Table II. Coordinates ($\times 10^4$) for 1,5-$(Ph_2PN)_2(NSBr)_2$, Space Group $P2_1/n$

atom	x	y	z	B_{eq}[a]
Br(1,2)	−306 (1)	−3190 (1)	1228.1 (5)	4.48 (2)
S(1,2)	−672 (2)	−2670 (3)	−253 (1)	2.76 (4)
P(1,2)	−1766 (2)	898 (3)	−96 (1)	2.74 (4)
N(1,3)	−1657 (6)	−1175 (9)	−442 (3)	3.24 (14)
N(2,4)	−546 (5)	2035 (9)	345 (3)	3.02 (13)
C(11,41)	−2568 (7)	756 (12)	663 (4)	2.84 (17)
C(12,46)	−2412 (8)	2061 (12)	1281 (5)	4.35 (19)
C(13,45)	−3082 (9)	1953 (16)	1832 (6)	5.97 (24)
C(14,44)	−3922 (9)	574 (16)	1781 (5)	5.23 (23)
C(15,43)	−4071 (8)	−710 (14)	1182 (6)	4.59 (21)
C(16,42)	−3413 (8)	−629 (12)	619 (5)	3.87 (18)
C(21,31)	−2690 (7)	2143 (11)	−961 (5)	3.03 (18)
C(22,32)	−3054 (8)	1378 (12)	−1741 (5)	4.02 (19)
C(23, 33)	−3763 (9)	2364 (16)	−2392 (5)	5.18 (24)
C(24,34)	−4091 (10)	4134 (19)	−2273 (7)	6.62 (30)
C(25,35)	−3719 (10)	4947 (14)	−1507 (8)	6.36 (32)
C(26,36)	−3008 (9)	3941 (14)	−849 (5)	4.60 (23)

[a] See footnote *a* of Table I.

Moreover, many bond lengths became disparate; for example, the P–C distances ranged from 1.74 (3) to 1.90 (2) Å and the Ta–H distances were 1.86 (11) and 1.16 (12) Å. These sorts of difficulties (which were not noted in ref 1) are typical of attempts to refine an approximately centrosymmetric model in a noncentrosymmetric space group.[4]

As usual,[5] refinement in the centrosymmetric space group $C2/c$ has led to equality of some bond lengths that appeared to be unequal in Cc; for instance, the Ta–Cl distance is now 2.551 (1) Å rather than 2.542 (5) and 2.563 (5) Å.[1] The two Ta–P distances remain unequal, at 2.564 (1) annd 2.631 (1) Å, but the P–C distances are statistically equal at 1.830 (3) Å. The Ta–H distance is 1.69 (6) Å, appreciably shorter than the values 1.94 (11) and 1.85 (11) Å reported in ref 1; as noted there, the most accurate Ta–H bond length available, from a neutron diffraction study[6] of Cp_2TaH_3, is 1.774 (3) Å.

1,5-$(Ph_2PN)_2(NSBr)_2$. The structure of this 8-membered-ring compound was described[7] in space group Pn (monoclinic; a = 11.476 (3) Å, b = 7.240 (1) Å, c = 16.914 (4) Å, β = 106.42 (1)°, Z = 2). It should be described in $P2_1/n$, with the molecule lying on a crystallographic center of symmetry.

After the coordinates in Table II of ref 7 were decremented so that the origin lay at the approximate center of symmetry (x = 0.655, y = 0.25, z = 0.665) and the coordinates of symmetry-related atoms were averaged,[8] full-matrix least-squares refinement quickly converged at an R of 0.042, a weighted R of 0.046, and a goodness-of-fit of 1.33 for 1199 observed reflections and 154 parameters; corresponding values reported for the Pn structure are 0.043, 0.047, and 1.34 for 185 parameters. Our refinement included anisotropic U_{ij}'s for the Br, S, P, and C atoms; in the earlier Pn refinement the C atoms were treated as isotropic.[9] In both refinements the hydrogen sites were assumed. The $P2_1/n$ parameters are given in Table II.

