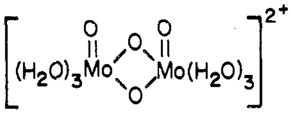
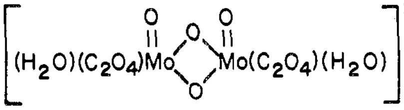


III



IV

Further support for structure III is lent by the similarity of absorption spectra of III and IV. The oxalato complex has maxima at 256 and 305 mμ. After 24 hr of aquation in 1 M H_2SO_4, the maxima of the complex shift to 255 and 298 mμ.

In preliminary experiments we were able to demonstrate that the new Mo(V) ion was the main product of air oxidation of Mo(II) and Mo(III) solutions. This explains the appearance of the typical maxima at 293 and 254 mμ in the spectrum of partly oxidized Mo(III) solutions.[9,10]

Acknowledgment. The authors wish to thank Mr. L. Halicz for valuable assistance in performing cryoscopic measurements.

Registry No. III, 40804-49-7; molybdenum, 7439-98-7.

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Core Electron Binding Energy Study of Group IIb-VIIa Compounds[1]

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The binding energies[2] of group IIb-VIa compounds have recently been measured. A general agreement between ionic character and chemical shift was noted. No core electron binding energy studies dealing with group IIb halides have been reported although the binding energies of cadmium valence and 4d electrons in cadmium chloride[3] and the uv photoelectron spectra[4] of various mercury halides have been published. In this paper we present the results of measurements of the binding energies of core electrons in IIb-VIIa compounds. The purpose of this study was (1) to examine a variety of experimental techniques for determining accurate and precise binding energies which had been corrected for charging effects, (2) to discover the change in binding energy of the metal core levels as a function of the halogen and *vice versa*, and (3) to compare the experimental shifts with atomic electron charge based on a simple electrostatic model and known ionic character.

Table I. Sample Preparation of CdI_2[a]

Cadmium binding energy, eV		
$3d_{3/2}$	$3d_{5/2}$	
412.0	405.1	Sublimed–Au probe
411.9	405.0	Evaporated soln–Au probe
413.7	406.8	Au mesh

[a] Calibrant: Au $4f_{7/2}$, $4f_{5/2}$.

Experimental Section

The binding energies were measured with an AEI ES 100 photoelectron spectrometer using Al Kα radiation ($E = 1486.6$ eV) as the photon source. Data acquisition and spectrometer control were accomplished using the AEI DS 100 data system and a Digital PDP 8/e computer. Spectra were plotted using the MADCAP IV plotting routine on a Digital PDP 8/I computer. A Physical Electronics Industries argon ion etching apparatus (Model 20-005) was used to clean[5] metal surfaces. Samples were deposited onto one face of a four-sided gold-plated probe either by sublimation or by allowing several drops of a dilute solution of the sample to evaporate slowly. It was found that sublimed preparations and solvent-evaporated depositions gave identical binding energy results within experimental error.

Initially it was believed that intimate contact of the sample with gold-plated copper mesh would provide a process for charge removal. However, as the typical data for CdI_2 in Table I show, higher binding energies indicative of charging effects were obtained for the mesh samples relative to the sublimed or solvent-evaporated samples. Deposition of samples onto double-sided cellophane tape yielded even higher binding energies as well as erratic results.

Samples of the metal halides were reagent grade and were purchased from commercial sources. All chemicals were used without additional purification. Samples of the halides were dried at 100° *in vacuo* for 12 hr in order to remove water of crystallization prior to sublimation of a thin film of sample onto the gold-plated probe. Under the conditions of the sublimations it is known from mass spectrometric studies[6,7] that the materials sublime as monomers without decomposition. A decrease in the gold counts, monitoring Au $4f_{7/2}$, to a value one-half to one-tenth that for an argon ion etched gold surface was found to be an acceptable indication of adequate sample on the probe yet not so much as to cause charging effects of an unknown magnitude. The gold $4f_{5/2}$ and $4f_{7/2}$ binding energies were measured and used to evaluate the spectrometer work function and the extent of charging during each sample measurement.

Accurate binding energies for the gold levels were determined in a separate series of experiments by measuring the binding energy for each gold f level relative to the more accurately known carbon $1s_{1/2}$ level of graphite and carbon black (soot) (BE = 283.8 eV).[8] Gold was used as a calibrant rather than carbon because of fear that the pump oil contamination present might complicate the carbon $1s_{1/2}$ signal. The measured binding energies for the gold 4f levels were $BE(4f_{5/2}) = 87.1$ eV and $BE(4f_{7/2}) = 83.4$ eV.

