Electronic Spectra of Some Post-transition-metal Halide Complexes

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The electronic absorption spectra of tetrahalide complexes of Zn^{II}, Cd^{II}, Hg^{II}, and Tl^{III} have been measured either in solution or as thin films. The effects of second-order spin–orbit coupling account satisfactorily for the observed band intensities and splittings. The one-electron transitions responsible for the lowest-energy groups of absorption bands are all of the type $t_2 \rightarrow a_1$. There is no evidence for transitions from the non-bonding t_1 or e molecular orbitals, and an explanation is advanced for their non-appearance.

WHILST the charge-transfer spectra of transition-metal compounds have begun to receive much attention, very little work has been reported on the spectra of non-transition-metal complexes in spite of the fact that, lacking the complexities of a partly filled *d*-shell, they should in principle be easier to interpret. As with transitional-metal charge-transfer spectra, such interpretation is expected to provide quantitative information on bonding. Unambiguous assignments are, of course, a necessary pre-requisite to extracting information from the spectra, and for this purpose molecules of high symmetry and low complexity are not appropriate.[1,2] We have therefore examined the absorption spectra of a series of tetrahedral halide complexes of the post-transition metals Zn, Cd, Hg, and Tl. Evidence for the geometry of these complex ions comes mainly from measurements of far-i.r. and Raman spectra.[3,4] While a number of these electronic spectra have been reported,[5-9] it has not always been the custom to ensure that the complex ions do not dissociate in the solutions studied. For example the equilibrium constants of Eillendt and Cruse [10] for the Hg^{II}–X^- systems in acetonitrile (the solvent used for our measurements) show that dilute solutions of $(Et_4N)_2HgX_4$ require a considerable quantity of added halide ion to ensure complete formation of HgX_4^{2-}. Even in the case of those complex halides for which reliable data have appeared [8,9] we consider it worthwhile to determine the spectra again to obtain accurate band shapes, which could then be subjected to Gaussian analysis to yield reliable measures of transition intensity.

EXPERIMENTAL

Samples of the compounds $(Et_4N)_2MX_4$ (M = Cd, Hg; X = Cl, Br, I) were prepared by a method similar to that used by Gill and Nyholm [11] for the corresponding complex halides of zinc and a variety of transition metals. The compounds precipitate on mixing ethanolic solutions of the component halides, Et_4NX and MX_2. In the case of the mercury complexes, it is known [12] that reaction between Et_4NX and HgX_2 can lead to products of the type Et_4NHgX_3 and $Et_4NHg_2X_5$, in addition to $(Et_4N)_2HgX_4$. The precaution was taken of employing about twice the amount of Et_4NX required for complete formation of $(Et_4N)_2MX_4$ in each case. The mercury complexes were recrystallised from acetonitrile; the bromo-complex required additional recrystallisation from nitromethane. The cadmium complexes were adequately pure without recrystallisation, which in any case appears to cause some dissociation. Analyses are in Table 1.

TABLE 1

Analyses (%)

Compound	C		H		N	
	Found	Calc.	Found	Calc.	Found	Calc.
$(Et_4N)_2HgCl_4$	32·2	31·9	6·6	6·6	4·7	4·65
$(Et_4N)_2HgBr_4$	24·5	24·6	5·0	5·2	3·35	3·6
$(Et_4N)_2HgI_4$	19·4	19·8	4·3	4·2	2·8	2·9
$(Et_4N)_2CdCl_4$	37·6	37·3	8·15	7·8	5·7	5·4
$(Et_4N)_2CdBr_4$	27·5	27·75	6·0	5·8	4·1	4·0
$(Et_4N)_2CdI_4$	21·9	21·9	5·15	4·6	3·0	3·2

The zinc complexes $(Bu_4^nN)ZnX_4$ used were examined as thin films [8] prepared by the evaporation of ethanolic solutions of Bu_4NX and ZnX_2 in 2 : 1 mole ratio on a piece of silica. Samples of the compounds Et_4NTlX_4 were kindly made available by Dr. R. A. Walton.

