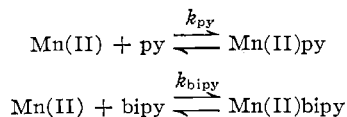data on the sum of the heights of the e.s.r. derivative curve for the six hyperfine lines of Mn(II). The yellow Mn(II)(bipy)$_3$ solution gave an asymmetric spectrum.

Considering ion association due to the Mn(II)–acetate, and complex formation due to the Mn(II)–pyridine, one can calculate

$$\text{Mn(II)} + \text{Ac} \xrightleftharpoons{K_a} \text{Mn(II)Ac} \quad \text{(ion association)}$$

$$K_a = \frac{[\text{Mn(II)Ac}]}{[\text{Mn(II)}][\text{Ac}]} = \frac{(0.00375 - 0.00268)}{(0.00268)(0.1)} = 4.0$$

Similar calculations hold for pyridine and bipyridine

$$\text{Mn(II)} + \text{py} \xrightleftharpoons{k_{py}} \text{Mn(II)py}$$

$$\text{Mn(II)} + \text{bipy} \xrightleftharpoons{k_{bipy}} \text{Mn(II)bipy}$$

From (3) and (4), k_{py} = 6.5 and 6.8, respectively; from (5) and (6), k_{bipy} = 3.16 $\times$ 10^3 and 1.86 $\times$ 10^3, respectively. Assuming complete complexation for solu-tions (7) and (8) one calculates $\beta_6$py = 23.3 and $\beta_3$bipy = 1.07 $\times$ 10^6. The latter value is interesting when compared with Brandt's[12] data from spectrophotometry in the near-ultraviolet: log β_3 = 6.33; this value (e.s.r.), log β_3 = 6.03.

To estimate the chelate effect from the e.s.r. data one may compare log k values for bipyridine and pyridine, respectively. The average values are 3.39 and 0.82, giving a ΔF_{chel} of -3.6 kcal./mole. This compares favorably with the potentiometric value and points out the good possibility of using e.s.r. to obtain reliable data on biological complex stabilities either by direct Mn(II)–ligand interaction or a competition between Mn(II) and another metal ion.

(12) R. R. Miller and W. W. Brandt, *J. Am. Chem. Soc,* **77**, 1384 (1955).

Magnetic Susceptibilities and Dilution Effects in Low-Spin d^4 Complexes: Osmium(IV)

BY ROLF B. JOHANNESEN AND GEORGE A. CANDELA

Magnetic susceptibility measurements were made on a series of hexachloro- and hexabromoösmates, M_2OsX_6, and on potassium hexachlororuthenate, K_2RuCl_6. The paramagnetism of the Os(IV) complexes is independent of temperature and increases as the osmium ions are separated. It is shown that the effect of dilution is described by the equation $\chi = \chi_\infty / (1 + \lambda d^{-n}\chi_\infty)$, where χ_∞ is the susceptibility at infinite dilution, d is the average distance between the osmium ions, λ is a constant, and n is approximately 2. An intermediate coupling scheme is necessary to explain the experimental results for the $5d^4$ configuration. The magnetic susceptibility and part of the optical absorption spectrum can be fit to theory by choosing the values of 2100 ± 100 cm.$^{-1}$ for the spin-orbit coupling constant and 2800 ± 100 cm.$^{-1}$ for the Coulomb interaction coefficient.

Introduction

In 1949 Kotani[1] proposed a theory to explain the magnetic susceptibilities of d^n octahedral complexes for n = 1–5. Kotani made the important assumption that the ligand field is much larger than the Coulomb repulsion between the d-electrons. He calculated energy levels and susceptibilities for the magnetically dilute complexes with the further assumption that the Coulomb interaction coefficient, $3B + C$, was much greater than the spin-orbit coupling constant, ζ. He obtained excellent agreement with experiment for the $3d^n$ complexes. Kotani predicted that a d^4 configuration would have a singlet ground state and a temperature independent paramagnetism given by the equation $\chi = 24N\beta^2/\zeta$ when $\zeta \gg kT$, where N is Avogadro's number and β is the Bohr magneton. The spin-orbit coupling constant is expected to be fairly large for the 4d and 5d electrons and in 1954 Johannesen and Lindberg[2]

reported a temperature independent paramagnetic susceptibility for ammonium hexabromoösmate of $(980 \pm 20) \times 10^{-6}$ cm.^{3} mole^{-1} over the temperature range of 100 to 400°K.[3] Using Kotani's theory and their susceptibility data they estimated a value of 6400 cm.$^{-1}$ for the spin-orbit coupling constant, which is considerably higher than that expected for the free osmium ion.

