Charge-transfer Spectra of Post-transition-metal Halide Complexes

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U.v. spectra of tetrahedral Group IIIB $[Et_4N][MX_4]$ (M = Ga or In; X = Cl, Br, or I), octahedral $[Et_4N]_2[SnX_6]$, and tetrahedral SnX_4 complexes have been measured in solution at room temperature, and of $[HgI_4]^{2-}$ doped in a crystal of $[NEt_4]_2[ZnI_4]$ at 300 to 4 K. The temperature variation of the half-width of the absorption band in the latter leads to an estimate of 0·21 Å for the expansion of the molecule in the excited state. The excitation is broadened by interaction with the totally symmetric stretching mode. Using results obtained in this and a previous paper, energies of the baricentres of the first halogen $(p_\pi)\rightarrow$metal(s) configurations are correlated for a wide range of B-subgroup elements, with respect to changing halogen, metal, and symmetry of the complex.

IN contrast to the great efforts made in recent years to derive precise assignments of charge transfer (c.t.) spectra of transition-metal halogeno- and oxo-complexes, comparatively little effort has been devoted to analysing, at a comparable level of detail, c.t. spectra of metals lying outside the transition elements. This is partly due to the high energy of many of the transitions, but experimental difficulties of working in the far-u.v. region may be compensated by the simplicity of the spectra themselves. Thus, with the *d* shell filled, and unable to accept electrons, the lowest-energy charge transfer from the ligands takes place into the empty *s* orbital on the metal atom, so complications of multiplet structure in partly filled shells are avoided. Indeed, since the acceptor orbital transforms as a_1 whatever the point group of the complex, the structure of the c.t. spectra parallels in an illuminating way the photoelectron spectra, in which an electron is removed from the highest-occupied molecular orbital, of mainly ligand character, to the continuum.

We showed in an earlier paper [1] that in some tetrahalogeno-complexes of post-transition elements, spin–orbit fine structure could be analysed with the same precision now conventional in analyses of transition-metal halide c.t. spectra, and that the observed pattern of energies and intensities could be fitted to yield empirical values of molecular-orbital based spin–orbit matrix elements and electron-repulsion parameters. In carrying out this analysis, we made no explicit use of the way in which energies of the baricentres of our spin–orbit components varied with changing ligand or central metal ion, contenting ourselves by treating the energy separations and relative dipole strengths alone of the transitions. The purpose of the present paper is to extend the data presented previously, by including complexes of Ga, In, and Sn, and then examine trends in the band energies, both vertically and horizontally, in the B subgroups for constant halide ion and for each metal atom with changing halide. In the later B subgroups, halogeno-complexes often have octahedral rather than tetrahedral co-ordination, and a further aim is to see how the energies, intensities, and spin–orbit structure of the $p_\pi(X) \rightarrow s(M)$ transitions is affected by change in symmetry.

Few complexes in this part of the Periodic Table can be examined optically at low temperatures because their transitions are intense and of sufficiently high energy that it is not easy to find isomorphous non-absorbing crystals into which they can be doped. (Indeed salts such as $A_2[SnCl_6]$ and $A_2[ZnX_4]$ have often been used as host lattices for studying transition-metal halide spectra.) In one instance, however, we have been able to dope a B-subgroup tetrahalogeno-complex, $[HgI_4]^{2-}$, into a crystal of another, $[Et_4N]_2$-$[ZnI_4]$, and so measure its spectrum as a function of temperature down to 4 K. The main effect of lowering the temperature is to narrow the lines which, however, remain unstructured throughout. We have previously demonstrated [2,3] that, under such conditions, one can apply the theory of line broadening by vibronic coupling, originally devised [4] to deal with spectra of point defects in continuous lattices (*e.g. F* centres). In the present instance values for the effective vibrational frequency broadening the line, the electron–phonon coupling constant, and (within the limitations of the harmonic approximation) an estimate of the expansion of the chromophore on passing into the excited state can all be derived from the spectrum.

EXPERIMENTAL

Salts $[Et_4N][MX_4]$ (M = Ga or In; X = Cl, Br, or I) were prepared by adding an aqueous solution of the halide MX_3, obtained by heating an excess of M_2O_3 in the appropriate hydrohalogenic acid and filtering and concentrating, to an ethanolic solution containing an equimolar amount of Et_4NX. The resulting precipitates were recrystallised from acetonitrile. Salts $[Et_4N]_2[SnX_6]$ were prepared by adding ethanolic solutions of anhydrous SnX_4 to ethanolic solutions containing a two-fold excess of Et_4NX. The resulting precipitates were recrystallised from acetonitrile. Analyses of both groups of salts are given in Table 1.

