detailed picture of the magnetic behavior can be but a reasonable speculation.

The low-temperature behavior (*i.e.*, below 20°K) is highly unusual. Presumably, in this temperature region, the material has ordered antiferromagnetically. Although this behavior may be due to an impurity, it is improbable that it is due to unreacted cobalt acetate since this material has been shown to be paramagnetic to 0.4°K.[8] As mentioned above, the magnetic susceptibility in this region is still field dependent and the observed behavior may be due to a spin reorientation which is affected by the small measuring field of the magnet.

Acknowledgments. This research was supported by the National Science Foundation through Grant GP-22887 and by the Materials Research Center of the University of North Carolina under Grant GH 33632 from the National Science Foundation. We wish to thank Dr. P. G. Slade for helpful comments concerning the crystal growth problem.

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X-Ray Photoelectron Spectroscopic Studies of Halide Complexes of Antimony(III)

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Received July 18, 1973

It is well known that binding energies of core levels are affected by changes in the valence shell of electrons and that these changes as measured by XPS can yield information on chemical bonding.[1] We report here an XPS study of a number of halide complexes of antimony. The complexes $M_3Sb_2X_9$ (M = alkali metal; X = Cl, Br, I) studied are virtually isostructural and contain antimony(III) in a halogen coordination close to octahedral.[2,3] $Co(NH_3)_6SbX_6$ complexes (X = Br, Cl) also contain six-coordinate antimony(III)[2-4] and consequently the differences in lattice potentials due to the distribution of charge in the lattice are hopefully minimized in this series of compounds. The fluoroantimonates(III) have more complex structures and these structures will be discussed in more detail later.

Results

The measured binding energy of the antimony 3d spin-orbit doublet and representative alkali metal and halogen core levels are presented in Table I. The antimony 3d levels are strong and consist of a well-separated spin-orbit doublet (9.3 ± 0.2 eV). The full widths at half-maximum height (FWHM) vary from 1.5 to 2.2 eV and the peak maxima were located with a precision of 0.1 eV. The binding energies presented are referenced against the C 1s contaminant line taken as 285 eV. [No attempt to correct for lattice potential effects by using an internal reference[5] (such as F 1s) has been made. This procedure is clearly incorrect for materials of differing structure and also incorrect for crystal structures with more than one site where lattice potentials can be different at each site.] The antimony 3d binding energies range from 539.3 and 530.1 eV for the $3d_{3/2}$ and $3d_{5/2}$ levels of $Rb_3Sb_2I_9$ to 540.8 and 531.5 eV for Na_2SbF_5, a spread of 1.5 eV.

Discussion

The measured 3d binding energies of the antimony(III) halides show a gross trend with ligand electronegativity; in general the fluoride-containing materials have the highest and the iodides the lowest antimony 3d binding energies. This is the expected result for decreasing ionicity of the antimony-halogen bond in going from Sb-F to Sb-I if the dominant term contributing to the total shift is the valence term. It has been demonstrated that for closely related series of compounds, *e.g.*, the series $Y_2Sn(8\text{-quinolinato})_2$, where Y = Et, Ph, or halogen[6] and mixed hexahalides of tin(IV),[7] a correlation is observed between Mossbauer isomer shifts and XPS chemical shifts. Further a correlation between ^{57}Fe Mossbauer isomer shift and the iron $2p_{1/2}$, $2p_{3/2}$ binding energies of a series of low-spin ferrous complexes has been observed.[8] The ^{121}Sb Mossbauer chemical shifts of the six-coordinate antimony(III) materials studied demonstrate[9] a large 5s character of the Sb(III) lone-pair orbital and also reflect the electrostatic nature of the antimony-halogen bond.[3] A reasonable correlation is found, for the chloride, bromides, and iodides studied, between the measured 3d binding energies and Mossbauer chemical shifts (Figure 1). However the parameters for the fluoroantimonates(III) do not fall on the same line. The Mossbauer isomer shift is determined by the total s-electron density at the nucleus, whereas the XPS chemical shifts are sensitive to change in population of all valence orbitals on the metal. Consequently for a series of materials where significant and varying 5s-5p mixing occurs as in the fluoroantimonates(III)[10] no correlation between Mossbauer and XPS chemical shifts can be expected. A linear correlation between Mossbauer and XPS chemical shifts for the chloride-, bromide-, and iodide-antimony(III) complexes implies therefore that the 5s character of the antimony lone pair is similar in all the materials, and changes in the Mossbauer isomer shift are brought about directly by any changes in residual 5s character of the antimony-halogen bonds and indirectly by shielding of 5s antimony electrons by antimony 5p electrons.

