Absorption Spectra of Post-Transition Group Halide Complexes

R. A. Walton, R. W. Matthews, and C. K. Jørgensen

The diffuse reflection spectra and the absorption spectra of solutions in acetonitrile have been measured of the d^{10}-systems $[SnCl_6]^{2-}$, $[SnBr_6]^{2-}$, $[SbCl_6]^-$, $[PbCl_6]^{2-}$ and the $d^{10}s^2$-systems $[SbCl_6]^{3-}$, $[SbBr_6]^{3-}$, $[BiCl_6]^{3-}$ and $[BiBr_6]^{3-}$. There is no definite evidence for or against the complete dissociation of the latter species to $[MX_5]^{2-}$ in acetonitrile. The excited levels are theoretically treated, and optical electronegativities derived from the electron transfer bands.

Introduction

The most common ground electron configurations of gaseous ions corresponding to chemical species formed by post-transition group elements terminate d^{10} (*e.g.* Sn^{IV}, Sb^V and Pb^{IV} studied here) or $d^{10}s^2$ (*e.g.* Sb^{III} and Bi^{III}). Under equal circumstances, the first excited levels have much higher energy than in the case of partly d-shells[1] and can be identified with electron transfer from filled molecular orbitals (M.O.) mainly localized on the ligands to the empty s-orbital in d^{10}-systems and with s→p transitions in $d^{10}s^2$-systems.

Theory for d^{10}-systems. The previous identifications[1] have recently been somewhat refined by two important observations. According to measurements of the Faraday effect[2] of $IrCl_6^{--}$, the order of M.O. energies in the hexahalides is

$$\pi t_{1g} > (\pi + \sigma) t_{1u} > \pi t_{2u} > \ldots \ldots > (\sigma + \pi) t_{1u} > \ldots \ldots \quad (1)$$

showing that ligand-ligand anti-bonding effects are stronger than the stabilization of the highest filled orbital set t_{1u} by bonding to the central atom empty p orbitals. This revised assignment agrees also with the spectra of mixed complexes[3] such as $IrCl_xBr_{6-x}^{--}$. The other recent change of interpretation comes from

the observation[4] of very strong absorption bands of ZnX_4^{--} at slightly lower energy than the np→(n+1)s transitions[1] of the ionically dissociated X^-, confirming the old suspicion[5] that the latter transitions survive to a large extent in complexes such as $PtBr_6^{--}$. The reason why we use the names, s,p,d,... for orbitals in spherical symmetry in our discussion of polyatomic species is that though these orbitals become somewhat delocalized on adjacent atoms and though they are deformed (i.e. no longer are exactly separable[6] in the product of a hydrogenic angular *l*-function and an arbitrary radial function), they still retain the degeneracy and symmetry types *as if* they had well defined *l*-values. Now, the charge separation effect[7] certainly produces a smaller wavenumber for np→(n+1)s excitations of an individual X^- than one would expect from a M.O. calculation evaluating the energy of the lowest empty totally symmetric orbital, say a_{1g} in the example above. Hence, we expect a mixture of central atom and ligand s-orbitals having no angular node-plane to constitute the excited orbital of a strong transition in the 50 kK region (1 kilokayser = 1000 cm^{-1}). Also, our cases of relatively high oxidation states are not expected to show d→s transitions of the central atom as are Cu^I, Ag^I and Au^I.[10]

In octahedral symmetry, d^{10}-systems are expected to show two strong electron transfer bands, one from $(\pi + \sigma) t_{1u}$ and the other from $(\sigma + \pi) t_{1u}$ in equation (1) to the lowest empty a_{1g} orbital, mainly constituted of central atom s. This assignment was previously made[8] for the bands at 32.6 kK (molar extinction coefficient $\varepsilon = 9700$) and at 48.1 kK ($\varepsilon = 24000$) of the species $[PbCl_6]^{2-}$ or $[PbCl_5(H_2O)]^-$ studied in aqueous hydrochloric acid.[9] By the same token, the band at 44.9 kK of $[SnCl_6]^{2-}$ and at 36.9 kK of $[SbCl_6]^-$ in strong HCl was ascribed[8] to the former

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transition. These bands are very broad, and it is not surprising that the weak, Laporte-forbidden $\pi t_{1g} \to s\ a_{1g}$ at slightly lower wavenumber is masked.