The $P2_1/n$ refinement has led to coordinate esd's about one-third as large as reported previously, presumably as a result of removing the near-singularities associated with refining an approximately centrosymmetric structure in a noncentrosymmetric space group.[4] It has again led to considerably more reasonable molecular geometry. For example, whereas the Pn model resulted in P–N distances ranging from 1.54 (2) to 1.68 (2) Å and S–N distances from 1.47 (2) to 1.57 (2) Å, the $P2_1/n$ refinement results in essentially equal values P–N = 1.613 (6), 1.629 (6) Å and S–N = 1.521 (6), 1.532 (6) Å. Even more dramatic are the changes in C–C distances (ref 1, supplementary material), which ranged from 1.12 (3) to 1.79 (3) Å for the Pn description but now range only from 1.351 (14) to 1.386 (15) Å.

The additional 2_1 axis requires the systematic extinction of reflections $0k0$ with k odd. Of the five such reflections included in the supplementary material, three are coded as "unobserved" and the other two as "$I_o < 0$".

Concluding Remarks. We can hear faint voices saying, "So what?"—the original, noncentrosymmetric descriptions of these two compounds showed the same atom connectivities as the revised centrosymmetric descriptions, and the average bond lengths are little changed. To many, these may be the only important considertions. But *reliable* bond lengths and angles are vital to many fields of chemistry. Refinement of a centrosymmetric structure in a noncentrosymmetric space group can well lead to inequalities in bond lengths so large (P–N, 1.54 (2) and 1.68 (2) Å, e.g.) as to invite fancy explanations when none is warranted. Moreover, the "wolf" syndrome is to be feared: if the reported accuracies of diffraction results cannot be trusted, further developments in such areas as bonding theory will surely be delayed. The centrosymmetric–noncentrosymmetric ambiguity is a particularly bothersome one, and we urge continual awareness of it and of its possible consequences.

Acknowledgment. This work was supported in part by Grant GM-16966 from the National Institutes of Health.

Registry No. $TaCl_2H_2(PMe_3)_4$, 85939-38-4; $(Ph_2PN)_2(NSBr)_2$, 90133-20-3.

Supplementary Material Available: Listings of anisotropic U_{ij} values and of hydrogen parameters for both compounds (Tables S1 and S2) (2 pages). Ordering information is given on any current masthead page.

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(3) The esd's were considerably larger than for the $C2/c$ refinement and varied greatly among atoms of the same type. These are manifesttions of the near-singularities (see ref 4).

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(8) There appear to be two misprints in Table II of ref 7: the y coordinate of N(2) should probably be 0.456 rather than 0.656, and the z coordinate of C(21) should probably be about 0.570 rather than 0.500. Also, the U values in the supplementary material (Table S1) are $\times 10^3$ rather than $\times 10^4$.

(9) Near-singularities in the least-squares matrix would presumably have led to severe convergence problems in the Pn refinement; the final shift-to-esd ratios are not given. Including anisotropic U_{ij}'s for the C atoms would probably have made the problem more severe.

Contribution from the Department of Chemistry,
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Surface-Selective Dispersion of $Os_3(CO)_{12}$ on Layered Silicate Clay. Reaction of $HOs_3(CO)_{12}^+$ with Hectorite

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A variety of metal complex catalysts may be immobilized by intercalation in smectite clays.[1,2] Oftentimes, the intercalated complex catalyst is more selective than the analogous complex in homogeneous solution. The steric requirements of surface transition states[3] or the position of surface equilibria[4] can provide the basis for enhanced catalytic selectivity.

Metal carbonyl cluster complexes represent a potentially important class of compounds for intercalation in clays, because they may exhibit interesting catalytic properties in their own right or they may serve as precursors for the formation of atomically dispersed metal centers.[5] Although metal carbonyls can be readily