The antimony 3d spectra of the fluoride complexes have slightly larger line widths than the other halide materials studied, but all three fluorides have similar line widths. The crystal structure[11] of K_2SbF_5 contains crystallographically equivalent antimony atoms and two groups of four equivalent fluorines in difference crystallographic sites resulting in an

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Table I. Observed Binding Energies (±0.3 eV) in Electron Volts for the Antimony Halide Complexes Studied[a]

Compd		Sb		Halogen	Alkali metal
		$3d_{3/2}$	$3d_{5/2}$		
Na_2SbF_6		540.8 (2.0)	531.5 (1.9)	F 1s 683.6 (2.2)	Na 2s 53.8 (1.8)
K_2SbF_5		540.5 (1.8)	531.2 (1.8)	684.1 (2.0)	K 2s 384.9 (1.9)
KSb_2F_7		540.7 (1.8)	531.4 (1.9)	684.5 (2.2)	384.7 (1.8)
$Co(NH_3)_6SbCl_6$	(1)	540.2 (1.7)	531.0 (1.8)	Cl 2p max[b] 199.1 (2.4)	
$Cs_3Sb_2Cl_9$	(3)	540.0 (1.6)	530.7 (1.6)	198.3 (2.4)	Cs $4d_{3/2}$ 77.9 Cs $4d_{5/2}$ 75.7
$Co(NH_3)_6SbBr_6$	(2)	540.1 (1.9)	531.0 (1.9)	Br 3d max[b,c] 69.1 (2.0)	
$Cs_3Sb_2Br_9$	(4)	539.6 (1.5)	530.3 (1.6)	71.0 (2.1)	Cs $4d_{3/2}$ 78.3
$Rb_3Sb_2Br_9$	(5)	539.4 (1.5)	530.1 (1.5)	70.3 (2.1)	Cs $4d_{5/2}$ 76.0
$Rb_3Sb_2I_9$	(6)	539.3 (1.5)	530.1 (1.7)	I $3d_{3/2}$ 632.6 (1.6) I $3d_{5/2}$ 621.0 (1.6)	
$CsSbCl_6$		540.6 (2.2)	531.1 (2.2)	Cl 2p max[b] 199.4 (2.6)	Cs $4d_{3/2}$ 78.2 Cs $4d_{5/2}$ 76.0

[a] Figures in parentheses are FWHM. The numbers in parentheses after compound formulas refer to Figure 1. [b] Unresolved spin-orbit doublet. [c] Excited by Mg Kα radiation.

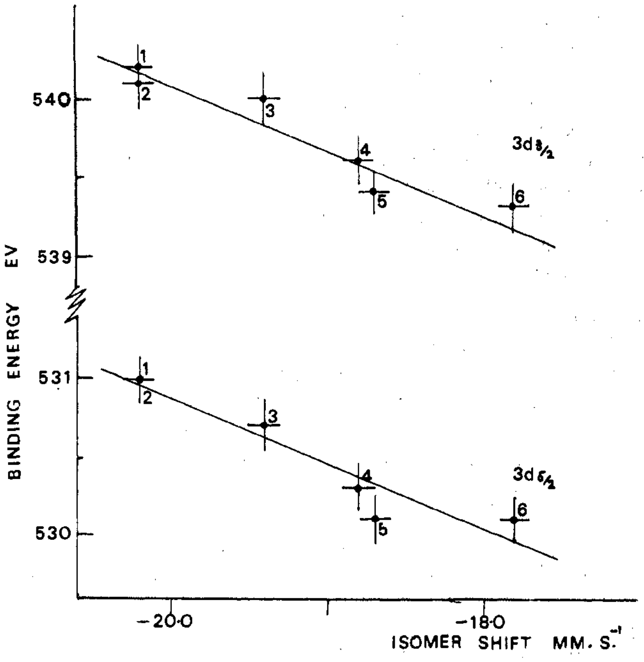

Figure 1. Correlation of Sb $3d_{3/2}$ and $3d_{5/2}$ binding energies with ^{121}Sb Mossbauer isomer shifts for chlorides, bromides, and iodides studied. Mossbauer isomer shifts are relative to $BaSnO_3$ source and taken from ref 3 and 10.

approximately square-pyramidal geometry of isolated $SbF_5{}^{2-}$ ions. The structure[12] of KSb_2F_7 contains antimony in two distinct sites and all fluorines in different sites. The structure does not contain a discrete $Sb_2F_7{}^-$ ion but is considered to consist of trigonal-bipyramidal $SbF_4{}^-$ ions and SbF_3 molecules. Na_2SbF_5 is not isostructural with K_2SbF_5 and its structure is at present unknown. The presence of two antimony sites in KSb_2F_7 material is not manifest in significantly broadened Sb 3d spectra nor are the inequivalent fluorine atoms obviously manifest in the XPS data. Further there is no significant splitting or broadening of the halogen spectra of the $M_3Sb_2X_9$ materials which, although not containing a discrete $Sb_2X_9{}^{3-}$ ion,[2,3] must contain both bridging and terminal halogens.[2,3]