TABLE 1

Analyses (%)

Salt	Found (Calc.)		
	C	H	N
$[Et_4N][InCl_4]$	24·5 (24·85)	5·65 (5·50)	3·75 (3·60)
$[Et_4N][InBr_4]$	16·7 (17·0)	3·50 (3·50)	2·40 (2·50)
$[Et_4N][InI_4]$	12·4 (12·75)	2·70 (2·70)	1·85 (1·85)
$[Et_4N][GaCl_4]$	28·4 (28·15)	5·85 (5·90)	4·20 (4·10)
$[Et_4N][GaBr_4]$	18·2 (18·5)	4·15 (4·00)	2·65 (2·70)
$[Et_4N]_2[SnCl_6]$	32·3 (32·45)	6·80 (6·85)	4·80 (4·75)
$[Et_4N]_2[SnBr_6]$	22·15 (22·9)	4·65 (4·85)	3·45 (3·35)
$[Et_4N]_2[SnI_6]$	17·25 (17·1)	3·65 (3·55)	2·45 (2·50)

With the above conditions of preparation, $GaI_3 + EtNI$ gave a solid {Found: C, 18·45; H, 4·00; N, 2·60. $[Et_4N]_3$-$[Ga_2I_9]$ requires C, 17·2; H, 3·60; N, 2·50%}. Crystals of the salt $[Et_4N]_2[ZnI_4]$ doped with $[HgI_4]^{2-}$ were grown by slowly cooling a methanolic solution of the constituents from 40 °C to room temperature over a period of 2 days.

All absorption spectra were obtained with a Cary 14 spectrophotometer, where necessary with nitrogen purging. Solution spectra were measured in acetonitrile, except for the halogenostannate(IV) ions which were measured in hexane. In each case the validity of Beer's law was investigated, both in the presence and absence of added excess of halide ions. The $[MX_4]^-$ species obeyed Beer's law without added halide; excess of bromide led to formation of the ion $[InBr_6]^{3-}$ while excess of I^- had no effect on $[InI_4]^-$. A ten-fold excess of Et_4NX was needed to suppress solvation of $[SnX_6]^{2-}$ species. For low-temperature crystal spectra, an Oxford Instruments liquid-helium cryostat was employed, with a gold–iron (0·03 atom %) chromel thermocouple.

RESULTS

Wavenumbers of the band maxima and absorption coefficients of the complexes measured in the present work are shown in Table 2. The ions $[GaCl_4]^-$ and $[InCl_4]^-$ have no maxima below 50 000 cm^{-1}, though the tail of an absorption band can be seen. Our results for the ions $[SnCl_6]^{2-}$ and $[SnBr_6]^{2-}$ agree quite well with previous measurements.[5] No u.v. spectra of any of the other halides

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[1] P. Day and R. H. Seal, *J.C.S. Dalton*, 1972, 2054.

[2] P. Day and E. A. Grant, *Chem. Comm.*, 1969, 123.

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

[4] J. J. Markham, *Rev. Mod. Phys.*, 1959, **31**, 956.

[5] R. A. Walton, R. W. Matthews, and C. K. Jørgensen, *Inorg. Chim. Acta*, 1967, **1**, 355.

or halogeno-complexes appear to have been reported, with the exception of SnI_4, which was measured in $CHCl_3$ and butanol solutions by Katzin[6] and in benzene as part of a solvent-extraction study.[7] Both the latter agree with our results in hexane, in particular with the observation that the lower in energy of the two absorption bands is the most intense. When SnI_4 was dissolved in acetonitrile, on the other hand, the intensity ratio was reversed, and became closer to that found for the ion $[SnI_6]^{2-}$. The separation between the two peaks also diminished, a feature which we associate below with a change of symmetry from tetrahedral to octahedral. In this weakly co-ordinating solvent, therefore, we probably have either formation of a six-co-ordinate adduct $SnI_4,2MeCN$ or partial disproportionation of SnI_4 into the ions $[SnI_2(MeCN)_4]^{2+}$ and $[SnI_6]^{2-}$. In any case, only the spectrum of the hexane solution of SnI_4 is included in the comparative survey below.

TABLE 2

Solution spectra of B-subgroup halogeno-complexes (all in acetonitrile, except SnX_4 in hexane)

Complex	$10^3\tilde{\nu}_{max.}/cm^{-1}$	$\varepsilon_{max.}/l\ mol^{-1}\ cm^{-1}$
$[GaCl_4]^-$	50	
$[GaBr_4]^-$	46·0	12 850
	49·9	15 400
$[InCl_4]^-$	50	
$[InBr_4]^-$	42·6	8 900
	47·6	31 000
$[InI_4]^-$	34·0	15 000
	39·4	50 700
$SnCl_4$	48·6	14 000
$SnBr_4$	37·5	3 600
	42·1	13 050
SnI_4 (hexane)	27·9	12 000
	35·1	6 800
(acetonitrile)	27·9	13 000
	34·4	17 000
$[SnCl_6]^{2-}$	43·6	13 200
$[SnBr_6]^{2-}$	32·0	9 000
	35·1	10 000
$[SnI_6]^{2-}$	26·8	5 300
	32·5	10 500

