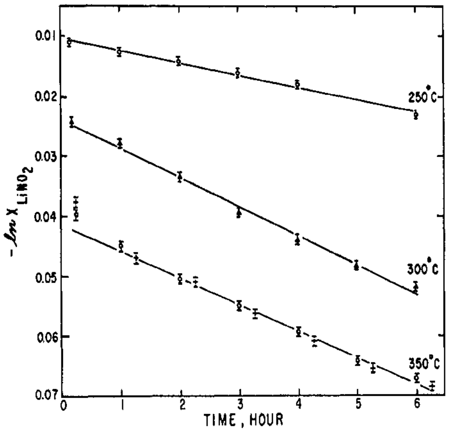

Figure 11.—First-order rate equation plots for the decrease of lithium nitrite.

250°, $k = (1.30 \pm 0.07) \times 10^{-6}$ sec^{-1} at 300°, and $k = (1.25 \pm 0.07) \times 10^{-6}$ sec^{-1} at 350°.

Although it is not possible to distinguish between the rate constants at 300 and 350°, it is clear that the rate of decomposition at 250° is slower. It is also clear that the initial rates of decomposition are very strongly dependent on temperature as indicated by the wide spread in the curves on Figure 11 despite identical starting compositions. Because of the complex nature of the nitrite decomposition, which involves consecutive, conjugate, and reversible reactions, there is no reason to expect that there would be a simple temperature dependency for the rate constants.

Stabilization of a $LiNO_2$–$LiNO_3$–Li_2O Mixture.—The initial rate of decomposition of pure nitrite is fast, but it decreases quickly to a low steady value depending on the rates of formation of nitrate and gaseous products. Using the prediction method of Lee and Johnson[17] the solubilities of the gaseous products in lithium nitrite are estimated to be of the order of 10^{-6} mol (cm^3 of melt)$^{-1}$ atm^{-1}. These solubilities are small, and consequently the concentrations of the gases in the melt rapidly approach the equilibrium concentrations and so depress the decomposition of nitrite.

The observed low rates of decomposition of lithium nitrite melts containing lithium nitrate and lithium oxide could be decreased further by pressurizing the melt with the gaseous products of the decomposition. By appropriate choice of gas composition and pressure the melt composition could be stabilized readily in the temperature range studied here.

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The Electronic Spectra of the Hexahalo Anions of Osmium(IV) and Iridium(IV)

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The electronic spectra of the hexahalo anions of osmium(IV), OsX_6^{2-} (X = F, Cl, Br, I), and of iridium(IV), IrX_6^{2-} (X = F, Cl, Br), have been studied by diffuse reflectance between 4 and 50 kK. All the salts investigated show well-marked band systems of moderate intensity between 4 and 8 kK, which are interpreted as arising from transitions between the spin–orbit split components of the $^3T_{1g}$(Os(IV), d^4) and of the $^2T_{2g}$(Ir(IV), d^5) ground states, respectively. The spectra of the chloro, bromo, and iodo species are dominated by much stronger bands, assigned as Laporte-allowed charge-transfer transitions, which extend upward from between 10 and 20 kK and prevent the derivation of fitting parameters for the d–d excitations, but for the hexafluoro complexes the other d–d bands identified lead to the parameters $Dq = 2600$ cm^{-1}, $B = 500$ cm^{-1}, and $\xi = 2900$ cm^{-1}, for OsF_6^{2-}, and $Dq = 2700$ cm^{-1}, $B = 510$ cm^{-1}, and $\xi = 3300$ cm^{-1}, for IrF_6^{2-}. For OsF_6^{2-} the peak at 5.4 kK is ascribed to the $^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$ transition, and the weaker bands at 12.7 and 18.5 kK and the shoulder at 23 kK are assigned to the formally spin-forbidden excitations $^3T_{1g}(\Gamma_1) \rightarrow {}^1E_g$, $^1T_{2g}$, $^3T_{1g}(\Gamma_1) \rightarrow {}^5E_g$, and $^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}$, respectively. The stronger absorptions at about 30 and 42 kK are attributed to numerous spin-allowed $t_{2g}^4 \rightarrow t_{2g}^3e_g$ excitations, and the intense peak indicated slightly above 50 kK is attibuted to a $\pi \rightarrow t_{2g}$ charge-transfer transition. Similarly, for IrF_6^{2-} the prominent peak at 6.7 kK is assigned as the $^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$ excitation, and the less intense bands at 19.8 and 25.0 kK are attributed to the spin-forbidden transitions $^2T_{2g}(\Gamma_7) \rightarrow {}^4T_{1g}$ and $^2T_{2g}(\Gamma_7) \rightarrow {}^4T_{2g}$. The stronger broad bands at 30 and 38 kK again represent many spin-allowed transitions, here $t_{2g}^5 \rightarrow t_{2g}^4e_g$, while the Laporte-allowed $\pi \rightarrow t_{2g}$ band appears at 47.8 kK. From these data a measure of the extent of covalency for the OsF_6^{2-} and IrF_6^{2-} anions may be deduced, but for all the complexes the value of the effective spin–orbit coupling constant may be estimated from the low-energy bands, thus yielding some indication of this effect. The degree of covalency is found in both cases to increase in the sense $MF_6^{2-} < MCl_6^{2-} < MBr_6^{2-} < MI_6^{2-}$, but for the fluoro anion is found, predictably, to be appreciably smaller than for the corresponding Os(V) and Ir(V) species. Finally, consideration is given to the factors influencing the intensities and bandwidths of the low-energy transitions (and to the effects produced by the change of cation), and the derived ξ values are used for the calculation of relativistically corrected optical electronegativities.

Introduction

Although the M(V) and M(VI) hexahalo species of the 5d elements W to Pt are exemplified only by hexafluoro derivatives, many M(IV) hexahalo compounds are known, and numerous spectroscopic studies have been reported. Thus, the chloro, bromo, and iodo complexes of Os(IV) and the chloro and bromo derivatives of Ir(IV) have been studied in solution by Jørgensen,[2] and most of the intense bands which occur from between 10 and 20 kK upward were assigned as

(1) Ph.D. students supported by the Royal Saudi Arabian Government.

(2) C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

Laporte-allowed, $\pi \rightarrow t_{2g}$, charge-transfer transitions. On the other hand Dorain, *et al.*,[3] have measured the optical spectrum of $OsCl_6^{2-}$ in single cubic crystals up to about 35 kK and concluded that all the observed bands may be assigned to d–d excitations, while Douglas[4] has demonstrated that the single-crystal spectrum of $IrCl_6^{2-}$ up to about 25 kK contains both d–d and charge-transfer type transitions. The assignment of the stronger bands remains however a matter of some controversy, and in a more recent review Jørgensen[5] has reinforced and elaborated his earlier interpretation of these absorptions for the $MHal_6^{2-}$ complexes.

Nevertheless, electronegativity considerations indicate that for the hexafluoro anions the electron-transfer bands should occur at substantially higher energies than for the other halo complexes and that an unequivocal assignment of several more d–d bands should therefore be possible. For both OsF_6^{2-} and IrF_6^{2-} some fragmentary observations of the solution spectra were recorded by Hepworth, Robinson, and Westland,[6] and diffuse reflectance measurements for Cs_2OsF_6 and Cs_2IrF_6 were reported by Brown, Russell, and Sharp.[7] In neither case though were the spectra reproduced diagramatically, and the latter workers studied only the range 10–40 kK and virtually neglected the effects of spin–orbit coupling in making their assignments. Our study of the spectra of the OsF_6^{2-} and IrF_6^{2-} anions, over the wider energy range of 4–50 kK, has revealed a number of important differences between our results and those of Brown, *et al.*, and we now therefore report our findings for the hexafluoroosmate(IV) and hexafluoroiridate(IV) anions, together with the fitting parameters obtained using the full strong-field electrostatic and spin–orbit matrices for d^4 and d^5 systems. At the same time we record our results for the other hexahalo anions of Os(IV) and Ir(IV) and the values of the effective spin–orbit coupling constants deduced from the low-energy d–d bands.

Experimental Section

Potassium and Cesium Hexafluoroosmate(IV) and Potassium Hexafluoroiridate(IV).—These were obtained by hydrolysis of the corresponding hexafluoroosmate(V) and hexafluoroiridate(V) complexes, according to the method of Hepworth, Robinson, and Westland.[6] *Anal.* Calcd for K_2OsF_6: Os, 49.7; F, 29.8. Found: Os, 49.1; F, 30.05. Calcd for Cs_2OsF_6: Os, 33.4; F, 20.0. Found: Os, 33.9; F, 19.85. Calcd for K_2IrF_6: Ir, 50.0; F, 29.7. Found: Ir, 49.3; F, 30.0.

Potassium Hexachloroosmate(IV), Sodium, Potassium, and Ammonium Hexachloroiridate(IV), and Potassium Hexabromoiridate(IV).—These were obtained as high-purity products from Johnson Matthey and Co. Ltd.

Potassium Hexabromoosmate(IV).—This was obtained according to Turner, *et al.*,[8] by the action of concentrated hydrobromic acid on OsO_4. *Anal.* Calcd for K_2OsBr_6: Os, 25.4; Br, 64.1. Found: Os, 25.2; Br, 64.6.