Absorption spectra of the compounds $(Et_4N)_2HgX_4$ in acetonitrile solution were obtained with a pathlength of 1 mm. In the absence of free halide ion, Beer's law was not obeyed, owing to extensive dissociation.[10] The minimum of X^- required for essentially complete formation of HgX_4^{2-}, used in obtaining the spectra of Figure 1, was *ca.* 10 times the amount of $(Et_4N)_2HgX_4$ for the chloro- and bromo-complexes, and 20 times for the iodo-compound. Satisfactory Beer's law plots were obtained under these conditions.

The tetrahalogenothallates were also examined in acetonitrile solution: in this case there is no appreciable dissociation, and addition of halide is not required. (Added halide causes changes in the spectra of Et_4NTlCl_4 and Et_4NTlBr_4 which are attributable to associations leading to five- and six-co-ordinated species; in contrast, the iodo-complex shows no such change. This is consistent with the known existence of such higher co-ordinated complexes with Cl^- and Br^-, and the lack of evidence for any similar complex with I^-.[13]) Figure 2 shows the spectra of the ions TlX_4^-.

Solution spectra of the tetrahalogenocadmates cannot

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[1] C. K. Jorgensen, *Mol. Phys.*, 1959, **2**, 309.

[2] B. D. Bird and P. Day, *J. Chem. Phys.*, 1968, **49**, 392.

[3] J. G. Spiro, *Inorg. Chem.*, 1967, **6**, 569.

[4] A. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, 1964, **86**, 17.

[5] H. Fromherz, *Z. Elektrochem.*, 1931, **37**, 553.

[6] C. Merritt, jun., H. M. Hershenson, and L. B. Rogers, *Analyt. Chem.*, 1953, **25**, 572.

[7] G. B. Deacon and B. O. West, *J. Chem. Soc.*, 1961, 3929.

[8] B. D. Bird and P. Day, *Chem. Comm.*, 1967, 741.

[9] R. A. Walton, *Co-ordination Chem. Rev.*, 1971, **6**, 1.

[10] G. Eillendt and K. Cruse, *Z. phys. Chem.* (*Leipzig*), 1952, **201**, 130.

[11] R. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.

[12] 'Gmelins Handbuch der Anorganischen Chemie,' Hg, Part Bl, Verlag Chemie, Weinheim, 1965.

[13] 'Stability Constants of Metal-ion Complexes; Part II: Inorganic Ligands,' eds. J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, Chemical Society, London, 1964.

be obtained in the presence of excess of halide ion as the absorptions of CdX$_4^{2-}$ and X$^-$ in acetonitrile lie in the same spectral region. The spectra of these compounds were therefore obtained by doping samples into polymer films, a method successfully employed by Briat and Rivoal.[14]

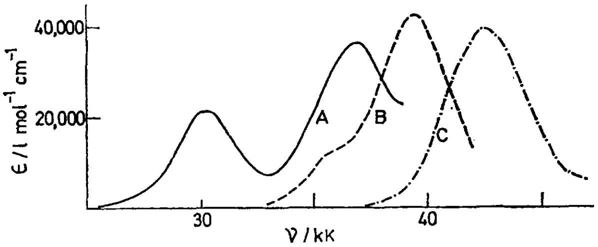

FIGURE 1 Spectra of the ions HgX$_4^{2-}$ in acetonitrile solution: A, HgI$_4^{2-}$; B, HgBr$_4^{2-}$; and C, HgCl$_4^{2-}$

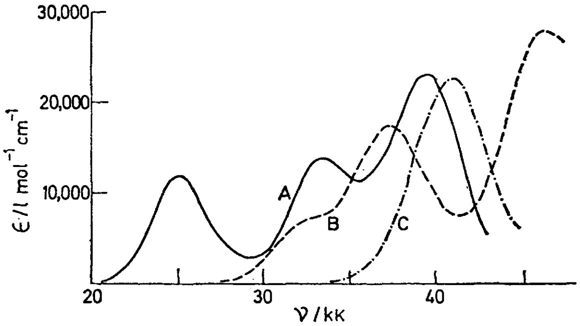

FIGURE 2 Spectra of the ions TlX$_4^-$ in acetonitrile solution: A, TlI$_4^-$; B, TlBr$_4^-$; and C, TlCl$_4^-$