Previous workers[13] have commented on the sharp narrow F 1s spectra observed for LaF_3, YbF_3, and UF_4 where, assuming full ionicities, markedly different shifts for each crystallographically distinct fluoride should be observed. A proportional reduction of charge due to covalency on all ions in the structure cannot account for the lack of resolution. A possible ground-state explanation for the observation of narrow spectra for these ionic materials could arise from varying sizes and partial charges on ions within a structure. Fajans first observed[14] that the radius and charge of a particular ion are dependent on its environment and that there is a contraction of electronic shells of anions in the presence of cations and an expansion of the electronic shells of cations in the presence of small anions. Recent Hartree-Fock calculations[15] also substantiate these observations. Within the context of the Siegbahn point charge model, variation of the radius of the effective sphere of charge caused by the local nature of the environment of the ions of the same atom at each crystallographic site, or indeed a change in partial charge, could account for the observation of narrow signals. For example, increasing the positive potential due to the lattice around an anion will result in a contraction of the sphere of effective charge describing the valence region thus further increasing the negative potential experienced by the anion core electrons, producing a further tendency toward equalization of the total potential.

Gross changes in oxidation state of cations are however reflected in their XPS spectra and the usefulness of XPS in the study of mixed-valence compounds of antimony has been previously exploited.[16] In particular the antimony 3d region of $Cs_4Sb^{III}Sb^{V}Cl_{12}$ is considerably broader than the 3d spectra of materials containing Sb(III) or Sb(V) alone. The chlorine 2p region of this material is also broad (3.2 eV) in contrast to the antimony(III) materials. This broadening may be due to inhomogeneity in surface charging but probably demonstrates the presence of two chemically different chloride sites and a marked difference in the nature of the Sb(III)-Cl and Sb(V)-Cl bond. It is further noted that the antimony 3d bonding energies are similar for $CsSb^{V}Cl_6$ and the fluoroantimonates(III). If not attributable to lattice potential effects this implies that the charge in the antimony(III) in the fluoroantimonates is similar to the Sb(V) in $CsSbCl_6$ presumably reflecting the greater covalency of antimony(V)-halogen bonds.

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Experimental Section

Spectra were measured by use of an AEI ES 200 electron spectrometer using Al Kα as the exciting radiation. The vacuum in the sample chamber was approximately 10^{-7} Torr and there was no evidence for any O 1s signal which is coincident with the Sb 3d region. The binding energies were measured with respect to C 1s contaminant signal taken as 285 eV. In all cases the C 1s spectrum was a singlet and repeated determinations of binding energies were consistent to 0.3 eV. FWHM are accurate to ±0.2 eV. Materials were prepared by literature methods and their antimony analyses agreed with the formula given.

Acknowledgments. We thank the SRC for financial support. J. T. Southern is thanked for the gift of the fluoroantimonates(III) and Professor J. M. Thomas for a stimulating discussion.

Registry No. Na_2SbF_5, 36732-24-8; K_2SbF_5, 20645-41-4; KSb_2F_7, 11088-88-3; $Co(NH_3)_6SbCl_6$, 17805-63-9; $Cs_3Sb_2Cl_9$, 12016-49-8; $Co(NH_3)_6SbBr_6$, 36527-01-2; $Cs_3Sb_2Br_9$, 12011-43-7; $Rb_3Sb_2Br_9$, 12234-36-5; $Rb_3Sb_2I_9$, 12532-41-1; $CsSbCl_6$, 19578-48-4; ^{121}Sb, 14265-72-6.

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Photolytic and Electrolytic Reduction of Iodobenzenenonahydro-*closo*-decaborate(1−) Ion, an Anionic Analog of Diphenyliodonium Ion, and Preparation of 1-Iodononahydro-*closo*-decaborate(2−) Ion

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Received August 13, 1973

In its formula, structure, and susceptibility to substitution reactions, the decahydro-*closo*-decaborate ion, $B_{10}H_{10}^{2-}$, has many similarities to benzene, C_6H_6. Thus, derivatives of the general type $B_{10}H_9X^{2-}$ are known, analogous to C_6H_5X compounds, where X can be any of a host of functional groups.[1] The iodobenzene derivative $B_{10}H_9IC_6H_5^-$, obtained by the reaction of $B_{10}H_{10}^{2-}$ with C_6H_5IO,[2] is an analog of the diphenyliodonium ion $(C_6H_5)_2I^+$, with the formal 2− charge of the boron cage conferring an overall negative charge on the formally positive iodine derivative. The cesium salt $CsB_{10}H_9IC_6H_5$ is reported to have a uv absorption maximum at 296 nm in acetonitrile.[2] Uv irradiation of diphenyliodonium iodide in chloroform has been reported to yield iodobenzene and benzene.[3] The $B_{10}H_9IC_6H_5^-$ ion was subjected to uv irradiation to see if a similar reaction would occur and if so, whether the boron-iodine or carbon-iodine bond would be broken.

