 -configurations are considered first, being the most comprehensive. The results for the d^3 -configuration are given in the next paper. A preliminary report has already been given.² The complexes studied were chosen, so far as possible, to have six equivalent ligands surrounding the central metal ion, for only then can the environment

TABLE I. *Estimated spin-orbit coupling constants (ζ_{nd}) and interelectronic repulsion parameters for the second and third transition-series ions of d^4 -configuration.⁸*

	Ion	ζ_{nd} (cm. ⁻¹)	$\frac{3F_2 + 20F_4}{3B + C}$ (cm. ⁻¹)		Ion	ζ_{nd} (cm. ⁻¹)	$\frac{3F_2 + 20F_4}{3B + C}$ (cm. ⁻¹)
$4d^4$	Ru ^{IV}	1400	5000	$5d^4$	Os ^{IV}	4000	3500
$5d^4$	Re ^{III}	2500	3250	$5d^4$	Ir ^V	5500	3650

F_2 and F_4 are the Condon-Shortley parameters or interelectronic repulsion, B and C are those due to Racah.

of the central ion be, in the first approximation at least, of cubic symmetry. The effect of ligand fields of symmetry lower than cubic on the magnetic properties of the ions will be considered elsewhere. However, as found for the t_{2g}^5 -configuration, ligand fields of low symmetry whose magnitude is of the same order as, or less than, the spin-orbit coupling constant do not much affect the average magnetic moment of the t_{2g}^4 -configuration, so that we may largely neglect them in dealing with regular octahedral complexes of the second and third transition series.⁶

The ligand field parameter, $10Dq$, which measures the separation between the t_{2g} - and the e_g -orbital subsets in the ligand field from an octahedral arrangement of co-ordinating groups, is known to be consistently $\sim 50\%$ larger for $4d$ - than for $3d$ -electron configurations. In the $5d$ -shell, $10Dq$ is $\sim 70\%$ larger than in the $3d$ -shell.⁷ On the other hand it seems

¹ Figgis, *J. Inorg. Nuclear Chem.*, 1958, **8**, 482.

² Figgis, Lewis, Nyholm, and Peacock, *Discuss. Faraday Soc.*, 1959, **26**, 103.

³ Griffith, *Discuss. Faraday Soc.*, 1959, **26**, 173.

⁴ Kamimura, Koide, Sekiyama, and Sugano, *J. Phys. Soc. Japan*, 1960, **15**, 1264.

⁵ Fred, Goodman, Moffitt, and Weinstock, *Mol. Phys.*, 1959, **2**, 109.

⁶ Figgis, unpublished work.

⁷ Jørgensen, 10th Conseil de l'Institut International de Chimie, Solvay, 1956, p. 355.

⁸ Dunn, personal communication.

that spin-pairing energies are smaller for the 4*d*- and 5*d*- than for the 3*d*-shell, because of reduced interelectronic repulsion terms. Consequently, although complexes of both the spin-free type (where the spin-pairing energy is greater than the ligand field) and the spin-paired type (where the converse is true) exist for many first transition-series ions, only spin-paired complexes are known for the later two series. For the second and third transition-series ions spin-orbit coupling constants are undoubtedly larger than in the first series. Table 1 gives estimated spin-orbit coupling and interelectronic repulsion parameter values for 4*d*- and 5*d*-ions which are pertinent to the present work.⁸

It is believed that in transition-metal complexes, particularly those of the spin-paired type, the electrons in *t*_{2*g*}-orbitals may be delocalised on to the ligand atoms for a part of their time. This phenomenon has been allied with π-bonding between the metal and the ligand atoms.^{9,10} Its effect on the magnetic properties of the *t*_{2*g*}-electrons has been described by supposing that the orbital angular momentum associated with the subset is lost for the fraction of time spent on the ligands. Accordingly¹¹ the orbital angular momentum operator may be reduced by a factor, *k*. *k* has been estimated to lie mostly between ~0.7 and 1.