The bands at 43.4 kK ($\varepsilon = 26000$) of $[HgCl_4]^{2-}$, 40.3 kK ($\varepsilon = 30000$) of $[HgBr_4]^{2-}$ and 30.9 kK ($\varepsilon = 22000$) of $[HgI_4]^{2-}$ were previously assigned[10,11] to the similar transition $(\pi + \sigma)t_2 \to s\ a_1$ in tetrahedral symmetry, but in view of Bird and Day's observation,[4] the truth may be slightly more complicated, since the three $[ZnX_4]^{2-}$ have their first band at 56.7, 49.2 and 40.5 kK, respectively.

Discussion of d^{10}-systems measured here. The electron transfer bands of hexahalides containing a partly filled 5d-shell are moderately shifted towards lower wavenumbers by formation of salts with relatively small alkali metal cations,[13] by organic solvents relative to water[14] and by extremely high pressures.[15] Hence, the most plausible explanation of the results in Table I is

spectrum tends to separate into two maxima surrounding an apparent minimum caused by the metallic reflectance. This effect can be detected by isomorphous dilution in the crystals, or by finely dividing the sample and mixing it with a non-absorbing material. Thus, powdered KI showed two maxima at 43.2 and 46.4 kK which coalesced to one maximum at 43.4 kK by dilution with MgO. Thorough mixing of $[NH_4]_2$-$[SnCl_6]$ with MgO shifted the 36.6 kK band to 38.7 but a chemical reaction cannot be entirely excluded. Grinding alone of $(NMe_4)_2SnBr_6$ removed the band at 27.0 kK, making it probable that it is an effect of metallic reflectance of the 30.6 kK band. However, dilution with MgO produced the first band at 28.0 kK (Figure 1). The $1.7 \times 10^{-4} M$ solution of $[SnBr_6]^{2-}$ in CH_3CN apparently dissociates to some extent forming species such as $[SnBr_4(CH_3CN)_2]$ by analogy to the behaviour[17,18] of $[TiCl_6]^{2-}$ and $[ZrCl_6]^{2-}$ in CH_3CN. When a sufficient excess of Br^- is added (to give a

Table I. Electronic absorption spectra of d^{10} complexes. Maxima in kK ($= 1000\ cm^{-1}$), shoulders in parentheses

$[NH_4]_2[SnCl_6]$		diffuse reflectance (d.r.)		36.6, 45.6
»	+LiF	d.r.	ref. 20	36.0, (38), 45.2
$[NEt_4]_2[SnCl_6]$		d.r.		39.2, 45.2
»	+LiF	d.r.	ref. 20	37.0, (39), 44.5
»		in CH_3CN		43.9 ($\varepsilon = 15000$)
$[SnCl_6]^{2-}$		in 12 M aq. HCl	ref. 8	44.9
$Cs[SbCl_6]$	+LiF	d.r.	ref. 20	28.9, 37.9
$[NEt_4][SbCl_6]$		d.r.		29.4, 37.5, 44.5
»		ground up, d.r.		31.6, 37.2, 45.4
»		in CH_3CN		(29.4) ($\varepsilon = 100$), 36.9 ($\varepsilon = 9500$)
$[SbCl_6]$		in 12 M aq. HCl	ref. 8, 12	36.9 ($\varepsilon = 8000$)
$[NH_4]_2[SnBr_6]$		d.r.		24.3, (25.5), 30.2, 36.2, 43.8
$K_2[SnBr_6]$		d.r.		24.7, (27.0), 30.7, 36.8, 43.8
$[NMe_4]_2[SnBr_6]$		d.r.		27.0, (31.0), 36.0, 43.8
»		ground up, d.r.		30.6, 35.0, 47.4
»		in CH_3CN		(26.3) ($\varepsilon \sim 600$), (32.3), 35.5 ($\varepsilon = 8700$)
»	+$[NMe_4]Br$	in CH_3CN		(26.3) ($\varepsilon \sim 900$), 31.9 ($\varepsilon \sim 9000$), 34.9 ($\varepsilon \sim 10400$)
$[NH_4]_2[PbCl_6]$		d.r.		23.9, 32.0, 37.3, 43.5
$[NEt_4]_2[PbCl_6]$		d.r.		$\sim$27, $\sim$32.5, $\sim$35.5, 46.1
»		in CH_3CN		31.35 ($\varepsilon = 10500$), 46.5 ($\varepsilon = 30000$)
$[PbCl_6]^{2-}$ or $[PbCl_5(H_2O)]^-$		in aq. HCl	ref. 9	32.6 ($\varepsilon = 9700$), 48.1 ($\varepsilon = 24000$)