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Table I. Infrared CO Stretching Frequencies for Reaction Products and Reference Compounds

sample	descripn	freq, cm^{-1}
I	$[HOs_3(CO)_{12}]^+$ + hectorite reacn product	2066 s, 2060 s, 2038 m, 2025 s, 2017 s, 1997 m, 1987 m
II	$[HOs_3(CO)_{12}][PF_6]$	2177 m, 2148 m, 2119 m, 2084 m, 2073 s, 2058 vs, 2021 s, 2009 s, 1986 s
III	$Os_3(CO)_{12}$	2068 s, 2060 s, 2040 m, 2027 s, 2015 vs, 1998 s, 1987 s
IV	$Os_3(CO)_{12}$ + hectorite reacn product	2066 s, 2060 m, 2037 m, 2027 s, 2014 vs, 1998 s, 1986 s
V	$[(\equiv SiO)_2Os(CO)_n]_x$–hectorite	2123 m, 2039 s, 1958 m

immobilized on solid supports by reaction with surface hydroxyls[6-8] or with covalently linked ligands,[9-11] analogous methodology is not suitable for intercalation of metal complexes in clays. Typically, the immobilization of metal complexes in clays requires positively charged species capable of electrostatic binding to the negatively charged silicate layers.

The present study examines the reaction of the protonated metal carbonyl cluster $HOs_3(CO)_{12}^+$ with a typical smectite clay, Na^+–hectorite. Remarkably, the binding of the cationic cluster leads to the preferential dispersal of $Os_3(CO)_{12}$ centers at the hydroxylated edge sites of the silicate layers rather than at the more abundant basal surfaces. We believe the reaction of the protonated cluster to be an unusual example of site-selective metal complex binding to a layered silicate surface.

Experimental Section

Materials. Natural sodium hectorite with an idealized unit cell formula of $Na_{0.67}[Mg_{5.33}Li_{0.67}](Si_{8.00})O_{20}(OH,F)_4$ was obtained from the Baroid Division of NL Industries. The mineral was allowed to sediment 24 h as a 1 wt % aqueous slurry to remove dense impurities, saturated with Na^+ by reaction with excess aqueous NaCl, washed free of chloride by dialysis, and then freeze-dried.

$Os_3(CO)_{12}$ was purchased from Strem Chemicals, Inc. $HOs_3(CO)_{12}^+$ was prepared as the hexafluorophosphate salt according to the method described by Knight et al.[12]

Cluster–Clay Reactions. Na^+–hectorite (0.10 g, 0.070 mequiv) in 10 mL of water was added with stirring to 0.0070 mequiv of $HOs_3(CO)_{12}^+$ or $Os_3(CO)_{12}$ dissolved in the minimum amount of acetone. After a reaction time of 10 min, the slurry was poured onto a polyethylene sheet and allowed to dry in air. The dried, self-supporting clay film was then removed from the polyethylene sheet. These clay films, though turbostratic, have the silicate layers oriented essentially parallel to the plane of the film.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 475 grating spectrophotometer. Spectra of the clay-supported products were obtained as oriented films. The reference compounds were run as KBr disks. X-ray basal spacings were determined for oriented film samples with use of Ni-filtered Cu Kα radiation.

Results and Discussion

The reaction of Na^+–hectorite (1.0 mequiv) in aqueous suspension with $HOs_3(CO)_{12}^+$ (0.10 mmol) in acetone results in a product (I) that contains a bound osmium carbonyl complex. The IR spectrum of I in the terminal CO stretching region is shown in Figure 1, along with the spectra of authentic samples of $[HOs_3(CO)_{12}][PF_6]$ (II) and $Os_3(CO)_{12}$ (III). The CO stretching frequencies are provided in Table I for each compound.

It is apparent from the IR spectrum that the osmium complex in I is immobilized on the clay surface as the *neutral* cluster $Os_3(CO)_{12}$, and not as the initial cation $HOs_3(CO)_{12}^+$. In addition, the X-ray diffraction pattern of I reveals an 001 spacing of 12.5 Å, a value that corresponds to an interlayer thickness of approximately 2.9 Å and the presence of a monolayer of water. Therefore, the bound $Os_3(CO)_{12}$ is not intercalated but instead is bound to the external surfaces of the clay. These conclusions also are compatible with the observation that the carbonyl complex is readily desorbed by washing with acetone.