The Magnetic Behaviour of the t⁴_{2g}-Configuration.—Kotani¹² showed that the spin-paired configuration of *d*⁴ in the ligand field from an octahedral distribution of ligand atoms *t*⁴_{2*g*}, has, under the action of a modified form of Russell-Saunders coupling within the *t*_{2*g*} subset, a ³T₁ term lying lowest. Spin-orbit coupling was found to lift the degeneracy of this term and the magnetic susceptibility of the system is

$$\chi_M = \frac{N\beta^2}{3kT} \cdot \frac{48 + (x - 18) \exp(-x/2) + (5x - 30) \exp(-3x/2)}{2x[1 + 3 \exp(-x/2) + 5 \exp(-3x/2)]}$$

with $x = \zeta/kT$. When x is very much greater than unity ($\zeta \gg kT$) only the lowest non-degenerate level of the system is occupied at available temperatures, and the susceptibility arises only from the second-order Zeeman effect between this and higher levels, and is of the temperature-independent type.

Then:

$$\chi_M = 24N\beta^2/\zeta.$$

When x is of the order of unity ($\zeta \sim kT$) the dependence of the susceptibility on temperature is complicated. For Ru^{IV} [(NH₄)₂RuCl₆] ($x \approx 8$ at 300° K) the dependence of the susceptibility on temperature has been found to be small, and it is absent for Os^{IV} (K₂OsBr₆) ($x \approx 16$ at 300° K). For Mn^{III} spin-paired [K₃Mn(CN)₆] ($x \approx 2$ at 300° K) the susceptibility varies with temperature in a somewhat unusual manner. These results may be explained, in the first approximation at least, on the basis of this theory. However, as pointed out in the preliminary communication,² the values which it is necessary to assign to ζ' * in order to obtain the observed susceptibilities of the Ru^{IV}, Os^{IV}, and other iso-electronic ions in complexes are considerably higher than expected on other grounds. This is surprising because, on account of the delocalisation of the *t*_{2*g*} electrons on to the ligand atoms, it is generally accepted that ζ' is likely to be lower in the complex than in the free ion.

Griffith¹³ improved Kotani's theory by introducing the factor *k* into the matrix elements of orbital angular momentum, thus allowing for the effects of *t*_{2*g*}-electron delocalisation, so that the magnetic moment operator is $\mu = (kL + 2S)\beta$ rather than $(L + 2S)\beta$. He also

* We reserve ζ for the free-ion value of the spin-orbit coupling, and the primed symbol, ζ', for the quantity in the complex, but not including the effective reduction resulting from delocalisation. It should be noted that ζ', the spin-orbit coupling constant for use within the *t*_{2*g*} set, is not quite equivalent even [after allowance for the factor (±2*S*)] to the quantity λ' which has been used to denote the effective spin-orbit coupling constant between the *t*_{2*g*} and *e_g* sets.¹⁰

⁹ Dunn, *J.*, 1959, 623.

¹⁰ Owen, *Proc. Roy. Soc.*, 1955, *A*, 227, 183.

¹¹ Stevens, *Proc. Roy. Soc.*, 1953, *A*, 219, 542.

¹² Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

¹³ Griffith, *Trans. Faraday Soc.*, 1958, **54**, 1009.

demonstrated the relation between the configurations (t_{2g}^n) and p^n which allows the properties of the former to be obtained from those of the latter by the substitution of $-L$ for L in the magnetic moment operator. The expression for the susceptibility for $\zeta' \gg kT$ then becomes

$$\chi_M = 8N\beta^2(2 + k)^2/3k\zeta'.$$

However, this treatment makes little difference to the values of ζ' which must be invoked to account for the experimental susceptibilities of the ions concerned.