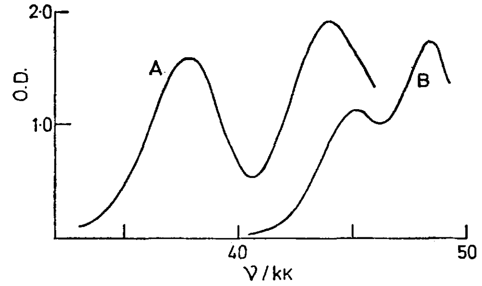

FIGURE 3 Spectra of the ions A, CdI$_4^{2-}$; B, CdBr$_4^{2-}$ as doped polymer films

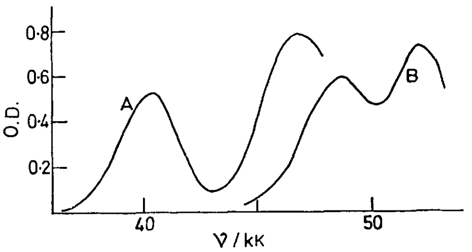

FIGURE 4 Spectra of the ions A, ZnI$_4^{2-}$; and B, ZnBr$_4^{2-}$ as evaporated films of the tetrabutylammonium salts

Polyvinyl chloride of molecular weight *ca.* 100,000 gave a film with good transmission up to about 48 kK when a solution in dichloromethane was evaporated. Doped films were prepared by adding solutions of the cadmium complex halides in this solvent to the polyvinyl chloride solution before evaporation. Both the bromo- and iodo-complexes gave satisfactory absorption spectra (Figure 3). The chloro-complex showed no appreciable absorption up to 50 kK.

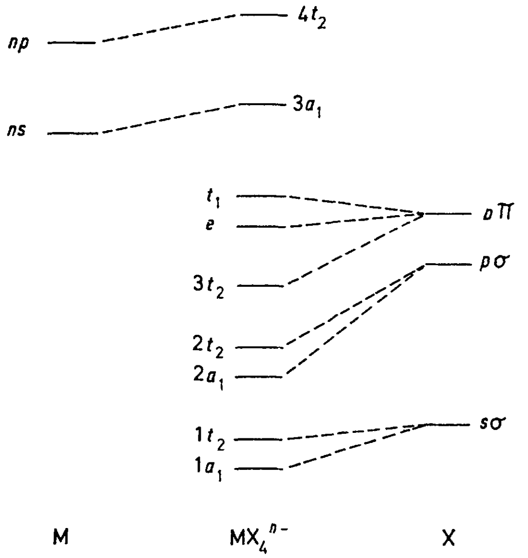

FIGURE 5 Molecular orbital scheme for tetrahedral complex ions MX$_4^{n-}$: broken lines indicate the atomic orbital expected to make the largest contribution to each molecular orbital

In the case of the tetrahalogenozincates, the high energy of the transitions again prevents the measurement of solution spectra, and we employed thin evaporated films, as in our earlier study of the far-u.v. spectra of transition-metal halide complexes. The tetrachlorozincate complex has no absorption maximum within the range of our spectrophotometer (185 nm). The spectra of the other two complexes are shown in Figure 4.

All absorption spectra were obtained with a Cary 14 spectrophotometer, where necessary with nitrogen purging, and were measured at room temperature.

DISCUSSION

Theory and Interpretation.—Figure 5 shows a qualitative molecular orbital scheme for a post-transition-metal tetrahalide complex. It is similar to that used for first transition series tetrahalide complexes,[2] but excluding the metal $(n-1)d$ orbitals, which in the post-transition metals become a part of the core (as indicated by atomic energy levels[15]). Thus in the post-transition-metal complexes, the e molecular orbital, which is bonding in transition-series complexes, becomes non-bonding like t_1. The relative positions of t_1 and e orbitals in Group IVB tetrahalides have been discussed by Green *et al.*,[16] who concluded both from

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[14] B. Briat and J. C. Rivoal, *Compt. rend.*, 1970, **271**, 1166.