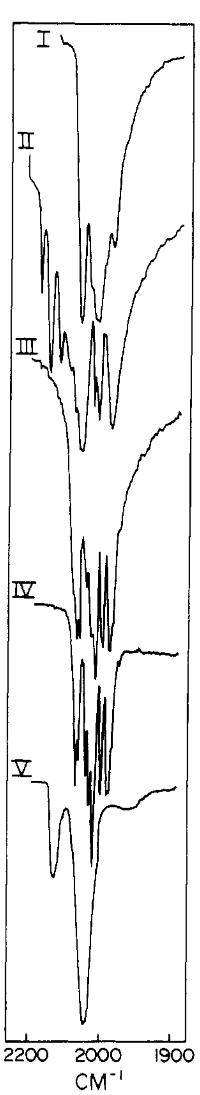

Figure 1. Infrared spectra in the terminal CO stretching region: (I) $Os_3(CO)_{12}$–hectorite preparted from $HOs_3(CO)_{12}^+$; (II) $[HOs_3(CO)_{12}]PF_6$; (III) $Os_3(CO)_{12}$; (IV) $Os_3(CO)_{12}$–hectorite prepared by impregnation of $Os_3(CO)_{12}$; (V) sample I after heating in air at 150 °C for 12 h.

To verify the presence of neutral metal carbonyl clusters in I, we investigated the binding of an authentic sample of $Os_3(CO)_{12}$ to Na^+–hectorite. The neutral carbonyl (0.10 mmol) in acetone solution was mixed at room temperature with a 1 wt % aqueous slurry of hectorite (1.0 mequiv), and the product was air-dried to form an oriented, self-supporting film. This method of sample preparation is analogous to the impregnation techniques typically used for supporting metal carbonyl clusters on silica and alumina. However, these latter supports, unlike clays, do not form highly oriented films when air-dried.

The CO stretching frequencies for the clay-supported $Os_3(CO)_{12}$ prepared by impregnation of $Os_3(CO)_{12}$ (IV) are given in Table I and Figure 1. It is seen that the spectrum is similar to, but not identical with, the spectrum observed for the clay product prepared by reaction with $HOs_3(CO)_{12}^+$ (I). Significantly, the bands for I are broader and less resolved than those observed for IV. Also, the relative intensities of the bands differ for the two products. These spectral differences are due in part to differences in cluster dispersion. For instance, IV exhibits sharp X-ray reflection

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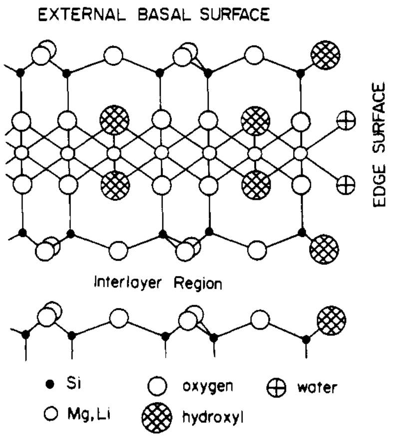


Figure 2. Schematic illustration of the two types of external surfaces for a smectite clay. The edge surfaces are hydroxylated whereas the basal planes contain only siloxane oxygens. Sodium exchange ions (not shown) occupy mainly the interlayer regions.

characteristic of a segregated $Os_3(CO)_{12}$ phase. Phase segregation also is known to occur for metal carbonyls supported on silica and alumina by impregnation methods.[13] In marked contrast to the low degree of cluster dispersion in IV, product I shows no X-ray evidence for a segregated carbonyl phase. Thus we conclude that the supported carbonyl clusters derived from proton dissociation of $HOs_3(CO)_{12}^+$ are highly dispersed with an aggregate size less than 50 Å.