Potassium Hexaiodoosmate(IV).—This was prepared according to Fenn, *et al.*,[9] by the interaction of potassium iodide, concentrated hydrochloric acid, and OsO_4. *Anal.* Calcd for K_2OsI_6: Os, 18.5; I, 73.9. Found: Os, 18.1; I, 75.0.

Potassium Hexaiodoiridate(IV).—There exists in the literature a very early reference to this compound,[10] but in our hands attempts to prepare it were unsuccessful.

Tetraethylammonium Salts.—These were prepared as required either by methods similar to those described above or by appropriate double-decomposition reactions.

Diffuse Reflectance Measurements.—These were made as before[11] using a Beckman DK 2A spectroreflectometer with a magnesium oxide reference. Intensities are expressed in terms of the Kubelka-Munk function, F_R, but uncertainty concerning the appropriate scattering coefficient for the 5d series prevents their conversion to approximate extinction coefficients.

Results and Discussion

In Table I we list our results and assignments for the potassium salts of the OsF_6^{2-}, $OsCl_6^{2-}$, $OsBr_6^{2-}$, and OsI_6^{2-} anions, while Table II similarly gives our findings for the potassium salts of the IrF_6^{2-}, $IrCl_6^{2-}$, and $IrBr_6^{2-}$ ions. The corresponding diffuse reflectance spectra are shown in Figures 1 and 2, respectively. For the hexachloro, hexabromo, and hexaiodo compounds the spectra are dominated to such an extent by strong bands, assigned as charge-transfer excitations, that it is not possible to derive reliable crystal

TABLE I

THE DIFFUSE REFLECTANCE SPECTRA OF POTASSIUM HEXAFLUORO-, HEXACHLORO-, HEXABROMO-, AND HEXAIODOOSMATE(IV)

Band position, kK	F_R	Assignment
		K_2OsF_6
3.0–3.4	(?)	$^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_4)$
5.62	2.4	$^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$
12.7	0.4	$^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}, {}^1E_g$
18.5	0.75	$^3T_{1g}(\Gamma_1) \rightarrow {}^5E_g$
22.5	2.3	$^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}$
30.0 br	5.7	Spin-allowed $t_{2g}^4 \rightarrow t_{2g}^3e_g$
42.0	(?)	
>50	Intense	$(\pi + \sigma)\ t_{1u} \rightarrow t_{2g}$
		K_2OsCl_6
5.15	5.9	$^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$
11.3	1.2	$^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}, {}^1E_g$
19.0 br	4.3	$\pi\ t_{1g} \rightarrow t_{2g}$, $^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}$ and ^5E_g (?)
26.3	14.6	$(\pi + \sigma)\ t_{1u} \rightarrow t_{2g}$
30.0	19.7	$\pi\ t_{2u} \rightarrow t_{2g}$
37.7	18.8	$(\sigma + \pi)\ t_{1u} \rightarrow t_{2g}$ (?)
43–47 br	*Ca.* 20	$(\pi + \sigma)\ t_{1u} \rightarrow e_g$
		K_2OsBr_6
4.90	7.8	$^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$
7.7	0.5	(?)
10.9	2.5	$^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}, {}^1E_g$
17.2	19.5	$\pi\ t_{1g} \rightarrow t_{2g}$ (a $\gamma_{8g} \rightarrow t_{2g}$)
20.0	22.6	$(\pi + \sigma)\ t_{1u} \rightarrow t_{2g}$ (a $\gamma_{8u} \rightarrow t_{2g}$)
23.4 sh	23.7	$\pi\ t_{2u} \rightarrow t_{2g}$ ($\gamma_{7u} \rightarrow t_{2g}$)
24.9	25.0	$\pi\ t_{2u} \rightarrow t_{2g}$ (b $\gamma_{8u} \rightarrow t_{2g}$)
33.0	20.6	$(\pi + \sigma)\ t_{2u} \rightarrow e_g$ (a $\gamma_{8u} \rightarrow e_g$)
37.0	19.4	$\pi\ t_{2u} \rightarrow e_g(\gamma_{7u} \rightarrow e_g)$
41–42 br	*Ca.* 20	$\pi\ t_{2u} \rightarrow e_g$ (b $\gamma_{8u} \rightarrow e_g$)
		K_2OsI_6
4.62	9.0	$^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$
9.0	10.4	$\pi\ t_{1g} \rightarrow t_{2g}$ (a $\gamma_{8g} \rightarrow t_{2g}$)
10.6	12.7	$(\pi + \sigma)\ t_{1u} \rightarrow t_{2g}$ (a $\gamma_{8u} \rightarrow t_{2g}$)
15.4 br	28.0	$\pi\ t_{2u} \rightarrow t_{2g}$ (γ_{7u}, b $\gamma_{8u} \rightarrow t_{2g}$)
35.0 v br	14.8	$(\pi + \sigma)\ t_{1u} \rightarrow e_g$ (a $\gamma_{8u} \rightarrow e_g$) $\pi\ t_{2u} \rightarrow e_g$ (γ_{7u}, b $\gamma_{8u} \rightarrow e_g$)
44–46 br	*Ca.* 20	$(\sigma + \pi)\ t_{1u} \rightarrow e_g$ (c $\gamma_{8u} \rightarrow e_g$)

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(3) P. B. Dorain, H. H. Patterson, and P. C. Jordan, *J. Chem. Phys.*, **49**, 3845 (1968).

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(5) C. K. Jørgensen, *Progr. Inorg. Chem.*, **12**, 101 (1970).

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(7) D. H. Brown, D. R. Russell, and D. W. A. Sharp, *ibid.*, *A*, 18 (1969).

(8) A. G. Turner, A. F. Clifford, and C. N. Ramachandra Rao, *Anal. Chem.*, **30**, 1708 (1958).

(9) E. Fenn, R. S. Nyholm, P. G. Owston, and A. Turco, *J. Inorg. Nucl. Chem.*, **17**, 387 (1961).

(10) T. Oppler, Dissertation, University of Gottingen, 1857, p 25; cited in "Gmelin's Handbuch der anorganischen Chemie," Iridium, Vol. 67, Verlag Chemie, Berlin, 1939, pp 106, 119.

(11) (a) G. C. Allen and K. D. Warren, *Inorg. Chem.*, **8**, 753 (1969); (b) *ibid.*, **8**, 1895 (1969).

TABLE II

THE DIFFUSE REFLECTANCE SPECTRA OF POTASSIUM HEXAFLUORO-, HEXACHLORO-, AND HEXABROMOIRIDATE(IV)

Band position, kK	F_R	Assignment
		K_2IrF_6
6.65	3.1	$^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$
19.8	2.5	$^2T_{2g}(\Gamma_7) \rightarrow {}^4T_{1g}$
24.9	2.5	$^2T_{2g}(\Gamma_7) \rightarrow {}^4T_{2g}$
30.0 br	4.5	Spin-allowed $t_{2g}{}^5 \rightarrow t_{2g}{}^4e_g$
38.0 br	6.85	
47.8	21.9	$(\pi + \sigma)\ t_{1u} \rightarrow t_{2g}$
		K_2IrCl_6
5.25	5.3	$^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$
17.4	15.4	$\pi\ t_{1g} \rightarrow t_{2g}$, $^2T_{2g}(\Gamma_7) \rightarrow {}^4T_{1g}$
19.6	20.0	$(\pi + \sigma)\ t_{1u} \rightarrow t_{2g}$
23.5	19.6	$\pi\ t_{2u} \rightarrow t_{2g}$
35.5 br	12.25	$(\sigma + \pi)\ t_{1u} \rightarrow t_{2g}$ (?)
45.0 br	*Ca.* 20	$(\pi + \sigma)\ t_{1u} \rightarrow e_g$
		K_2IrBr_6
4.70	6.2	$^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$
13.5	18.3	$(\pi + \sigma)\ t_{1u} \rightarrow t_{2g}$ (a $\gamma_{8u} \rightarrow t_{2g}$)
16.7	20.7	$\pi\ t_{2u} \rightarrow t_{2g}$ (γ_{7u}, b $\gamma_{8u} \rightarrow t_{2g}$)
26.3	16.9	$(\sigma + \pi)\ t_{1u} \rightarrow t_{2g}$ (c $\gamma_{8u} \rightarrow t_{2g}$)
36.0 br	13.0	$(\pi + \sigma)\ t_{1u} \rightarrow e_g$, $\pi\ t_{2u} \rightarrow e_g$ (a $\gamma_{8u} \rightarrow e_g$; γ_{7u}, b $\gamma_{8u} \rightarrow e_g$)
46.0	*Ca.* 20	$(\sigma + \pi)\ t_{1u} \rightarrow e_g$ (c $\gamma_{8u} \rightarrow e_g$)

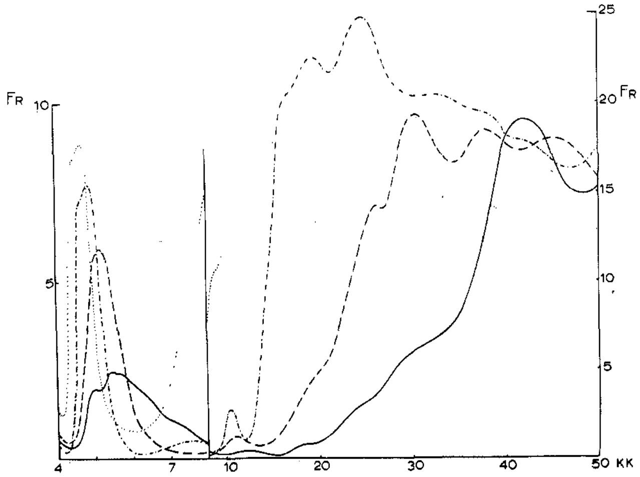

Figure 1.—The diffuse reflectance spectra of potassium hexahalo-osmates(IV): ———, F; – – – – – –, Cl; –·–·–·, Br; ······, I.

field fitting parameters, Dq, B, and ξ, from the observed d–d transitions, but for the hexafluoro complexes, $OsF_6{}^{2-}$ and $IrF_6{}^{2-}$, sufficient bands of this type were observed for such parameters to be derived.