Apart from those which absorb at too high a frequency, all the B-subgroup halogeno-complexes, either in this or our previous paper, show a single band (chlorides), a band with a weaker shoulder to low frequency (bromides), or two resolved bands, that occurring at higher frequency being the more intense (iodides). This pattern of behaviour is characteristic of spin–orbit splitting of a hole state mainly localised on the halide ions, and we were able earlier[1] to analyse the observed frequency separations and relative dipole strengths of the pairs of bands in the bromides and iodides in terms of only two parameters, an empirical electron-repulsion parameter defining the separation between ${}^1T_2$ and ${}^3T_2$ upper states and the reduced-matrix element of the molecular spin–orbit operator $\langle \tfrac{1}{2}t_2 || \mathbf{su} || \tfrac{1}{2}t_2 \rangle$. These we called respectively K and S. The new data in Table 2 may be analysed in the same way, and yield values of the two parameters shown in Table 3. To obtain these the absorption curves were analysed into Gaussian components.

Fundamental to the theoretical treatment of the absorption spectra in our previous paper, and also to our discussion here, is the assumption that both the weaker and stronger bands are electric-dipole allowed, the lower-frequency one having its parentage in ${}^3T_2$ being rendered allowed by second-order spin–orbit mixing with ${}^1T_2$. To verify this point we measured the intensity and bandshape of the lower-frequency band of the ion $[HgI_4]^{2-}$, doped into a $[NEt_4]_2[ZnI_4]$ crystal down to 4 K. The bandshape is important because, if the transition is only vibronically allowed, 'hot' vibronic transitions will make an important contribution to the overall envelope at higher temperatures. We found that the integrated area of the band remained nearly constant (actually increasing slightly), demonstrating that it is allowed. Konitzer and Markham[8] showed that one may test the constancy of the shape function of an absorption band with temperature by plotting $\varepsilon : \varepsilon_{max.}$, the absorption constant as a ratio of the maximum, against ν/H, where H is the width of the band at half height. The result of such a plot, for $[HgI_4]^{2-}$ at 300 and 4 K, is shown in Figure 1. From this it is clear that the shape is indeed constant.

TABLE 3

Parameters S and K obtained from data in Table 2

Complex	$10^3S/cm^{-1}$	$10^3K/cm^{-1}$
$[InBr_4]^-$	−7·3	2·3
$[InI_4]^-$	−10·2	4·5
$SnBr_4$ *	−7·6	2·4
SnI_4 *	−15·1	0·3
$[SnBr_6]^{2-}$	−6·5	1·2
$[SnI_6]^{2-}$	−11·7	3·3

* In hexane.

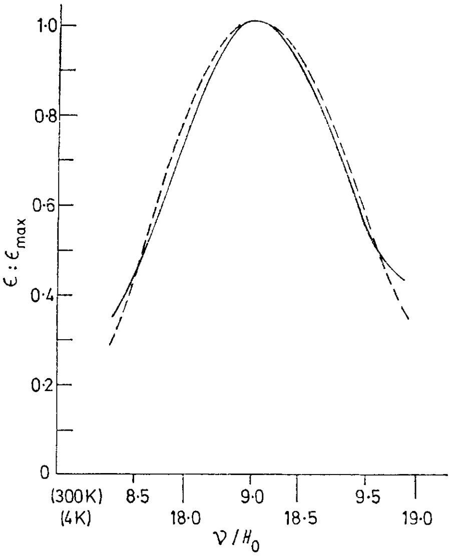

FIGURE 1 Shape plot for the first absorption band of the ion $[HgI_4]^{2-}$ doped in $[NEt_4]_2[ZnI_4]$ at 300 (——) and 4 K (— — —)

Now it may be shown[4] that if a chromophore undergoes a large displacement Δq in its equilibrium geometry on excitation from the ground to excited state, the resulting

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[6] L. Katzin, *J. Chem. Phys.*, 1955, **23**, 2057.

[7] D. D. Gilbert and E. B. Sandell, *J. Inorg. Nuclear Chem.*, 1962, **24**, 990.