We next consider the type of surface occupied by the dispersed $Os_3(CO)_{12}$ clusters in I. There are two chemically distinct surfaces available for the binding of an adsorbate to a smectite clay particle: edge surfaces and basal surfaces. As shown in Figure 2, the basal surfaces are composed of siloxane-type oxygen atoms, whereas the edge surfaces are hydroxylated. $Os_3(CO)_{12}$ is known to react with surface hydroxyls of silica[6,7] and alumina[6-8] to give molecular species such as those represented in eq 1 for a silica surface. This

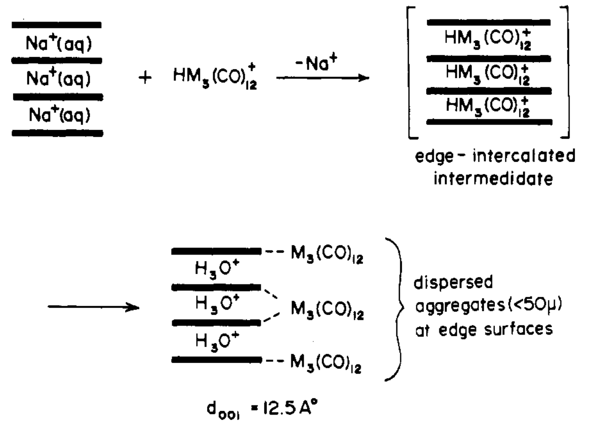
$$2(SiOH) + Os_3(CO)_{12} \xrightarrow{\Delta} [(\equiv SiO)_2Os(CO)_n]_x \quad (1)$$
$$n = 2, 3$$

reaction provides a chemical means of distinguishing between $Os_3(CO)_{12}$ at edge and basal plane sites. Under conditions where surface migration is slow, as is the case with our oriented film samples (see below), edge-bound clusters should react according to eq 1, whereas clusters adsorbed on basal planes should be stable.

In a typical smectite clay particle composed of a few tens of layers, each 9.6 Å thick and approximately 10^4 Å in diameter, the basal surface area is at least 1 order of magnitude greater than the edge surface area. In the case of IV, where much of the $Os_3(CO)_{12}$ is segregated as a separate phase, we might expect the cluster to migrate onto the basal surfaces and eventually to edge sites for reaction with hydroxyl groups. For instance, $Os_3(CO)_{12}$ supported on alumina by impregnation reacts according to eq 1 at 150 C, even though the cluster initially is poorly dispersed at room temperature. However, the highly oriented nature of our clay film samples impedes migration of the metal clusters across the basal planes. Thus we observe no reaction of IV after 12 h at 150 °C. The importance of sample orientation in impeding surface migration was demonstrated by impregnating a random, freeze-dried clay sample with $Os_3(CO)_{12}$ and observing reaction according to eq 1.

In contrast to the behavior of the neutral clusters in IV, the clusters in I do react in air at 150 °C to form new surface species, *despite the oriented condition of the sample.* As shown in Figure 1 and Table I, the new surface species exhibit three terminal CO stretching frequencies. These three bands are indicative[6-8] of both the molecular tricarbonyl (n = 3) and the bicarbonyl (n = 2) species depicted in eq 1. On the basis of these observations, we may conclude that the initial binding of $HOs_3(CO)_{12}^+$ and the subsequent formation of $Os_3(CO)_{12}$ occurs at or near the edge surface sites.

Scheme I.



The selective formation of $Os_3(CO)_{12}$ from $HOs_3(CO)_{12}^+$ at edge surfaces may be explained in terms of Scheme I, wherein M = Os. Unlike the neutral cluster, the protonated cluster is capable of ion exchange with intercalated Na^+. This exchange reaction provides the driving force for the initial binding of the cluster cation near the edge of the clay platelet. However, the cluster cation is unstable because the aquated interlayer is more basic than the corresponding neutral cluster. Though $HOs_3(CO)_{12}^+$ undergoes deprotonation in acetone/H_2O even in the absence of clay, the deprotonation in homogeneous solution[12] is slower than the rate of ion exchange, which occurs in a matter of seconds. Consequently, it is the *protonated* complex that binds initially to the clay. The proton is then transferred to interlayer water, and the neutral cluster is selectively formed in a dispersed state at edge sites where a reaction according to eq 1 can occur.

