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Photoelectron Spectroscopy of Tin Compounds

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Photoelectron spectroscopy of core electrons is a technique capable of yielding information pertinent to the study of chemical bonds in that the binding energy of an inner shell electron is characteristic of both its elemental identity and the chemical environment of the atom.² As the sensitivity of the binding energy to valence state depends on the element, the first objective of this work was to determine this sensitivity for tin core electrons. It should be noted that some tin binding energies have already been interpreted in terms of a specific oxidation state.³ In addition, the tin nucleus is amenable to the Mossbauer technique and communications reporting relationships between isomer shifts and core electron binding energies for some Sn(IV) compounds and some Fe(II) compounds appeared during the course of this work.^{4,5} Our second objective was to investigate the existence of such a correlation for selected complexes of tin(IV) chloride. Finally, the differences in binding energies between coordinated and uncoordinated ligand atoms have been used to support arguments concerning π back-bonding in some coordination compounds.^{6,7} As such an interaction can also be important in coordination to tin, another objective of this work was to investigate the changes in core electron binding energies of a variety of ligand atoms upon coordination to tin.

Experimental Section

This work was carried out on a Varian IEE-15 spectrometer employing an electrostatic electron analyzer and controlled by a Varian 260/i digital computer. Powdered samples, mounted with double-faced tape on cylindrical aluminum holders, were bombarded with either Al $K\alpha_{1,2}$ or Mg $K\alpha_{1,2}$ X-rays with energies of 1.487 and 1.254 keV, respectively. Three samples were investigated with both sources and the measured binding energies were found to be independent of the X-ray source. Instrument resolution at an analyzer energy of 100 eV corresponded to a 1.9-eV peak width at half-height for the carbon 1s electrons from a graphite standard. Other typical line widths were as follows: Sn 4d, 2.5 eV; Sn 3d, 2.2 eV; P 2p, 2.5

eV; Au 4f, 1.9 eV; N 1s, 2.2 eV; S 2p, 3.3 eV; O 1s, 3.2 eV. All compounds were run at least once with a gold standard deposited on the mounted sample under vacuum conditions and most were examined on at least two separate occasions with this standard. Several compounds were examined as many as eight separate times over the course of 1 year. The standard deviation for these measurements was typically 0.3 eV and, although the reproducibility was much better for many samples, we have taken this as a measure of the precision of all the determinations.

To support the standardization technique, we have measured the phosphorus 2p binding energies in three compounds that have been examined in other laboratories. Our results and those reported by others^{8,9} are compared in Table I. With one exception, the agreement between our values and those reported by other laboratories using phenyl carbon as an internal standard is good. As the absolute binding energy for the Au 4f_{5/2} line was not determined, the values in the tables are only relative.

Most compounds were also run without deposited gold and the relative binding energies of the core electrons of the various atoms present were independent of the presence of gold. In measuring the binding energies, the reference line was always measured before and after the lines of interest. Instrument drift was rarely observed but when it was the determination was discarded.

The Sn(IV) compounds examined were gifts of Professor Columba Curran and Drs. Data Naik and Merle Arnold. The preparations and characterizations have been reported elsewhere.¹⁰⁻¹⁷ Selected compounds were rechecked for purity by elemental analysis or by infrared spectroscopy. The Sn(II) compounds were commercial samples as were the free ligands.

Results and Discussion

Chemical Shift. The observed binding energies for the Sn (4d) and (3d_{5/2}) electrons for a variety of tin compounds are presented in Table II. The agreement between the chemical shifts for the two levels measured is good. For the compounds measured the values span a mere 2 eV although charges (q , Table II) estimated using Pauling's electronegativities² span about 3 units. Clearly the tin core electron binding energies are fairly insensitive to their chemical environment. This behavior can be understood in that the change in binding energy with reference to a standard is roughly proportional to the change in atomic charge. The constant of proportionality is in turn inversely proportional to atomic radius.^{2,9,18,19} Thus as the radii of tin are fairly large,²⁰ the insensitivity of the core electron binding energies of tin to chemical environment is reasonable. Unfortunately, this technique will not be extremely useful in examining the bonding of tin compounds. Thus the tin binding energies in platinum-tin cluster compounds³ do not allow one to distinguish unambiguously the Sn(IV) oxidation state from that of Sn(II).