We suggested that a way out of the difficulty might be to take into consideration the fact that when ζ' is large it may no longer be negligibly small compared with the electrostatic repulsions between the t_{2g} electrons, *i.e.*, that a form of coupling intermediate between Russell-Saunders and $j.j$ may be required.² It was estimated that, in intermediate coupling, the observed susceptibilities for $4d^4$ - and $5d^4$ -ions could be accounted for with very reasonable values of ζ' . Griffith³ has completed the calculations for the susceptibility of t_{2g}^4 with $\zeta' \gg kT$, based on its equivalence to p^2 . He finds that

$$\chi_M = \frac{2N\beta^2(1 + \cos \theta)(2 + k)^2}{3\delta(8^{-\frac{1}{2}} \tan \theta - 1 + \sec \theta)}, \quad \dots \quad (1)$$

with $\delta = \frac{1}{2}(15B + 5C + \zeta')k$ and $\tan \theta = 2k\zeta'/\delta$. [It is presumed that the interelectronic repulsion parameters are reduced in the complex by the same factor, k , as is ζ' , and eqn. (1) differs in this way from the expression given by Griffiths.]

The magnetic moment for t_{2g}^4 has been worked out also in intermediate coupling for $\zeta' \gg kT$ by Kamimura *et al.*,⁴ but no allowance for the effects of electron delocalisation was made. With reasonable estimates of interelectronic repulsion parameters and ζ' , it has been possible to account for the observed moments of some compounds of Ru^{IV} , Os^{IV} , and Ir^V . The results of Kamimura *et al.* are not presented in a form which is convenient for use when ζ' is very much greater than kT . However, for this case, an investigation of theory shows that the only contribution to the susceptibility is from the second-order Zeeman effect between the ground level and one non-degenerate higher level. Consequently, the susceptibility can be shown of the form

$$\chi_A = \chi_A^0 \tanh(a/2kT) \quad \dots \quad (2)$$

where χ_A^0 is the limiting susceptibility at zero temperature, and a is the separation between the ground and the higher level.

Results.—The results of the measurements of the magnetic susceptibilities of nineteen complexes of Re^{III} , Ru^{IV} , Os^{IV} , and Ir^V between 80° and $300^\circ K$ are set out in Table 3. In Figs. 1—5, the susceptibility is plotted against temperature. For the ruthenium complexes the solid lines are plots of eqn. (2) for the values of a and χ_A^0 given in Table 2. For the other

TABLE 2. (a) *Magnetic properties, at 300° K, of the complexes studied.*

Compound	$10^6 \chi_A$ (c.g.s./ mole)	μ_{eff} (B.M.)	$10^6 \chi_A^0$	Compound	$10^6 \chi_A$ (c.g.s./ mole)	μ_{eff} (B.M.)	$10^6 \chi_A^0$
K_2RuF_6	3380	2.86	3960	Cs_2OsF_6	935	1.50	950
K_2RuCl_6	3018	2.70	3700	K_2OsCl_6	941	1.51	940
$(NH_4)_2RuCl_6$	3150	2.76	3620	Cs_2OsCl_6	1162	1.67	1200
Rb_2RuCl_6	3750	3.01	4280	K_2OsBr_6	603	1.21	610
K_2RuBr_6	3322	2.84	3570	Cs_2OsBr_6	1285	1.76	1320
Rb_2RuBr_6	3270	2.81	3420	K_2OsI_6	788	1.38	820
$ReD_2Cl_2(ClO_4)$ * ..	1908	2.14	1960	Cs_2OsI_6	1128	1.65	1150
$ReD_2Br_2(ClO_4)$	1690	2.02	1664	$KIrF_6$	670	1.27	712
$ReD_2I_2(ClO_4)$	1260	1.74	1260	$CsIrF_6$	687	1.29	700
K_2OsF_6	713	1.31	713				

* D = *o*-phenylenebisdimethylarsine.

(b) *Values of a, from eqn. (2), for the complexes of ruthenium.*

Compound	K_2RuF_6	K_2RuCl_6	$(NH_4)_2RuCl_6$	Rb_2RuCl_6	K_2RuBr_6	Rb_2RuBr_6
a (cm. ⁻¹)	508	486	480	546	664	660

Plots of χ_{Metal} against temperature.

FIG. 1. A, Rb_2RuCl_6 ; B, K_2RuCl_6 ; C, $(\text{NH}_4)_2\text{RuCl}_6$.