In 1958 Griffith[4] noted the isomorphism between the octahedral $(dt_2)^n$ and p^{6-n} configurations and reported another derivation of the Kotani formulas for susceptibilities of low-spin d^n complexes. At a conference in 1958 Figgis and co-workers[5] reported tem-

(1) M. Kotani, *J. Phys. Soc. Japan,* **4**, 293 (1949).

(2) R. B. Johannesen and A. R. Lindberg, *J. Am. Chem. Soc.,* **76**, 5349 (1954).

(3) In 1943 the susceptibility of the same complex was reported by D. P. Mellor (*J. Proc. Roy. Soc. N. S. Wales,* **77**, 145 (1943)); however, the measurements were made at room temperature only.

(4) J. S. Griffith, *Trans. Faraday Soc.,* **54**, 1109 (1958).

(5) B. N. Figgis, J. Lewis, R. S. Nyholm, and R. D. Peacock, *Discussions Faraday Soc.,* **26**, 103 and 175 (1959).

perature independent paramagnetism for several complexes of osmium(IV) and iridium(V). They noted a moderate change in susceptibility with temperature and extrapolated their data to zero temperature; however, their values for the paramagnetism of osmium ranged over a factor of two, yielding high coupling constants of 5200 to 10,300 cm.$^{-1}$ when used with Kotani's equation. They proposed that perhaps the assumption that the Coulomb interaction coefficient was much larger than the spin-orbit coupling constant was not valid and pointed out that j–j coupling would reduce the paramagnetism to $\chi = 16N\beta^2/3\zeta$. They also suggested that some intermediate form of coupling is more applicable and at the same conference Griffith[6] reported his calculations based on an intermediate scheme. Griffith, following Condon and Shortley,[7] calculated the energy levels and susceptibilities for low-spin d^4 ions. By making the Coulomb interaction coefficient approximately equal to the spin-orbit coupling constant, by using orbital reduction of the magnetic moment, and by assuming reasonable values for the parameters Griffith obtained good agreement with experiment for Ru^{+4}, Os^{+4}, and Ir^{+5}. Griffith also calculated that the high-frequency elements arising from the t_2^3e configuration contribute a value of 50–70×10^{-6} cm.^{3} mole^{-1} to the paramagnetism. However, he also commented on the apparently haphazard experimental values for osmium, and used an average value for its susceptibility.[8] In 1959 Moffitt, *et al.*,[9] obtained the same ligand field theory results for 5d^n hexafluorides. Jørgensen has examined the spectra of OsCl$_6^{-2}$ and OsBr$_6^{-2}$ and has reported different sets of values for ζ and $3B + C$[10,11]: $\zeta = 2800$–3600 cm.$^{-1}$ and $3B + C = 2100$–2600 cm.$^{-1}$.

In 1960 Kamimura and co-workers[12] reported a calculation they performed for intermediate coupling which yielded the same results as the intermediate scheme of Griffith, and they obtained the same energy levels as Condon and Shortley. They assumed that magnetic interactions between the ions were present and corrected the experimental values of the susceptibilities for the small temperature effect using a Curie–Weiss expression. They calculated reasonable values for ζ; however, no attempt was made to explain the large spread in the osmium data. In 1961 Westland and Bhiwandker[13] reported their measurements on solid solutions of K$_2$OsCl$_6$ and K$_2$OsBr$_6$ diluted with the corresponding Pt salts. Their experiments clearly showed that the paramagnetism of Os^{+4} increased with dilution and using Kotani's equations with an extrapo-

lated value for the susceptibility of 1900×10^{-6} cm.^{3} mole^{-1} calculated a spin-orbit coupling constant of 3200 cm.$^{-1}$. They proposed that superexchange and π-bonding occur in these osmium complexes.

It was decided to prepare and measure the susceptibility of a series of osmium(IV) octahedral complexes with varying degrees of magnetic dilution in an attempt to resolve the discrepancy in the values of susceptibility, the considerable variations in the temperature dependence of susceptibility, and the calculated values of the spin-orbit coupling constant reported in the literature.

Experimental

Osmium tetroxide was prepared by the combustion in oxygen of highly purified metallic osmium which had been shown by spectrographic examination to be free of other platinum group metals. Solutions of chloroösmic and bromoösmic acids were prepared by reducing the tetroxide with the respective hydrohalogen acids at reflux temperatures. The reduction of osmium tetroxide was aided by the addition of small amounts of ethanol. The major oxidation product of ethanol appeared to be the highly volatile acetaldehyde; if any dissolved organic material remained in the solution after evaporation, it is most unlikely that it would be paramagnetic. The analogous acids of platinum were prepared by dissolving the metal in aqua regia or in hydrobromic acid plus bromine.