[15] C. E. Moore, ' Atomic Energy Levels,' National Bureau of Standards, Circular 467, vols. II and III, Washington, 1958.

[16] J. C. Green, M. L. H. Green, P. J. Joachim. A. F. Orchard, and D. W. Turner, *Phil. Trans. Roy. Soc.*, 1970, *A*, **268**, 111.

the experimental evidence of photoelectron spectroscopy and from calculations of the interactions within the X_4 tetrahedron that the t_1 orbital lies above the e orbital. We adopt the same ordering in Figure 5 though it is not essential to our treatment. In the ground state all orbitals up to and including the non-bonding levels are filled, giving a $^1A_1$ term.

In what follows we employ the co-ordinate system and symmetry-adapted combinations of ligand orbitals of Ballhausen and Gray.[17] Molecular orbital mixing coefficients for t_2 orbitals are defined in Table 2 to be consistent with those used previously.[2] Electronic transitions are allowed from the $^1A_1$ ground term to $^1T_2$ excited terms, which can result from the one-electron transitions $nt_2 \rightarrow 3a_1$ (n = 1, 2, or 3). No doubt the transition $1t_2 \rightarrow 3a_1$, and in some cases $2t_2 \rightarrow 3a_1$ also, occur at energies outside the range of our measurements, and we similarly discount the possibility of transitions to the $4t_2$ orbital in view of the high energy [15] of the np metal orbitals. Under the influence of spin–orbit coupling one may expect to see transitions to the T_2 spinor states arising from excited terms $^3T_2$, ^3E, and $^3T_1$ as well as $^1T_2$: the last two terms, resulting from one-electron transitions $e \rightarrow 3a_1$ and $t_1 \rightarrow 3a_1$ respectively, may be expected to lie lower in energy than $^3T_2$ and $^1T_2$.

TABLE 2

Metal	Ligand		
np	$p\sigma$	$p\pi$	s
c_3	c_5	c_7	c_6

TABLE 3

Band parameters from Gaussian analysis of absorption spectra: for thin films the values of the extinction coefficient, E, and dipole strength, D, are relative to those of band 1

Complex	Band	$\nu_{max.}$/kK	ε/l mol^{-1} cm^{-1}	D/D^2
$HgCl_4^{2-}$	1	42·6	39,200	38·0
$HgBr_4^{2-}$	1	35·5	8760	6·25
	2	39·5	41,400	40·0
HgI_4^{2-}	1	30·3	20,600	21·9
	2	36·9	35,400	40·9
$TlCl_4^{-}$	1	41·0	22,200	27·5
$TlBr_4^{-}$	1	32·0	5150	5·97
	2	37·3	17,000	23·8
	3	46·7	27,600	36·1
TlI_4^{-}	1	25·2	11,600	18·0
	2	33·5	13,200	18·3
	3	39·5	22,900	27·4
$CdBr_4^{2-}$	1	45·0	1	1
	2	48·5	1·52	1·10
CdI_4^{2-}	1	37·7	1	1
	2	44·2	1·24	1·17
$ZnBr_4^{2-}$	1	48·6	1	1
	2	52·4	1·22	0·864
ZnI_4^{2-}	1	40·3	1	1
	2	47·0	1·53	1·73

According to the experimental evidence, the development of the spectra of the Group IIB tetrahalide anions from the chloro- to the iodo-complex suggests the emergence of a spin-forbidden band.

To obtain more precise transition energies and intensities from the overlapping bands, we have carried out a Gaussian analysis of each of the spectra in Figures 1—4, giving the parameters of Table 3. The separation of the two bands in the bromo- and iodo-complexes of the Group IIB metals is then seen to be rather greater than the halogen spin–orbit coupling constant (Table 4).[18]

TABLE 4

Spin–orbit coupling constants/kK, from Jørgensen's tabulation [18] or calculated by us from atomic spectral data [15]