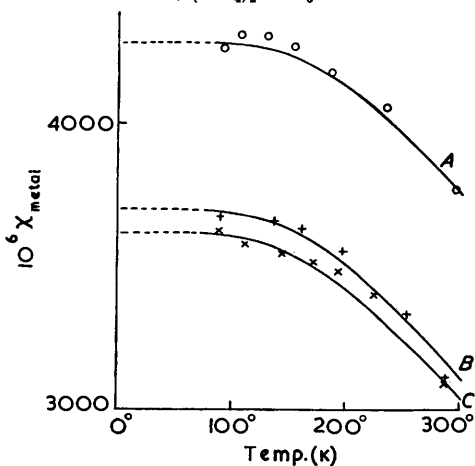


FIG. 2. A, K_2RuF_6 ; B, K_2RuBr_6 ; C, Rb_2RuBr_6 .

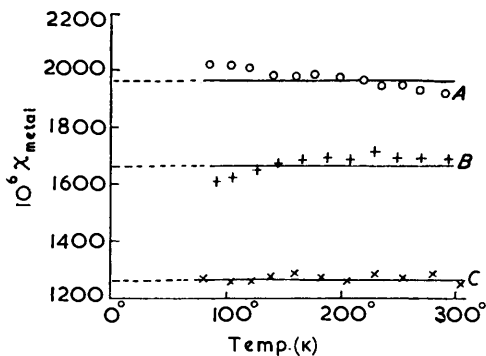
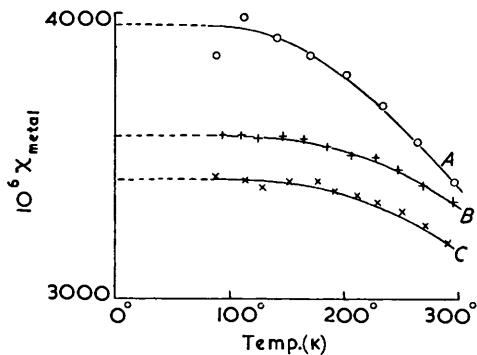


FIG. 3. A, $\text{ReD}_2\text{Cl}_2, \text{ClO}_4$; B, $\text{ReD}_2\text{Br}_2, \text{ClO}_4$; C, $\text{ReD}_2\text{I}_2, \text{ClO}_4$.

FIG. 4. A, Cs_2OsBr_6 ; B, Cs_2OsF_6 ; C, K_2OsF_6 ; D, CsIrF_6 ; E, K_2OsBr_6 .

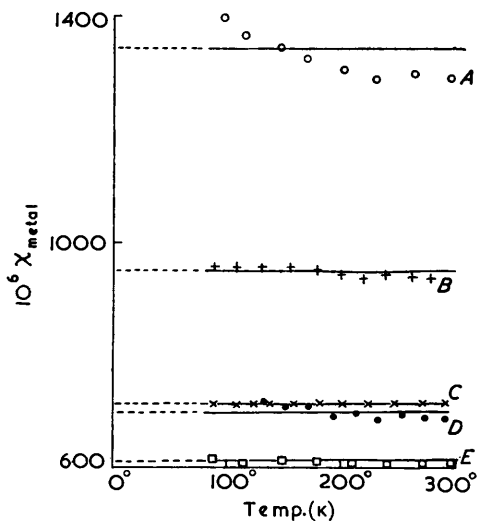
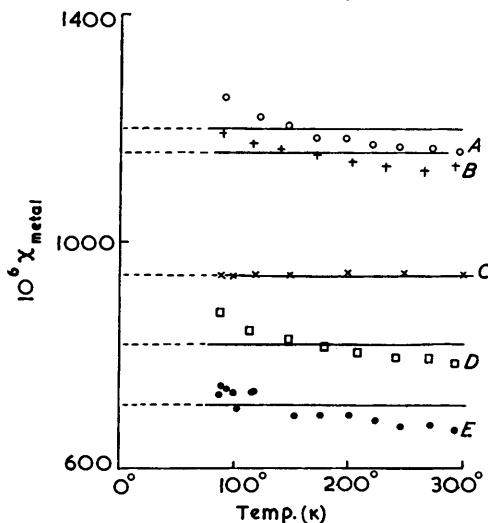


FIG. 5. A, Cs_2OsCl_6 ; B, Cs_2OsI_6 ; C, K_2OsCl_6 ; D, K_2OsI_6 ; E, KIrF_6 .



complexes ζ' is so large that $\tanh(a/2kT)$ is unity and the plot is of χ^0_{Λ} . The magnetic susceptibilities and moments at 300°K are also summarised in Table 2.