The various salts whose susceptibilities are reported in Table II were prepared by adding solutions of the appropriate halide to the corresponding haloösmic or haloplatinic acid. In most cases, the salts were of low solubility and crystallized as the solutions were mixed. The salts of the tetra-*n*-butylammonium cation were relatively soluble and it was necessary to evaporate the solutions to recover the product. The solubility of the tetra-*n*-butylammonium chloro salts was very much greater in concentrated acid than in dilute. The osmium solutions were not diluted to less than about 6 *N* acidity because of hydrolysis, but the platinum solutions could be diluted safely to 1 *N* and a better recovery made.

Commercial tetramethylammonium bromide (Eastman Kodak White Label) was recrystallized from a mixture of alcohol and ether. Tetra-*n*-butylammonium bromide was prepared by allowing tri-*n*-butyl amine and *n*-butyl bromide (both Eastman Kodak White Label) to stand in a sealed ampoule until largely solid. The product was twice recrystallized from ethyl acetate. This salt was converted into the corresponding chloride by treatment in aqueous solution with excess silver oxide, followed by neutralization of the quaternary ammonium hydroxide with hydrochloric acid. The solution of the chloride was used directly in the preparation of the chloroösmate and chloroplatinate. The ammonium halides were prepared by distilling ammonia directly into solutions of the redistilled hydrohalogen acids and evaporating to recover the salts. The cesium halides were prepared starting with pollucite and purified by recrystallizing the dichloroiodide from dilute hydrochloric acid.[14] Spectrophotometric and flame photometric analyses showed foreign cations to be present to the extent of 0.01% or less; tests similar to those for reagent chemicals[15] showed the amounts of foreign anions to be within the limits established for ACS reagent grade potassium chloride or bromide.

The mixed crystals of (NH$_4$)$_2$(Pt,Os)Br$_6$ were prepared by mixing solutions of the bromoacids in the desired proportions and then adding a solution of ammonium bromide. X-Ray and microscopic examination of the product in comparison with known mechanical mixtures of (NH$_4$)$_2$OsBr$_6$ and (NH$_4$)$_2$PtBr$_6$

(6) J. S. Griffith, *Discussions Faraday Soc.*, **26**, 173 (1959).

(7) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge Press, 1953.

(8) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge Press, 1961.

(9) W. Moffitt, G. L. Goodman, M. Fred, and B. Weinstock, *Mol. Phys.*, **3**, 109 (1959).

(10) C. K. Jørgensen, *Discussions Faraday Soc.*, **26**, 175 (1959).

(11) C. K. Jørgensen, *Mol. Phys.*, **3**, 201 (1960).

(12) H. Kamimura, S. Koide, H. Sekiyama, and S. Sugano, *J. Phys. Soc. Japan*, **15**, 1264 (1960).

(13) A. D. Westland and N. C. Bhiwandker, *Can. J. Chem.*, **39**, 1234 (1961).

(14) R. West and R. P. Anderson, *Inorg. Syn.*, **4**, 9 (1953).

(15) Reagent Chemicals, American Chemical Society Specifications, 1955.

showed that we most probably were dealing with a true solid solution. Potassium hexachlororuthenate was prepared by the method of Howe.[16]

The results of analyses for heavy metals are reported in Table I. The salts were analyzed by ignition in hydrogen (followed by extraction of CsX and re-ignition where necessary). Analyses also were made by precipitating hydrated osmium dioxide from solution at pH 4.0 followed by ignition in hydrogen.[17] The mixed crystal material was analyzed by a spectrophotometric method in which the spectrum of the unknown was exactly matched by mixing standard solutions of bromoplatinic and bromoösmic acids in the reference cell of a Cary Model 14 recording spectrophotometer. The results are estimated to be accurate to within ±2% of the amount of osmium in the sample.

TABLE I

Salt	Calcd.	Found
$(NH_4)_2OsCl_6$	43.31	43.09, 43.10, 43.12, 41.93
$(NH_4)_2OsBr_6$	26.96	26.21, 26.88, 27.12, 27.17
Cs_2OsCl_6	28.44	28.64
Cs_2OsBr_6	20.33	20.10, 20.45
$[(CH_3)_4N]_2OsBr_6$	23.25	23.34
$[(C_4H_9)_4N]_2OsCl_6$	21.44	21.21, 21.45
$(NH_4)_2PtBr_6$	27.47	27.40, 27.41
$[(C_4H_9)_4N]_2PtCl_6$	21.87	21.62, 21.89
K_2RuCl_6	25.90	25.71, 25.90
$(NH_4)_2(Pt,Os)Br_6$	Os/(Os + Pt) = 0.0763 mole/mole	