In the tin(IV) chloride and bromide complexes, the binding energies of the Cl 2p electrons and Br 3d electrons

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Table I. Reproducibilities of Binding Energies (eV) between Laboratories

Compd	P 2p	C 1s	Au 4f _{5/2}	No. of runs	Ref
(C ₆ H ₅) ₃ P	131.3 ± 0.3	(285.0) ^b		5	This work ^a
	131.3 ± 0.3	(285.0)		5	8
	130.6	(285.0)		9	9
	131.9 ± 0.4	(285.0)		7	7
	132.0 ± 0.3	(285.0)	87.9 ± 0.3	6	This work
(C ₆ H ₅) ₃ PO	131.2 ± 0.3	284.1 ± 0.3	(87.0)	6	This work
	132.5	(285.0)		1	This work ^a
	132.8 ± 0.2	(285.0)		5	8
	132.7	(285.0)		9	9
	132.9 ± 0.1	(285.0)		4	7
(C ₆ H ₅) ₃ PS	132.6 ± 0.3	(285.0)	87.0 ± 0.3	3	This work
	132.5 ± 0.3	285.0 ± 0.3	(87.0)	3	This work
	132.3	(285.0)		9	9
	132.9 ± 0.1	(285.0)		5	8
	132.2 ± 0.3	(285.0)	87.7 ± 0.3	3	This work
	131.5 ± 0.3	284.3 ± 0.3	(87.0)	3	This work

^a No gold deposited. ^b Parentheses indicate assumed value.

Table II. Observed Binding Energies for Tin Compounds

No.	Compd	Binding energy, ^a eV			δ, b mm/ sec
		g	Sn 4d	Sn 3d _{5/2}	
1	SnF ₂	1.44	26.0	486.4	3.51
2	SnCl ₂	0.62	25.2	485.8	4.02
3	SnCl ₂ ·2H ₂ O	0.32	26.5	486.8	3.56
4	SnBr ₂	0.46	26.0	486.2	3.85
5	SnI ₂	0.24	26.2	486.6	4.06
6	SnO	1.38	25.9	485.9	2.62
7	Sn(C ₂ H ₅) ₂ (NCS) ₂ - (<i>o</i> -C ₁₂ H ₈ N ₂)	0.04	25.5	485.7	283.7 1.40
8	SnBr ₄ (C ₆ H ₅ S) ₂	-0.32	25.6	486.1	283.7 0.97
9	SnCl ₄ [(C ₆ H ₅) ₃ P] ₂	-0.34	25.2	485.4	0.85
10	SnBr ₄ (α,α'-C ₁₀ H ₈ N ₂)	0.12	26.3	486.3	283.7 0.71
11	Sn(C ₆ H ₅) ₂ (C ₉ H ₇ NO) ₂	0.32	25.5	485.7	283.7 0.70
12	SnCl ₄ {[(CH ₃) ₂ N] ₂ CS} ₂	0.18	25.8	486.0	284.0 0.68
13	SnBr ₄ [(CH ₃) ₂ SO] ₂	0.50	26.0	486.3	283.7 0.64
14	SnBr ₄ [(C ₆ H ₅) ₃ PO] ₂	0.50	25.8	486.4	283.7 0.61
15	SnCl ₄ (C ₅ H ₅ N) ₂	0.44	25.3	485.8	0.49
16	(NH ₄) ₂ SnCl ₆	-0.06	26.1	486.0	0.43
17	SnCl ₄ [(CH ₃) ₂ SO] ₂	0.84	26.1	486.2	283.9 0.35
18	SnCl ₄ {[(CH ₃) ₂ N] ₂ CO} ₂	1.00	26.1	486.2	283.9 0.33
19	SnCl ₄ {[(CH ₃) ₂ N] ₃ PO} ₂	1.00	26.4	486.5	284.4 0.29
20	SnO ₂	2.68	26.0	486.0	-0.02
21	SnF ₄	2.88	27.0	487.2	-0.27
22	Pt(SnCl ₃) ₂ {[(CH ₃) ₂ N] ₂ - CS} ₂	0.05	25.4	485.4	1.63
23	Pd(SnCl ₃) ₂ {[(CH ₃) ₂ N] ₂ - CS} ₂	0.05	25.4	485.6	284.0 1.97
24	PtCl(SnCl ₃)[(C ₆ H ₅) ₂ - P(CH ₂) ₂ P(C ₆ H ₅) ₂]	0.05	25.8	485.7	284.0 1.66
25	PdCl(SnCl ₃)[(C ₆ H ₅) ₂ - P(CH ₂) ₂ P(C ₆ H ₅) ₂]	0.05	25.6	485.6	1.72
26	Pt(SnCl ₃) ₂ [(C ₅ H ₁₀ N) ₃ PS] ₂	0.05	25.6	486.0	1.67
27	Pd(SnCl ₃) ₂ [(C ₅ H ₁₀ N) ₃ PS] ₂	0.05	25.7	485.8	284.1 1.71
28	PtCl(SnCl ₃)[(C ₆ H ₅) ₂ Sb] ₂	0.05	25.3	485.6	283.6 1.75
29	PtCl(SnCl ₃)[(C ₆ H ₅) ₂ As] ₂	0.05	25.4	485.3	283.7 1.63
30	PtCl(SnCl ₃)[(C ₆ H ₅) ₃ P] ₂	0.05	25.5	485.8	284.0 1.59
31	Au(SnCl ₃)[(C ₆ H ₅) ₃ P] ₃	0.10	25.0	485.8	283.6 1.65
32	Ag(SnCl ₃)[(C ₆ H ₅) ₃ P] ₃	0.02	25.2	485.8	283.6 1.71
33	Cu(SnCl ₃)[(C ₆ H ₅) ₃ P] ₃	0.02	25.3	485.6	283.6 1.83
34	(CH ₃) ₄ NSnCl ₃	-0.12	25.6	485.7	284.4 3.54
35	KSnF ₃	1.09	26.2	486.0	283.9