Finally, we should note that the formation of mononuclear $[(\equiv SiO)_2Os(CO)_n]_x$ from $Os_3(CO)_{12}$ on silica[6,7] according to eq 1 is known to occur via a $[HOs_3(CO)_{10}$–O–surface] intermediate. The same intermediate has been detected on alumina.[6-8] We do not observe this intermediate species upon heating the clay system in air at 150 °C, as expected under oxidizing conditions. Attempts to observe the intermediate by heating the $HOs_3(CO)_{12}^+$–hectorite reaction product in vacuo at various temperatures in the range 100–150 °C resulted in complex IR spectra indicative of the mononuclear complex, the $Os_3(CO)_{12}$ cluster, and possibly a $HOs_3(CO)_{10}$–O–clay intermediate. However, the metal cluster intermediate is formed as the principal product when Na^+–hectorite that has been predried in vacuo at 350 °C is allowed to react with $Os_3(CO)_{12}$ in refluxing octane (125 °C) under argon for 24 h. The presence of ($HOs_3(CO)_{10}$–O–surface) is clearly indicated by CO bands in the IR spectrum at 2115 w, 2071 m, 2055 s, 2020 vs, and 2001 sh cm^{-1}, in agreement with earlier assignments.[6-8] Differences in reaction conditions are expected to influence cluster reactivity. For instance, Knözinger[8] has noted that the stability of triosmium clusters on silica and alumina depends on the surface hydroxyl content, as well as on the presence of water or oxygen. Such factors also appear to be important in governing the reactivity of the triosmium clusters in the clay-supported system.

Conclusions

Although the initial intent of this work was to intercalate $HOs_3(CO)_{12}^+$ cluster cations in smectite clay, the cations proved to be unstable with regard to proton dissociation at exchange sites near the platelet edges. Thus other routes must be explored to achieve carbonyl cluster intercalation in clays.[14] Nevertheless, the observed chemistry is rather novel in that the metal clusters are selectively dispersed at or near edge surface sites and the degree of cluster dispersion is much greater than can be achieved by

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impregnation of neutral clusters from solution. These results may have important implications for optimizing the turnover frequencies of clay-supported metal catalysts. Also, the surface selectivity of the reaction may be useful for estimating the edge surface area of layered silicates and for selectively decorating edge surfaces with heavy elements for studies of clay particle morphology by electron microscopy.

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Registry No. $HOs_3(CO)_{12}^+$, 47558-24-7; $Os_3(CO)_{12}$, 15696-40-9; hectorite, 12173-47-6.

Contribution from the Department of Chemistry,
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Magnetic Circular Dichroism Spectra for Thallium(I), Lead(II), and Bismuth(III) Ions in Aqueous Acid Solution

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The metal ions of $6s^2$ electronic configuration, Tl(I), Pb(II), and Bi(III), in aqueous acid solution each exhibit an intense broad band in the UV region 4.2–5.2 μm^{-1}. These bands have been assigned as $6s^2 \rightarrow 6s6p$ metal-localized transitions primarily on the basis of their analogy to the intense UV absorptions observed for a variety of ns^2 ions doped into cubic alkali-metal halide lattices.[1] A considerable body of experimental data has been accumulated for these doped lattices,[1-5] including absorption, magnetic circular dichroism (MCD), and emission spectra, with some studies over a wide temperature range. The ns^2 ions are believed to occupy cubic sites, and the states of the excited $nsnp$ configuration that give rise to the UV bands (labeled A, B, and C in order to increasing energy) are designated $^3T_{1u}$ (allowed by spin–orbit coupling, intensity parallels ζ_{np}), $^3E_u + {}^3T_{2u}$ (weak, both states vibronic), and $^1T_{1u}$ (intense, allowed), respectively, in order of increasing energy.[2] These states correlate with $^3P_1$, $^3P_2$, and $^1P_1$ atomic states of the free ions. A $^3A_{1u}$ state correlating with $^3P_0$ is also predicted but not observed because it is strongly forbidden.