The measured binding energies, Tables I-III, for all samples represent the average of no less than four separate deposits. The deviation reported is one standard deviation.

Results and Discussion

The measured binding energies for metal and halogen core electrons are summarized in Tables II and III, respectively. The measured chemical shift relative to the element is also presented in the tables for each core level investigated. The chemical shift for all metal ions is positive and negative for all nonmetallic ions as expected from a consideration of formal oxidation states. A typical spectrum is shown in Figure 1. The measured spin-orbit splittings for the metal iodides, summarized in Table IV, are in agreement with those

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(1) Presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972.

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Table II. Metal Binding Energies (BE) and Chemical Shifts (CS) for Core Electrons of MX_2 (eV)

	Zinc				Cadmium				Mercury			
	BE($2p_{1/2}$)	CS	BE($2p_{3/2}$)	CS	BE($3d_{3/2}$)	CS	BE($3d_{5/2}$)	CS	BE($4f_{5/2}$)	CS	BE($4f_{7/2}$)	CS
F					412.4 ± 0.2	+1.7	405.6 ± 0.2	+1.6	104.8 ± 0.2	+1.5	100.6 ± 0.2	+1.4
Cl	1045.7 ± 0.2	+2.9	1022.5 ± 0.2	+2.8	412.4 ± 0.1	+1.7	405.5 ± 0.1	+1.6	105.0 ± 0.1	+1.7	100.8 ± 0.2	+1.6
Br	1045.9 ± 0.1	+3.1	1022.8 ± 0.2	+3.1	412.2 ± 0.1	+1.5	405.4 ± 0.1	+1.4	104.5 ± 0.2	+1.2	100.4 ± 0.2	+1.3
I	1045.5 ± 0.1	+2.7	1022.5 ± 0.1	+2.8	412.0 ± 0.1	+1.3	405.1 ± 0.1	+1.2	104.2 ± 0.1	+0.9	100.1 ± 0.1	+0.9
M	1044.6 ± 0.1	(ZnO[a])	1021.6 ± 0.1	(ZnO[a])	410.7 ± 0.1		404.0 ± 0.1		103.3 ± 0.1		99.2 ± 0.1	
	1042.8 ± 0.6	*b*	1019.7 ± 0.6	*b*								

[a] See text. [b] Reference 9.

Table III. Binding Energies and Chemical Shifts For Nonmetals in MX_2 Compounds (eV)[a]

		Zn		Cd		Hg	
		BE	CS	BE	CS	BE	CS
F	$1s_{1/2}$			684.3 ± 0.1	−1.7	685.4 ± 0.1	−0.6
Cl	$2p_{1/2}$	200.6 ± 0.2	−1.4	200.0 ± 0.1	−2.0	199.6 ± 0.1	−2.4
	$2p_{3/2}$	199.1 ± 0.2	−0.9	198.4 ± 0.1	−1.6	198.1 ± 0.1	−1.9
Br	$3d_{3/2,5/2}$	69.4 ± 0.2	−0.6	68.6 ± 0.2	−1.4	68.40 ± 0.1	−1.6
I	$3d_{3/2}$	630.8 ± 0.1	−0.2	630.7 ± 0.2	−0.3	630.3 ± 0.1	−0.7
	$3d_{5/2}$	619.1 ± 0.1	−0.9	618.8 ± 0.2	−1.2	618.8 ± 0.1	−1.2

[a] Elemental binding energies of halogens taken from ref 10.

Table IV. Spin–Orbit Splittings for Metal Iodides (eV)

	Zn	Cd	Hg
This work	23.1	6.9	4.2
Ref 1 (MTe)	23.1	6.8	4.1
Ref 9 (M)	23.1	6.8	3.7
This work (M)	23.0[a]	6.7	4.1

[a] See text.

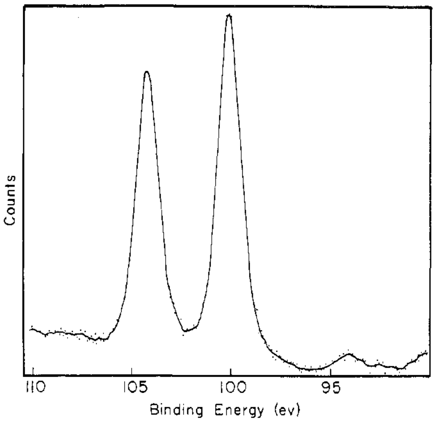

Figure 1. Photoelectron spectrum of Hg $4f_{7/2}$ and $4f_{5/2}$ levels in HgI_2 (net counts 5200, 3 sec/channel, and 6 scans).

published for metal chalcogenides and with those listed in a summary of metal binding energies.[9] The spin-orbit splittings for the other halides are in similar agreement with previously reported splittings within experimental error.