For complexes of the 5d series the spin–orbit coupling constant is of course substantial, being comparable to the crystal field splitting parameter, Dq, and considerably greater than the Racah electrostatic parameter, B. Spin–orbit coupling cannot therefore be treated as a minor perturbation, and the data for the hexafluorides were accordingly fitted using the strong field electrostatic matrices of Tanabe and Sugano,[12] together with the d^4 and d^5 spin–orbit matrices of Schroeder.[13,14] In our fitting the assumed value of the ratio of the Racah parameters, C/B, was obtained using the same considerations as in our treatment[15] of the $OsF_6{}^-$ and $IrF_6{}^-$ anions, the ratios being taken as 4.75 for Os(IV) and 4.90 for Ir(IV). In this way we were able to avoid the wild variations in the derived C/B value, within a series of similar complexes, which often ensue when C and B are allowed to vary independently. Similarly we used, as before,[15] only a single value of B and of ξ in our fitting, since our inability to resolve the bands corresponding to the spin-allowed d–d excitations renders the use of separate B_{35} and B_{55}, and ξ_{35} and ξ_{55}, parameters inappropriate. Finally, we determined the nephelauxetic ratio, β ($=B_{\text{complex}}/B_{\text{gas}}$), and the relativistic ratio, β^* ($=\xi_{\text{complex}}/\xi_{\text{gas}}$), for the $OsF_6{}^{2-}$ and $IrF_6{}^{2-}$ anions by evaluating the free-ion values of B and ξ in the same way as before. Thus we assume Jørgensen's[16] approximation $B_{\text{gas}}(\text{M}, 5d^n) = 0.6B_{\text{gas}}(\text{M}, 3d^n)$ and the proportionality between ξ and B^3 found by Cole and Garrett,[17] from which we obtain $B_{\text{gas}}(\text{Os(IV)}) = 677\ \text{cm}^{-1}$, $B_{\text{gas}}(\text{Ir(IV)}) = 712\ \text{cm}^{-1}$, $\xi_{\text{gas}}\ (\text{Os(IV)}) = 3870\ \text{cm}^{-1}$, and $\xi_{\text{gas}}(\text{Ir(IV)}) = 4500\ \text{cm}^{-1}$.

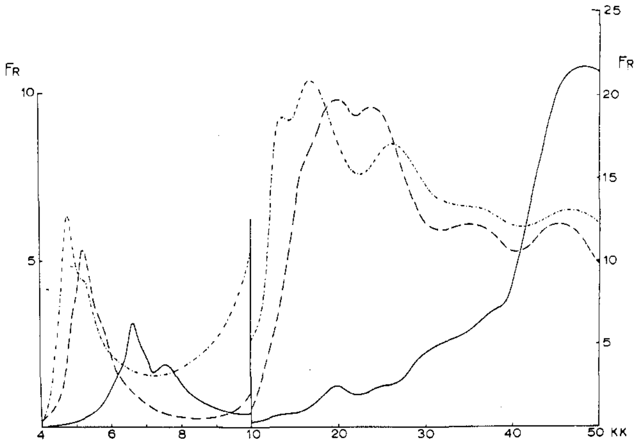

Figure 2.—The diffuse reflectance spectra of potassium hexahalo-iridates(IV): ———, F; – – – – – –, Cl; –·–·–·, Br.

For all but one of the potassium salts studied X-ray crystallographic data are available. Thus K_2OsF_6 and K_2IrF_6 both have trigonal K_2GeF_6-type lattices in which the MF_6 octahedra are only slightly distorted from perfect O_h symmetry,[6] while K_2OsCl_6 and K_2OsBr_6 possess the cubic K_2PtCl_6 type structure.[18] Similarly K_2IrCl_6 and K_2IrBr_6 both show the cubic lattice, but esr data indicate that although the $IrCl_6{}^{2-}$ unit is strictly O_h, the $IrBr_6{}^{2-}$ ion exhibits a small tetragonal distortion.[19] Nevertheless, the departures from regular octahedral symmetry about the metal are always small, and we have therefore analyzed our data throughout on the assumption of regular O_h geometry.

Assignment of Charge-Transfer Bands.—As indicated in the Introduction, the assignments of the intense bands observed in the solution spectra[1] of the hexahalo complexes of Os(IV) and of Ir(IV) have recently become the subject of some controversy. Thus Dorain and his coworkers have suggested[3,20,21] that the intensity criterion may sometimes be inadequate and

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[12] Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 753, 766 (1954).

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[19] J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc., Ser. A*, **226**, 96 (1954).

[20] P. B. Dorain and R. G. Wheeler, *J. Chem. Phys.*, **45**, 1172 (1966).

[21] P. C. Jordan, H. H. Patterson, and P. B. Dorain, *ibid.*, **49**, 3858 (1968).

that such bands could in fact represent d–d transitions for which a change in the t_{2g}, e_g orbital occupation enables the vibronic coupling mechanism to provide sufficient strength. Much of this reasoning however involves arguments based on the assignment of the observed vibrational detail to the coexcitation of odd vibrational modes, thereby implying the presence of a Laporte-forbidden, g–g, transition. In this event, though, it is always difficult to assign excited-state vibronics on the basis of ground-state frequencies, and even if established the involvement of odd modes would not be inconsistent with the occurrence of parity-forbidden charge-transfer bands or with the superposition of d–d and Laporte-allowed transitions.

Thus Douglas[4] found evidence for both d–d and u–g charge-transfer bands in the 18–25-kK region of $IrCl_6^{2-}$, and for the same ion the magnetic circular dichroism studies of McCaffery, *et al.*,[22,23] both in solution and for single crystals, have provided further support for the charge-transfer assignments of Jørgensen,[2] although the results did show the necessity of revising the energetic order assumed[2] for the ligand orbitals. A similar very recent study of $IrBr_6^{2-}$ also provides unequivocal confirmation[24] of the charge-transfer assignment for the 10–20-kK bands, and preliminary MCD results[25] for Os^{4+} in O_h Cl^- environments also favor the assignment of most of the intense bands to charge-transfer transitions. Additional evidence favoring the charge-transfer interpretation for the strong bands in the hexachloro and hexabromo complexes of both Os(IV) and Ir(IV) has been summarized by Bird, Day, and Grant,[26] and furthermore both the semiempirical molecular orbital calculations of Cotton and Harris[27] and optical electronegativity considerations suggest that the charge-transfer bands for the hexahalo complexes of Os(IV) should not lie more than about 5–10 kK higher than in the corresponding Ir(IV) compounds.

On these grounds therefore we have assigned the more intense bands ($F_R > 10$), above 10 kK, as charge-transfer excitations, and in Tables I and II our assignments and nomenclature follow that of Jørgensen[5] and of Jørgensen and Preetz.[28] Thus the lowest lying mainly ligand levels from which electron transfer may occur are the $\pi\ t_{1g}$, $\pi\ t_{1u}$, $\pi\ t_{2u}$, and $\pi\ t_{2g}$ sets. Of these the $\sigma\ t_{1u}$ will interact with the lower lying $\sigma\ t_{1u}$ level, giving a higher energy, predominantly, π, $(\pi + \sigma)$ t_{1u} orbital, and a lower, mainly σ, $(\sigma + \pi)$ t_{1u} level. From the MCD studies of McCaffery, *et al.*,[22–24] the order of MO energies was found to be $\pi\ t_{1g} > (\pi + \sigma)\ t_{1u} > \pi\ t_{2u} > \ldots > (\sigma + \pi)\ t_{1u}$. The $\pi\ t_{2g}$ level would be expected to lie close to the $\pi\ t_{2u}$ level, but transitions from it to the mainly metal orbitals are parity forbidden and probably indistinguishable from the Laporte-allowed bands. When relativistic effects due to the ligands become important (*e.g.*, for Br^- and I^-), consideration must be given to the spin–orbit splitting of the ligand levels. Thus[5,28] $\pi\ t_{1g}$ yields a γ_{8g} + a γ_{6g}, $(\pi + \sigma)\ t_{1u} \rightarrow$ a γ_{8u} + a γ_{6u}, $\pi\ t_{2u} \rightarrow \gamma_{7u}$ + b γ_{8u}, and $(\sigma + \pi)\ t_{1u} \rightarrow$ c γ_{8u} + b γ_{6u}, a detailed description and a full splitting diagram being given by Jørgensen and Preetz.[28]