Atom	ζ_M	Atom	ζ_X
Zn	0·39	Cl	0·59
Cd	1·14	Br	2·46
Hg	4·27	I	5·07
Tl	5·20		

In view of our remarks above it is reasonable to assume that the lowest-energy group of bands in these spectra arises from the transition $3t_2 \rightarrow 3a_1$. The two Russell–Saunders terms $^1T_2$ and $^3T_2$, of the configuration $3t_2^5 3a_1^1$ could then be mixed *via* second-order spin–orbit coupling, so that the transition to the latter becomes partially allowed. We now test this hypothesis, using the vector coupling method in Griffith's [19] formulation (1) for calculation of matrix elements of the spin–orbit coupling Hamiltonian,[20] where κ indexes the electrons and $\mathbf{u}$ is given by equation (2), the summation being

$$\mathscr{H}_{\mathrm{so}} = \sum_{\kappa=1}^{n} \mathbf{s}(\kappa)\mathbf{u}(\kappa) \qquad (1)$$

$$\mathbf{u} = \sum_{i} \zeta_i(r)\mathbf{l}_i \qquad (2)$$

over all nuclei. Writing spinor group wavefunctions as kets such as $|ShJt\tau\rangle$, where τ is a component of a spinor irreducible representation t arising from a term ^{2S+1}h, and J is a number to distinguish the t's if more than one occurs in the term, one may reduce matrix elements of $\mathscr{H}_{\mathrm{so}}$ (which is diagonal in t and τ) according to (3) where

$$\langle ShJt\tau|\mathscr{H}_{\mathrm{so}}|S'h'J't\tau\rangle = \langle Sh||\mathscr{H}_{\mathrm{so}}||S'h'\rangle \Omega_{JJ'}\begin{pmatrix} S S' T_1 \\ h' h\ t \end{pmatrix} \qquad (3)$$

the Ω-coefficients have been tabulated (ref. 20, Table E1). Further reduction to one-electron reduced matrix elements can be achieved for particular types of electron configuration, *e.g.*, if the terms ^{2S+1}h and $^{2S'+1}h'$ both arise from a configuration $a^m b^n$ having two open shells one may use equation (10.14) of ref. 20 to give a sum of contributions from $\langle \tfrac{1}{2}a||\mathrm{su}||\tfrac{1}{2}a\rangle$ and $\langle \tfrac{1}{2}b||\mathrm{su}||\tfrac{1}{2}b\rangle$, the reduced matrix elements of one-electron wavefunctions.

In our case we have, by applying equation (3),

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[17] C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' Benjamin, New York, 1964.

[18] C. K. Jorgensen, 'Orbitals in Atoms and Molecules,' Academic Press, London, 1962.

[19] J. S. Griffith, 'The Irreducible Tensor Method for Molecular Symmetry Group,' Prentice-Hall, Englewood Cliffs, N.J., 1962.

[20] A. A. Misetich and J. Buch, *J. Chem. Phys.*, 1964, **41**, 2524.

equations (4) and (5). Further, we have equation (6), and finally equations (7)—(9).

$$\langle {}^1T_2T_2|\mathscr{H}_{\text{so}}|{}^1T_2T_2\rangle = 0 \tag{4}$$

$$\langle {}^3T_2T_2|\mathscr{H}_{\text{so}}|{}^3T_2T_2\rangle = \tfrac{1}{6}\langle {}^3T_2||\mathscr{H}_{\text{so}}||{}^3T_2\rangle \tag{5}$$

$$\begin{aligned}\langle {}^3T_2||\mathscr{H}_{\text{so}}||{}^3T_2\rangle &= \\ &\langle t_2^{\,5}({}^2T_2)a_1({}^2A_1){}^3T_2||\mathscr{H}_{\text{so}}||t_2^{\,5}({}^2T_2)a_1({}^2A_1){}^3T_2\rangle \\ &= -\langle \tfrac{1}{2}t_2||\text{su}||\tfrac{1}{2}t_2\rangle\end{aligned} \tag{6}$$

$$\langle {}^3T_2T_2|\mathscr{H}_{\text{so}}|{}^1T_2T_2\rangle = \langle {}^1T_2T_2|\mathscr{H}_{\text{so}}|{}^3T_2T_2\rangle \tag{7}$$

$$= \tfrac{1}{3}\langle {}^3T_2||\mathscr{H}_{\text{so}}||{}^1T_2\rangle \tag{8}$$

$$\langle {}^3T_2||\mathscr{H}_{\text{so}}||{}^1T_2\rangle = -\frac{1}{\sqrt{2}}\langle \tfrac{1}{2}t_2||\text{su}||\tfrac{1}{2}t_2\rangle \tag{9}$$