^a Based on $E_B(\text{Au } 4f_{5/2}) = 87.0 \text{ eV}$. ^b Relative to a barium stannate source; values from ref 10-18.

were also measured. These remained constant at $198.0 \pm 0.3 \text{ eV}$ (13 compounds) and $68.1 \pm 0.3 \text{ eV}$ (4 compounds), respectively. In all cases the reference line was Au 4f_{5/2} and the midpoint of the unresolved doublet was measured.

Table III. Comparison of Ligand Donor Atoms in Free and Complexed Forms

Compd ^a	Binding energy, eV		
	Ligand atom ^b	Complex minus free	Au 4f _{5/2}
(CH ₃) ₄ NSnCl ₃	26.2		87.6
Compd 22-33, Table II, av	26.5	0.3	88.2
(C ₆ H ₅) ₃ P	131.3		^c
(C ₆ H ₅) ₃ PO	132.0		87.9
[(C ₆ H ₅) ₃ P] ₂ PtCl(SnCl ₃)	132.5	0.8	87.9
[(C ₆ H ₅) ₃ P] ₃ Au(SnCl ₃)	132.2	0.5	88.4
[(C ₆ H ₅) ₃ P] ₃ Ag(SnCl ₃)	131.7	0.0	88.4
[(C ₆ H ₅) ₃ P] ₃ Cu(SnCl ₃)	131.7	0.0	88.4
[(C ₆ H ₅) ₃ P] ₂ PtCl ₂	131.3	-0.4	88.0
(C ₆ H ₅) ₃ PB ₉ H ₁₃	132.2	0.5	88.9
(C ₆ H ₅) ₃ PO	132.5		^c
(C ₆ H ₅) ₃ PO	132.6		87.0
[(C ₆ H ₅) ₃ PO] ₂ SnBr ₄	132.7	0.2	88.1
[(C ₆ H ₅) ₃ PO] ₂ SnCl ₄	132.8	0.2	89.2
[(CH ₃) ₂ N] ₂ CS	161.7		87.2
{[(CH ₃) ₂ N] ₂ CS} ₂ SnCl ₄	162.6	0.9	88.0
α,α'-C ₁₀ H ₈ N ₂	398.6		^c
(α,α'-C ₁₀ H ₈ N ₂)SnBr ₄	400.3	1.7	88.3
C ₅ H ₅ N	398.0 ^d		
(C ₅ H ₅ N) ₂ SnCl ₄	400.0	2.0	^c

^a Ligand atom in bold face type. ^b Based on $E_B(\text{C } 1s) = 285.0 \text{ eV}$. ^c No gold deposited. ^d References 2 and 6.

The average binding energies of the C 1s electrons referenced to that of Au 4f_{5/2} (87.0 eV) for the compounds reported in Table II is $283.9 \pm 0.3 \text{ eV}$.

