$$1 + 2 + 3 + 4 = a_7\sqrt{4}$$

and for s's

$$1 + 2 + 3 + 4 = a_9\sqrt{4}$$

$$1 + 2 - 3 - 4 = z_8\sqrt{4}$$

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Spectra and Constitution of Antimony(III), Antimony(V) Hexahalide Salts and Related Compounds

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Reflection spectra of Sb(III), Sb(V); Bi(III), Sb(V); In(III), Sb(V); and Tl(III), Sb(V) hexahalide complexes diluted in hexahalostannate(IV) crystals are reported for a number of cations. The pure compounds $Cs_2Bi_{0.5}Sb_{0.5}Cl_6$, $Cs_2In_{0.5}Sb_{0.5}Cl_6$, and $Cs_2Tl_{0.5}Sb_{0.5}Cl_6$ also have been prepared and characterized from their X-ray powder photographs. The Bi and In compounds show evidence of superlattice formation which is assumed to exist, undetected, in the Sb(III), Sb(V) compounds. On this evidence the solid spectra have been assigned to electron transfer transitions from the ns^2 or $(n + 1)s^2$ shell of the trivalent ion to the ns_0 shell of the pentavalent ion. The abnormally deep colors of the In and Tl compounds also are discussed.

The "interaction color" of Sb(III), Sb(V) in HCl solution was studied some time ago,[2] but the spectra of the corresponding solids have not been reported, although the appearance of the crystals suggests that they must be quite different. The cesium salt Cs_2SbCl_6 was first prepared by Wells,[3] who showed that it was isomorphous with Cs_2PbCl_6, and the ammonium compound also forms mixed crystals with $(NH_4)_2SnCl_6$ and $(NH_4)_2PtCl_6$.[4] Early authors thought that these compounds were derivatives of $SbCl_4$, but Elliot showed that $(NH_4)_2SbBr_6$ was diamagnetic,[5a] and therefore presumably contained equal amounts of Sb(III) and Sb(V). Sb(IV) remains a possibility if the compounds were antiferromagnetic, with a very high Néel temperature. There is a simple theory[5b] for antiferromagnetism in the isostructural K_2IrCl_6 which invokes electron transfer from chlorine to iridium, but when it is applied to the antimony case, one finds that the maximum amount of charge transfer could not give a Néel temperature above 50°K., so the compounds would be strongly paramagnetic at room temperature. This is further strong evidence against Sb(IV).

However, the X-ray powder diagrams[6] can be indexed quite accurately in terms of a pure K_2PtCl_6 lattice, *i.e.*, the $Sb(III)Cl_6$ and $Sb(V)Cl_6$ units are either indistinguishable or randomly distributed. Since these units carry different charges if there really are two different valences present, a random distribution is perhaps not likely. The X-ray scattering powers of Sb(III) and Sb(V) must be so similar that a superlattice could not be detected.

The intense colors of mixed valence solids make it very difficult to measure their transmission spectra, and only a few are recorded in the literature.[7] Their diffuse reflection spectra also are broadened and distorted. Because the antimony(III),(V) solids can be homogeneously diluted with Sn(IV), this problem is avoided. Only diffuse reflection spectra are reported here, but we hope later to obtain oscillator strengths as a function of concentration from single crystal spectra using a microscope.

If this class of compounds contains Sb(III) and Sb(V), we would expect analogous Bi(III), Sb(V) salts, and the cesium compound has been prepared. In an effort to discover whether there is a superlattice of trivalent and pentavalent ions, we also prepared In(III), Sb(V), and Tl(III), Sb(V), salts.

Experimental

Preparations.—All the preparations were carried out in 12 *M* HCl solution. For the Sb(III), Sb(V) compounds Weinland and Schmidt's method[4] is convenient. A solution of Sb_2O_3 is divided into two equal portions, one of which is saturated with chlorine, and then warmed to remove the excess. Recombining the two solutions produces the characteristic yellow "interaction color." When anhydrous $SnCl_4$ is added, followed by an alkali metal halide solution, mixed Sb(III), Sb(V), Sn(IV) compounds crystallize on cooling.

For equal ratios of Sb to Sn, more concentrated solutions deposit chlorostannate crystals containing more Sb (*i.e.*, darker color). Thus, because the chlorostannates become more soluble in 12 *M* HCl with decreasing size of the alkali metal cation,

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[1] University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, England.