We define S by equation (10) and construct the

$$S = \langle \tfrac{1}{2}t_2||\text{su}||\tfrac{1}{2}t_2\rangle \tag{10}$$

secular determinant (11) for the interaction of $|{}^1T_2T_2\rangle$

$$\begin{vmatrix} -\tfrac{1}{6}S - K - E & -\dfrac{1}{3\sqrt{2}}S \\ -\dfrac{1}{3\sqrt{2}}S & -E \end{vmatrix} = 0 \tag{11}$$

and $|{}^3T_2T_2\rangle$, where K is the interelectron repulsion separating the terms ${}^3T_2$ and ${}^1T_2$. The wavefunctions after interaction are the linear combinations (12) and (13). Solution of the secular determinant gives the

$$\psi = b_1|{}^3T_2T_2\rangle + b_2|{}^1T_2T_2\rangle \tag{12}$$

$$\psi' = b'_1|{}^3T_2T_2\rangle + b'_2|{}^1T_2T_2\rangle \tag{13}$$

energies (14) and hence the separation of the two bands

$$\begin{aligned}E &= -S/12 - K/2 \pm [(S/4 + K/2)^2 - SK/6]^{\frac{1}{2}} \\ &= -S/12 - K/2 \pm X\end{aligned} \tag{14}$$

will be given by (15). Solution of the secular equations for b_2 and b_2' gives the relation (16) where the positive

$$d = 2X \tag{15}$$

$$b_2, b_2' = \left|1 + \frac{S^2}{18(S/12 + K/2 \pm X)^2}\right|^{-\frac{1}{2}} \tag{16}$$

sign refers to b_2 and the negative to b_2', and ψ is taken to be the higher-energy wavefunction. The ratio, R, of intensities of high and low energy transitions can now be obtained from equation (16), and is shown by equations (17) and (18). We now have two relationships [equations (15) and (18)] involving the observables, d and R, and the parameters of the theory, S and K. Writing the latter explicitly in terms of the former, however, we find that the sign of S is indeterminate. However, the limiting value of R as $K/S \rightarrow 0$ depends on the sign of S, being $\frac{1}{2}$ if $S < 0$ and 2 if $S > 0$. In nearly every case the experimental ratio of intensities is less than 2, suggesting that S is negative in these systems. This agrees with the photoelectron spectroscopy results of Green *et al.*,[16] who find that the highest occupied t_2 molecular orbital in the Group IVB tetrahalides has a value of S which is negative, and close to its maximum possible value. To determine this maximum we recall that one-electron reduced matrix elements of the type $\langle \frac{1}{2}t_2||\text{su}||\frac{1}{2}t_2\rangle$ can be expressed[2,21] in terms of molecular orbital coefficients and atomic spin–orbit coupling constants. Neglecting many-centre integrals, we have equation (19) where ζ_M and ζ_X are the

$$R = \frac{|\langle {}^1A_1|r|\psi\rangle|^2}{|\langle {}^1A_1|r|\psi'\rangle|^2} = \frac{b_2^{\,2}}{b_2'^{\,2}} \tag{17}$$

$$= \frac{X + S/12 + K/2}{X - S/12 - K/2} \tag{18}$$

$$\langle \tfrac{1}{2}t_2||\text{su}||\tfrac{1}{2}t_2\rangle = -3[c_3^{\,2}\zeta_M - (\sqrt{2}c_5c_7 - \tfrac{1}{2}c_7^{\,2})\zeta_X] \tag{19}$$

spin–orbit coupling constants of metal and halogen respectively in the p valence shell. Green *et al.*[16] pointed out that when ζ_M is small, S has its negative maximum of $-3\zeta_X$ for $c_5 = -\sqrt{\frac{1}{3}}$, $c_7 = +\sqrt{\frac{2}{3}}$, $c_3 = c_6 = 0$ and that the Group IVB tetrabromides exhibited values of S in the region of $-3\zeta_{Br}$.