The experimental data for the metals, except zinc, are in agreement with previously reported photoelectron values[10] and recent tabulated results.[9] The binding energies for zinc metal are higher than those tabulated[9] but are in excellent agreement with the measured binding energies for the Zn $2p_{1/2}$ and $2p_{3/2}$ values for zinc oxide.[2] Thus it is apparent that under the experimental conditions (10^{-7}–10^{-8} Torr) in this study it is either not possible to clean the oxide coating from the zinc metal or the surface is reoxidized before or during the measurements. It is likely that the latter process is responsible for the observations in this work, since it has been possible to remove surface oxide contamination from other metals by argon ion etching.

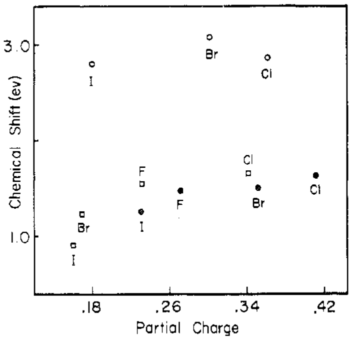

Figure 2. Chemical shift *vs.* partial charge for MX_2 compounds: ○, Zn; ●, Cd; □, Hg.

An important result of this study is that the metal core electron binding energies in the metal halides are almost independent of the halogen. For cadmium and mercury there is a slight increase in the binding energy as indicated from the chemical shift data in proceeding from iodide to chloride. This result is in accord with the expected greater ionic character of the metal-chloride ion bond compared to the metal-iodide ion bond. A calculation of per cent ionic character[11,12] for each combination supports this hypothesis. However, for zinc the chemical shift reaches a maximum at bromide ion while chloride and iodide are in the expected order. This discrepancy is not too unexpected since the ionicities of $ZnCl_2$ (16%) and $ZnBr_2$ (13%) are practically the same.[11] Surprisingly the chemical shifts for cadmium and mercury fluorides are equal to or slightly less than those of the chlorides although fluorides are predicted to be more ionic. The predicted chemical shift based on the Pauling per cent ionic character is about 1.5 times greater than the measured value for cadmium fluoride and about 3 times the measured value for mercuric fluoride. This observation reflects the notion that core electron binding energies as well as chemical shifts are functions of both the electron density and the crystal or molecular potential of the solid. Therefore, although the IIb fluorides are probably more electrovalent, their calculated crystal potentials[12] are 100–200 kcal/mol larger than their congeners which have approximately the same crystal potentials.[12] All things being equal, a greater bond ionicity suggests a larger binding energy chemical shift whereas a larger crystal potential is expected to lower the chemical shift. It is suggested that these offsetting factors account for the rather small chemical shift differences that are found for a particular metal with different halides.

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A comparison of the observed chemical shift with the calculated metal partial charge according to Sanderson[13] is presented in Figure 2. An increase in chemical shift with increasing partial positive charge is observed. The comparison here is more favorable than with ionic character as evidenced by the predicted lower binding energy for fluorides relative to chlorides which we have observed. The observed core electron binding energy trend in HgX_2 ($X^- = Cl^-, Br^-, I^-$) is also in agreement with the calculated charges on mercury in these compounds as estimated from measurement of the $5d^{10}$ ionization potential using uv photoelectron spectroscopy.[4]

Comparison of core electron binding energies for a series of halides with a common metal is not advisable since the same electron level has not been studied for each halogen and the extent of spin-orbit coupling for an identical electron level differs markedly in some cases. The trend in chemical shift for a common halogen with different metal ions is in partial agreement with the idea that more ionic compounds should exhibit larger halide chemical shifts. The calculated ionicities are in the order $Zn < Cd > Hg$. Only with the more highly covalent bromides and iodides do we find a discrepancy.

