The exchange field splittings are all around 190 cm^{-1} with these assignments.

The MCD in this region is not very well defined, except for the region around 21,000 cm^{-1}, and it is difficult to make clear assignments of features to absorption peaks due to the overlap of phonons in the first band of this region, but the MCD is generally consistent with this assignment. Above 26,000 cm^{-1} an intense absorption sets in which could not be penetrated optically. This presumably represents a charge-transfer transition and gives an indication of the energy barrier ($\sim$3.5 eV) in the conduction process as electrons are transferred from nickel ion to nickel ion throughout the lattice.

Conclusion

Previous interpretations of the spectrum of NiO have assumed the model of a d^8 ion perturbed only by the crystal field. We find this approximation is not able to explain the details of the absorption spectrum at liquid helium temperatures and is completely inadequate for describing the MCD. We have found that it is essential to include explicitly the exchange field and have obtained a good fit to experiment using a molecular field model with H_E 190 cm^{-1}, somewhat larger than the ground-state exchange field. We conclude that in NiO and in other antiferromagnets where $H_E \sim kT$, the effect should be included. The regions of the spin-forbidden regions are not sufficiently sharp at low temperatures for us to identify magnon side bands or magnon assistance in the spectra.

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X-Ray Photoelectron Spectroscopy of Tin. I. Hexahalostannates

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X-Ray photoelectron spectroscopy (ESCA) has been used to measure the tin (3d$_{5/2}$) electron binding energies for octahedral tin complexes of formula $[(CH_3CH_2)_4N]_2[SnX_{6-n}Y_n]$. The binding energies are found to correlate linearly with average ligand electronegativities, Mössbauer isomer shifts, and estimated atomic charges on the tin atom. The results are discussed in terms of these molecular parameters.

Introduction

Although there is still some uncertainty concerning the exact relation between core-electron binding energies measured *via* X-ray photoelectron spectroscopy (ESCA) and atomic charges,[2-7] this technique promises to be a useful tool in determining the electronic environment of atoms in molecules. ESCA binding energies have been shown to correlate with ligand electronegativities for a rather large number of compounds.[2,5,8] In addition, Gelius and coworkers[9] have calculated group electronegativities for a large number of organic functional groups using ESCA data. Barber and coworkers[10] have reported a linear relationship between the Mössbauer isomer shifts of ^{119}Sn and the tin (4d) binding energies for some tin complexes in which the tin atom had constant stereochemistry and oxidation state. The authors point out that since Mössbauer data have been shown to correlate with ligand electronegativity,[11-14] their data further verify the correlation between ESCA binding energies and ligand electronegativities. Several workers[5,15-20] have attempted to correlate measured electron binding energies with atomic charges obtained from calculative techniques of varying degrees of sophistication. In this article we wish to report an ESCA study of octahedral tin in hexahalostannates of formula $[(CH_3CH_2)_4N]_2[SnX_{6-n}Y_n]$, in which the tin (3d$_{5/2}$) electron binding energies are found to correlate with the average electronegativities of the halide ligands, the Mössbauer isomer shifts reported for the compounds, and

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the relative atomic charges calculated by a simple method of electronegativity equalization.

Experimental Section

The tetraethylammonium hexahalostannates were prepared by adding dropwise a stoichiometric amount of the appropriate tetraethylammonium halide dissolved in a 50:50 mixture of chloroform and methanol to the appropriate tin tetrahalide dissolved in chloroform.[13] After precipitation, the salts were separated by filtration, washed with a 50:50 mixture of chloroform–methanol followed by anhydrous ether, and dried under vacuum. All preparations were performed in a drybox.

The potassium hexafluorostannate and the molybdenum trioxide were purchased from the Research Organic/Inorganic Chemical Corporation and were used without further purification.

The spectra were obtained from powdered samples mounted on cellophane tape using a Varian Associates IEE-15 electron spectrophotometer. In all cases, Mg Kα X-rays were used as the excitation source. In order to compensate for the charging of the powdered samples which occurs during the photoelectron ejection process, an internal standard, MoO_3, was homogeneously mixed into each sample. The $Mo(3d_{5/2})$ electrons in MoO_3 have been reported to have a binding energy of 232.5 eV.[21] It was assumed that this energy remained constant except for variation in sample charging and all experimental data were corrected by the appropriate amount. The charging corrections ranged from -0.9 to -2.8 eV for all of the determinations. For a given sample, the correction was constant to within ± 0.3 eV. Molybdenum trioxide was chosen as an internal standard since the $Mo(3d_{5/2})$ electrons have a large cross section for photoexcitation and no molybdenum electron lines interfere with those from tin.[21]

An attempt was made to calibrate the spectra using the C(1s) electron line which arises not only from the carbon present in the sample but also from any hydrocarbon contaminants present in the system. The resulting C(1s) line was usually very broad, 2.5–3.0 eV, and often was resolved into a doublet. Therefore it was felt that using the C(1s) calibration would introduce significant error into the data.