In our case, assuming S to be negative, we obtain the values of S and K for the Group IIB complexes given in Table 5. S approaches the limit of $-3\zeta_X$ fairly closely in most cases (only once does S exceed this limiting value, and then by a small amount). For the lighter metals Zn and Cd, which have quite small ζ_M (Table 4), our results therefore indicate that in the $3t_2$ level there is little metal participation and the mixing of halogen $p\sigma$- and $p\pi$-orbitals is considerable. The value of ζ_{Hg} is not small compared with ζ_X, so that one cannot draw reliable conclusions about the LCAO coefficients in the mercury complexes.

TABLE 5

The parameters S and K, derived from experimental results. See text for explanation of assignments (*i*) and (ii) of TlX_4^-

Complex		S/kK	K/kK
$ZnBr_4^{2-}$		−8·1	1·1
ZnI_4^{2-}		−13·7	4·1
$CdBr_4^{2-}$		−7·4	1·4
CdI_4^{2-}		−13·8	2·8
$HgBr_4^{2-}$		−5·7	3·8
HgI_4^{2-}		−13·4	4·3
$TlBr_4^-$	(i)	−9·1	4·7
	(ii)	−19·4	5·2
TlI_4^-	(i)	−17·5	3·0
	(ii)	−12·5	3·3

We now investigate the tetrahalogenothallate spectra in the light of the preceding discussion. The third band seen in the spectra of the bromo- and iodo-complexes could reasonably originate in one of two ways: it might be an orbitally-forbidden transition from t_1 or e to $3a_1$ at low energy, the other two bands corresponding to those of the Group IIB complexes; alternatively it may be that the latter are paralleled in the two lowest-energy bands of the TlX_4^- spectra, the highest-energy

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[21] B. D. Bird, D.Phil. Thesis, Oxford, 1969.

band resulting from a more deeply lying molecular orbital.

Transition energies alone suggest that the latter interpretation is the correct one. The first absorption peak of $TlCl_4^-$, which is not split by spin–orbit coupling, lies at lower energy than $HgCl_4^{2-}$ in agreement with our expectation that Tl^{III} is the more oxidising metal ion. One might expect then that the behaviour of the other halogen-complexes would parallel that of the chlorides. Table 3 and the spectra themselves show that this is consistent with the assignment of bands 1 and 2, but not 2 and 3, to the excited configuration $3t_2^5 3a_1$.

Band splittings and intensities support the same assignment, for $TlBr_4^-$ at least, when the method used above is applied to pairs of adjacent bands in each spectrum to obtain values of S and K (Table 3). Assignment (i) assumes that bands 1 and 2 come from the configuration $3t_2^5 3a_1$, while assignment (ii) assumes that bands 2 and 3 come from this configuration. In the case of $TlBr_4^-$, (ii) gives a value of S which is numerically far too large to be credible; (i) also gives $S < -3\zeta_{Br}$, but since ζ_{Tl} is more than twice as large as ζ_{Br}, a small amount of metal participation in the $3t_2$ molecular orbital leads to a value of the magnitude observed. The situation is less clear for TlI_4^-; (ii) leads to a value of S closer to those found in the Group IIB complexes, but this does not preclude (i). A fairly small contribution from the metal, if slightly positively charged, could result in the larger value (we calculate ζ for Tl^+ from atomic spectral data [15] to be 8·18 kK). Considerable metal participation in the bonding molecular orbitals is to be expected in this complex of a tervalent metal ion with iodide, the most polarisable of the halides, particularly as the spectrum of $TlBr_4^-$ suggests that c_3 is not negligible in the $3t_2$ molecular orbital of this complex.