For the d^5 Ir(IV) complexes the electronic spectrum arising from electron transfer from the ligand orbitals to the metal should be relatively simple since only the Γ_1, t_{2g}^6 level ($\gamma_8^4\gamma_7^2$ in the jj nomenclature) is available,[2,5] and each $\pi \rightarrow$ d excitation should therefore give rise only to a single energy state. For Os(IV) complexes the situation is fortuitously as simple: the Γ_1, $^3T_{1g}$ ground state for the d^4 system is predominantly γ_8^4 in the jj scheme, and since the accessible Γ_7 and Γ_8, t_{2g}^5 states correspond, respectively, to $\gamma_8^4\gamma_7^3$ and $\gamma_8^3\gamma_7^2$, only the former represents a one-electron jump, which should be readily observable. We have accordingly assigned our observed bands on this basis, and the reflectance data are found to parallel quite closely the earlier solution results.[2,5] The degree of resolution obtainable by reflectance studies is not of course high, but it is interesting to note that the bands assigned as $\pi \rightarrow t_{2g}$ are appreciably sharper than those ascribed to $\pi \rightarrow e_g$ transitions, in agreement with the observations and explanation advanced previously by Jørgensen.[2] In our spectra the apparent intensities of the $\pi \rightarrow e_g$ bands are slightly less than those of the $\pi \rightarrow t_{2g}$ transitions, in contrast to Jørgensen's findings, but it must be remembered that the scattering coefficient usually increases quite sharply above about 25 kK, thereby causing diffuse reflectance spectra significantly to underestimate the intensities of the higher energy bands. For the hexafluoro complexes the only bands which may reasonably be identified as charge-transfer transitions are of course at much higher energies than for the other halides. For IrF_6^{2-} the band at 47.8 kK corresponds quite closely to that reported as $\pi \rightarrow t_{2g}$ at 47 kK by Westland, *et al.*,[6] from solution measurements, but for OsF_6^{2-} the rather strong band at 42 kK seems somewhat too low to represent a charge-transfer transition. More probably it corresponds to a number of superimposed spin-allowed $t_{2g}^4 \rightarrow t_{2g}^3e_g$ transitions which are gaining intensity by virtue of their proximity to the $\pi \rightarrow t_{2g}$ band reported by Westland, *et al.*, just above 50 kK. This assignment is certainly more acceptable on the basis of optical electronegativities, but we defer treatment of this until the d–d fitting parameters have been established.

Assignment of d–d Bands.—For the hexafluoro anions OsF_6^{2-} and IrF_6^{2-} diffuse reflectance spectra have already been reported by Brown, *et al.*,[7] and solution data by Westland, *et al.*[6] The former authors record absorptions at 23.5, 30.0, and 33.0 kK for Cs_2OsF_6 and at 13.0, 19.0, 24.2, 30.5, and 34.0 kK for Cs_2IrF_6, while the solution spectra show peaks at 32.5 and at 31.6 kK, which were attributed to spin-allowed $t_{2g} \rightarrow e_g$ transitions in OsF_6^{2-} and in IrF_6^{2-}, respectively. However, even in the 10–40-kK region our spectra for OsF_6^{2-} and IrF_6^{2-} differ significantly from those of Brown, *et al.* Thus for K_2OsF_6 we find two fairly weak bands, at 12.7 and 18.5 kK, followed by a shoulder at around 23 kK and broader, stronger absorptions at about 30 and 42 kK. For the low-spin d^4 system indicated by the magnetic data,[29] a $^3T_{1g}(t_{2g}^4)$ state will con-

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[22] G. N. Henning, A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Chem. Phys.*, **48**, 5656 (1968).

[23] A. J. McCaffery, P. N. Schatz, and T. E. Lester, *ibid.*, **50**, 379 (1969).

[24] S. B. Piepho, T. E. Lester, A. J. McCaffery, J. R. Dickinson, and P. N. Schatz, *Mol. Phys.*, **19**, 781 (1970).

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[26] B. D. Bird, P. Day, and E. A. Grant, *J. Chem. Soc. A*, 100 (1970).

[27] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 376 (1967).

[28] C. K. Jørgensen and W. Preetz, *Z. Naturforsch. A*, **22**, 945 (1967).

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

stitute the ground state, and the lowest lying transitions should be the formally spin-forbidden, intrasubshell, excitations to the $^1T_{2g}$, ^1E_g and to the $^1A_{1g}$ levels, together with the also spin-forbidden transition to the $^5E_g(t_{2g}{}^3e_g)$ level. In the related $OsCl_6{}^{2-}$ ion the $^3T_{1g} \rightarrow {}^1T_{2g}$, ^1E_g transition has been located by Dorain, *et al.*,[3] and by Dickinson and Johnson,[30] at 10.6–11.1 kK, so that our band at 12.7 kK in $OsF_6{}^{2-}$ is reasonably assigned in the same way: its intensity is consistent with the assignment as a spin-forbidden band, and its slightly greater energy with the expectation that the electrostatic repulsion parameters should be somewhat larger for fluoro than for chloro complexes. The assignment of the next two bands though is less simple, since for $OsCl_6{}^{2-}$ both the $^3T_{1g} \rightarrow {}^1A_{1g}$ and the $^3T_{1g} \rightarrow {}^5E_g$ transitions are found at virtually the same energy, *ca.* 17.1–17.2 kK. However, on passing from the chloro to the fluoro compound, both Dq and B would be expected to increase: for the ^5E_g level these trends would tend to counterbalance each other, but for the $^1A_{1g}$ state an increase in the energy should occur because only the change in B will be effective. Accordingly we assign the 18.5-kK peak as $^3T_{1g} \rightarrow {}^5E_g$ and the 23-kK shoulder as $^3T_{1g} \rightarrow {}^1A_{1g}$, and assuming that this corresponds to the peak of Brown, *et al.*, at 23.5 kK, we disagree with their assignment of it as $^3T_{1g} \rightarrow {}^5E_g$. This latter conclusion was reached without proper consideration of the substantial spin–orbit coupling, but our calculations show that when this is included, all the observed levels can be satisfactorily reproduced. Our values, shown in Figure 3 and Table III, appear to suggest that the $^1A_{1g}$ level is somewhat underestimated, but gaussian analysis indicates that the 23-kK shoulder should correspond to a fairly weak band, with a maximum not higher than 22.5 kK, and quite possibly lower.

TABLE III

CALCULATED ENERGY LEVELS FOR $OsF_6{}^{2-}$ (Dq = 2600 CM^{-1}, B = 500 CM^{-1}, ξ = 2900 CM^{-1}, AND C/B = 4.75)

$^3T_{1g}(t_{2g}{}^4)$	$^5E_g(t_{2g}{}^3e_g)$	$^3E_g(t_{2g}{}^3e_g)$
Γ_1 0.00	Γ_2 17.06	Γ_4 28.53
Γ_4 3.09	Γ_5 17.22	Γ_5 29.19
Γ_5 5.47	Γ_3 17.39	
Γ_3 5.52	Γ_4 17.46	$^3T_{2g}(t_{2g}{}^3e_g)$
	Γ_1 17.56	Γ_3 29.16
$^1T_{2g}(t_{2g}{}^4)$		Γ_4 29.96
Γ_5 12.51	$^1A_{1g}(t_{2g}{}^4)$	Γ_5 30.77
	Γ_1 21.50	Γ_2 32.29
$^1E_g(t_{2g}{}^4)$		
Γ_3 12.95	$^3T_{1g}(t_{2g}{}^3e_g)$	$^3A_{2g}(t_{2g}{}^3e_g)$
	Γ_4 27.19	Γ_5 30.64
	Γ_1 28.09	
	Γ_3 31.21	$^3A_{1g}(t_{2g}{}^3e_g)$
	Γ_5 31.57	Γ_4 31.31
		$^3E_g(t_{2g}{}^3e_g)$
		Γ_5 33.05
		Γ_4 33.46

In the 30–35-kK region we succeeded in resolving only one band, rather than the two reported[7] at 30 and 33 kK, but this is very broad and we agree with Brown, *et al.*, in assigning this to spin-allowed $t_{1g}{}^4 \rightarrow t_{2g}{}^3e_g$ transitions to the spin–orbit split components of the $^3T_{1g}$, ^3E_g, $^3T_{2g}$, $^3A_{1g}$, and $^3A_{2g}$ levels (see Tables I and III). For K_2OsF_6 we found a further, stronger absorption at about 42 kK, which we also assign as spin-allowed $t_{2g} \rightarrow t_{2g}{}^3e_g$ transitions, to higher lying $^3T_{1g}$ and $^3T_{2g}$ states. For the potassium salt the absorption in this region tended to be very high but difficult to reproduce and we are inclined to think that the F_R value is exaggerated in this region. It is probably noteworthy that for the cesium salt the intensity is only slightly greater than that of the 30-kK band, supporting its d–d assignment, and in both compounds a very steep increase in intensity occurs at around 48.5 kK in agreement with the $\pi \rightarrow t_{2g}$ band reported by Westland, *et al.*, at above 50 kK. In the cesium salt the bands at 12.8 and 18.5 kK were also much weaker than in K_2OsF_6, and the 23-kK shoulder was more pronounced, thus possibly accounting for the failure of Brown, *et al.*, to detect the former two absorptions.