TABLE 3. *Magnetic susceptibilities of the compounds studied.*(Temperatures are in °K, susceptibilities in 10⁻⁶ c.g.s./mole.)

K ₂ RuF ₆		K ₂ RuCl ₆		(NH ₄) ₂ RuCl ₆		Rb ₂ RuCl ₆		K ₂ RuBr ₆	
Temp.	Ru	Temp.	Ru	Temp.	Ru	Temp.	Ru	Temp.	Ru
297.0°	3397	288.1°	3112	288.1°	3189	296.1°	3765	296.5°	3338
264.4	3541	254.3	3328	226.4	3399	234.8	4057	270.0	3396
234.2	3670	197.0	3549	194.3	3474	186.2	4169	248.5	3448
203.0	3777	162.5	3629	172.1	3505	154.5	4264	228.8	3486
172.8	3856	138.4	3654	145.0	3540	131.0	4306	207.2	3507
141.8	3914	91.3	3652	111.6	3577	108.4	4303	187.2	3535
113.5	3985			92.0	3616	92.7	4266	166.2	3556
88.8	3853							147.3	3562
								125.8	3564
								110.0	3576
								95.7	3573

Rb ₂ RuBr ₆		ReD ₂ Cl ₂ (ClO ₄) *		ReD ₂ Br ₂ (ClO ₄) *		ReD ₂ I ₂ (ClO ₄) *		K ₂ OsF ₆	
Temp.	Ru	Temp.	Re	Temp.	Re	Temp.	Re	Temp.	Os
292.5°	3194	290.7°	1919	293.6°	1687	304.1°	1247	291.0°	713
271.8	3249	269.4	1936	268.9	1691	279.6	1282	271.7	713
252.9	3299	252.8	1954	228.6	1710	254.3	1270	245.7	713
231.1	3337	235.8	1954	207.8	1687	230.3	1283	224.0	713
211.7	3359	219.2	1963	187.6	1695	206.8	1259	200.9	713
192.2	3377	199.1	1963	166.9	1684	183.1	1270	182.3	713
154.2	3412	178.3	1981	146.7	1675	161.1	1282	159.2	713
129.3	3389	160.9	1976	127.1	1654	138.2	1270	138.0	713
114.3	3413	141.2	1976	106.4	1621	121.5	1259	124.1	713
88.8	3433	120.7	2003	93.0	1610	105.4	1259	109.8	713
		104.0	2017			79.4	1270	88.9	713
		87.4	2012						

* D = *o*-phenylbisdimethylarsine.

Cs ₂ OsF ₆		K ₂ OsCl ₆		Cs ₂ OsCl ₆		K ₂ OsBr ₆		Cs ₂ OsBr ₆	
Temp.	Os	Temp.	Os	Temp.	Os	Temp.	Os	Temp.	Os
278.5°	937	300°	941	296.5°	1162	295.3°	603	295.4°	1285
261.7	937	250	941	272.4	1166	272.4	604	264.4	1293
240.0	934	200	941	244.5	1171	239.6	604	231.3	1285
220.1	937	150	941	220.6	1175	209.5	604	202.4	1300
200.7	940	120	941	196.6	1188	179.2	610	171.1	1327
179.8	950	100	941	171.1	1188	148.9	609	146.8	1342
155.6	957	90	941	147.1	1209	115.0	609	115.6	1365
131.0	954			122.6	1222	87.4	617	98.0	1392
108.7	957			91.0	1257				
89.8	957								