The magnetic susceptibilities were measured by an absolute Gouy method. A double-ended sample tube with a partition at the center was used. The sample was finely powdered and carefully packed in the upper half of the tube. Both sections were evacuated and filled with helium gas at 20 cm. pressure. Blank runs were made on all sample tubes used. An enclosure contained the tube and a Mettler semimicro balance and was filled with helium or "prepurified" nitrogen gas. The absolute gram susceptibilities were calculated by the equation

$$\chi = \frac{2\Delta wgl}{m(B_1^2 - B_0^2)}$$

where Δw is the change in weight on application of the field B_1, B_0 is the field at the top of the sample, g is the acceleration due to gravity, l is the length, and m the mass of the sample. B_1 was measured by a proton resonance magnetometer and B_0 was measured by a calibrated General Electric gaussmeter. The maximum field used was 8000 gauss and $B_0^2 < 0.02B_1^2$ at al fields. The largest source of error is due to the non-uniformity of the density, which depends upon the particular sample. Measurements were made at 298 and 78°K.; K_2RuCl_6 was measured at 63°K. also. A calibrated thermocouple was used to measure the temperature. The susceptibilities of the various complexes studied are listed in Table II. Each figure in Table II is the average of the results obtained from several runs using different tube fillings, and in some cases different preparations. In all cases the gram susceptibility for a given compound at any one temperature was repeatable within 0.01×10^{-6} cm.^{3} g.$^{-1}$ or 1%, whichever was larger. Each run was made at several field strengths and each showed a susceptibility independent of field strength.

The spectra of H_2OsCl_6 and H_2OsBr_6 in solution in the respective hydrohalogen acids were measured with a Cary Model 14 recording spectrophotometer. The wave length scale was calibrated at several points using lines from hydrogen and mercury vapor sources and found to be within 5 Å. of the indicated values. The solutions were measured from 1300 to 200 mμ (7700 to 50,000 cm.$^{-1}$). The wave numbers and extinction coefficients of the observed peaks are listed in Table III (s indicates a shoulder).

(16) J. L. Howe, *J. Am. Chem. Soc.*, **49**, 2381 (1927).

(17) R. Gilchrist, *Bur. Std. J. Res.*, **6**, 421 (1931).

The spectrum of $[(n-C_4H_9)_4N]_2OsCl_6$ in the form of a mull in hexachlorobutadiene was recorded between 0.6 and 2.6 μ (3850–16,600 cm.$^{-1}$). Only relative intensities can be indicated since the concentration and thickness of the mull were not accurately known. Peaks were recorded at 17,320 (s); 17,170; 16,990; 10,930 (broad); 10,470 (?); 8403 (w); 8065 (s); and 7843 (w) cm.$^{-1}$ (s = strong, w = weak). Several bands were observed between 4500 and 5600 cm.$^{-1}$. At least some of these bands also were present in $(n-C_4H_9)_4NBr$, but the agreement of lines in the two spectra was not exact and some of the absorption is believed to be due to the $OsCl_6^{-2}$ ion.

Solutions of these acids diluted to a lower acidity with water showed no visible change at room temperature in a day. At a temperature of 90–95°, however, the H_2OsCl_6 in 1.5 N acid changed color visibly in 1 or 2 hr., and the H_2OsBr_6 in 1.5 N acid changed color visibly in 10 or 15 min. These changes were reversed in about the same length of time upon heating the diluted solutions with concentrated acid. The spectral changes that were most pronounced in the case of H_2OsCl_6 were a very large increase in absorption at 39,400 cm.$^{-1}$ and a simultaneous loss of absorption at 30,000 cm.$^{-1}$ as the solution was diluted and heated. Under similar conditions the spectrum of H_2OsBr_6 changed to give only a single strong, broad absorption at 23,300 cm.$^{-1}$. Presumably these changes are due to hydrolysis of one or more of the halogen atoms, but no definite species was isolated. The values given above may be compared with those reported by Jørgensen.[18] The observed positions of the peaks are in close agreement, except for a few values in the near-infrared which are not listed by Jørgensen. The values of the extinction coefficients are roughly the same, but the agreement is not so good as might be desired. Our spectra were run in more concentrated acid than those reported in the literature, and it is possible that this difference in conditions may account for some of the lack of correspondence between the two sets of data. A broad absorption from 3000–5000 cm.$^{-1}$ is reported by Turner,[19] which may correspond to the absorption found here around 5000 cm.$^{-1}$. Turner also reports spectra in the visible with which the above data generally agree.