that the $(\pi + \sigma)t_{1u} \to s\ a_{1g}$ transition of $[SnCl_6]^{2-}$ at 44.9 kK in aqueous HCl is shifted 1 kK towards lower energy in acetonitrile solution, 5.7 kK in the solid tetraethyl-ammonium salt and 8.3 kK in the ammonium salt. The ligand-ligand anti-bonding effects are expected to be much larger at decreasing M–X internuclear distances.[13-15]

However, the measurements of reflectance spectra[16] of undiluted solids must be treated with caution. If the imaginary part of the complex refractive index (essentially proportional to the product of ε and the molar concentration of the absorbing substance) is sufficiently large, metallic reflectance occurs (as well known from the green glitter from $KMnO_4$ or liquid Br_2). Hence, a maximum in the actual solution
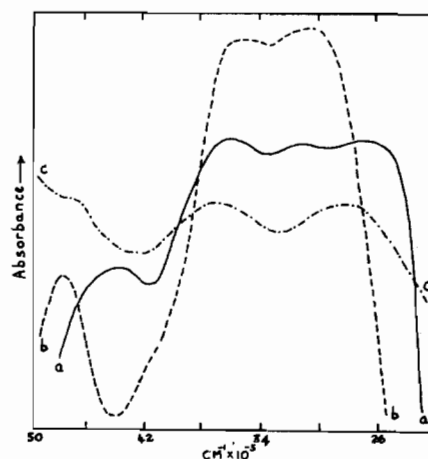
Figure 1. Diffuse reflectance spectrum of $[NMe_4]_2SnBr_6$. (a) Crystals. (b) Finely ground-up powder. (c) Diluted with MgO ($\sim$1:5 v/v).

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saturated solution of NMe_4Br) a constant spectrum of $[SnBr_6]^{2-}$ is obtained. Besides the two maxima at 31.9 and 34.9 kK representing the relativistic (spin-orbit coupling) splitting[1,19] of the transition $(\pi + \sigma)t_{1u} \rightarrow$ s a_{1g}, a weak band ($\varepsilon \sim 600$) is observed at 26.3 kK, giving some credence to the 27-28 kK bands mentioned above. The latter transition may be $\pi t_{1g} \rightarrow$ s a_{1g}.

In the case of $(NEt_4)SbCl_6$, grinding made the 29.4 kK band somewhat broader and moved it to 31.6 kK. On the other hand, dilution with MgO produced bands at 28.6, 36.0 and 45.0 kK (Figure 2). The solution spectrum of $[PbCl_6]^{2-}$ in CH_3CN showed a shoulder at 36 kK of variable intensity, always increasing with time. There is little doubt that this shoulder is caused by an impurity of Pb^{II}. Addition of Cl^- made the reduction go to completion.
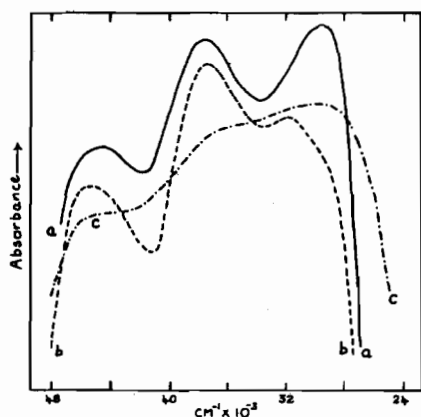

Figure 2. Diffuse reflectance spectrum of $[NEt_4]SbCl_6$. (a) Crystals. (b) Finely ground-up powder. (c) Diluted with MgO ($\sim 1:1$ v/v).