K ₂ OsI ₆		Cs ₂ OsI ₆		KIrF ₆		CsIrF ₆			
Temp.	Os	Temp.	Os	Temp.	Ir	Temp.	Ir		
296.2°	789	294.4°	1132	294.3°	670	104.3°	708	289.1°	687
269.5	794	267.1	1128	272.5	678	98.9	732	272.3	687
241.9	798	233.3	1132	246.8	673	94.1	739	253.0	691
208.4	808	202.7	1142	224.1	685	91.9	744	233.0	687
179.9	818	173.0	1153	201.6	694	89.5	755	213.9	695
149.8	827	141.9	1163	177.2	694			193.1	691
114.3	844	116.3	1177	154.7	694			172.0	706
88.4	877	90.7	1191	115.7	735			151.9	709
								133.1	713

DISCUSSION

Ruthenium.—As pointed out by Griffith,³ the application of eqn. (1) to the estimated values of the parameters of spin-orbit coupling and interelectronic repulsion for Ru^{IV} (free ion) [$\zeta = 1400$ cm.⁻¹; $\delta = 13,200$ cm.⁻¹] leads to a susceptibility of 3590×10^{-6} c.g.s./mole at zero temperature. To this figure a small contribution from the second-order Zeeman effect with higher-lying ligand field levels, probably about 60×10^{-6} c.g.s./mole,

should be added, giving a total of 3650×10^{-6} c.g.s./mole. If ζ' is less than ζ , or if k is less than 1.00, this figure is increased—to 5400×10^{-6} c.g.s./mole if $k = 0.7$. It may be compared with the figure of 4435×10^{-6} c.g.s./mole obtained from Kotani's theory applied in the same way. The values of χ_{Ru}^0 listed in Table 2 range from 3420 to 4280×10^{-6} c.g.s./mole. It seems, then, that the low-temperature susceptibility of the ruthenium complexes may be very satisfactorily accounted for, in the first approximation at least, on the intermediate coupling scheme and by employing spin-orbit coupling and inter-electronic repulsion parameters little if any lower than for the free ion. In the theory the only mechanism for differences appearing between individual complexes lies in the variation of the constant k . It might be expected that k should decrease in the series of ligands F, Cl, Br, and consequently, that χ_{Ru}^0 should rise in that order. However, no correlation between the value of χ_{Ru}^0 and the halogen ligand atom can be seen, and the difference between values for the same halogen with different cations may be larger than that between different halogens. From the theory of Kamimura *et al.*⁴ it may be calculated, by employing $\zeta' = 1400$ cm.⁻¹ and $3B + C = 5000$ cm.⁻¹ (obtained from $\delta = 13,200$ cm.⁻¹) that the level (W_1) with which the second-order Zeeman effect is developed by the ground level (W_3) lies about 900 cm.⁻¹ higher. Accordingly, the temperature-dependence of the magnetic susceptibility of the ruthenium complexes should obey the law $\chi_{\text{Ru}} = \chi_{\text{Ru}}^0 \tanh(450/kT)$, *i.e.*, $a = 900$ cm.⁻¹. However, from Table 3 this is obviously not so. Figs. 1 and 2 show that the susceptibilities are of the form required by eqn. (2) to a fair degree of accuracy, but the values of a required are too low, by about a factor of 2, for all the compounds. The presence of ligand-field components of symmetry lower than cubic could probably lower the W_1 - W_3 separation (a) which was, of course, derived on the basis of a field of cubic symmetry, without much affecting the susceptibility. However, if this is the cause of the reduction, it is remarkable that the low symmetry fields act in the same direction and to much the same amount for each of the six complexes.