Discussion

In Table IV the magnetic susceptibilities of osmium complexes reported in Table II and those of other workers are listed. The average distance between osmium ions listed in Table IV was calculated from the X-ray data and dilution of each compound. K_2OsF_6 and Cs_2OsF_6 are trigonal with two osmium ions closer than the other six and the average distance listed is a mean value of the two different distances. All the other complexes have twelve nearest neighbors at the same distance.

Unfortunately there are some large discrepancies among the reported values for the paramagnetism of the complexes. These differences are most likely due to lack of purity. All of the measurements of this investigation display a very small change of susceptibility with temperature whereas other workers have reported some rather large temperature effects. Any increase in the susceptibility of Os^{+4} with decrease in temperature most likely is due to impurities because the next higher magnetic state is at least 1500 cm.$^{-1}$ above the ground state and temperature effects should not be

(18) C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959); *Acta Chem. Scand.*, **16**, 793 (1962).

(19) A. G. Turner, Dissertation, Purdue University, *Dissertation Abstr.* **19**, 2458 (1959).

Inorganic Chemistry

<div align="center">Table II</div>

Complex	Temp., °K.	Specific susceptibility $10^6\chi_g$, cm.³ g.⁻¹	Molar susceptibility $10^6 M\chi_g$, cm.³ mole⁻¹	Molar diamagnetic susceptibility $10^6\chi_d$, cm.³ mole⁻¹	Susceptibility of d^n electrons $10^6\chi$, cm.³ mole⁻¹	Molecular weight M
$(NH_4)_2OsCl_6$	298	1.594	700	−208	908	439.02
	78	1.609	706	−208	914	
$(NH_4)_2OsBr_6$	298	1.030	727	−268	995	705.78
	78	1.020	720	−268	988	
Cs_2OsCl_6	298	0.990	662	−247	909	668.76
	78	1.002	670	−247	917	
Cs_2OsBr_6	298	0.721	675	−307	982	935.52
	78	.734	687	−307	994	
$[(CH_3)_4N]_2OsBr_6$	298	.849	694	−374	1068	817.99
	78	.902	738	−374	1112	
$[(C_4H_9)_4N]_2OsCl_6$	298	.434	385	−599	984	887.89
	78	.445	395	−599	994	
$(NH_4)_2(Os_{0.076}Pt_{0.924})Br_6$	298	−0.171	−122	−230	1420	710.42
	78	−0.165	−117	−228	1460	
$(NH_4)_2PtBr_6$	298	−0.324	−230	−272	42	710.81
	78	−0.321	−228	−272	44	
K_2RuCl_6	298	8.30	3250	−200	3450	392.04
	78	9.36	3670	−200	3870	
	63	9.42	3690	−200	3890	
$[(C_4H_9)_4N]_2PtCl_6$	298	−0.630	−562	−599	37	892.73
	78	−0.626	−558	−599	41	

noted over the range of temperatures in which any of the measurements were made.

X-Ray studies of $[(n\text{-}C_4H_9)_4N]_2OsCl_6$ showed a non-cubic structure and the average distance between osmium ions listed in Table IV was estimated. Compared to the other complexes, one might expect a somewhat larger value than 990×10^{-6} cm.³ mole⁻¹ for the susceptibility. This "low" measured value might be due to lower symmetry.[20]

A comparison of the measurements on the osmium complexes reported in Table IV indicates that the paramagnetism increases as the osmium ions are separated. Westland and Bhiwandker have clearly shown this effect for $K_2Pt_{1-n}Os_nBr_6$ and $K_2Pt_{1-n}Os_nCl_6$. In Table IV the complexes are listed by increasing osmium ion separation, d, and the average experimental paramagnetism increases as the distance and does not appear to be strongly influenced by the nature of the cations. The different halogens also appear to have

<div align="center">Table III</div>

$\bar{\nu}$, cm.⁻¹	OsCl₆⁻² ϵ, mole⁻¹ cm.⁻¹	$\bar{\nu}$, cm.⁻¹	OsBr₆⁻² ϵ, mole⁻¹ cm.⁻¹
8,580	1.1	8,550	2.0
10,825	5.3	10,530	20.6
11,780	4.4	11,380	25.9
17,235	6.7	17,700 s	1344
17,433	3.4	20,400	6220
17,575	2.1	22,600	8530
17,640	4.9	23,700 s	5030
24,100 s	1220	25,100	5370
27,100	8650	28,750	1070
29,400 s	9300	36,100	12250
30,000	9380		
33,100 s	1270		
36,400 s	965		
39,400	2330		

little influence on the dilution effect. This is because although the particular halogen has an important effect on the magnitude of the very strong crystal field, the contribution to the paramagnetism from the high de levels is estimated by Griffith to be only about $50\text{–}70 \times 10^{-6}$ cm.³ mole⁻¹. Measurements on two different platinum compounds give a value of 40×10^{-6} cm.³ mole⁻¹ for the temperature independent paramagnetism of Pt^{+4} (Table II), in agreement with Griffith. If the dilution effect were due to superexchange *via* the halogen ion then the particular halogen would be very important in determining the amount of exchange. This does not appear to be the case.