[2] J. E. Whitney and N. Davidson, *J. Am. Chem. Soc.*, **71**, 3809 (1949).

[3] H. L. Wells and F. J. Metzger, *Am. Chem. J.*, **26**, 268 (1901).

[4] R. F. Weinland and H. Schmidt, *Ber.*, **38**, 1080 (1905).

[5] (a) N. Elliot, *J. Chem. Phys.*, **2**, 298 (1934); (b) J. H. E. Griffiths, J. Owen, J. G. Park, and M. F. Partridge, *Proc. Roy. Soc.* (London), **A250**, 84 (1959).

[6] K. A. Jensen, *Z. anorg. allgem. Chem.*, **232**, 193 (1937).

[7] S. Yamada and R. Tsuchida, *Ann. Rept. Sci. Works, Fac. Sci. Osaka Univ.*, **4**, 79 (1956).

and the chlorides less soluble, potassium chlorostannate will not incorporate a high proportion of Sb. Sodium chlorostannate is in any case hydrated, and has a different structure.

Sb(III), Sb(V) hexabromides and their hexabromostannate-(IV) dilutions were made according to Ephraim and Weinberg.[8a]

$Cs_2Bi_{0.5}Sb_{0.5}Cl_6$.—Sb_2O_3 (0.12 g.) in 8 ml. of 12 *M* HCl is oxidized with chlorine; the solution is warmed to 60° and added to a solution if 0.23 g. of Bi_2O_3 in 4 ml. of HCl at the same temperature. This mixture is added to a 60° solution of 0.75 g. of CsCl in 8 ml. of HCl and the immediate dark red precipitate is quickly filtered. In this way the product showed no signs of contaminating $CsSbCl_6$ crystals under the microscope. Washing with cold 12 *M* HCl caused some decomposition, so the crystalline precipitate was sucked dry and pressed between filter paper.

$Cs_2In_{0.5}Sb_{0.5}Cl_6$ and $Cs_2Tl_{0.5}Sb_{0.5}Cl_6$.—Sb_2O_3 (0.14 g.) and 0.22 g. of $InCl_3$ in 10 ml. of 12 *M* HCl are oxidized with chlorine and added to a solution of 0.67 g. of CsCl in 10 ml. of HCl, to give a finely divided pale yellow precipitate. The Tl(III)Sb(V) salt was prepared in the same way using a Tl(III) solution prepared by passing chlorine through a suspension of 0.25 g. of Tl_2SO_4 in 20 ml. of HCl until it had all dissolved. Both mixed salts precipitate at room temperature at concentrations for which neither In(III), Tl(III), nor Sb(V) will give a solid with CsCl, even on strong cooling. In(III)Sb(V) and Tl(III)Sb(V) compounds already have been reported briefly,[8b] but without details of preparation or analysis.

Analyses.[9]—Calcd. for $Cs_2Bi_{0.5}Sb_{0.5}Cl_6$: Cs, 41.3; Bi, 16.3; Sb, 9.5. Found: Cs, 41.0; Bi, 15.5; Sb, 9.0. Calcd. for $Cs_2In_{0.5}Sb_{0.5}Cl_6$: Cs, 44.5; In, 9.6; Sb, 10.2. Found: Cs, 44.0; In, 9.6; Sb, 10.7. Calcd. for $Cs_2Tl_{0.5}Sb_{0.5}Cl_6$: Cs, 41.4; Tl, 15.9; Sb, 9.5. Found: Cs, 41.8; Tl, 15.3; Sb, 9.6.

X-Ray Powder Photographs.—A Siemens counter diffractometer was used with Ni filtered CuKα radiation. Each μ-parameter in Table IV is the mean of the values giving the best agreement with the calculated intensity for each (*hkl*). Intensities were measured by making several photostat copies of each trace and then cutting the peaks out and weighing them. Tables I, II, and III contain the observed and calculated spacings and intensities.

Visible Spectra.—In powder reflection spectra, intense absorption bands often are flattened and distorted because small amounts of stray light become dominating, and the Rayleigh scattering powers of sample and standard are not the same. A Beckman DU spectrophotometer with a diffuse reflection attachment therefore was used to measure the spectra as the difference between two samples homogeneously diluted with different amounts of Sn(IV), but prepared at the same concentration. The particle sizes were further matched by grinding each sample for the same length of time in the same agate mortar. Figure 1 gives the Sb(III), Sb(V) difference spectra, and all the absorption maxima are in Table V.