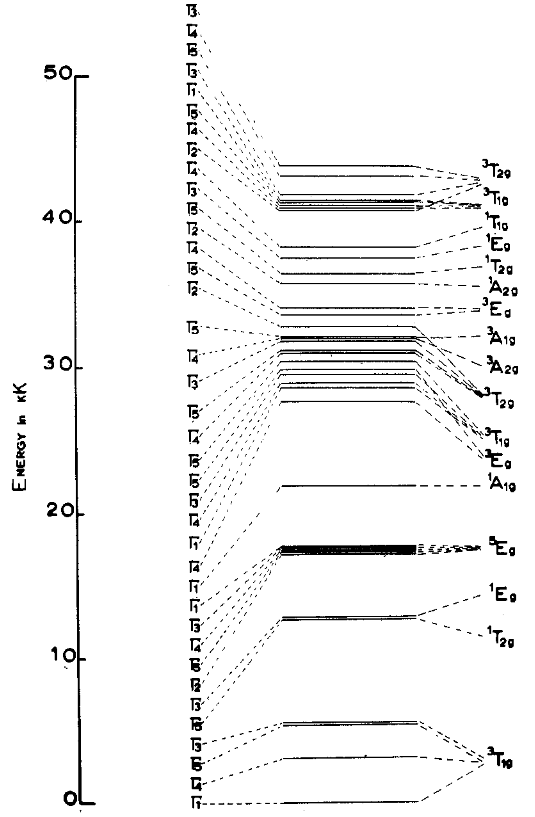

Figure 3.—Calculated energy levels for $OsF_6{}^{2-}$; Dq = 2600 cm^{-1}, B = 500 cm^{-1}, ξ = 2900 cm^{-1}, and C/B = 4.75.

It is however in the region below 10 kK that the most prominent new features are found. Thus in K_2OsF_6 a moderately strong (F_R = 2.4) band, showing a considerable amount of structure, is observed at 5.6 kK, and similar peaks are also found for the $OsCl_6{}^{2-}$, $OsBr_6{}^{2-}$, and $OsI_6{}^{2-}$ anions in the 4.5–5.2-kK region. Furthermore, the corresponding Ir(IV) complexes (*quod vide*) also display a similar, moderate-intensity band in the low-energy region, at 6.6 kK for $IrF_6{}^{2-}$ and between 4.7 and 5.2 kK for the hexachloro and hexabromo compounds. For the Os(IV) complexes these low-energy bands are readily assigned as formally spin-allowed transitions between the spin–orbit split components of the $^3T_{1g}$ ground state, and such an interpretation has already been advanced by Dickinson and Johnson[30] for $OsCl_6{}^{2-}$ as a result of melt and KBr disk studies of the sodium salt. For the d^4 Os(IV) systems the $^3T_{1g}$ ground state will be split by spin–orbit coupling into four components Γ_1, Γ_3, Γ_4, and Γ_5

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[30] J. R. Dickinson and K. E. Johnson, *Mol. Phys.*, **19**, 19 (1970).

in the O* double group, and in the strong-field scheme Γ_3 and Γ_5 will be approximately degenerate, at $^3/_2\xi$ above the Γ_1 ground state, with the Γ_4 level at $^1/_2\xi$. In fact, such systems are better reflected in the jj coupling scheme in which, using the p^n isomorphism, the first-order energies are found to be Γ_1, 0 with Γ_3, Γ_4, and Γ_5 all at $+^3/_2\xi$. For K_2OsF_6 though our fitting parameters (Table III), using the complete strong-field scheme, indicate an intermediate coupling situation, with Γ_3 and Γ_5 almost degenerate at 5.5 kK and Γ_4 at 3.1 kK, and in all the hexahaloosmate(IV) complexes the beginnings of the Γ_4 band can clearly be seen in the spectral region just above 4 kK (the lower limit of our instrument). In the case of the potassium salt of the hexafluoro anion however we did obtain further confirmation of this prediction by observing a weak band in the infrared region between 3.0 and 3.4 kK, using a hexachlorobutadiene mull.

Thus, in the 5d series the values of the effective spin–orbit coupling constants in the hexahalo complexes can be large enough (*ca.* 3–4 kK) for the splittings of the ground state to be directly observable. Such an effect would therefore be anticipated for the d^4 $^3T_{1g}$ and d^5 $^2T_{2g}$ (*quod vide*) ground states but not for the d^3 $^4A_{2g}(\Gamma_8)$ and d^6 $^1A_{1g}(\Gamma_1)$ ground states, and in accordance with this expectation we have found no trace of low-energy bands for PtF_6^{2-} and $PtCl_6^{2-}$ (d^6) or for $IrCl_6^{3-}$ (d^6), while for ReF_6^{2-}, $ReCl_6^{2-}$, and OsF_6^- (d^3), no bands were found above 4 kK which could not be attributed to spin-forbidden intra-subshell (t_{2g}^3) excitations. On the other hand, the d^4 IrF_6^- ion was found [15] to show a low-energy band at 6.5 kK similar to that observed for the Os(IV) complexes. Moreover, analogous low-energy bands, arising from the spin–orbit splitting of the ground state, have also been recorded by Moffitt, *et al.*,[31] for the d^1, d^2, and d^4 systems—ReF_6, OsF_6, and PtF_6.

From the observed ground-state splitting for K_2OsF_6 it is possible to make a first-order estimate of the effective spin–orbit coupling constant, but it should be noted that our fitting parameters, obtained *via* the complete spin–orbit and electrostatic matrices, indicate that the actual separation of the Γ_1 and the Γ_3, Γ_5 components is appreciably more than $^3/_2\xi$. Thus our data are well fitted by the values $Dq = 2600$ cm^{-1}, $B = 500$ cm^{-1}, and $\xi = 2900$ cm^{-1}, and consequently the use of the p^n(jj) isomorphism to fit the bands arising from t_{2g}^4 only is likely appreciably to overestimate ξ, since this formalism leads to $^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5) \approx 1.5\xi$.

For IrF_6^{2-} ion our results (Table IV) again differ from those of Brown, *et al.*, who studied Cs_2IrF_6. Our main results refer here to the potassium salt, but our spectra for K_2IrF_6 and for Cs_2IrF_6 do not disagree in any significant way. Thus, for K_2IrF_6 we find only an extremely faint absorption at 13 kK (which we consider to be spurious) and our findings concerning the intensity of the band near 19 kK and the assignment of the peak at 24.9 kK also differ. For the d^5 IrF_6^{2-} anion, the magnetic data again indicate[6] a low-spin ground state, $^2T_{2g}(t_{2g}^5)$, for which the lowest lying excited states will be the $t_{2g}^4e_g$ $^4T_{1g}$ and $^4T_{2g}$ levels. For the related ion, $IrCl_6^{2-}$, the positions of some of the spin–orbit components of these levels have been established by Douglas,[4] the former lying between 18.8 and 21.1 kK and the latter lying close to 22.9 kK. Again, on passing from the hexachloro to the hexafluoro complex, the values of both *Dq* and *B* would be expected to increase, and once more these changes would influence the positions of both the quartet levels in mutually contrary directions. We do not therefore feel that a decrease in the $^2T_{2g} \rightarrow {}^4T_{1g}$ energy of some 7 kK between $IrCl_6^{2-}$ and IrF_6^{2-} is reasonable, and we therefore assign the two relatively weaker bands at 19.8 and 24.9 kK as $^2T_{2g} \rightarrow {}^4T_{1g}$ and $^2T_{2g} \rightarrow {}^4T_{2g}$, respectively. Furthermore our results do not indicate any anomalously high intensity for the $^2T_{2g} \rightarrow {}^4T_{1g}$ transition. Formally this excitation is of course spin forbidden, but the F_R value appears entirely reasonable in view of the large spin–orbit coupling constant which ensures substantial mixing with the doublet $t_{2g}^4e_g$ levels beginning less than 10 kK higher. There is, moreover, no substantial difference in intensities for any of the bands between the potassium, rubidium, and cesium salts.

TABLE IV

CALCULATED ENERGY LEVELS FOR IrF_6^{2-} ($Dq = 2700$ CM^{-1}, $B = 510$ CM^{-1}, $\xi = 3300$ CM^{-1}, AND $C/B = 4.90$)

$^2T_{2g}(t_{2g}^5)$	$^2T_{1g}(t_{2g}^4e_g)$	$^2E_g(t_{2g}^4e_g)$
Γ_7 0.00	Γ_8 27.52	Γ_8 33.30
Γ_8 6.27	Γ_6 30.49	
		$^2T_{2g}(t_{2g}^4e_g)$
$^4T_{1g}(t_{2g}^4e_g)$	$^2T_g(t_{2g}^4e_g)$	Γ_8 34.19
Γ_8 17.30	Γ_7 28.91	Γ_7 39.32
Γ_7 19.22	Γ_8 32.44	
Γ_8 20.64		$^2T_{1g}(t_{2g}^4e_g)$
Γ_6 21.67	$^2A_{2g}(t_{2g}^4e_g)$	Γ_6 36.29
	Γ_7 31.59	Γ_8 37.77
$^4T_{2g}(t_{2g}^4e_g)$		
Γ_6 24.18		$^2A_{1g}(t_{2g}^4e_g)$
Γ_8 24.55		Γ_6 39.58
Γ_7 24.77		
Γ_8 24.77		

For the two quartet $t_{2g}^4e_g$ levels our calculations indicate that the spin–orbit splitting of their components should be somewhat greater for the $^4T_{1g}$ than for the $^4T_{2g}$ state. In agreement with this, the band at 19.8 kK does seem to be rather broader than the 24.9-kK absorption, and in Cs_2IrF_6 some splitting of the former peak is discernible with the maximum at 19.5 kK and a shoulder at 20.1 kK. In addition our observation of essentially two groups of spin-allowed $t_{2g}^5 \rightarrow t_{2g}^4e_g$ transitions, represented by broad bands at *ca.* 30 and 38 kK, is also paralleled in our calculations, which suggest that the former should correspond mainly to transitions to $^2T_{1g}$, $^2A_{2g}$, $^2T_{2g}$, and ^2E_g levels, and the latter to transitions to higher lying $^2T_{2g}$ and $^2T_{1g}$ levels and to a $^2A_{1g}$ state.