In order to explain the increase in susceptibility with increasing separation of osmium ions, let us consider an "effective" Weiss interaction $\lambda'M$, where M is the magnetic moment at infinite dilution.[21] λ' is a function of the crystal field, the various other ions besides the magnetic osmium ion, and the distance between the osmium ions. For the series of complexes listed in Table IV, λ' appears to be mainly a function of the dilution and it is assumed that $\lambda' = \lambda d^{-n}$, where λ is a constant and d is the distance between the osmium ions. Then for a temperature independent paramagnetism the susceptibility is

$$\chi = \frac{\chi_\infty}{1 + \lambda d^{-n}\chi_\infty}$$

where χ_∞ is the paramagnetism at infinite dilution. The average susceptibility data listed in Table IV could be fit graphically with n between 1 and 2. With

(20) H. Kamimura, *J. Phys. Soc. Japan*, **11**, 1171 (1956).

(21) If the moment at infinite dilution contains both a temperature dependent term, c/T, and a temperature independent term, a, then one obtains, assuming the above Weiss interaction

$$\chi = \frac{c + aT}{T + \lambda'(c + aT)} \neq \frac{c}{T + \theta} + \alpha$$

TABLE IV

MOLAR SUSCEPTIBILITIES OF OSMIUM(IV) COMPLEXES

Complex		Literature	This research	Average[a]	Calcd.[b]	d, Å[k]
K_2OsF_6		759,[c] 713,[d] (760–2180)[e]		736	740	5.41
Cs_2OsF_6		937–957[d]		947	801	5.84
K_2OsCl_6		918,[f] 913,[g] 941,[d] 860,[h] (560–1270)[e]		908	963	6.92
$(NH_4)_2OsCl_6$		924,[f] 932[g]	911	922	943	6.99
Cs_2OsCl_6		1162–1257[d,i]	913	1017	967	7.23
K_2OsBr_6		(603–617),[d] (560–1110),[e] 964,[g] 985[h]		975	977	7.30
$(NH_4)_2OsBr_6$		981,[f] 1041,[g] 992[i]		1005	982	7.35
Cs_2OsBr_6		1285–1392[d,i]	988	1110	1001	7.54
K_2OsI_6		789–877,[d,i] (diamagnetic)[g]		770	1044	7.99
Cs_2OsI_6		1132–1191[d,i]		1106	1050	8.06
$[(CH_3)_4N]_2OsBr_6$			1090	1090	1147	9.28
$[(n\text{-}C_4H_9)_4N]_2OsCl_6$			990	990	1254	11.1
$K_2(Os,Pt)Br_6$	10.4% Os	1320–1590[h]		1470	1402	15.52
$(NH_4)_2(Os,Pt)Br_6$	7.6% Os		1440	1440	1438	17.30
$K_2(Os,Pt)Cl_6$	100% Os	860[h]		860	936	6.92
$K_2(Os,Pt)Cl_6$	67.5% Os	980[h]		930	1035	7.89
$K_2(Os,Pt)Cl_6$	50.3% Os	950[h]		950	1103	8.68
$K_2(Os,Pt)Cl_6$	33.6% Os	1000[h]		1000	1190	9.93
$K_2(Os,Pt)Cl_6$	18.9% Os	1250[h]		1250	1300	12.15
$K_2(Os,Pt)Cl_6$	7.9% Os	1570[h]		1570	1410	15.93

[a] Values in parentheses omitted in averaging. [b] Calculated from $\chi = (1600 \times 10^{-6})/(1 + 34d^{-2})$. [c] M. A. Hepworth, P. L. Robinson, and G. J. Westland, *J. Chem. Soc.*, 4269 (1954). [d] Ref. 5 and 25. [e] Ref. 19. [f] Ref. 3. The literature values were corrected using Klemm's diamagnetic corrections. [g] V. I. Belova and Ya. K. Syrkin, *Zh. Neorgan. Khim.*, 3, 2016 (1959). [h] Ref. 13. [i] Ref. 2. [i] The reported values for these compounds showed a large temperature dependence. It was assumed this was due to an impurity obeying Curie's law and a correction calculated from this assumption was subtracted to give the value used in obtaining the average listed in the table. [k] d = Average distance between Os^{+4} ions, Å.