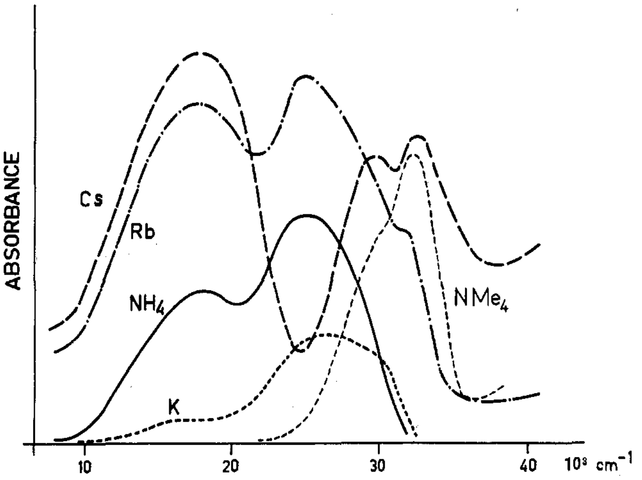

Fig. 1.—Difference spectra of $A_2[Sb(III)_{0.5}Sb(V)_{0.5}]_vSn(IV)_{1-v}Cl_6$.

TABLE I

X-RAY POWDER DATA FOR $Cs_2Bi_{0.5}Sb_{0.5}Cl_6$

hkl	10^4Q_{obsd}[a]	10^4Q_{calcd}	I_{hkl}/I_{220}[b]	$\|F_{hkl}\|^2Lp\cdot p''$[c]
111	272	272	0.51	0.53
200	...	...	.00	.002
211	592	...	vw	...
220	726	725	...	...
300/221	834	816	vw	...
311	1007	997	.28	.25
222	1097	1089	.60	.30
320	1186	1179	vw	...
400	1456	1451	.52	.63
331	1737	1723	.13	.09
420	...	1814	.00	.007
422	2186	2176	.43	.68
511	2445	2440	.15	.12
333				.01
440	2897	2901	.46	.43
531	3166	3174	.12	.12
600	...	3265	.00	.00
442				.002
620	3618	3625	.14	.22
533	3905	3899	.03	.03
622	3983	3990	.06	.11
444	4351	4350	.22	.15
711	4620	4622	.07	.02
551				.05
640	...	4718	.00	.001
642	5074	5080	.14	.25
731	5348	5349	.06	.03
553				.03
800	5808	5803	vw	...
733	6092	6078	vw	...
822	6530	6532	vw	...
660				
751	6810	6800	vw	...
555				
840	7252	7252	vw	...

[a] $Q_{obs} = 1/d^2$. [b] Intensity tabulated relative to (220). [c] Lp = Lorentz and polarization factors, p'' = multiplicity factor.

Results and Discussion

The X-ray powder diagrams of $Cs_2Bi_{0.5}Sb_{0.5}Cl_6$, $Cs_2In_{0.5}Sb_{0.5}Cl_6$, and $Cs_2Tl_{0.5}Sb_{0.5}Cl_6$ all can be indexed as O_h^5 (Fm 3m), isomorphous with K_2PtCl_6. In the Bi and In compounds, however, there are several very weak reflections not allowed by that space group (mixed even and odd indices). They are quite close to the noise level of the counter so that their spacings cannot be observed very accurately, but they are reproducible in different samples and at different instrument noise levels. They do not appear to be impurity lines, because the powder diagrams of likely impurities such as $CsSbCl_6$, $CsInCl_5\cdot H_2O$, etc., do not have strong reflections at the appropriate spacings, and their more intense reflections do not appear. In any case, with the accuracy attainable, the Q_{hkl} values of the weak lines agree with the unit cell dimensions calculated from stronger reflections. It appears, then, that we have evidence for a doubled unit cell, *i.e.*, a superlattice.

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(8) (a) F. Ephraim and S. Weinberg, *Ber.*, **42**, 4450 (1909); (b) A. Tovberg-Jensen and S. E. Rasmussen, *Acta Chem. Scand.*, **9**, 708 (1955).