Dr. Peter Day, Oxford, was so kind as to inform us that he had measured the reflection spectra of $[NH_4]_2[SnCl_6]$, $[NEt_4]_2[SnCl_6]$ and $Cs[SbCl_6]$ diluted with LiF. These results are included in Table I marked ref. 20; his spectrum of $[NH_4]_2[SnBr_6]$ was very similar to ours.

Theory for $d^{10}s^2$-systems. Seitz[23] proposed that the ultraviolet absorption of thallium(I) in alkali metal halide crystals is due to transitions from the ground-state ^1S_o having the preponderant configuration $6s^2$ to the levels ^3P_o, $^3P_1$, $^3P_2$ and $^1P_1$ belonging to $6s6p$. Of these transitions, the first is very severely forbidden in spherical symmetry, whereas the second is spin-forbidden and gets its intensity by intermediate coupling from the very intense transition to $^1P_1$. The variation of these absorption bands as a function of the ligands and of the central atom In^I, Sn^{II}, Sb^{III}, Te^{IV}, Hg^0, Tl^I, Pb^{II}, Bi^{III}, Po^{IV} has been extensively discussed.[10,24,25] The radial functions must be considerably changed from those of the corresponding gaseous ion since the Landé

parameter ζ_p has been decreased to about half and the exchange integral K (s,p) to about a third of the values for the isolated ion (ref. 10, p. 186). This suggests a strong delocalization of the s and p shells in an extended M.O. Also, the energy difference between s and p decreases when the electronegativity of the ligands decreases, much in the same way as the $4f \rightarrow 5d$ transitions in cerium(III) complexes.[26] With a given set of ligands, the s—p energy difference tends to stay constant in an isoelectronic series such as Tl^I, Pb^{II}, Bi^{III} rather than to increase as for the gaseous ions Tl^+, Pb^{2+} and Bi^{3+}.

It is striking that the $s \rightarrow p$ transitions are invariant with respect to the symmetry and coordination number of the complexes studied. Actually, the stereochemistry of s^2-systems is extraordinarily complicated[27-29] and suggests that frequently, one of the ligands is replaced by a lone-pair, stabilizing pyramidal NH_3, PCl_3, SO_3^{2-}, IO_3^- and XeO_3 and square-pyramidal MX_5. On the other hand, crystallographic studies[30] sometimes indicate perfectly regular octahedra MX_6. However, the difficulty is that the high symmetry reported may refer only to the time average, and that a kind of dynamic second-order Jahn-Teller effect would distort the instantaneous picture.[31] A characteristic case of how relatively unhelpful absorption spectra have been for s^2-systems relative to the d and f groups is the observation[21] that the $^1S_o \rightarrow {}^3P_1$ transition of lead(II) smoothly changes from 37.5 kK in 4 M aqueous hydrochloric acid to 36.7 kK in 10 M HCl. There is no clear-cut evidence available as to whether the species present in instantaneous equilibria in these solutions are $PbCl_4^{2-}$, $[PbCl_5]^{3-}$ or $[PbCl_6]^{4-}$, nor is their symmetry known.

In a sense, the high-spin p-shells can be said to behave nearly as if the symmetry were spherical, in strong contrast to low-spin linear p^4- and p^2-complexes.[1] Thus, the $6p^1$-system Tl^0 has a nearly unperturbed transtion $^2P_{1/2} \rightarrow {}^2P_{3/2}$ at 6-7 kK[32] and nearly all the $6p^2$-transitions from the groundstate ^3P_o have been identified[33] in Bi^+ in molten $AlCl_3$-NaCl eutectic. Though s^1 systems tend to dimerize to stable species such as Au_2 and Hg_2^{2+}, they have been studied in irradiated crystals and Cu^0 [34] and Ag^0 [35] show intense $d^{10}s \rightarrow d^{10}p$ and $d^{10}s \rightarrow d^9sp$ transitions.