$n = 1$ the expression for the susceptibility becomes

$$\chi = \frac{2500 \times 10^{-6}}{1 + 12.5d^{-1}}$$

and with $n = 2$

$$\chi = \frac{1600 \times 10^{-6}}{1 + 34d^{-2}}$$

The data could not be fit with λ' as an exponential function of d. While other forms of functional dependence on d might be suggested, the precision of the experimental data is not high enough to warrant more elaborate efforts at curve fitting. Nevertheless, the present data do show that the above equation cannot be used assuming $n = 3$, as might be expected for direct exchange. Westland and Bhiwandker[13] extrapolated their curve of susceptibility *vs.* concentration of osmium to zero concentration and obtained a value of 1900×10^{-6} cm.³ mole⁻¹ for χ_∞. In Table IV the susceptibilities calculated with $n = 2$ are listed for comparison with experiment. The value of 2500×10^{-6} cm.³ mole⁻¹ for χ_∞ for $n = 1$ appears to be very high and leads to a very small value of ζ. In the dilute solutions the measurements are very difficult to make and the experimental error is very large; therefore, extreme caution must be used in extrapolation. Also, the distances between osmium ions in the Pt–Os solutions are average values. If the interaction arises from overlap of the orbitals and if the orbitals are considered spherical then the overlap volume would decrease as d^2. If the orbitals are somewhat ellipsoidal then the overlap volume would decrease by a lower power of d. This, of course, is a very naïve model. Table IV demonstrates that a large dilution effect is present in these Os(IV) complexes, which is surprising in view of the fact that the paramagnetism arises from admixture by the magnetic field of a ground singlet with a higher magnetic state resulting in an effective lowering of the upper state.

Griffith[4,8] pointed out the isomorphism between the octahedral $(dt_2)^n$ and p^{6-n} configurations and noted that Condon and Shortley[7] had calculated the energy levels for the intermediate coupling scheme. These energy levels also were calculated by Kamimura and co-workers.[12] The energy level differences are

$$({}^3T_{11} - {}^3T_{10}) = \Delta W_1 = -\frac{5}{2}(3B + C) + \frac{1}{2}\sqrt{[5(3B + C) + \zeta]^2 + 8\zeta^2}$$

$$({}^3T_{12} - {}^3T_{10}) = \Delta W_2 = -\frac{3}{2}(3B + C) + \frac{3\zeta}{4} + \frac{1}{2}\sqrt{[5(3B + C) + \zeta]^2 + 8\zeta^2} - \frac{1}{4}\sqrt{[4(3B + C) - \zeta]^2 + 8\zeta^2}$$

$$({}^1E{}^1T_2 - {}^3T_{10}) = \Delta W_3 = -\frac{3}{2}(3B + C) + \frac{3\zeta}{4} + \frac{1}{2}\sqrt{[5(3B + C) + \zeta]^2 + 8\zeta^2} + \frac{1}{4}\sqrt{[4(3B + C) - \zeta]^2 + 8\zeta^2}$$

$$({}^1A_1 - {}^3T_{10}) = \Delta W_4 = \sqrt{[5(3B + C) + \zeta]^2 + 8\zeta^2}$$

Griffith calculated the expression for the susceptibility of low-spin d⁴ complexes

$$\chi = \frac{2N\beta^2(K + 2)^2}{3\Delta W_1}\left[1 + \frac{5(3B + C) + \zeta}{\sqrt{[5(3B + C) + \zeta]^2 + 8\zeta^2}}\right] + \frac{32N\beta^2K'^2}{3\bar{E}}$$

The last term is the contribution from the high frequency elements. The constants K and K' are orbital reduction factors.

The spectral peaks below 17,700 cm.$^{-1}$ presumably are caused by transitions within the t_{2g}^4 configuration of the Os^{+4}, while the peaks at and above 17,700 cm.$^{-1}$ presumably are due to charge transfer but also may contain transitions to higher energy configurations (*e.g.*, $t_{2g}^3e_g$). If the four lines at 8600, 10,800, 11,800, and 17,200 cm.$^{-1}$ are due to transitions within this ground configuration, then no choice of the parameters ζ and $3B + C$ in the expressions for the energy levels can account for more than two lines of this observed spectrum. The value of ΔW_1 is almost entirely determined by χ and varies only slightly with $\zeta/(3B + C)$. By assigning a value to χ and by allowing $\zeta/(3B + C)$ to vary over a wide range the energy levels, ζ, and $3B + C$ can be calculated. Table V shows calculated values of ΔW_n for various choices of $\zeta/(3B + C)$ when χ is taken as 1800, 1900, and 2000 $\times$ 10^{-6} cm.^{3} g.$^{-1}$. A remarkably good fit can be obtained with the lines at 8600 and 17,200 cm.$^{-1}$, which yield very reasonable values for both ζ and $3B + C$ and are in good agreement with the experimental value for the susceptibility if K is chosen between 0.9 and 0.7.