Again however the most striking feature of the spectrum lies in the region below 10 kK, where for K_2IrF_6 a broad, moderately strong band, showing considerable vibrational detail, is observed at 6.6 kK. As for the d^4 Os(IV) complexes, the $^2T_{2g}$ low-spin ground state of the d^5 Ir(IV) compounds is split under the influence of spin–orbit coupling. In this case the overall ground state is the $^2T_{2g}(\Gamma_7)$ level, and in both the strong-field and the p^n(jj) schemes the first-order separation between this and the upper Γ_8 component is $^3/_2\xi$. Thus, since the spin–orbit coupling constants of the order of 3–4 kK are to be expected in this part of the 5d series, the low-energy band is readily assigned as the $^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$ transition, its intensity

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(31) W. Moffitt, G. L. Goodman, M. Fred, and B. Weinstock, *Mol. Phys.*, **2**, 109 (1959).

being consistent with a formally spin-allowed excitation. Once more the position of the low-energy band affords a first-order estimate of the effective spin–orbit coupling constant in the complex, but as in the case of the Os(IV) compound a complete fitting, using the strong-field electrostatic and spin–orbit matrices, indicates that the actual splitting of the Γ_7 and Γ_8 components of $^2T_{2g}(t_{2g}{}^5)$ is appreciably greater than 1.5ξ. A very satisfactory fit of the bands for $IrF_6{}^{2-}$ was in fact obtained from the parameters Dq = 2700 cm^{-1}, B = 510 cm^{-1}, and ξ = 3300 cm^{-1}, as illustrated in Figure 4.

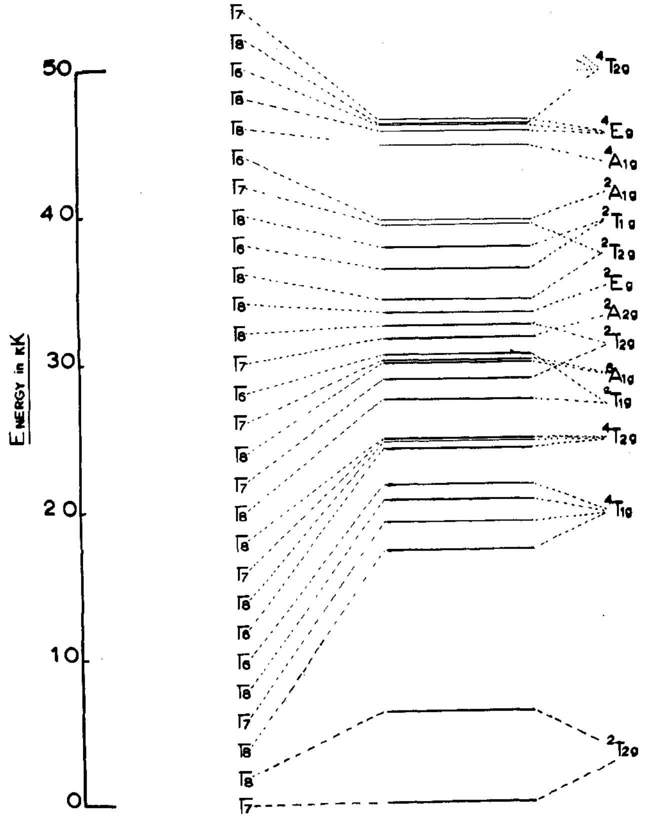

Figure 4.—Calculated energy levels for $IrF_6{}^{2-}$; Dq = 2700 cm^{-1}, B = 510 cm^{-1}, ξ = 3300 cm^{-1}, and C/B = 4.90.

For the remaining hexahalo complexes of Os(IV) and Ir(IV) there are not enough d–d bands accessible for a complete fitting to be attempted, but some approximate parameterization is possible. Thus, low-energy bands are found in all the complexes, similar to those observed for $OsF_6{}^{2-}$ and $IrF_6{}^{2-}$, which permit an estimate to be made of the effective spin–orbit coupling constant, even though this necessitates the use of second-order perturbation theory because of the inadequacy of the approximation $\Delta E \approx 1.5\xi$.

For $OsCl_6{}^{2-}$ we identify only two d–d bands with certainty—the $^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$ peak at 5.15 kK and the $^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}, {}^1E_g$ band at 11.3 kK. The latter observation is in good agreement with the location of the $^1T_{2g}$ and ^1E_g levels at 10.56 and 11.10 kK by Dorain, *et al.*,[3] and with the reflectance spectrum of $OsCl_6{}^{2-}$ in a KCl–LiCl melt reported by Dickinson and Johnson.[30] The latter workers were successful in resolving this band into components at 10.4 and 11.65 kK and also in finding the $^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}, {}^5E_g$ transitions at 17.25 kK, but our spectrum shows only one peak for the $^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}, {}^1T_{2g}$ transitions, and the $^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}, {}^5E_g$ transitions, found by Dorain, *et al.*, at 17.1–17.3 kK, are obscured by the onset of the π $t_{1g} \rightarrow t_{2g}$ charge-transfer band. However, our d–d bands, together with the reported values for the $^3T_{1g}(\Gamma_1) \rightarrow {}^1A_{1g}, {}^5E_g$ transitions, can be approximately reproduced with the parameters $B \approx 425$ cm^{-1} and $\xi \approx 2650$ cm^{-1}.

For $OsBr_6{}^{2-}$ we identify the 4.8- and 10.9-kK bands as transitions from $^3T_{1g}(\Gamma_1)$ to $^3T_{1g}(\Gamma_3, \Gamma_5)$ and to $^1T_{2g}$ and ^1E_g, respectively, the origin of the 7.7-kK absorption being obscure. This yields the values $B \approx 400$ cm^{-1} and $\xi \approx 2500$ cm^{-1}. However, for $OsI_6{}^{2-}$ just the $^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3, \Gamma_5)$ band is found, permitting only the estimate $\xi \approx 2350$ cm^{-1}.

For $IrCl_6{}^{2-}$ we identify only the $^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$ band, since we were unable to resolve the $^2T_{2g}(\Gamma_7) \rightarrow {}^4T_{1g}$ transition from the beginning of the π $t_{1g} \rightarrow t_{2g}$ charge-transfer band. The fragmentary d–d band positions reported by Douglas[4] can however be roughly satisfied using Dq = 2300 cm^{-1} $B \approx 450$ cm^{-1}, and $\xi \approx 2750$ cm^{-1}, but for $IrBr_6{}^{2-}$ only the $^2T_{2g}(\Gamma_7) \rightarrow {}^2T_{2g}(\Gamma_8)$ band is available, giving the approximation $\xi \approx 2500$ cm^{-1}.

The estimation of the parameters for $OsCl_6{}^{2-}$, $OsBr_6{}^{2-}$, $OsI_6{}^{2-}$, $IrCl_6{}^{2-}$, and $IrBr_6{}^{2-}$ is of course handicapped by the absence of information concerning the spin-allowed d–d bands, which prevents any reliable estimate of Dq being made and introduces considerable uncertainty into the B and ξ values obtained. The ξ results should though be somewhat the more reliable, and the data are all collected in Tables V and VI. We have throughout assumed C/B = 4.75 for Os(IV) and 4.90 for Ir(IV).

TABLE V

NEPHELAUXETIC AND RELATIVISTIC PARAMETERS FOR OSMIUM(IV) COMPLEXES

	Ligand			
	F	Cl	Br	I
B, cm^{-1}	500	425	(400)	?
ξ, cm^{-1}	2900	(2650)	(2500)	(2350)
β	0.74	0.66	0.59	?
β^*	0.75	0.68	0.65	0.61
$a_5{}^2$	0.90	0.87	0.84	. . .
(Z/Z_0)	0.91	0.88	0.84	. . .
$a_\pi{}^2$	0.74	0.66	0.51	. . .

TABLE VI

NEPHELAUXETIC AND RELATIVISTIC PARAMETERS FOR IRIDIUM(IV) COMPLEXES

	Ligand		
	F	Cl	Br
B, cm^{-1}	510	(425)	?
ξ, cm^{-1}	3300	(2750)	(2500)
β	0.72	0.60	?
β^*	0.73	0.61	0.56
$a_5{}^2$	0.90	0.84	. . .
(Z/Z_0)	0.90	0.85	. . .
$a_\pi{}^2$	0.73	0.59	0.41

As noted above, all the hexahalo complexes of Os(IV) and of Ir(IV) show well-marked low-energy bands which we ascribe to the spin–orbit splitting of the ground states. There are though certain features of these bands which merit further attention, especially considerations regarding their energies, their intensities, their shapes, and the effect of change of cation. The most obvious aspect lies however in the positions of the band maxima which are found in both series to decrease in energy in the sense of $MF_6^{2-} > MCl_6^{2-} > MBr_6^{2-} > MI_6^{2-}$ (see Figures 1 and 2), thus implying a decrease in the effective spin–orbit coupling constants in the same order. This in turn is readily interpreted in terms of the well-known increasing tendency toward covalency for the ligand series F^-, Cl^-, Br^-, I^-, since, as shown below, even the large spin–orbit coupling constants of the Br^- and I^- ligands are not sufficient to offset the diminishing contribution of the metal ion to the effective ξ value.