Discussion of $d^{10}s^2$-systems measured here. As seen from Table II, the transitions to $^3P_1$ at 34.8 kK and to $^1P_1$ at 43.9 kK of Sb^{III} in aqueous HCl are represented in the salt of $[SbCl_6]^{3-}$. There is some evidence that a shoulder occurs between the two intense bands. This can be readily assigned to $^3P_2$, the excited level becoming accessible to electric dipole radiation because of deviations from spherical symmetry. It is improbable that these deviations separate the sub-levels of $^3P_1$ to

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a large extent, when a comparison is made with mixed halides [TlX$_n$Y$_{6-n}$]$^{5-}$ studied in crystals[36] or with bismuth(I).[33] The limiting species, [SbCl$_5$]$^{2-}$ or [SbCl$_6$]$^{3-}$, in CH$_3$CN needs a considerable excess of Cl$^-$ in order to be formed. Haight and Ellis[37] report solubility measurements in aqueous solution indicating an equilibrium between [SbCl$_4$]$^-$ and [SbCl$_6$]$^{3-}$ in 1 to 4M Cl$^-$.

Apparently, the spectra of Sb^{III} bromides had not been reported previously. In CH$_3$CN, ^{3}P$_1$ seems to be the excited level at 27.8 kK and ^{1}P$_1$ at 37.0 kK agreeing with the general tendency to lower wavenumbers in bromides compared with chlorides. The shoulder at

the band at 30.7 kK (ε = 6500) suggesting the beginning of dissociation. Since solutions of [NBu^{n}H$_3$]$_2$-[BiCl$_5$] have similar spectra (2.3×10^{-4}M at 30.0 kK (ε = 8000); 1.1×10^{-4}M 30.4 kK (ε = 7500); 4×10^{-5}M 31.1 kK (ε = 7000)) we conclude that either the limiting species is [BiCl$_5$]$^{2-}$ or [BiCl$_5$(CH$_3$CN)]$^{2-}$, or the spectrum of [BiCl$_6$]$^{3-}$ in CH$_3$CN is the same. Similar remarks can be made about Bi^{III} bromides in acetonitrile. The very intense ($\varepsilon\sim$ 45,000) band at 46.5 kK (having a shoulder at 43.5 kK) shown by very dilute solutions in CH$_3$CN may essentially represent the 4p^6→4p^{5}5s bromide transitions. The solid state spectra of [BiBr$_6$]$^{3-}$ are shown in Figure 3.

Table II. Electronic absorption spectra of d^{10}s^2 complexes. Notation as in Table I

[NBu^{n}H$_3$]$_3$[SbCl$_6$]		d.r.		31.8, (35.0), (38), 45.2
»		ground up, d.r.		34.4, 37.8, 45.4
»		in CH$_3$CN		(35) ($\varepsilon\sim$2000), (39) ($\varepsilon\sim$4500)
»	+[NEt$_4$]Cl	in CH$_3$CN		32.7 (ε=1600), 37.3 ($\varepsilon\sim$5000), >40 (intense)
Sb^{III}		in 12 M aq. HCl	ref. 10	34.8 ($\varepsilon\sim$2000), 43.9 (ε=13000)
[NEt$_2$H$_2$]$_3$[SbBr$_6$]		d.r.		27.0, ($\sim$28.5), 37.9, 46.0
»		ground up, d.r.		26.6, (29.0), 37.9, 45.5
»		in CH$_3$CN		(30.3) ($\varepsilon\sim$1200), (33), (42) ($\varepsilon\sim$12000), 45 ($\varepsilon\sim$38000)
»	+[NEt$_4$]Br	in CH$_3$CN		27.8 ($\varepsilon\sim$3000), (32.3) ($\varepsilon\sim$10000), 37.0 ($\varepsilon\sim$37000)
[NBu^{n}H$_3$]$_2$[SbBr$_5$]		d.r.		23.0, 25.5, 31.2, (35.0), 46.8
[NBu$_2^n$H$_2$]$_3$[BiCl$_6$]		d.r.		(28), 29.5, (36), 37.4, 45.0
»		ground up, d.r.		(29), 30.0, 38.2, 45.2, (46)
»		^{a} diluted with MgO		29.2, $\sim$39.0, $\sim$45.0
»		in CH$_3$CN		30.0 (ε=7900), 43.9 (ε=18000)
[NBu^{n}H$_3$]$_2$[BiCl$_5$]		d.r.		28.0, 31.2, 36.0, 46.1, 49
»		ground u.p., d.r.		29.4, 31.4, 38.0, 46.0, 49
Bi^{III}		in strong aq. HCl	ref. 21, 22	30.5 (ε=16100), 45.0 ($\varepsilon\sim$44000)
[NBu$_2^n$H$_2$]$_3$[BiBr$_6$]		d.r.		24.4, 27.0, (29.0), (38), 39.2, 42.6, (44)
»		ground up, d.r.		(25.6), 26.5, 32.0, 38.4, 42.3, 44.5
»		^{a} diluted with MgO		26.0, 31.8, 37, (41), 45
»		in CH$_3$CN		25.9 (ε=9000), 38.5 (ε=20000), $\sim$46.5 (more intense)
Bi^{III}		in aq. HBr	ref. 21, 22	26.8 (ε=18000), 38.5 (ε=42000)