To obtain comparative data for mercury(I) salts the binding energies of selected mercury and chlorine energy levels were measured for Hg_2Cl_2 (Hg $4f_{5/2,7/2}$, 103.7 ± 0.2, 99.4 ± 0.2; Cl $2p_{1/2,3/2}$, 198.8 ± 0.2, 197.2 ± 0.2). The physical and chemical properties of Hg_2Cl_2 are consistent with the fact that the mercury-chlorine bond is predominantly ionic and that the ionicity is greater than that for the mercuric halides. In addition Scaife[14] has estimated that the ionicity of the Hg-Cl bond is about 79% in Hg_2Cl_2. Thus it might be expected that a significant shift in the binding energy of mercury would result. On the other hand it is known from spectroscopic studies[15] that mercurous mercury is Hg_2^{2+}, and a chemical shift indicative of the covalent mercury-mercury bond might result. That the latter result is in fact realized is noted by examining the chemical shifts for the mercury 4f levels. The chemical shifts for Hg $4f_{7/2,5/2}$ of +0.4 and +0.2 eV, respectively, compare with a shift of about +1.6 eV for mercury in mercuric chloride. This result adds support to the notion that the dimeric mercurous mercury species, Hg_2^{2+}, is apparently characterized by strong covalent bonding although the mercury-chlorine bond is extremely ionic. That the Hg-Cl bond is more ionic than those noted in mercuric chloride is indicated by the greater negative chemical shift (greater electron density) for the chlorine $2p_{1/2,3/2}$ (CS = −2.8 eV for both levels) levels in Hg_2Cl_2. Thus the core binding energies for mercury and chlorine in mercurous mercury reinforce the conclusions from other studies which suggest that Hg_2Cl_2 be formulated as $Hg_2^{2+}{:}2Cl^-$.

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Registry No. $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; ZnI_2, 10139-47-6; CdF_2, 7790-79-6; $CdCl_2$, 10108-64-2; $CdBr_2$, 7789-42-6; CdI_2, 7790-80-9; HgF_2, 7783-39-3; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; Hg_2Cl_2, 10112-91-1.

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Electrochemical Reduction of Phenylcyclopolyphosphines[1]

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A great amount of work on the alkali metal reduction of phenylcyclopolyphosphines has been done, largely by Issleib and coworkers.[2] However, most of the experiments were performed when it was believed that phenylcyclopolyphosphine was a tetrameric species, $(C_6H_5P)_4$. It is now known from X-ray crystallographic work that the so-called "A" and "B" forms are pentameric[3] and hexameric,[4] respectively, although it is still not clear whether these species are different in solution.[5] In order to clarify the confusion concerning the solution structures of these compounds, and also to reexamine their reduction under carefully controlled conditions, the results of an electrochemical investigation of pentaphenylcyclopentaphosphine (A) and hexaphenylcyclohexaphosphine (B) are reported. The only known cyclic trimeric phosphine,[2d,6] $K_2(C_6H_5P)_3$, which is formed by potassium reduction of pentaphenylcyclopentaphosphine, was also reexamined.

Experimental Section

Instrumental. Electrochemical experiments were made using a Wenking Model 66TS10 potentiostat and a Chemtrix Type 800-A waveform generator in conjunction with a Plotamatic Model 715 x-y recorder or, for fast techniques, a Tektronix Type 564B storage oscilloscope. Some measurements were also performed on a Princeton Applied Research Corp. (PAR) electrochemical system, Model 170. A Varian Associates nmr spectrometer Model XL-100-15 was used for ^{31}P spectra. Proton nmr spectra were run on the same instrument or on a Varian A-60. Raman spectra were recorded on a Jarrell-Ash Model 25-500 laser Raman, and ir spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Uv-visible spectra were obtained on a Cary 17 spectrophotometer.

Preparations. (a) Pentaphenylcyclopentaphosphine, $(C_6H_5P)_5$. Pentaphenylcyclopentaphosphine[9] was prepared by dropwise addition of 8.95 g (0.05 mol) of dichlorophenylphosphine to 1.22 g (0.05 mol) of magnesium turnings in 50 ml of tetrahydrofuran (THF). After complete addition of the phosphine, 60 ml of H_2O was added to form a two-phase system with the resultant precipitation of the pentamer in the organic layer. Recrystallization from THF yielded crystals melting at 149–150°. A Raman spectrum run of the solid in a sealed glass tube agreed well with that previously reported,[10] as did a Nujol mull ir spectrum.[9] A uv spectrum run under anaerobic conditions in THF exhibited peaks at 323, 293, and 241 nm. A ^{31}P nmr spectrum in THF exhibited a single resonance at +4.0 ppm (relative to 85% H_3PO_4), and a proton nmr spectrum[9] in CS_2 exhibited absorptions at 7.05, 7.19, 7.13, and 7.25 ppm (relative to TMS) in order of

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(1) Presented in part before the Inorganic Division, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

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