It is also noticeable that the F_R values of the low-energy bands increase progressively in the sense F < Cl < Br < I, while the bandwidths show a marked decrease in that order. This latter finding can though be readily rationalized. Thus the measurements of Dorain, *et al.*,[3] and of Douglas[4] suggest that for $OsCl_6^{2-}$ and for $IrCl_6^{2-}$ the vibrational mode principally involved in vibronic coupling is the mainly bending ν_4, τ_{1u} mode. For the hexachloro species the frequency of this mode is about 170–180 cm^{-1}, and if we assume the same enabling vibration to operate for all the hexahalo complexes, we should anticipate values of 250–300, 120–130, and 70–80 cm^{-1}, respectively, for the fluoro, bromo, and iodo compounds. The observed decrease in bandwidths is therefore easily understood since the appearance of the d–d band depends upon the coexcitation of the odd vibrational mode. The decrease of the enabling frequency from F to Cl, etc., would also have the effect of enhancing the band intensity *via* the coth $(h\nu/2kT)$ term, in the sense observed, but it is not possible to reach an unequivocal conclusion on this point since the band intensities will also depend upon the extent of vibronic mixing with the Laporte-allowed levels and on the energy separations between these and the low-energy d–d excitations. Thus the band intensity should be inversely proportional[32,33] to the third power of the energy gap between the upper g and the lowest u states, so that from the positions of the corresponding Laporte-allowed charge-transfer bands we should also predict the intensities to increase from F to Cl to Br, etc. Since however the intensity should in addition depend upon the ΔE value for the g–g transition and on the extent of vibronic mixing, it is not feasible to make quantitative estimates, and consequently we are unable to decide whether the u–g mixing or the coth $(h\nu/2kT)$ factor is the predominant influence in determining the intensity sequences.

The effect of change of cation on the position of the maximum of the low-energy band was also investigated for all the Os(IV) and Ir(IV) hexahalo anions. In every case but one the general appearance of these bands was unchanged and it was found throughout that the band maxima were moved to slightly higher energies as the size of the cation was increased. Thus, for example, for $IrCl_6^{2-}$ the maxima lie at 5.24, 5.25, 5.29, 5.32, and 5.32 kK, respectively, for the Na, K, Cs, NH_4, and NEt_4 salts, while for $OsBr_6^{2-}$ the K, Cs, and NEt_4 salts show maxima at 4.90, 4.99, and 5.04 kK. For d–d transitions it is well established that a decrease in the metal–ligand distance is accompanied by a blue shift, so that if it is assumed that the MX_6^{2-} units are compressed by increase in the size of the cation, then the observed behavior can be understood. In the present case though it must be inferred that instead of the effect being due to an accentuation of the difference between the t_{2g} and e_g orbital energies, a similar circumstance obtains for the double-group orbitals γ_7 and γ_8. The one exception to the regular behavior described above is afforded by the OsF_6^{2-} ion. In this case the change of cation from K to Cs results in an increase in the position of the band maximum of just over 0.5 kK, which is much larger than would be expected to arise from any lattice compression effects, and the actual shape of the band is appreciably changed. Since both the K and the Cs salts belong to the trigonal, K_2GeF_6-type lattice, it is clear that the differences cannot arise in this way, but it is possible that the effect could be due to a change in the odd enabling vibration from ν_4, τ_{1u} to the higher energy ν_3, τ_{1u} mode. Alternatively, the band maximum in the Cs salt might correspond to the coexcitation of a greater number of the fully symmetric ν_1, α_{1g} vibrational quanta, but the reason for this anomaly is really not as yet properly understood.

As noted above the decrease in the effective spin–orbit coupling constants for the hexahalo complexes of Os(IV) and Ir(IV) in the sense F > Cl > Br > I can easily be understood qualitatively in terms of an increasing tendency toward covalency, but a quantitative assessment of this trend is less straightforward. Thus, Owen and Thornley[33] ascribed the reduction of the free-ion value of ξ, due to complex formation, entirely to symmetry-restricted covalency, leading to the expression $\xi_{obsd} = N_\pi^2(\xi_d + {}^1/_2\alpha_\pi^2\xi_p)$, where the normalizing constant N_π is equal to $[1 - 4\alpha_\pi S + \alpha_\pi^2)^{-1/2}$. If, in the absence of reliable values for the metal–ligand overlap integrals, we assume the approximation $S \approx 0$, the fractional contributions of the metal and ligands are equal to $(1 + \alpha_\pi^2)^{-1}$ and ${}^1/_2\alpha_\pi^2(1 + \alpha_\pi^2)^{-1}$, respectively, and the appropriate coefficients, a_π^2, for the t_{2g} (π) metal orbitals of the Os(IV) and Ir(IV) complexes are readily found to have the values given in Tables V and VI. The neglect of central field covalency in this approach does however tend to overestimate the extent of the symmetry-restricted contribution, and it is not at the moment clear that this approximation is strictly justifiable, even though the spin–orbit coupling constant is dominantly an inner radial function quantity, which would not be expected to show large central field covalency effects. Thus, Jørgensen[34] has shown that the nephelauxetic and relativistic ratios, β_{55} and β^*_{55}, should be related to the metal orbital contribution coefficient, a_5^2, and the relative reduction of the effective nuclear charge by the expressions $\beta_{55} = a_5^4(Z/Z_0)$ and $\beta^*_{55} = a_5^2(Z/Z_0)^2 + {}^1/_2(1 - a_5^2)(\xi_p(\text{lig})/\xi_d(\text{metal}))$, where again we assume $S \approx 0$. (When the spin–orbit coupling constant of the ligand is small compared with that of the metal, the last term in the second expression may be neglected.) Thus, if both β_{55} and β^*_{55} are known for a given complex, a_5^2 and (Z/Z_0) can each be determined, and the values calculated in this way are also shown in Tables V and VI. In the present work only the results for the two hexafluoro complexes can be regarded as properly reliable, because of the uncertainty in B for the other species, but in all cases the results show the usual

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[32] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 188.

[33] J. Owen and J. H. M. Thornley, *Rep. Progr. Phys.*, **29**, 675 (1966).

[34] C. K. Jørgensen, *Struct. Bonding (Berlin)*, **1**, 3 (1966).

trend in covalency effects for the halide series and suggest that the neglect of central-field effects tends to exaggerate the overall extent of the ligand contributions.

For the Ir(IV) complexes it is possible to compare our present results with the results obtained[19] for the fraction of unpaired electron spin density per ligand, as deduced from esr measurements of the g values and ligand hyperfine splittings. The most recent interpretation[35] of these data involves some assumptions concerning the degree of interaction of the e_g (σ) metal orbitals with the ligands, but for the F, Cl, and Br complexes the f_π values calculated from the g factors were, respectively, 11.5, 14.1, and 14.1%, while the ligand hyperfine splittings yielded the figures 8.1, 8.0, and 7.5%. From our a_π^2 values we calculate the corresponding results of 6.9, 10.3, and 14.8%, which agree as well with Thornley's[35] two sets of values as these do with each other. In view of the approximations made here the agreement is reasonably satisfactory, but our results do tend to support the view that the consideration only of symmetry-restricted covalency does lead to an overestimate of the ligand contributions. It is though noteworthy that the Os(IV) and Ir(IV) hexafluoro complexes both lead to much larger values of a_5^2 and appreciably more reduced values of (Z/Z_0) than for the corresponding Os(V) and Ir(V) anions, which, overall, show much stronger covalent tendencies.[15]

For the Ir(IV) complexes the progressive reduction of the effective spin–orbit coupling constant on descent of the halogen series is closely reflected in the corresponding values of the magnetic moments, which, for a low-spin, $^2T_{2g}$ ground state, would be expected to increase as ξ decreased. Thus, for Cs_2IrF_6, a moment of 1.42 BM at 300°K is reported,[6] while K_2IrCl_6 and $(NH_4)_2IrCl_6$ give 1.77 and 1.84 BM, respectively, and $(NH_4)_2IrBr_6$ yields a value of 2.09 BM.[36] For the Os(IV) complexes the low-spin, $^3T_{1g}$ ground state also leads to the expectation that the magnetic moment should tend to increase with a decreasing spin–orbit coupling constant. However, although there is some evidence to suggest that this is the general trend, the magnetic moments appear to be appreciably cation dependent and there is some suggestion that the situation may be complicated by antiferromagnetic effects.[29] Thus the magnetic data are qualitatively in agreement with our findings for the values of the spin–orbit coupling constants in both series, but we have not attempted to assess the extent of covalency effects *via* the orbital reduction factor, k, since it has been shown by Gerloch and Miller[37] that this factor cannot be assumed to be equivalent to a_5^2 and in fact provides only a qualitative guide to the magnitude of covalent contributions. It is therefore not possible to make an independent estimate of the magnitude of a_5^2, with a view to deciding whether the Owen and Thornley[33] or the Jørgensen[34] approach affords the better description of the situation. On the whole we are inclined to believe that the former tends to overestimate a_π^2 and the latter to exaggerate the reduction in (Z/Z_0), and we have previously[15] indicated our reservations concerning the combination of Jørgensen's two expressions for the purpose of calculating a_5^2 and (Z/Z_0).