^{a} Dilution with LiF gave a similar spectrum.

32.3 kK may be due to ^{3}P$_2$; its absolute intensity is not larger than of ^{3}P$_1$ because it is superimposed on a strongly increasing band corresponding to ^{1}P$_1$.

The limiting species BiCl$_5^{2-}$ or [BiCl$_6$]$^{3-}$ has only a slightly smaller wavenumber for its two bands in CH$_3$CN than in aqueous HCl. Newman and Hume[22] are convinced about the penta-coordination whereas other authors[38,39] give evidence for the second alternative. The solubility measurements[40] again suggested and equilibrium between [BiCl$_4$]$^-$ and [BiCl$_6$]$^{3-}$. The compound [Co(NH$_3$)$_6$][BiCl$_6$] has the same powder-diagram[41] as [Co(NH$_3$)$_6$][TlCl$_6$] which is known[42] to contain octahedral ions. Our solutions in CH$_3$CN dissociate much less than the corresponding Sb^{III} chlorides and obey Beer's law to a high degree. Thus, the Gaussian shaped band corresponding to ^{3}P$_1$ is shifted only to 30.3 kK (ε = 7400) for 1.2×10^{-4}M [NBu$_2^n$H$_2$]$_3$[BiCl$_6$], whereas 6×10^{-5}M solutions have
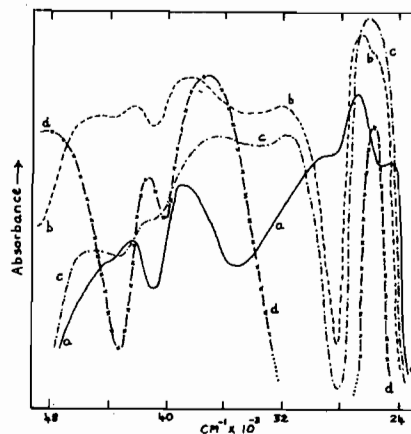

Figure 3. Diffuse reflectance spectrum of [NBu$_2^n$H$_2$]$_3$BiBr$_6$. (a) Crystals. (b) Finely ground-up powder. (c) Diluted with MgO ($\sim$1:1 v/v). (d) Diluted with LiF ($\sim$1:15 v/v).

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Experimental Section

Preparative procedures. The compounds [NH$_4$]$_2$-[SnCl$_6$], [NEt$_4$]$_2$[SnCl$_6$], [NH$_4$]$_2$[PbCl$_6$], [NEt$_2$]$_2$-[PbCl$_6$], K$_2$[SnBr$_6$], [NBu$_2^n$H$_2$]$_3$[BiCl$_6$] and [NBu$_2^n$H$_2$]$_3$-[BiBr$_6$] were prepared as previously described in the (Found: C, 45.6; H, 3.0; N, 8.9%).