[8] J. D. Konitzer and J. J. Markham, *J. Chem. Phys.*, 1960, **32**, 43.

absorption band envelope has a Gaussian shape with a half-width given by equation (1), where the summation

$$H^2 = \sum_i 4 \ln 2 \,.\, \hbar\omega_i{}^3 \Delta q_i \coth(\hbar\omega_i/2\boldsymbol{k}T) \qquad (1)$$

is over all normal modes contributing to band broadening. In deriving this expression assumptions are made that the frequencies of the normal vibrations in the ground and excited states are equal, that the potential-energy surfaces in both states are harmonic, and that the energy of the zero-phonon transition does not vary with temperature. In favourable cases only one normal mode (usually the totally symmetric stretch) is strongly excited so one may drop the summation and test equation (1) by plotting $\coth^{-1}(H^2/H_0{}^2)$ against $1/T$, where H_0 is the limiting half-width approaching absolute zero (Figure 2). The plot shown is quite a good straight line, passing close to the origin. From its gradient we find ω *ca.* 116 cm^{-1}. This value is very close to that of the totally symmetric stretching frequency of the ion $[HgI_4]^{2-}$ measured by Raman spectroscopy [9] (119 cm^{-1}). Further, from H_0, by assuming that the reduced mass of the ion is that of four iodine atoms, we find that the excited state is expanded by 0·21 Å from the ground state. Naturally, there is no immediate means of verifying this figure, but it is worth noting that it is much larger than that obtained from a similar analysis [2] of a c.t. band in the ion $[OsBr_6]^{2-}$. In the latter, an electron is transferred from a non-bonding t_{2u} combination of bromine 4*p* to the weakly π-antibonding t_{2g} shell of mainly metal character. In the case of the ion $[HgI_4]^{2-}$ we proposed earlier [1] that the transition is from the t_2 bonding combination of iodine 5*p* to the empty, highly expanded and antibonding, 6*s* orbital on Hg. It is clear from this single example that quantitative examination of the way in which a smooth broad absorption band changes with temperature can tell one quite a lot about the molecular vibrations responsible for broadening the transition, and changes occurring in the geometry of the excited state. Unfortunately we have not been able to prepare suitably doped crystals which would enable us to carry out similar experiments on any of the other post-transition-metal halide systems.

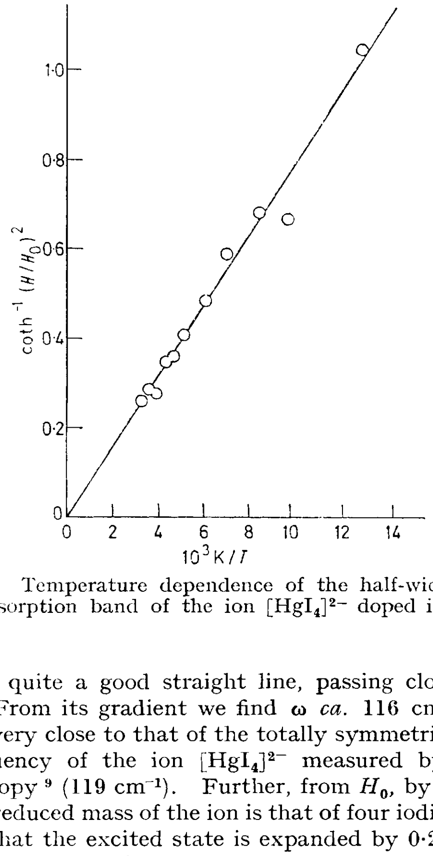

FIGURE 2 Temperature dependence of the half-width of the first absorption band of the ion $[HgI_4]^{2-}$ doped in $(NEt_4)_2$-$[ZnI_4]$

DISCUSSION

Energy Variation of the Bands.—The results given in Table 2, together with those reported in our earlier paper, are sufficient to allow both horizontal and vertical comparisons among the isoelectronic ions across Groups IIB, IIIB, and IVB. Spectra of the tetrahedral complexes in Table 2 are very similar in shape and general appearance to those reported before for Group IIB ions, and we therefore assign the entire set to spin–orbit and electron-repulsion components of the orbital excitation $t_2{}^6a_1{}^0 \rightarrow t_2{}^5a_1{}^1$ proposed earlier. When comparing the energies of the bands it is important to take the baricentre of the $t_2{}^5a_1{}^1$ configuration, and not simply the frequency of the first transition as the experimental observable, because spin–orbit coupling and electron repulsion may cause quite large splittings. The two bands seen in the bromides and iodides are assigned as $T_2({}^3T_2)$ and $T_2({}^1T_2)$, the other spin–orbit components of ${}^3T_2$, as well as all those from the configuration $t_1{}^5a_1{}^1$, remaining unobserved for the reasons given in our previous paper. Thus to obtain a true baricentre for the $t_2{}^5a_1{}^1$ configuration we cannot simply take the baricentre of its two observed T_2 components, but must make a further correction to allow for the unobserved $A_2({}^3T_2)$, $E({}^3T_2)$, and $T_1({}^3T_2)$. Relative to the baricentre of the two T_2, the energies of the unobserved components may be shown to be $-(K/2) - (S/4)$ (A_2) and $-(K/2) - (S/12)$ (E and T_1). We therefore get the true baricentre of the $t_2{}^5a_1{}^1$ configuration by subtracting $(K/4) + (S/18)$ from the baricentre of its two observed T_2 components. The results of this procedure are shown in Table 4.