From the positions of the lowest Laporte-allowed charge-transfer transitions in the Os(IV) and Ir(IV) complexes studied it is possible to calculate optical electronegativity values for the metals in the usual way.[38] Such values have already been obtained by Jørgensen[2] from solution measurements for the chloro, bromo, and iodo species, the values of χ_{opt} for the metal being essentially independent of the ligand, Os(IV) and Ir(IV) having χ_{opt} values of 2.2 and 2.35, respectively. These values were however derived by applying to σ_{obsd} (the lowest Laporte-allowed charge-transfer band) only the corrections due to changes in the spin-pairing energy accompanying the $d^q \rightarrow d^{q+1}$ transition, the relativistic (spin–orbit) effects being neglected, but in the 5d series the values of ξ are substantial and these contributions should not be ignored. For t_{2g}^n ground states the spin–orbit corrections are readily derived using the p^n isomorphism and the approximation of jj coupling in which the spin–orbit matrices are diagonal, whence we obtain for d^4 and d^5 systems the results $\sigma_{\text{cor}}(d^4) = \sigma_{\text{obsd}} - {}^4/_3D - \xi$ and $\sigma_{\text{cor}}(d^5) = \sigma_{\text{obsd}} - {}^2/_3D - \xi$, where D is the spin-pairing energy. Note that in these cases the relativistic correction acts in the same sense as the spin-pairing term whereas for d^3 systems (*e.g.*, Re(IV),[39] Os(V)[15]) the contributions are opposed since $\sigma_{\text{cor}}(d^3) = \sigma_{\text{obsd}} - 2D + 2\xi$.

For the chloro, bromo, and iodo complexes the present σ_{obsd} values agree quite closely with the solution data[2] and we have thus used them as outlined above to calculate the optical electronegativity values, $\chi_{\text{opt(rel)}}$, containing the spin–orbit corrections. For IrF_6^{2-} σ_{obsd} is well established as 47.8 kK, but for OsF_6^{2-} we have assumed $\sigma_{\text{obsd}} = 50\text{–}55$ kK, in agreement with the findings of Hepworth, *et al.*,[6] and with the indications in our own spectrum of the beginning of the charge-transfer region just below 50 kK. The $\chi_{\text{opt(rel)}}$ values thus derived are listed in Table VII, together with the σ_{obsd}, σ_{cor}, and D parameters. As expected, the $\chi_{\text{opt(rel)}}$ values for Os(IV) and Ir(IV) are somewhat smaller than the corresponding figures for Os(V) and Ir(V),[15] 2.53 and 2.76, respectively, reflecting the reduced tendency for electron accession to the metal in the M(IV) series, which is also paralleled in the larger β values for the hexafluoro complexes: Os(IV), 0.74; Os(V), 0.56; Ir(IV), 0.72; Ir(V), 0.47. The increased tendency toward covalency for the higher oxidation states is also reflected in the β values of 0.48 and 0.37 calculated[16] for Os(VI) and Ir(VI) in OsF_6 and IrF_6.

TABLE VII

OPTICAL ELECTRONEGATIVITY PARAMETERS FOR OSMIUM(IV) AND IRIDIUM(IV) ANIONS

Ligand	σ_{obsd}, kK	σ_{cor}, kK	D, kK	$\chi_{\text{opt(rel)}}$
		Os(IV)		
F	50–55	44	4.22	2.43 ± 0.08
Cl	26.3	18.6	3.81	2.38
Br	20.0	13.0	3.38	2.37
		Ir(IV)		
F	47.8	41.6	4.40	2.51
Cl	19.6	14.4	3.67	2.52

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(35) J. H. M. Thornley, *Proc. Phys. Soc. London* (*Solid State Phys.*), [2] **1**, 1024 (1968).

(36) V. Norman and J. C. Morrow, *J. Chem. Phys.*, **31**, 455 (1959).

(37) M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, **10**, 1 (1968).

(38) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, p 94.

(39) C. K. Jørgensen and K. Schwokau, *Z. Naturforsch. A*, **20**, 65 (1965).

For the M(IV) series the familiar increase in covalency (decrease of β) toward the end of the d block is again observed. Thus, the data of Jørgensen and Schwokau[39] for ReF_6^{2-} yield $\beta_{55} \approx 0.85$, as compared with our values of 0.74 and 0.72 for OsF_6^{2-} and IrF_6^{2-}, while for PtF_6^{2-} the data[40] require $\beta \approx 0.55$. In a similar way the optical electronegativity shows a progressive increase along the 5d series, the values of $\chi_{\text{opt(rel)}}$ for Re(IV) and Pt(IV) being approximately 1.9 and 2.6, respectively, so that the relationship between β and χ_{opt}, for which we have previously suggested a rationalization,[41] appears to hold in the 5d block as well as in the first transition series. This connection appears to be rather less exact in the 5d series than for the 3d complexes since the $\chi_{\text{opt(rel)}}$ value for Re(IV) is surprisingly low, but our own diffuse reflectance measurements confirm the σ_{obsd} value of 35.6 kK for $ReCl_6^{2-}$ and also show no indication of charge-transfer bands below 50 kK for ReF_6^{2-}. In fact, though, a fairly substantial difference in $\chi_{\text{opt(rel)}}$ between d^3 and d^4 systems is not altogether unexpected, since the relativistic corrections operate in a contrary sense in the two cases.

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[41] G. C. Allen and K. D. Warren, *Mol. Phys.*, **20**, 379 (1971).

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The Enthalpies of Formation of Arsine and Biarsine[1]

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The enthalpies of formation of AsH_3 and As_2H_4 have been determined by the method of explosion in mixtures with SbH_3, and the thermochemical bond energies have been derived. Results are $\Delta H_f°(AsH_3(g)) = +14.9 \pm 0.4$ kcal mol^{-1}, $\Delta H_f°(As_2H_4) = +28.2 \pm 1.3$ kcal mol^{-1}, E(As–H) = 71.2 kcal mol^{-1}, and E(As–As) = 39.9 kcal mol^{-1}.

Introduction

As part of a continuing program of investigation of the enthalpies of formation and thermochemical bond energies of the binary[2–8] and ternary[9] hydrides of boron and the group IV–VI elements, the enthalpies of decomposition of arsine and biarsine have been measured. No previous calorimetric studies have been reported for biarsine, but a mass spectrometric appearance potential study exists.[10]

The method used was explosion of the gaseous hydride in mixtures with stibine, as in earlier studies.[2–6,8,9] The enthalpy of decomposition of arsine was previously measured by this method[2] but only at a single AsH_3:SbH_3 ratio. Since elemental arsenic and antimony form a continuous range of solid solutions, the enthalpy of mixing of the metals might have a significant effect upon the deduced enthalpy of formation. Accordingly, in the present work the measurements were performed over a range of AsH_3:SbH_3 ratios.

Experimental Section

Stibine and arsine were obtained from the Matheson Chemical Co.[11] The stibine cylinder was held at −78° while the gas was withdrawn into flasks at −196°; a middle fraction was used. The arsine was passed twice through a trap at −126°. A single flask of each gas was used for all of the calorimetric work; melting curve analysis[12] of both indicated the mole fraction of liquid-soluble, solid-insoluble impurities to be less than 2×10^{-5}.

Biarsine was prepared as described by Shriver and Jolly,[13] using an ozonizer-type discharge tube operated at 12.5 kV with arsine passed through at low pressure and without diluent gas. About 25 mmol of arsine was condensed in a U trap (without packing) at −196°. The surrounding dewar was removed and the liquid nitrogen was dumped out of it; when the discharge started, the cold, empty dewar was replaced around the trap and adjusted to a height such as to keep the trap at a temperature at which the vapor pressure of the arsine was barely adequate to maintain the discharge. About 30–45 min was required to pass the total batch of arsine; the rate of production of biarsine was roughly 0.15 mmol hr^{-1}. To a first approximation, this rate was unaffected by passing the arsine considerably more rapidly at a higher pressure.

Biarsine is fairly stable as a gas, even at somewhat elevated temperatures, but is extremely unstable in the condensed phase above *ca.* −100°. Accordingly, the biarsine was always condensed, in the preparation, purification, and calorimeter-loading vacuum lines, into special traps having electrically heated reentrant inlet tubes so that the gas went directly to a surface at −126° (methylcyclohexane slush), as described by Shriver and Jolly.[13] The biarsine was always volatilized rapidly from the trap by removing a surrounding dewar of liquid nitrogen and immediately replacing it with water at *ca.* 60°. The biarsine was purified by several trap-to-trap distillations at −126°. The volume of gas decreased 10–20% per pass, indicating this to be the amount decomposed at each volatilization.

The vapor pressure of biarsine is very difficult to determine because of the instability of the liquid; Shriver and Jolly[13] estimated 10 mm at room temperature. In the course of the present work, experiments were done wherein the pressure in a bulb was observed as the temperature of a surrounding bath was lowered.

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

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