On balance the first of the possible assignments seems more reasonable for both complexes but it is surprising that no trace of the orbitally-forbidden excited states can be found in the absorption spectra. We therefore pursue the spin–orbit analysis further to find an explanation why they do not appear. The large number of parameters involved in a full perturbation treatment of the mixing of $^1T_2$, $^3T_2$, $^3T_1$, and ^3E terms prevents a useful comparison with experimental results since one would have to include the three separations between the terms and several matrix elements of $\mathscr{H}_{so}$. It turns out, however, that the spin–orbit matrix alone is informative.

Matrix elements governing the mixing of $^1T_2$ into the $^3T_1$ and ^3E terms involve three open shells, $3t_2$, $3a_1$, and t_1 or e. Although Griffith [19] has not extended the irreducible tensor method to three open shells, Bird [21] has given the necessary reduction formula. We find equation (20) by equation (3). Reducing the right

$$\langle {}^3T_1T_2|\mathscr{H}_{so}|{}^1T_2T_2\rangle = -\tfrac{1}{3}\langle {}^3T_1\|\mathscr{H}_{so}\|{}^1T_2\rangle \qquad (20)$$

hand side further we obtain equations (21) and (22).

$$\begin{aligned}\langle {}^3T_1\|\mathscr{H}_{so}\|{}^1T_2\rangle &= \\ \langle t_2^6({}^1A_1)t_1^5({}^2T_1)a_1({}^2A_1){}^3T_1\|\mathscr{H}_{so}\|t_2^5({}^2T_2)t_1^6({}^1A_1)a_1({}^2A_1){}^1T_2\rangle &= -\frac{1}{\sqrt{2}}\langle \tfrac{1}{2}t_2\|\mathrm{su}\|\tfrac{1}{2}t_1\rangle \qquad (21)\end{aligned}$$

$$\begin{aligned}\langle {}^3ET_2|\mathscr{H}_{so}|{}^1T_2T_2\rangle &= \tfrac{1}{3}\langle {}^3E\|\mathscr{H}_{so}\|{}^1T_2\rangle \\ &= \frac{1}{3\sqrt{2}}\langle \tfrac{1}{2}t_2\|\mathrm{su}\|\tfrac{1}{2}e\rangle \qquad (22)\end{aligned}$$

The one-electron reduced matrix elements have been evaluated [21] as in equation (23) and (24).

$$\langle \tfrac{1}{2}t_2\|\mathrm{su}\|\tfrac{1}{2}t_1\rangle = \frac{\sqrt{3}}{2}(\sqrt{2}\,c_5 + c_7)\zeta_X \qquad (23)$$

$$\langle \tfrac{1}{2}t_2\|\mathrm{su}\|\tfrac{1}{2}e\rangle = \frac{\sqrt{3}}{2}(\sqrt{2}\,c_5 + c_7)\zeta_N \qquad (24)$$

We have already noted that the values of S derived from the absorption spectra imply a halogen contribution close to the maximum permitted, which in turn implies a ratio of c_2/c_7 of *ca.* $-1/\sqrt{2}$. Such a ratio makes the reduced matrix elements of equations (8) and (9) vanish, so the absence of the orbitally-forbidden transitions is explained.

CONCLUSION

We have obtained a satisfactory interpretation of these absorption spectra in terms of the one-electron transition $3t_2 \rightarrow 3a_1$, the highest-energy band in the cases of $TlBr_4^-$ and TlI_4^- probably being due to $2t_2 \rightarrow 3a_1$.

Our analysis has taken no account of the halogen $(n + 1)s$ orbitals, which may contribute significantly to the $3a_1$ molecular orbital.[8] Such an admixture will not affect the discussion of spin–orbit effects, and our conclusions about the composition of the $3t_2$ molecular orbital remain valid. Increasing effective nuclear charge of the halogen, resulting from greater covalence in the M–X bond, will cause an increase in the energy of a ligand-localised transition of the type $np \rightarrow (n + 1)s$.[8] In ZnX_4^{2-} the transitions observed are rather close to those of halide in ionic salts such as Bu_4NX, but in descending Group IIB the bands move to lower energy though the bonding is likely to become more covalent. Only for ZnX_4^{2-} is the participation of halogen $(n + 1)s$ in the $3a_1$ molecular orbital likely to be important.

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