Rhenium.—If we assume the free-ion parameters $\zeta = 2500$ cm.⁻¹ and (estimated by comparison with Griffith's values³ for other ions) $3B + C = 3250$ cm.⁻¹ for Re^{III} , application of eqn. (1) gives a susceptibility of 1640×10^{-6} c.g.s./mole for χ_{Re}^0 . A correction for the second-order Zeeman effect with higher ligand-field levels, of 60×10^{-6} c.g.s./mole, increases this to 1700×10^{-6} c.g.s./mole. The spin-orbit coupling is so large that the susceptibility is not expected to vary with temperature over the range studied. The complexes of rhenium studied differ from those of the other ions in that there are not six equivalent ligand atoms surrounding the central metal atom; consequently, since the ligand field produced by the two halogen atoms will differ markedly from those of the four arsenic atoms, it must be expected that the ligand field experienced by the rhenium atom departs a good deal from cubic symmetry. The values of χ_{Re}^0 observed lie between 1960 and 1260×10^{-6} c.g.s./mole and decrease as the atomic number of the halogen atom involved increases. This range includes the value predicted by the theory for a symmetrical rhenium ion. However, it is much larger than that which can be obtained by modifying the theory by reducing k . The temperature-independence of the susceptibility required by the large spin-orbit coupling is nevertheless observed.

Osmium.—The free-ion parameters are $\zeta = 4000$ cm.⁻¹ and $3B + C = 3500$ cm.⁻¹. From eqn. (1), χ_{Os}^0 is calculated to be 880 cm.⁻¹, which is increased to 940×10^{-6} c.g.s./mole by the second-order Zeeman effect with higher ligand-field levels. Again, the large spin-orbit coupling requires that the susceptibility be independent of temperature over the range studied. The susceptibilities were found to range from 600 to 1350×10^{-6} c.g.s./mole, and, while several of them are independent of temperature within experimental error, others change with temperature by amounts which are well outside that error. For the compounds of the latter type, obviously, the value to be chosen for χ_{Os}^0 is ambiguous. The mean value of χ_{Os} was taken to be χ_{Os}^0 . Where the susceptibility varies with temperature it is higher at lower temperatures; consequently, it is tempting to ascribe the variation to the presence of a paramagnetic impurity obeying a Curie law. The presence

of a very small amount of the ion OsX_6^{3-} , whose effect on the analytical results would be negligible, could account for the phenomenon. For this reason the method of choosing χ_{Os}^0 may not be the best; perhaps the high-temperature limit might be better. Nevertheless, the fact remains that the values found for χ_{Os}^0 differ by a factor of more than two. While the range of values found spans the value predicted by theory, there seems to be no way in which the theory can be modified to account for such a range. The problem is more difficult than for the rhenium complexes, for it is expected that the ligand field cannot depart much from cubic symmetry. The susceptibilities are independent of temperature and we are investigating the possibility that magnetic exchange could be consistent with this and responsible for the range of χ_{Os}^0 found. No correlation between χ_{Os}^0 and the halogen involved or the cation is apparent.

Iridium.—If the free-ion parameters are taken to be $\zeta = 5500 \text{ cm}^{-1}$ and $3B + C = 3650 \text{ cm}^{-1}$, eqn. (1) predicts that χ_{Ir}^0 is $590 \times 10^{-6} \text{ c.g.s./mole}$. The second-order Zeeman effect contribution from higher ligand-field levels increases this to $650 \times 10^{-6} \text{ c.g.s./mole}$. The susceptibility is expected to be independent of temperature. The complexes studied are confined to the fluorides; both have χ_{Ir}^0 close to $700 \times 10^{-6} \text{ c.g.s./mole}$, and χ_{Ir} is essentially independent of temperature.

Experimental.—The preparation of the fluoride complexes has been described elsewhere. The remaining halide complexes were prepared and analysed by standard methods. The authors are indebted to Dr. J. E. Fersusson for loan of the rhenium complexes. The measurements of magnetic susceptibility were performed on equipment described previously.¹⁴ The accuracy of the measurement of the absolute susceptibilities of the substances was 2–3%; that of the relative susceptibilities of the same compound at different temperatures was about $\pm 10 \times 10^{-6} \text{ c.g.s./mole}$ for the rhenium, osmium, and iridium complexes, and about $\pm 20 \times 10^{-6} \text{ c.g.s./mole}$ for the ruthenium complexes.

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¹⁴ Figgis and Nyholm, *J.*, 1959, 331.