Correlation with Mossbauer Isomer Shifts. It has been suggested that in a closely related series of compounds where the stereochemistry and oxidation number of the central atom is constant there should be a relationship between the isomer shifts and the core electron binding energies.⁴ The preliminary results of an investigation of the correlation of binding energies with Mossbauer isomer shifts for Sn(IV) octahedral complexes have appeared.⁴ Comparing the series of compounds L₂SnCl₄ where L = (C₆H₅)₃P, [(CH₃)₂N]₂CS, C₅H₅N, (CH₃)₂SO, [(CH₃)₂N]₂CO, and [(CH₃)₂N]₃PO shows that here too there does appear to be a trend of increasing binding energy with decreasing isomer shift as expected. However, the observed change is barely outside of the precision of the data and the correlation is not the same as nor is it as dramatic as that reported previously.⁴ Consequently, we have measured the binding energies of two of the compounds upon which the published correlation is based: namely, SnO₂ and Sn(C₆H₅)₂(C₉H₆NO)₂ (points 7 and 2, respectively, in the figure of ref 4). We agree on the binding energy of SnO₂ but differ by ca. 2.5 eV on the latter compound. The purity of our sample was checked by elemental analysis and was found to be unchanged from that reported originally.¹⁶ It should be noted that no standardization was reported by Barber, *et al.*⁴

Change in Binding Energy with Coordination. It has been shown that the difference in binding energies between coordinated and uncoordinated ligands can give insight into the character of the coordinate bond. For example, the nitrogen 1s binding energy of ammonia increases upon coordination, that of the nitro ligand remains the same, and that of cyanide decreases.⁶ These changes are qualitatively explained in terms of metal-ligand σ bonding and π back-bonding. The changes in ligand atom core electron binding energies upon coordination to tin and other metals are presented in Table III. Here the carbon 1s binding energy is used as a standard. The assumption is made that the charge

on the carbon atoms of the ligands does not change upon coordination.

For nitrogen as the ligand atom, the binding energy increases about 2 eV indicating an increased positive character of the nitrogen donor atom as expected.⁶ In the case of phosphorus there is no significant change in the binding energy upon coordination to a variety of metals. The same observation has been made previously for Ni, Pd, and Cd⁷ and was interpreted in terms of π back-donation. Thus ligand π back-bonding would also appear to be important for the interesting acceptor B₃H₃ (Table III). If so, this is support for the argument that the lack of reactivity of the phosphine compound with respect to ligand displacement is due to donation from the boron cage to the phosphorus d orbitals.²¹ There is also no change in the phosphorus 2p binding energies in (C₆H₅)₃PO upon coordination in agreement with the observation of others.⁸ For sulfur there is a barely significant increase in the binding energy upon coordination. As in the case of nitrogen, this would indicate that there is a net transfer of electrons to tin upon coordination. For tin, in the ligand SnCl₃⁻, there is no significant change in the binding energy upon coordination to a variety of metals. Unfortunately, this may merely reflect the insensitivity of the tin core electrons to their chemical environment. This is easy to understand (Table II) in that a coordinate interaction causing a 2-V shift for nitrogen would cause only a 0.1-V shift for tin. No conclusion can be drawn concerning the role of π back-bonding in this situation.²²

Registry No. SnF₂, 7783-47-3; SnCl₂, 7772-99-8; SnCl₂·2H₂O, 10025-69-1; SnBr₂, 10031-24-0; SnI₂, 10294-70-9; SnO, 21651-19-4; Sn(C₄H₉)₂(NCS)₂(*o*-C₁₂H₈N₂), 38882-72-3; SnBr₄(C₄H₈S)₂, 38894-35-8; SnCl₄[(C₄H₉)₃P]₂, 38966-48-2; SnBr₄(α, α' -C₁₀H₈N₂), 16918-62-0; Sn(C₆H₅)₂(C₆H₅NO)₂, 19568-50-4; SnCl₄[(CH₃)₂N]₂CS₂, 21470-12-2; SnBr₄[(CH₃)₂SO]₂, 21470-09-7; SnBr₄[(C₆H₅)₃PO]₂, 17927-31-0; SnCl₄(C₅H₅N)₂, 17100-04-8; (NH₄)₂SnCl₆, 16960-53-5; SnCl₄[(CH₃)₂SO]₂, 19979-07-8; SnCl₄[(CH₃)₂N]₂CO₂, 12085-24-4; SnCl₄[(CH₃)₂N]₃PO₂, 16971-36-1; SnO₂, 18282-10-5; SnF₄, 7783-62-2; Pt(SnCl₃)₂[(CH₃)₂N]₂CS₂, 38882-68-7; Pd(SnCl₃)₂[(CH₃)₂N]₂CS₂, 38960-89-3; PtCl(SnCl₃)(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂, 38894-43-8; PdCl(SnCl₃)(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂, 38882-69-8; Pt(SnCl₃)₂[(C₅H₁₀N)₃PS]₂, 38960-50-8; Pd(SnCl₃)₂[(C₅H₁₀N)₃PS]₂, 38882-70-1; PtCl(SnCl₃)(C₆H₅)₃Sb₂, 38966-51-7; PtCl(SnCl₃)(C₆H₅)₃As₂, 38894-44-9; PtCl(SnCl₃)(C₆H₅)₃P]₂, 32535-75-4; Au(SnCl₃)(C₆H₅)₃P]₃, 38894-46-1; Ag(SnCl₃)(C₆H₅)₃P]₃, 38894-47-2; Cu(SnCl₃)(C₆H₅)₃P]₃, 38882-71-2; (CH₃)₄N₃SnCl₃, 14877-00-0; KSnF₃, 13782-23-5; (C₆H₅)₃P, 603-35-0; (C₆H₅)₃PO, 791-28-6; [(CH₃)₂N]₂CS₂, 2782-91-4; α, α' -C₁₀H₈N₂, 366-18-7; (C₆H₅)₃PS, 3878-45-3.