The data for β tin were obtained from a sample which had been vacuum deposited upon a MoO_3 powder sample. The deposition was done using a tungsten filament coated with tin. To verify that the β form was the one actually present, the sample was cooled to approximately 77°K and the spectrum of α tin was obtained. Upon heating the sample again to room temperature, the β form was regenerated as evidenced by a shift in the binding energy to the original position.

The data for the hexafluorostannate anion were obtained from the potassium salt whereas all other data were obtained from the tetraethylammonium salts. Varying the cation in two otherwise identical compounds is expected to affect the experimentally determined electron binding energies of the atoms in the anion. The "cation effect" was determined in this case by comparing the $Sn(3d_{5/2})$ binding energies obtained for K_2SnBr_6 and $[(CH_3CH_2)_4N]_2SnBr_6$. Since the only difference between these two compounds is the nature of the cations, any difference in binding energy must be attributed to the "cation effect." The $Sn(3d_{5/2})$ binding energies differed by 0.4 eV, with that for the potassium salt being greater. One would expect differences in cations to have similar effects for all other pairs of salts. Therefore, by subtracting 0.4 eV from the binding energy obtained for K_2SnF_6 one can normalize the data to that of the tetraethylammonium salt. This was done in plotting the data.

Implicit in any correction for a "cation effect" or for direct correlation of binding energies with measures of atomic charges is the assumption that in a homologous series of compounds other effects may be ignored. The experimentally determined binding energies of core electrons are, however, affected not only by the immediate electronic environment of the atom but also by the electrostatic potential of all of the charges in the crystal.[22] The work presented here ignores the Madelung potential and considers the chemical shift to be a result of changes in charge density of the tin atom alone. Although this is a common assumption made by other workers in the field (see references listed) it is obviously an oversimplification. In the present study the use of a homologous series of compounds with similar $[SnX_6]^{2-}$ anions probably minimizes errors resulting from differences in Madelung potential.

TABLE I

TIN($3d_{5/2}$) BINDING ENERGIES (E_b), AVERAGE LIGAND ELECTRONEGATIVITIES ($\bar{\chi}_P$), MÖSSBAUER ISOMER SHIFTS (IS), AND ESTIMATED ATOMIC CHARGES (δ) FOR THE HEXAHALOSTANNATES, $[SnX_{6-n}Y_n]^{2-}$

Compound	$Sn(3d_{5/2})$ E_b, eV	IS,[a] mm/sec	$\bar{\chi}_P$[b]	δ[c]
1. K_2SnF_6	488.3 ± 0.1[d]	-2.46	3.98	0.339
2. $(Et_4N)_2SnCl_4F_2$	487.3 ± 0.1	-1.81	3.43	0.227
3. $(Et_4N)_2SnBr_4F_2$	487.2 ± 0.1	-1.57	3.30	0.230
4. $(Et_4N)_2SnCl_6$	487.1 ± 0.2	-1.58	3.16	0.250
5. $(Et_4N)_2SnCl_4Br_2$	487.2 ± 0.2	-1.43	3.09	0.227
6. $(Et_4N)_2SnCl_4I_2$	487.4 ± 0.1	-1.32	2.99	0.213
7. $(Et_4N)_2SnBr_6$	487.2 ± 0.1	-1.26	2.96	0.188
8. $(Et_4N)_2SnBr_4Cl_2$	487.1 ± 0.1	-1.33	3.02	0.207
9. $(Et_4N)_2SnBr_4I_2$	487.0 ± 0.1	-1.14	2.86	0.177
10. $(Et_4N)_2SnI_4Cl_2$	486.9 ± 0.1	-1.11	2.82	0.146
11. $(Et_4N)_2SnI_4Br_2$	486.8 ± 0.2	-1.01	2.76	0.173
12. $(Et_4N)_2SnI_6$	486.7 ± 0.2	-0.87	2.66	0.157
13. K_2SnBr_6	487.6 ± 0.1			
14. Sn(β)	486.9 ± 0.2	$+0.60$	1.96	0.000

[a] Reference 13. [b] Reference 23. [c] Charge in electrons. See reference 24. [d] Experimentally determined value; see text for explanation of cation effect.

Results and Discussion

Table I contains the tin($3d_{5/2}$) binding energy data. Each reported binding energy is the average of at least three replicate measurements with the indicated standard deviation. Also contained in the table are the average Pauling-type electronegativities ($\bar{\chi}_P$), the Mössbauer isomer shifts relative to α tin (IS), and the estimated atomic charges on the tin atom (δ).

The experimentally obtained binding energies correlate well ($r = 0.94$) with average Pauling-type electronegativities[23] of the halide ligands. A least-squares fit of the data yielded

$$E_b = 483.8 + 1.09\bar{\chi}_P$$

The $Sn(3d_{5/2})$ binding energy for the tetrachlorodiiodostannate anion shows the greatest deviation from linearity. A similar deviation is observed in the Mössbauer data, and Herber and Cheng[12] have postulated a distortion for the $[SnCl_4I_2]^{2-}$ anion resulting from cis-iodo ligands.