TABLE V^a

$\zeta/(3B + C)$	ΔW_1	ΔW_2	ΔW_3	ΔW_4	ζ	$3B + C$
		χ = 1800 $\times$ 10^{-6} cm.^{3} g.$^{-1}$				
0.1	1738	4879	67920	164701	3225	32245
.5	1712	3887	13405	28639	2522	5043
1.0	1656	3115	7296	13452	2028	2028
2.0	1546	2319	4638	6957	1546	773
0.79	1681	3394	8844	17297	2202	2787
.81	1679	3365	8660	16838	2184	2696
		χ = 1900 $\times$ 10^{-6} cm.^{3} g.$^{-1}$				
0.75	1597	3273	8765	17345	2123	2830
.76	1596	3258	8663	17091	2113	2780
		χ = 2000 $\times$ 10^{-6} cm.^{3} g.$^{-1}$				
0.72	1520	3151	8628	17225	2043	2837

^{a} All energy values are in units of cm.$^{-1}$.

The values of 2100 $\pm$ 100 cm.$^{-1}$ for the spin-orbit coupling constant and 2800 $\pm$ 100 cm.$^{-1}$ for the Coulomb interaction coefficient are obtained. The Kotani equation with its assumption that $(3B + C) >> \zeta$ therefore cannot properly be applied to these 5d complexes.

This assignment of lines (ΔW_4 = 17,200 and ΔW_3 = 8600 cm.$^{-1}$) is unable to account for the observed lines at 10,800 and 11,800 cm.$^{-1}$ unless a field of lower symmetry is assumed. A trigonal field would split the $^1E^1T_2$ into two doublets and a singlet which then could explain the spectrum; however, the $^3T_{1i}$ level also would

be split into a doublet and singlet and this would affect the susceptibility. The $[(n\text{-}C_4H_9)_4N]_2OsCl_6$ complex is shown to be distorted by X-ray studies and its spectrum is different from that of the dilute solutions of the complex. Lines were observed at 17,320, 10,880, 10,470, and 8065 cm.$^{-1}$ for this complex. That the dilute solutions of the complexes have little if any distortion is a strong argument against using a crystal field of lower symmetry to remove the degeneracy. Large shifts in these lines would be expected from one complex to another if a lower symmetry field were present; this is not observed.

The spin-orbit interactions between configurations which have not been considered in any of the above treatments have been calculated by Runciman and Schroeder,[22] by Liehr and Ballhausen,[23] and by Eisenstein.[24] Liehr and Ballhausen have calculated the d^2 case. When the crystal field is large, d^2 becomes the same as d^4 with the sign of ζ reversed and the same results as Griffith's are obtained for the ground configuration. At present, there unfortunately appears to be no reasonable explanation for the complete spectrum.

It would be very interesting to see if dilution of the Ru^{+4} and Ir^{+5} ion would yield similar results. Figgis, *et al.*,[5,25] have measured the susceptibilities of six complexes of Ru^{+4} and noticed a temperature effect in each compound. The susceptibility of K_2RuCl_6 reported in Table II also shows an increase in paramagnetism with decrease in temperature (3450 and 3870 $\times$ 10^{-6} cm.^{3} mole^{-1} at 298 and 78°K., respectively). These results are somewhat higher than those reported by Figgis, *et al.* (3112 and 3652 cm.^{3} mole^{-1} at 288 and 91°K., respectively). Ruthenium has a much smaller spin-orbit coupling constant than osmium so that higher states may be occupied and may contribute a temperature dependent paramagnetism. Measurements on dilute ruthenium complexes at lower temperatures would be very valuable. The only two complexes of Ir^{+5} reported ($KIrF_6$ and $CsIrF_6$) are magnetically quite concentrated.[5,25]

(22) W. A. Runciman and K. A. Schroeder, *Proc. Roy. Soc.* (London), **A265**, 489 (1962).

(23) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N.Y.), **2**, 134 (1959).

(24) J. C. Eisenstein, *J. Chem. Phys.*, **34**, 1628 (1961).

(25) A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, *J. Chem. Soc.*, 3132 (1961)