In contrast to the solid-state studies, the nature of the excited state(s) exhibited by the ions in solution is not well understood. In fact the structure of the solution species for the $6s^2$ ions in acid is not known for certain. The coordination number of Tl(I) is ill-defined, similar to that of an alkali-metal ion,[6] and both Pb(II) and Bi(III) are known to form polynuclear hydroxo- or oxo-bridged clusters as the pH is raised. Thus $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_6^{6+}$ ions have been shown to crystallize from lead(II) perchlorate solutions,[7] and the $Bi_6O_4(OH)_4^{6+}$ ions have been identified in solution and in a solid perchlorate salt.[8]

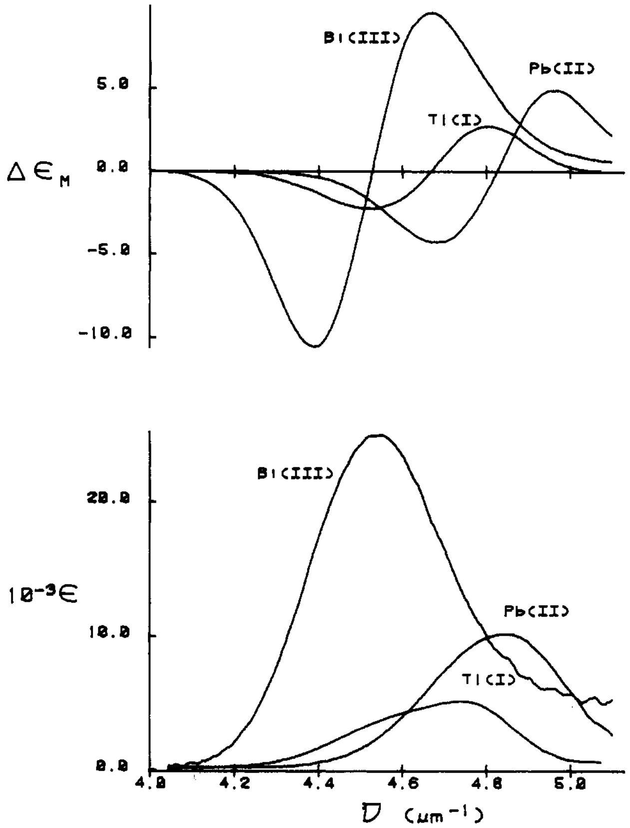

Figure 1. Electronic absorption (lower curves) and MCD (upper curves) spectra for Tl(I) in 0.100 M $HClO_4$, Pb(II) in 0.100 M $HClO_4$, and Bi(III) in 1.00 M $HClO_4$.

Table I. Spectral Data

absorption				MCD		
λ_{max}, nm	$\bar{\nu}$, μm^{-1}	ϵ, $M^{-1}\ cm^{-1}$	$\bar{D}_0$[a]	$\bar{\nu}$, μm^{-1}	$\Delta\epsilon_M$, $(M\ cm\ T)^{-1}$	$\bar{A}_1/\bar{D}_0$[a]
Tl(I) in 0.100 M $HClO_4$						
213	4.69	4860	1.4	4.48 4.62 4.76	−2.24 0 +2.76	+1.9[b]
Pb(II) in 0.100 M $HClO_4$						
208	4.80	9890	2.0	4.63 4.78 4.91	−4.25 0 +4.95	+2.1[c]
Bi(III) in 1.00 M $HClO_4$						
223	4.49	23800	5.4	4.35 4.49 4.63	−10.5 0 +9.6	+1.9[d]

[a] From a moment analysis of the data (see ref 9 for details). [b] $\bar{B}_0/\bar{D}_0 = -8 \times 10^{-5}/cm^{-1}$. [c] $\bar{B}_0/\bar{D}_0 = -5 \times 10^{-4}/cm^{-1}$. [d] $\bar{B}_0/\bar{D}_0 = -1 \times 10^{-4}/cm^{-1}$.

The purpose of this note is to report some MCD spectra[9] for Tl(I), Pb(II), Bi(III) in perchloric acid solution. These spectra provide some additional spectroscopic information on which to base the assignment of the UV absorptions and hopefully provide some insight into the nature of the solution species and their excited states.

Experimental Section

Solutions of Tl(I) were prepared by dissolving thallium metal in $HClO_4$ and diluting to give 0.100 M $HClO_4$; solutions of Pb(II) were prepared by dissolving $Pb(ClO_4)_2 \cdot 3H_2O$ in 0.100 M $HClO_4$, and those

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