(9) Analyses by Analix S.A., Geneva.

TABLE II

X-RAY POWDER DATA FOR $Cs_2In_{0.5}Sb_{0.5}Cl_6$

hkl	10^4Q_{obsd}	10^4Q_{calcd}	I_{hkl}/I_{220}	$\|F_{hkl}\|^2Lp \cdot p''$
111	280	278	. . .	. . .
200	. . .	370	0.00	0.13
300/221	840	834	vw	. . .
220	741	740	. . .	. . .
310	919	926	vw	. . .
311	1021	1018	.26	.17
222	1114	1111	.61	.49
320	1212	1213	vw	. . .
400	1480	1480	.66	.68
331	. . .	1759	.05	.04
420	. . .	1851	.00	.04
422	2225	2221	.37	.44
510/431	2414	2408	vw	. . .
511	2500	2499	.12	.11
333				.007
440	2960	2961	.55	.46
531	3238	3238	.09	.10
600	. . .	3330	.00	.000
442				.02
620	3710	3704	.08	.23
533	3982	3982	.04	.02
622	4071	4072	.10	.17
444	4422	4441	.10	.15
711	4708	4721	.06	.01
551				.05
640	. . .	4816	. . .	.007
642	5181	5181	.14	.25
731	5430	5462	.03	.009
553				.03
800	5935	5922	.05	.07
822 660	6665	6663	vw	. . .
751 555	6944	6941	vw	. . .
662	7041	7039	vw	. . .
840	7404	7408	vw	. . .
911	7682	7682	vw	. . .

Atoji and Watanabe[10] also found extra lines in the powder diagram of the mixed valence compound $Co(NH_3)_6PbCl_6$. This compound, of a deep purple color, and evidently containing Pb(II) and Pb(IV), is otherwise isomorphous with $Co(NH_3)_6TlCl_6$ and $Co(NH_3)_6BiCl_6$. $PbCl_6^{4-}$ is known to form a regular octahedron,[11] and $PbCl_6^{2-}$ is also octahedral, so that superlattice formation in the mixed compound will only be detectable through the changed metal–halogen distance. The group VB hexachloride units have not been closely studied crystallographically, but we know from the cobalt(III) hexaammine salts above that $BiCl_6^{3-}$ is a regular octahedron, and the powder diagram of the rather unstable Cs_3SbCl_6 also can be indexed as O_h^5 (anti-BiF_3), so it seems that $SbCl_6^{3-}$ is not greatly distorted by its $5s^2$ electrons. The ns^0 systems, $SbCl_6^-$, $TlCl_6^{3-}$, and $InCl_6^{3-}$, all should be undistorted octahedra. No structures containing $SbCl_6^-$ or $InCl_6^{3-}$ are available, but $TlCl_6^{3-}$ has been determined in potassium[12] and cobalt(III) hexaammine salts.[13]

TABLE III

X-RAY POWDER DATA FOR $Cs_2Tl_{0.5}Sb_{0.5}Cl_6$

hkl	10^4Q_{obsd}	10^4Q_{calcd}	I_{hkl}/I_{220}	$\|F_{hkl}\|^2Lp \cdot p''$
111	277	277	. . .	. . .
200	370	369	0.02	0.002
220	746	738	. . .	. . .
311	1019	1014	.19	.25
222	1114	1107	>1.2	.31
400	1474	1476	.42	.63
331	1756	1753	.11	.08
420	. . .	1845	.00	.007
422	2210	2214	.39	.45
511	2489	2491	.13	.10
333				.01
440	2954	2954	.37	.42
531	3239	3229	.10	.12
600	. . .	3321	.00	.00
442				.002
620	3689	3689	.05	.22
533	3955	3965	.02	.03
622	4055	4060	.04	.10
444	4445	4430	.31	.14
711	4728	4705	.06	.02
551				.05
640	. . .	4800	.00	.001
642	5177	5168	.15	.18
731	5431	5446	.06	.03
553				.03
800	5935	5903	vw	. . .
733	. . .	6182	vw	. . .
822 660	6630	6642	vw	. . .
751 555	6935	6920	vw	. . .