TABLE 4

Baricentre energies of configurations $t_2{}^5a_1{}^1$ ($\times 10^{-3}$ cm^{-1}) relative to the ground state for $[MX_4]^{n-}$ ions

	Zn	Ga	
Cl	56·7		
Br	50·7	(48·0)	
I	41·9		
	Cd	In	Sn
Cl			48·6
Br	46·8	44·9	39·6
I	41·0	36·1	33·1
	Hg	Tl	
Cl	42·6	41·0	
Br	36·9	34·0	
I	33·2	29·6	

To summarise the chemical conclusions from Table 4 it is most convenient to look at variations with respect to different changes within the molecules.

(1) *Constant metal, varying halogen.* For a very large number of hexahalogeno-complexes of the second and

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[9] M. L. Delwaulle, *Compt. rend.*, 1938, **207**, 340.

third transition series, Jørgensen[10] showed many years ago that a nearly constant energy difference existed between corresponding c.t. bands in $[MCl_6]^{n-}$ and $[MBr_6]^{n-}$, and between $[MBr_6]^{n-}$ and $[MI_6]^{n-}$, irrespective of the central atom M. There is a similar relation between c.t. bands of tetrahedral halogeno-complexes of 3*d* elements.[11] Because of this one can define a set of additive parameters,[12] called 'optical electronegativities,' transferable from one complex to another, which enable one to predict frequencies of c.t. transitions. The important point about the data on the B-subgroup tetrahalides presented here is that even if one takes care to compare baricentres of the t^5a^1 configuration, and not simply energies of the first absorption bands, the energy differences between the ions $[MCl_4]^{n-}$ and $[MBr_4]^{n-}$ and $[MBr_4]^{n-}$ and $[MI_4]^{n-}$ are by no means constant. In fact, with the exception of Sn^{IV}, they diminish down each Group, and also from Group IIIB to IIB. Thus the optical electronegativity of a halide is not constant throughout the set.

The reason for the success of the optical-electronegativity concept among transition-metal complexes is not simply that the electron undergoing the transition is excited from a nearly non-bonding (t_{1u} in $[MX_6]^{n-}$) or completely non-bonding (t_1 in $[MX_4]^{n-}$) set of ligand orbitals, but that it is transferred into an orbital (t_{2g} in $[MX_6]^{n-}$ or e in $[MX_4]^{n-}$) which is sufficiently localised on the metal atom for charge separation in the excited state to be almost complete. The filled t_2 shell, which acts as electron donor in the present set of tetrahedral complexes, has some bonding character but, additionally, the empty s (a_1) forming the acceptor must be highly antibonding and may be considerably delocalised over the halide ions. Indeed, as we remarked some time ago,[13] the character of this type of transition may well be intermediate between that of pure c.t. $t_2(X\ p) \rightarrow a_1(M\ s)$ and local excitation $t_2(X\ p) \rightarrow a_1(X\ s)$ on the halide ions.

(2) *Constant halogen, varying metal.* For a given halogen two kinds of variation among the metal atoms are of interest: vertical, down a Group; and horizontal, across the Groups. Baricentre energies are plotted in both senses in Figures 3 and 4. Again, in the extreme case that observed transitions were purely ligand localised, *i.e.* that the a_1 orbital had much more X s than M s character, one would anticipate little variation in baricentre energy for a given halogen as one changed the central metal atom. That there is in fact a strong variation in the baricentre energy of the $t_2^5a_1^1$ configuration for the isoelectronic ions both down and across the Groups argues a substantial contribution of charge transfer to the excitation, *i.e.* of M s to the acceptor a_1. The direction of the energy variation agrees qualitatively with expectations, for example with increasing oxidation state in Cd^{II}, In^{III}, and Sn^{IV}. Thus, if the a_1 orbital were purely M s one would expect the baricentre of the $t_2^5a_1^1$ configuration to correlate with the electron affinity $s^0 \rightarrow s^1$ of M. This is indeed the case for the isoelectronic set Cd^{II}, In^{III}, and Sn^{IV}, as shown in Figure 5 where we have plotted the average of the baricentre energies for the tetrabromo- and tetraiodo-complexes against electron affinity, A_M.

