those reported by Clune and Cohn.[1] The ^{19}F nmr showed a 1:1 doublet at δ 75.6 ppm from $CFCl_3$ (J_{PF} = 1170 Hz), each member of which was split into a septet (J_{HCNPF} = 3.5 Hz). The proton nmr spectrum showed a doublet (δ −2.8 ppm from TMS; J_{PNCH} = 13 Hz), each member of which was split into a second doublet (J_{FPNCH} = 3 Hz). The ^{31}P spectrum showed a broad doublet (J_{FP} = 1170 Hz; δ = −187 ppm from OPA).

(e) **Synthesis of PFClBr.** A 6.7-mmol sample of $(CH_3)_2NPFCl$ was mixed with a 13.7-mmol sample of HBr in a 500-ml gas reaction flask equipped with a stopcock. The system was warmed gradually to room temperature. After the reaction mixture had been standing 15 min, the volatiles were fractionated through traps held at −78, −126, and −196°. The PFClBr was retained in the −126° trap in 41% yield, while unreacted $(CH_3)_2NPFCl$ was found in the trap at −78°. Some PF_3, HBr, HCl, and SiF_4 were found in the −196° trap. White solid, identified as $[(CH_3)_2NH_2]^+Br^-$ by its X-ray powder pattern, remained in the reaction vessel. All properties of PFClBr except its mass spectrum have been given in an earlier section. The mass spectrum is again reported as *m/e*, assignment, peak intensity. The values are 168, $PF^{37}Cl^{81}Br^+$, 3.7; 166, $PF^{37}Cl^{79}Br^+$ and $PF^{35}Cl^{81}Br^+$, 16.8; 164, $PF^{35}Cl^{79}Br^+$, 13.0; 131, $PF^{81}Br^+$, 9.2; 129, $PF^{79}Br^+$, 9.2; 112, $P^{81}Br^+$, 1.8; 110, $P^{79}Br^+$, 1.8; 87, $PF^{37}Cl^+$, 33.3; 85, $PF^{35}Cl^+$, 100; 81, $^{81}Br^+$, 36.1; 79, $^{79}Br^+$, 36.1; 68, $P^{37}Cl^+$, 1.9; 66, $P^{35}Cl^+$, 8.1; 50, PF^+, 16.7; 37, $^{37}Cl^+$, 2.5; 35, $^{35}Cl^+$, 7.8; 31, $^{31}P^+$, and 19, $^{19}F^+$, 1.4. In addition, peaks assignable to $PFCl_2$ and $PFBr_2$ were observed. When the same reaction was carried out at −78° in a sealed reaction tube for 16 hr, the yield as estimated from the recovered $(CH_3)_2NPFCl$ was close to 90%.

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Registry No. $(CH_3)_2NPFCl$, 29246-85-3; $[(CH_3)_2N]_2PF$, 1735-82-6; $PFCl_2$, 15597-63-4; $(CH_3)_2NH$, 124-40-3; $(CH_3)_2NPFBr$, 21475-62-7; $PFBr_2$, 15597-39-4; PFClBr, 20464-11-3.

Contribution from the Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Molybdenum(V) in Aqueous Solution

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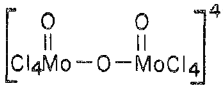
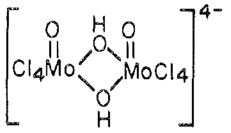
The role of molybdenum in the activity of various enzymes has renewed interest in the coordination chemistry of Mo(V). The structures of binuclear complexes of Mo(V) with oxalate, xanthate, and other chelating groups were elucidated;[1] yet, surprisingly little is known about the noncomplexed species of Mo(V) in aqueous solution.

Almost all the investigations concerned with the solution chemistry of Mo(V) were conducted in hydrochloric acid solutions. The well-characterized "Klason's salt"[2] $(NH_4)_2[MoOCl_5]$ dissolves in concentrated HCl (>10 *M*) without spectral change, and it is generally agreed[2] that the main species in this solution is the paramagnetic ion $MoOCl_5^{2-}$. Upon dilution of the solution to ~6 *M* HCl, another paramagnetic ion is formed for which structures I[2,3] and II[4] were suggested. Further dilution of this solution to <2 *M* HCl transforms the Mo(V) species into a diamagnetic ion. The two structures attributed to this diamagnetic ion are structure I by Colton and Rose[4] and a tetramer $(MoO_2^+)_4$ by Souchay.[5]



$$\left[Cl_4\overset{\overset{O}{\|}}{Mo}-O-\overset{\overset{O}{\|}}{Mo}Cl_4\right]^{4-}$$

I



II

The results of the investigation reported here show that the main Mo(V) species in dilute HCl, as well as in $HClO_4$ and other acids, is a binuclear *cation* charged +2 which is not coordinated to chloride. This ion exists in all acidic aqueous solutions of Mo(V) in which complex formation does not occur.

Two different preparative methods were used to obtain Mo(V) solutions. (a) Klason's salt solution was prepared by dissolving $MoO(OH)_3$ in concentrated HCl. This solution was diluted with water to a HCl concentration of 1 *M*. (b) Molybdic(VI) acid dissolved in $HClO_4$ (1 *M*) was reduced electrolytically. Both solutions were yellow orange and the absorption spectra of each had maxima at 254 and 293 mμ. The perchloric acid solution was free of Cl^- ions (no electrolytic reduction of ClO_4^- took place). Each solution was absorbed on a cation exchange column (Dowex 50 X2 acid form). The yellow Mo(V) species formed a distinct band on each column and was eluted with 1 *M* $HClO_4$. This ion exchange behavior indicated a minimum charge of +2. The oxidation state of Mo in the eluted solutions was determined by oxidation to Mo(V) with excess Fe^{3+} and back titration with permanganate. The 3:1 permanganate ratio for titration of an aliquot before and after reduction with a Jones reductor to Mo(III) confirmed the +5 oxidation state. The absorption spectra of the ion eluted from each column were identical with the spectra of the original solutions. The molar absorption was $\epsilon_{254} = 1999$ and $\epsilon_{293} = 1727$. No change occurred in the spectrum when the perchloric acid concentration was increased to 6 *M*, indicating the stability of the ion in strong acid media.[5] Cryoscopic measurements of Mo(V) were conducted in a eutectic perchloric acid solvent (5.27 *M*). The freezing point lowering of the solvent was approximately one-half of that expected for a mononuclear ion.[6] A solution containing 0.02 g-atom of Mo per kilogram of solvent lowered the freezing point by 0.052°. This corresponds to a molal depression of 2.6°, compared to 5.2° observed for mononuclear ions.

This result indicates that the Mo(V) ion is binuclear. This conclusion was confirmed by a determination of the charge per Mo atom and the charge per ion, according to the method of Cady and Connick.[7] Using acidified La^{3+} solutions as eluent, the charge per Mo atom derived from six determinations was 1.0 ± 0.1. The charge per ion derived from three batch experiments was +1.73 ± 0.05. This ionic charge is well within the accuracy of the method for a +2 ion.[7]

No definite conclusion can be drawn from these data about the detailed structure of the binuclear dipositive Mo(V) ion but we favor structure III. This structure is expected to be diamagnetic, like the oxalato complex, which is structurally related to it[8] (structure IV).

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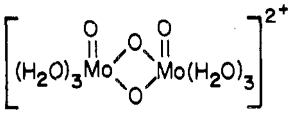
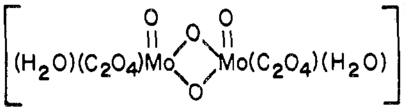


III



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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