TABLE IV

SUMMARY OF UNIT CELL DIMENSIONS AND PARAMETERS

	a/2, Å.	*u*
$Cs_2Bi_{0.5}Sb_{0.5}Cl_6$	10.50	0.239 ± 0.015
$Cs_2In_{0.5}Sb_{0.5}Sl_6$	10.39	0.232 ± 0.025
$Cs_2Tl_{0.5}Sb_{0.5}Cl_6$	10.41	0.238 ± 0.015

TABLE V

DIFFERENCE SPECTRA OF Sb(III), Sb(V) HEXAHALIDES (10^3 CM.$^{-1}$)

	Chlorides				Bromides	
K	18.5	27.0	. . .	. . .	8–9	19.0
NH_4	18.2	26.5	. . .	. . .	9.5	18.8
Rb	18.05	25.4	27–29	31–32	8–9	16.7
Cs	17.9	. . .	29.3	32.3	~9	17.6
$N(CH_3)_4$	. . .	. . .	27–29	32.3	. . .	18.9
$N(C_2H_5)_4$	. . .	. . .	. . .	~33	. . .	20.5

In the absence of information about Sb(V)–Cl and In(III)–Cl distances the unit cell dimensions and chlorine atom parameters recorded in Table IV cannot be interpreted conclusively, but determinations of suitable indium and antimony compounds are being planned. In any case, single crystal measurements will be necessary to improve the accuracy of the parameters in the mixed compounds because many of the F_{hkl} are not very steep functions of u in the region of interest.

The colors of the Sb(III), Sb(V) solids are quite different from the solutions that they precipitate from. This is caused by the broad new band at about 18,000 cm.$^{-1}$. Dilute (less than 5%) solids are yellow like the solutions, but deep blue Rb_2SbCl_6 is only about 8.5 *M* from its density, while in Whitney and David-

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(10) M. Atoji and T. Watanabe, *J. Chem. Phys.*, **20**, 1045 (1952).

(11) Chr. Kn. Møller, *Kgl. Danske Videnskab Selskab, Mat. Fys. Medd.*, **32**, No. 3 (1960).

(12) J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, **3**, 645 (1935).

(13) T. Watanabe, M. Atoji, and C. Okazacki, *Acta Cryst.*, **3**, 405 (1950).

son's 1.5 M solution spectrum[2] there is no trace of a shoulder between 15,000 and 20,000 cm.$^{-1}$. One possible reason for this striking change is that the Sb(III) species in solution is much more likely to be $SbCl_4^-$ than $SbCl_6^{3-}$ as in the solid. The positions of mixed-valence interaction bands in solution certainly change with chloride concentration, because McConnell and Davidson's[14a] Cu(I), Cu(II) spectrum in 0.3 M Cl^- has its peak at 400 mμ; at 6.0 M it has shifted to 490 mμ, and in some early measurements in 10 M chloride[14b] the peak has moved still further, to 550 mμ, which is also the wave length obtained from the difference spectrum of Mori's[15] solid cobalt(III) hexaammine chlorocuprates(I),(II). However, the yellow rather than pale blue color of diluted Sb(III), Sb(V) salts suggests that even in the solid, the long wave length band is much weaker than the ultraviolet band.

From Fig. 1 and Table V we see that there are several remarkable changes in the Sb(III), Sb(V) chloride and bromide spectra as the cation is changed. With increasing ionic radius from K to Cs, the long wave length band moves slightly to lower energy. In K and NH_4 salts the second band is single, but partly in Rb, and wholly in Cs, it has moved to higher energy and split into two components. Increasing the cation size still further produces a dramatic alteration. The $N(CH_3)_4$ and $N(C_2H_5)_4$ salts are no longer blue or dark brown but pale yellow, owing to the complete disappearance of the long wave length absorption. The former still shows the split higher energy band but in the latter this too has nearly disappeared. It may be that the solution in HCl is behaving in the same way as the large cation solids, with the electron transferring group separated by a cation such as $(H_3O^+)(H_2O)_3$.

We made a rough comparison of intensities of the long wave length bands in the NH_4 and Rb salts, by taking the reflection spectra of two pairs of solids containing similar proportions of Sb to Sn, and found that there was no significant difference, so this effect apparently is confined to the larger cations. Exactly the same phenomenon occurs in the bromides, though the whole spectrum has shifted to lower energy, with the first band now in the infrared. Also the second band is no longer split by the larger cations. Bi(III), Sb(V) hexachlorides are dark red, by an increase of 6000 cm.$^{-1}$ in the energy of the first band. Absorption by the component ions obscures the higher bands.