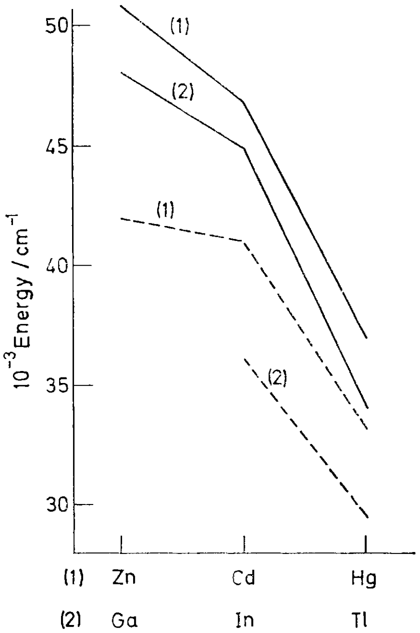

FIGURE 3 Baricentre energies of the $t_2^5a_1^1$ configuration for Group IIB and IIIB tetrabromides (——) and tetraiodides (— — —)

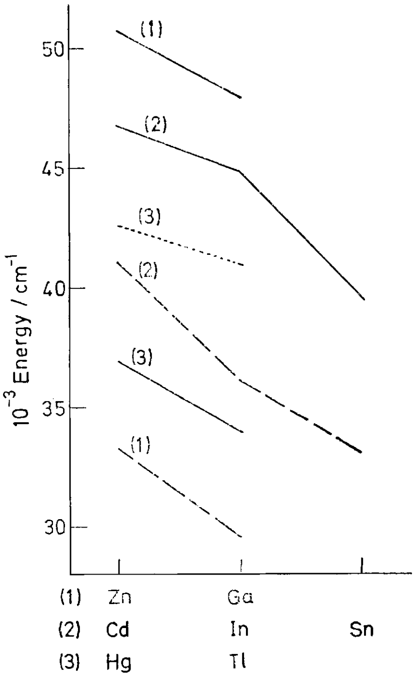

FIGURE 4 Baricentre energies of the $t_2^5a_1^1$ configuration for Group IIB, IIIB, and IVB tetrachlorides (· · · ·), tetrabromides (——), and tetraiodides (— — —)

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[10] C. K. Jørgensen, *Mol. Phys.*, 1959, **2**, 309.

[11] P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 1964, 5009.

[12] C. K. Jørgensen, *Progr. Inorg. Chem.*, 1970, **12**, 101.

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

However, in contrast to the simple behaviour across a Period, no straightforward correlation is found with electron affinity of the *ns* orbital in the free ion on descending a Group. Thus in Groups IIB and IIIB both the first- and second-ionisation potentials decrease from the fourth Period (Zn, Ga) to the fifth (Cd, In), increasing again to the sixth (Hg, Tl). This curiously non-monotonic behaviour is usually attributed to exceptional build-up of nuclear charge from the fifth to the sixth Period as a result of incorporating the 14 lanthanoids. Direct correlation of c.t. energy with electron affinity of the *ns* orbital would then demand a blue shift in the spectra on passing from Zn or Ga to Cd or In, followed by a strong red shift from Cd or In to Hg or Tl. In fact, as Figure 4 shows, the energies of the baricentres shift to the red down each Group, although the red shift from the fourth to the fifth Period is less than that from the fifth to the sixth.

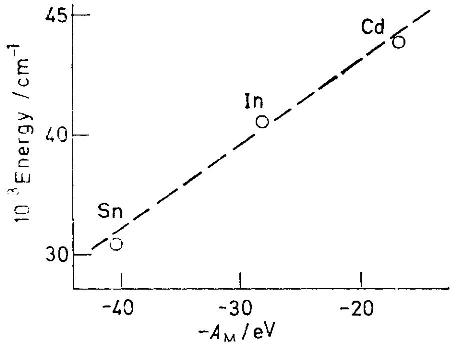

FIGURE 5 Average of the baricentre energies for tetrabromides and tetraiodides plotted atainst $-A_M$ ($5s^0 \rightarrow 5s^1$)

One possible explanation why there is no direct correlation between baricentre energies and electron affinities alone of the central metal ions might be that, as a result of the increase in effective nuclear charge on traversing the lanthanoids, radii of cations in a given B subgroup do not increase linearly from the fourth to the fifth to the sixth Period. Thus interaction in the excited state between the electron on the metal atom and the hole left behind on the ligands will not vary monotonically. Adopting for simplicity a purely ionic model of the c.t. process (*i.e.* assuming that the t_2 orbital consists entirely of X *p* and a_1 entirely of M *s*), the energy of the $t_2^6a_1^0 \rightarrow t_2^5a_1^1$ excitation would be given by equation (2), where I_X and A_M are energies