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(22) Note Added in Proof. See W. E. Swartz, Jr., P. H. Watts, Jr., E. R. Lippincott, J. C. Watts, and J. E. Huheey, *Inorg. Chem.*, **11**, 2632 (1972), for the report of a similar study of tin compounds.

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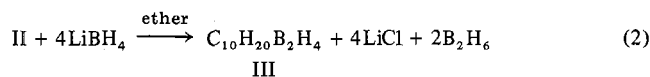
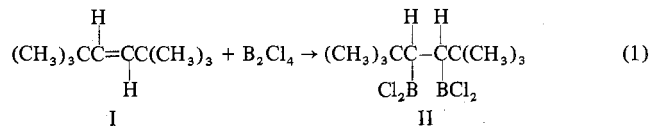
Hydrogenation of

3,4-Bis(dichloroboryl)-2,2,5,5-tetramethylhexane

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Recently Biallas¹ reported that the difunctional Lewis acid 1,2-bis(dichloroboryl)cyclohexane can react with LiBH₄ to give the corresponding 1,2-bis(dihydroboryl) compound. This new hydridic species was found to be relatively stable and exhibited infrared and nmr spectra consistent with those of a structure containing both terminal and bridged B-H bonds. We now wish to report the results of a study in which 3,4-bis(dichloroboryl)-2,2,5,5-tetramethylhexane (II), prepared from *trans*-2,2,5,5-tetramethyl-3-hexene and tetrachlorodiborane(4) (eq 1), is converted to the hydridic compound in a similar manner with a borohydride salt (eq 2).²



Product III is isolated at -45° by trap-to-trap fractional condensation and purified by sublimation. Compound III is a thermally stable, white, waxy solid with a molecular weight (cryoscopic) indicative of a monomeric substance. The ir spectra of II and III are summarized in the Experimental Section. Prominent features of the spectrum of III are the appearance of a sharp singlet absorption at 2495 cm⁻¹ characteristic of a terminal B-H stretching vibration³ and a strong relatively broad absorption at 1575 cm⁻¹ assigned to the complex vibrational mode of the bridging B-H-B group.⁴ Both of these bands in III seemingly occur at the expense of the broad BCl₂ stretching vibrations at 850-950 cm⁻¹ in II.² The spectrum of III is essentially unchanged whether observed in solution or as a smear between KBr disks.

The boron-11 nmr spectrum of III consists of a single broad resonance at -25 ppm relative to BF₃·Et₂O.⁵ The shape and position of the signal are independent of solvent and concentration.

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(2) A small quantity of ethyl chloride, presumably from a side reaction of diethyl ether and I, was detected in the material trapped at -196° on fractional condensation. Similar ether cleavages have been observed with other polyfunctional BCl₂ derivatives: M. Zeldin, *J. Inorg. Nucl. Chem.*, **33**, 1179 (1971).

(3) It has been well documented that diborane derivatives having two terminal hydrogens have both asymmetric in-phase and symmetric out-of-phase stretches which appear as a doublet in the ir near 2500 cm⁻¹: W. J. Lehmann, C. O. Wilson, J. F. Ditter, and I. Shapiro, *Advan. Chem. Ser.*, No. 32, 139 (1961).

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(5) The boron-11 chemical shift of III is consistent with the values obtained for similar compounds: 1,2-tetramethylenediborane, -18.6 ppm; 1,2-(1'-methyltrimethylene)diborane, -18.6 ppm (H. G. Weiss, W. J. Lehmann, and I. Shapiro, *J. Amer. Chem. Soc.*, **84**, 3840 (1962)); 1,2-dimethyldiborane, -20.5 ppm for *cis* and *trans* isomers (R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960)).