The simplest explanation for the strong colors of the Sb(III), Sb(V) and Bi(III), Sb(V) compounds is that we have an electron transfer from the $5s^2$ or $6s^2$ shell of the trivalent ion to the 5s shell of Sb(V). A convenient simple model for the interaction color of an isolated pair would be a transition from $H^- + H^+$ to $2H\cdot$ at about 7 Å. separation, which actually has a high negative energy. The reason why the ground state in the Sb system is Sb(III) + Sb(V) and not Sb(IV) therefore must be sought in the extra variable not present in the model, namely, the Sb–Cl separation. However, we can see at once that such a transition, whatever its energy, would have two components, a triplet and a singlet. To account for the number of bands in the solid spectrum it will be necessary to consider the increased number of nearest neighbors possible in the A_2MX_6 lattice.

Transfer to 5p of Sb(V) also may occur, but if we assume that the 5s level in Sb(III) has lower energy than in Sb(V), because it has trapped the "extra" two electrons, then the 5s [Sb(III)] → 5p [Sb(V)] transition must have a higher energy than 5s [Sb(III)] → 5p [Sb(III)], the triplet and singlet components of which are already far in the ultraviolet at 35,000 and 43,000 cm.$^{-1}$. We now have to try to account for the number of bands observed.

There are two ways of introducing a superlattice in a face-centered cubic lattice such as that of the MX_6 compounds in the antifluorite structure. One can have successive layers either in the (110) or in the (111) plane. However, the former probably would involve tetragonal distortion of the lattice, and only double the unit cell in one direction. Since this is not observed in the X-ray data we will assume the latter. This gives an octahedron of $M'X_6$ units surrounding every MX_6. The hole state of MX_6 after transferring an electron to the M' atoms is $5s^1$, *i.e.*, A_{1g} in O_h, and the excited electron, which can be on any of the six M' atoms, is also A_{1g} ($5s^1$), giving 6 × 4 = 24 possible excited states. The factor of four arises from the four possible spin states of the electron-hole pair.[16] Irreducible representations of the total wave functions for the 24 exciton states are given by the direct products of the representations of the hole and electron states, including the spin representations, as

$$\text{singlet: } A_{1g} \times (A_{1g} + E_g + T_{1u}) \times A_{1g} = A_{1g} + E_g + T_{1u}$$

$$\text{triplet: } A_{1g} \times (A_{1g} + E_g + T_{1u}) \times T_{1g} = A_{1u} + E_u + 2T_{1g} + T_{1u} + T_{2g} + T_{2u}$$

Only those states can be reached by dipole-allowed transitions which have a total symmetry of T_{1u}, so we have one singlet and one triplet only.

If we consider the possibility that the structure is random, and take the full cuboctahedron[17] of surrounding units, by the same procedure we have

$$\text{singlet: } A_{1g} \times (A_{1g} + E_g + T_{1u} + T_{2g} + T_{2u}) \times A_{1g} = A_{1g} + E_g + T_{1u} + T_{2g} + T_{2u}$$

$$\text{triplet: } A_{1g} \times (A_{1g} + E_g + T_{1u} + T_{2g} + T_{2u}) \times T_{1g} = A_{1u} + A_{2g} + A_{2u} + E_g + 2E_u + 3T_{1g} + 2T_{1u} + 2T_{2g} + 2T_{2u}$$

i.e., there are now two dipole-allowed triplets and one singlet.

If the superlattice ordering is in the (111) direction it is possible to introduce a trigonal distortion in the surrounding octahedron of MX_6 without producing any trigonal distortion in the lattice as a whole, but only an

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[14] (a) H. M. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3168 (1950); (b) E. Doelmann and H. Fromherz, *Z. physik. Chem.*, **171a**, 371 (1934).

[15] M. Mori, *Bull. Chem. Soc. Japan*, **33**, 985 (1960).

[16] A. W. Overhauser, *Phys. Rev.*, **101**, 1702 (1956).