Results

When 6 m*M* solutions of $CsB_{10}H_9IC_6H_5$ in water were irradiated with a medium-pressure mercury lamp fitted with a Corex filter (290-nm cutoff) for 4-5 hr, high-yield conversions according to eq 1 were achieved. The odor of biphenyl,

$$B_{10}H_9IC_6H_5^- + H_2O \xrightarrow{h\nu} B_{10}H_9I^{2-} + H^+ + {}^1/_2O_2 + C_6H_6 \tag{1}$$

$C_6H_5C_6H_5$, could be detected when ether extracts of the reaction mixture were allowed to evaporate, but no isolable quantities of biphenyl were obtained. Phenol was not detected. When $CsB_{10}H_9IC_6H_5$ was irradiated in a mixture of water and 2-propanol, the reaction proceeded according to eq 2.

$$B_{10}H_9IC_6H_5^- + (CH_3)_2CHOH \xrightarrow{h\nu} B_{10}H_9I^{2-} + H^+ + (CH_3)_2CO + C_6H_6 \tag{2}$$

The product $B_{10}H_9I^{2-}$ ion had no uv absorption maximum above 210 nm. Moderately strong ir absorptions at 1465, 1440, and 985 cm^{-1} of the starting material were not present in the product, but an absorption at 1000 cm^{-1} remained. The 32-MHz ^{11}B nmr spectrum consisted of a doublet of area 0.92 at 19.6 ppm (J_{BH} = 136 Hz), a singlet of area 0.92 at 27.1 ppm, and an apparent triplet due to two overlapping doublets of area 8.16 at 43.8 and 47.8 ppm (J_{BH} = 126 Hz), with chemical shifts upfield from external $B(OCH_3)_3$.

The $B_{10}H_9IC_6H_5^-$ ion was reduced at a dropping mercury electrode in acetonitrile at about −1.0 V (relative to sce), but not in a reversible, diffusion-controlled process. There was a pronounced maximum in the wave, the limiting current was much larger than expected, and the current-time curves for individual drops were somewhat irregular. In water, no wave was observed, but rather, there was a gradual increase in cathodic current with negative potential. Electrolysis at a mercury pool electrode at −1.2 V in acetonitrile or −1.5 V in acetonitrile-water yielded $B_{10}H_9I^{2-}$ ion and benzene. Coulometry gave *n* values of 1.3 ± 0.1 in acetonitrile and 1.8 ± 0.2 in acetonitrile-water.

Discussion

The synthesis of the $B_{10}H_9IC_6H_5^-$ ion results in apical substitution only,[2] and the ^{11}B nmr spectra confirm that this substitution geometry is retained in the product $B_{10}H_9I^{2-}$ ion. These reactions offer convenient routes to quite pure 1-$B_{10}H_9I^{2-}$ ion uncontaminated with the 2 isomer or with polyiodinated derivatives that are formed in the direct iodination of $B_{10}H_{10}^{2-}$.[4]

Although the experiments were designed and carried out primarily for purposes of product preparation rather than for mechanistic studies, some deductions concerning the course of the photoreduction can be made. The identification of $B_{10}H_9I^{2-}$ and C_6H_6 as the major products of the photolysis demonstrates that the carbon-iodine bond cleavage does *not* occur from the excited state directly. Homolytic cleavage would give a phenyl radical and a $B_{10}H_9I^{\cdot-}$ radical ion, which would dimerize to form the $B_{20}H_{17}I_2^{3-}$ ion and H^+.[5] Heterolytic cleavage to form the $B_{10}H_9I^{2-}$ ion directly would also form a phenyl cation which would react with water to give phenol. Formation of benzene could be explained by heterolytic cleavage to form a phenyl anion, but this would also generate neutral $B_{10}H_9I$, an unreasonably high-energy species analogous to a doubly ionized iodobenzene cation $C_6H_5I^{2+}$. Thus it can be concluded that reduction of the excited state precedes bond cleavage.

The photolysis of diphenyliodonium iodide in chloroform[3] yields iodobenzene, benzene, and iodine in amounts that are consistent with the results of a more detailed study of the photolysis of triphenylsulfonium iodide in chloroform, in which irradiation was carried out at the wavelength of the charge-transfer absorption.[6] The charge-transfer excited

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