A least-squares correlation of the $Sn(3d_{5/2})$ binding energies with the Mössbauer isomer shifts[13] observed for these compounds yields

$$E_b = 486.8 - 0.64\text{IS}$$

with $r = 0.94$. Chemical shifts in Mössbauer spectroscopy give a measure of the s-electron density at the nucleus. Therefore, as was pointed out by Barber and coworkers,[10] in a series of compounds where the stereochemistry and oxidation state of the central atom are constant, there should be a relationship between the s-electron density (Mössbauer isomer shift) and the total electron density around the central atom (ESCA binding energy). These restrictions are met for the hexahalostannates and thus the linear relationship is not surprising. Once again, the largest deviation from linearity occurs for the $[SnCl_4I_2]^{2-}$ anion. Distortions in the structure, as mentioned above, would change the stereochemistry and could

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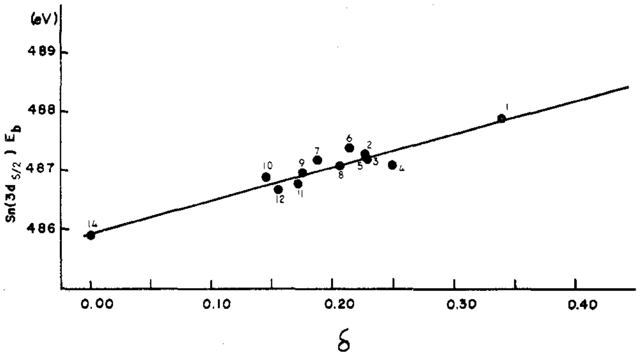

Figure 1.—$Sn(3d_{5/2})$ binding energies *vs.* estimated atomic charge on the tin atom.

thus result in the deviation observed, especially in view of the known dependence of the isomer shifts upon hybridization (s character).

Figure 1 is a plot of the estimated atomic charge (δ) on the central tin atom in this series of compounds *vs.* the measured $Sn(3d_{5/2})$ electron binding energy. The charges were obtained by a relatively simple method of electronegativity equalization.[24] While there is no way to obtain absolute charges experimentally to validate these estimates, their success in numerous applications[24-27] indicates that their relative magnitude is accurate. The least-squares fit of the binding energy data yields

$$E_b = 486.4 + 0.57\delta$$

with $r = 0.93$.

It is interesting to note that the values of the correlation coefficient do not vary greatly in the three correlations. It should be noted, however, that we have chosen Pauling-type empirical electronegativities[23,28] for the correlation given above and that other systems of electronegativities based on *a priori* assumptions such as the Allred-Rochow system of electrostatic electronegativities[29] yield somewhat poorer fits ($r = 0.92$). This is because purely empirical schemes such as that of Pauling tend to have "built-in" adjustments for such factors as orbital hybridization and charge capacity, shown to be extremely important in the determination of charge distribution.[24-27] Thus, although a simple, one-parameter system (summation of electronegativities) may often provide excellent correlation of experimental data, we feel that the increased power of a two-parameter, orbital electronegativity system provides significant advantages at a minimum increase in computational work.

We are currently studying additional compounds of this type to elucidate further the relationship among electron binding energy, Mössbauer isomer shifts, and molecular parameters.

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Synthetic and Structural Studies of Some Methyltin(IV) Chlorosulfonato Compounds

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The synthesis of some new methyltin(IV) chlorofluorosulfates and trifluoromethanesulfonates of the general type $(CH_3)_nSnCl_m(SO_3X)_{4-(n+m)}$, where n and m can be 0, 1, or 2 and X = F and CF_3, is described. Two general synthetic routes are employed: (a) the acid solvolysis of methyltin(IV) chlorides in the corresponding sulfonic acids and (b) ligand redistribution reactions of methyltin(IV) chlorides and sulfonates. Structural proposals are based on infrared, Raman, and ^{119}Sn Mössbauer studies.

A. Introduction

The solvolysis of methyltin(IV)–chloro compounds in some monobasic sulfonic acids of the type HSO_3X with X = F, Cl, CF_3, CH_3, or C_2H_5 has resulted in the preparation of the series $(CH_3)_2Sn(SO_3X)_2$[1] using $(CH_3)_3SnCl$ and $(CH_3)_2SnCl_2$ as solutes and the series $(CH_3)_3SnSO_3X$ with X = F,[2] CF_3,[3] and CH_3,[2] when an excess of $(CH_3)_4Sn$ has been used as solute.

Structural proposals were based on infrared and Raman spectra as well as on ^{119}Sn Mössbauer spectra.[1,2] In addition the detailed X-ray diffraction study of $(CH_3)_2Sn(SO_3F)_2$ has been carried out.[4] In all cases the SO_3X group was found to act as a bidentate bridging group with coordination to tin occurring through oxygen bridges, thus resulting in pentacoordination for the series $(CH_3)_3SnSO_3X$ and in hexacoordination for compounds of the type $(CH_3)_2Sn(SO_3X)_2$. The latter series was found to be closely related to compounds of the

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