[17] J. R. Canon and G. H. Duffey, *J. Chem. Phys.*, **35**, 1657 (1961).

isotropic expansion. We then would have to consider D_{3d}, with the direct product representations

$$\text{singlet: } A_{1g} \times (A_{1g} + A_{2u} + E_g + E_u) \times A_{1g} = A_{1g} + A_{2u} + E_g + E_u$$

$$\text{triplet: } A_{1g} \times (A_{1g} + A_{2u} + A_{2u} + E_g + E_u) \times T_{1g} = A_{1u} + A_{2g} + E_g + E_u$$

The state with the total symmetry A_{2u} is polarized along the *z*-direction, and E_u in the *xy* plane, so there are two singlets and one triplet allowed.

Assuming that the ordering in the Sb(III), Sb(V) hexachlorides and hexabromides is the same as that postulated for the Bi(III), Sb(V) and In(III), Sb(V) hexachlorides, the two bands in the K and NH_4 salts are easily assigned to the one singlet and one triplet allowed by an octahedral environment. It is not likely that we have the two triplets and one singlet required of the full cuboctahedral situation for, as we already have remarked, the lower energy band undoubtedly is less intense than the higher, perhaps by a factor of five or ten. It certainly is significant that only in the large light cations does the lowest band disappear, while in the large heavy Cs it is as intense as in K. Perhaps from K to Cs, increasing size and decreasing overlap roughly cancel with increasing *Z*. In the Rb and Cs salts, on the other hand, the splitting of the ultraviolet band might easily be accounted for by a small trigonal distortion to D_{3d}. We do not know, of course, how large a physical distortion would be needed to give the observed splitting, but it is worth noting the lack of splitting in the large hexabromo ion with even the largest cations.

Our assumption that charge transfer is occurring between the 5s states of Sb(III) and Sb(V), together with the hypothesis of superlattice formation, therefore leads to a correct prediction of the number and intensity ratio of the new absorption bands. However, the fact that dilute Sb(III), Sb(V) compounds are pale yellow rather than pale blue, and the complete disappearance of the long wave length band in the tetramethylammonium salt, might be taken to suggest that the two bands do not have the same concentration dependence. Single crystal spectra must be undertaken to settle this point.

The colors of the In(III), Sb(V) and Tl(III), Sb(V) compounds are altogether more difficult to rationalize. Their ease of formation, which must be related to the favorable energetics of the antifluorite A_2MX_6 lattice, compared with A_3MX_6 and AMX_6, also is surprising. Both compounds absorb at longer wave lengths than either component ion and, by making Sn(IV) dilutions, we find one new band in each Cs salt, at 30,800 $cm.^{-1}$ for In and 29,600 $cm.^{-1}$ for Tl. The In salt is pale yellow, and the Tl deep lemon yellow, though In(III) in HCl does not absorb until much further into the ultraviolet than $CsSbCl_6$, itself quite white. Watanabe, *et al.*,[13] noticed that their cobalt(III) hexaammine hexachlorothallate had a rather deeper color than expected from the cation alone, and correlated it with the abnormally short Tl–Cl bond length they found (2.48 Å. compared with 2.55 Å. for $K_3TlCl_6 \cdot 2H_2O$[12] and an average of 2.54 Å. for $Cs_2TlCl_5H_2O$[18]). They also discovered that on cooling in liquid air it became almost colorless, and on heating, deep orange. Cesium Tl(III), Sb(V) hexachloride behaves in exactly the same way.

Two possible explanations are that a chlorine to thallium charge transfer band is being shifted by compression, or that the hexachlorothallate group is transferring an electron to cobalt(III) hexaammine or $SbCl_6^-$. Neither alternative is very satisfactory. If the band has been shifted to the red by pressure, it ought not to be shifted back to the blue again by lowering the temperature, and though anions are known (*e.g.*, I^-)[19] which give charge transfer bands with $Co(NH_3)_6^{3+}$, $TlCl_6^{3-}$ does not seem a likely candidate. On the other hand, a formal consideration of the ionization potentials shows that the energy liberated when an electron is added to Sb^{5+} is greater than the energy needed to form Tl^{4+} from Tl^{3+} by 5.7 e.v. The corresponding figures for Sb(III), Bi(III), and In(III) are 11.5, 10.7, and −2.2 e.v. One could test the compression hypothesis by making the corresponding rhodium(III) hexaammine salt, which probably has the same structure, and whose first cation absorption bands lie much further into the ultraviolet.

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