$$E_{c.t.} = I_X - A_M + \Delta P \qquad (2)$$

of the processes $X^- \rightarrow X^0$ and $M^{n+}(s^0) \rightarrow M^{(n-1)+}(s^1)$ respectively, and P is the change in electrostatic energy of the molecule. To calculate the latter, we assume that 0·25 of an electron is donated to the central metal by each of the four halogen ions surrounding it. Taking the Group IIB complexes as examples, the total electrostatic energy of charge distribution $(M^{2+})(X^-)_4$ is $-(8/R) + (6/1{\cdot}632R) = -(4{\cdot}32/R)$, while after an electron has been transferred from the ligands to the metal, the charge distribution would be (M^+)-$(X^{-\frac{3}{4}})_4$, which has an electrostatic energy of $-(3/R) + (3{\cdot}375/1{\cdot}632R) = -(0{\cdot}93/R)$. Therefore ΔP is 14·37-(3·39/R) eV Å^{-1}, where R is the metal–halogen distance. To calculate $E_{c.t.}$ we use standard values for electron affinities of the halogen atoms and second-ionisation potentials of the Group IIB metals, together with Pauling's crystal radii.[14] The resulting values of $E_{c.t.}$ are compared with observed $t_2^5a_1^1$ baricentre energies in Figure 6. Over the set of eight Group IIB tetrahalogeno-complexes for which we have experimental data, correlation with the calculated $E_{c.t.}$ values is excellent, although, as might be expected, the simple ionic picture fails to reproduce absolute energies of the c.t. transitions. What should particularly be noticed in Figure 6 is that the discontinuous variation in the Group IIB ionisation potentials, which taken alone would suggest a discontinuous variation in $t_2^5a_1^1$ baricentre energy for a given halogeno-complex on passing down the Group, is almost exactly compensated by an opposed variation in ΔP, stemming from the non-uniform increase in R_M from Zn^{2+} to Cd^{2+} to Hg^{2+}. Thus the plot in Figure 6 is a nearly perfect straight line. Correlations at about the same level of precision can also be drawn for Group IIIB and IVB complexes.

(3) *Constant metal and halogen, varying symmetry.* In the later B subgroups halogeno-complexes tend to have octahedral rather than tetrahedral co-ordination. It would be interesting to see what effect this change of symmetry has on c.t. spectra, and also whether the spectra contain sufficient information to permit any detailed comparison between the bonding in the two types of complex. Spectra of Sn^{IV} halides are particularly illuminating in this respect, because the complexes can be prepared with either stereochemistry.

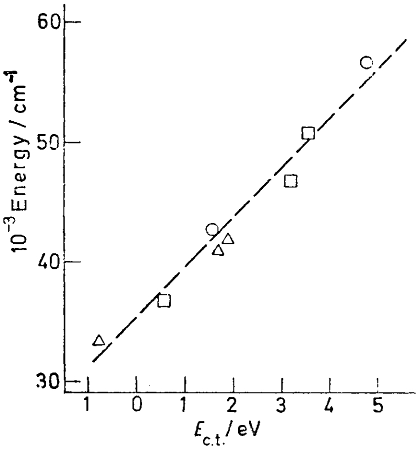

FIGURE 6 Observed c.t. baricentre energies for Group IIB tetrahalides plotted against $E_{c.t.}$ calculated as described in the text: ○, tetrachlorides; □, tetrabromides; △, tetraiodides

Comparing the spectra of SnX_4 and $[SnX]_6^{2-}$ in Table 2, we can make the following generalisations.

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[14] C. S. G. Phillips and R. J. P. Williams, ' Inorganic Chemistry,' vol. 1, Oxford University Press, 1965.

First, the baricentre of the two bands which make up the accessible part of the spectrum in both sets shifts to the red when the number of halide ligands is increased from four to six. The shift is very marked (5 000—6 000 cm^{-1}) for the chlorides and bromides, though less so (1 850 cm^{-1}) for the iodides. Secondly, the intensities of the transitions are slightly lower in the octahedral complexes, though this comparison is slightly obscured by the fact that, exceptionally among all the tetrahalides, the lowest-energy transition in SnI_4 is more intense than the next higher. Thirdly, the separation between the two bands is smaller in the octahedral bromo- and iodo-anions than in the tetrahedral neutral molecules.