literature.[43-47] [NEt4][SbCl6] was isolated as colourless crystals on mixing thionylchloride solutions of SbCl3 and [NEt4]+Cl− according to the general procedure of Adams et al.[44] Yellow [NH4]2[SnBr6] separated on reacting NH4Br with SnBr4 in conc. HBr,[48] and [NMe4]2[SnBr6] was prepared by a similar procedure. The compounds [NBunH3]3[SbCl6], [NEt2H2]3[SbBr6] and [NBunH3]2[SbBr5] were prepared by mixing solutions of the amine (3.3 moles) and Sb2O3 (0.5 mole) in the appropriate concentrated hydrohalic acid. The products (white, pale yellow and deep yellow, respectively) were isolated in rather low yield after washing with conc. HX and then drying in vacuo over NaOH. [NBunH3]2[BiCl5] was prepared by a similar procedure but using BiCl3 as the metal source. This general method has also been used by Whealey et al.[49,50] who found that the type of anion obtained depends upon the amine used and is essentially independent of the stoicheiometries of the reagents.

In all cases the composition of the compounds were confirmed by metal, halogen and nitrogen analyses.

Spectral measurements. Diffuse reflectance spectra were recorded on a Unicam S.P. 700C spectrophotometer fitted with a S.P. 735 diffuse reflectance attachment. MgO and LiF were used as reference standards. The 100% transmission baseline was adjusted with respect to the standard being used.

The spectra of solids in a given state were in all instances reproducible but quite marked spectral changes were observed on grinding the specimen. The affect of dilution with MgO or LiF was determined by thorough mixing with increasing amounts of the reference standard until no further spectral changes occurred. However, dilution was sometimes accompanied by a poorer resolution of the spectrum.

Solution spectra were measured in «spectrograde» acetonitrile on a Unicam S.P. 800 spectrophotometer using matched 1 cm. silica cells.

Conclusions

There is no doubt that the s- and p-shells are not so strongly localized on the central atoms as are the partly filled d- and f-shells in transition group compounds. The strong colours of Sb^{III,V} hexahalide crystals[51] indicate a strong individuality of the [SbCl6]$^{3-}$

and [SbCl6]− species, which is also consistent with their crystallographic non-equivalence.[52] Hence, it is not surprising that we find spectra of solid d^{10}- and d^{10}s^2-halide complexes not very different from the monomeric chromophores in aqueous hydrohalic acids or in acetonitrile. It is interesting that [SnBr6]$^{2-}$ and Sb^{III} halide complex anions show a perceptible tendency toward dissociation in the latter solvent. This is probably due to a considerable affinity between post-transition group ions and acetonitrile, whereas the lanthanide hexahalides [MX6]$^{3-}$ which are extremely sensitive to moisture are not so readily dissociated by CH3CN.[53] It is unfortunate that our results do not contribute much to resolve the enigmatic question whether the limiting complex of Sb^{III} and Bi^{III} is [MX5]$^{2-}$ or [MX6]$^{3-}$. However, it is not trivial to note that we have found no sign of coordination of *more* than six halide anions; the fact that [Mg(H2O)6]3[Bi(O2NO)6]2.6H2O is isotypic with the corresponding cerium(III) salt[54] shows that Bi^{III} sometimes can be twelve-coordinate.

The electron transfer spectra observed (and including orange [AsCl6]− recently reported[55] to have a band at 30.5 kK) indicate the following *optical electronegativities*[1,7] χ_{opt}:

[AsCl6]−	CH3CN	χ_{opt} As^V	=	1.99
[SnCl6]$^{2-}$	aq.	Sn^{IV}	=	1.50
»	CH3CN			1.54
[SnBr6]$^{2-}$	CH3CN			1.74
[SbCl6]−	aq.	Sb^V	=	1.77
»	CH3CN			1.77
[PbCl6]$^{2-}$	aq.	Pb^{IV}	=	1.91
»	CH3CN			1.95

(2)

showing the distinct variation 4s > 5s < 6s. The values are comparable to χ_{opt} for d^o-systems such as Ti^{IV} (2.06),[18] Zr^{IV} (1.6)[18] and Nb^V (1.82).[1] Optical electronegativities of central atoms of about 1.2 cannot be determined in halide complexes because the lowest empty s-orbital of the halide anion produces absorption bands in the region corresponding to χ_{opt} = 1.2. It must also be remenbered that since hexahalide complexes have fairly strong ligand-ligand anti-bonding[1,3,53] effects, χ_{opt} of the central atom will be higher than the value one would obtain for mono(halide)poly(solvent) complexes.

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