An adequate explanation for the red shift in the baricentre from SnX_4 to $[SnX_6]^{2-}$ would be increasing ligand–ligand interaction in the latter, which raises the energy of the donor orbital. The lower intensity of bands of the octahedral ions could result from the longer Sn–X distance, and hence smaller overlap, enforced by increased co-ordination number. On the other hand, the smaller interval between the pairs of bands of the octahedral bromide and iodide must reflect a change in atomic orbital make-up of the donor molecular orbitals. If we adopt a hypothesis for the origin of the two bands in the ions $[SnX_6]^{2-}$ similar to the one which we have used successfully to explain structure in tetrahalide spectra, the excited configuration in the former will be $t_{1u}{}^5a_{1g}{}^1$, since that alone can give rise to a fully allowed ${}^1A_{1g}\rightarrow{}^1T_{1u}$ transition. We then note that there also exists a ${}^3T_{1u}$ term from the same configuration, and that spin–orbit coupling splits it in first order into A_{1u}, T_{1u}, E_u, and T_{2u} components. Second-order spin–orbit coupling then allows the ${}^3T_{1u}T_{1u}$ state to mix with ${}^1T_{1u}T_{1u}$, so that electric-dipole intensity is shared between them. By arguments very similar to those we employed [1] when dealing with tetrahedral complexes, we find that relevant matrix elements are as in equations (3) and (4), *i.e.* the spin–orbit matrix is identical to that describing the ${}^1T_2$ and ${}^3T_2$ terms of $t_2{}^5a_1{}^1$ in $T_d{}^*$, with the simple replacement of $\langle\tfrac{1}{2}t_2|\mathbf{su}|\tfrac{1}{2}t_2\rangle$ by $\langle\tfrac{1}{2}t_{1u}||\mathbf{su}||\tfrac{1}{2}t_{1u}\rangle$. The former of these we previously called S, so the latter we now denote by S'. General expressions for S and S' in terms of LCAO–MO coefficients are set out in refs. 1 and 3, though in the latter, a sign error, pointed out by Lester *et al.*,[15] should be corrected. In ref. 1 we showed that values of S which fit Group IIB tetrahalide spectra are close to the upper limit, which is achieved when the halogen contribution to molecular spin–orbit coupling is dominant, and when $c_{p\sigma} = -(1/\sqrt{3})$ and $c_{p\pi} = +\sqrt{(2/3)}$, *i.e.* when mixing between p_σ and p_π orbitals is maximised. It therefore seems reasonable to assume in the hexahalides too that metal orbitals make a negligible contribution to t_{1u}. Under that assumption the expressions for S and S' become as in equation (5),

$$\langle{}^3T_{1u}T_{1u}|\Sigma\mathbf{su}|{}^3T_{1u}T_{1u}\rangle = (1/6)\langle{}^3T_{1u}||\Sigma\mathbf{su}||{}^3T_{1u}\rangle = -(1/6)\langle\tfrac{1}{2}t_{1u}||\mathbf{su}||\tfrac{1}{2}t_{1u}\rangle \qquad (3)$$

$$\langle{}^3T_{1u}T_{1u}|\Sigma\mathbf{su}|{}^1T_{1u}T_{1u}\rangle = (1/3)\langle{}^3T_{1u}||\Sigma\mathbf{su}||{}^1T_{1u}\rangle = -(1/32)\sqrt{\langle\tfrac{1}{2}t_{1u}||\mathbf{su}||\tfrac{1}{2}t_{1u}\rangle} \qquad (4)$$

$$S(S') = \pm 3[2^{\frac{1}{2}}c_{p\sigma}c_{p\pi} \mp (1/2)c_{p\pi}{}^2]\zeta_{\mathrm{X}} \qquad (5)$$

where the upper + and − signs refer to S and the lower to S'. Thus any difference between observed values of S and S' for a given metal and halogen atom reflects directly varying contributions of $c_{p\sigma}$ and $c_{p\pi}$ to the t_2 and t_{1u} orbitals. For example, in the limit of pure p_π character $S = S' = -(3/2)\zeta_{\mathrm{X}}$.

We can therefore state at once that, since experimentally $S > S'$ in SnX_4 and $[SnX_6]^{2-}$, the t_{1u} donor orbital in the latter has more p_π character than t_2 in the former. Indeed, one can go further, and use equation (5) to calculate values for $c_{p\sigma}$ and $c_{p\pi}$ if the further assumption is made that ligand–ligand overlap is neglected, in other words that $c_{p\sigma}{}^2 + c_{p\pi}{}^2 = 1$. The resulting values of $c_{p\sigma}$ and $c_{p\pi}$ are as follows: $[SnBr_6]^{2-}$ $c_{p\sigma}$ 0·32, $c_{p\pi}$ 0·95; $[SnI_6]^{2-}$ 0·21, 0·98. That the most loosely bound t_{1u} electrons in both hexahalogeno-complexes are mainly p_π underlines the similar conclusion already arrived at by analysing spin–orbit fine structure [3] and magnetic circular dichroism [15,16] of c.t. bands in transition-metal hexahalides, and suggests that this feature is characteristic of the X_6 octahedral cluster, and not determined by specific bonding with the central metal atom.

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[16] G. N. Henning, P. A. Dobosh, A. J. McCaffery, and P. N. Schatz, *J. Amer. Chem. Soc.*, 1970, **92**, 5377.