has been extended to polar media with some success by Buckingham.[12] However, the necessary data are not yet available for hydrogen fluoride systems, and we have not attempted any correlations with such theory. It is obvious that the effects are small and do not involve the formation of any new bonds. Indeed, the highly symmetrical ground states are essentially unperturbed. At the temperature at which the Raman spectra are observed, a significant number of vibrationally excited states are occupied and it is not clear to what extent these affect the observed band positions even for the pure materials.

We believe such slight shifts as are observed in solution can be rationalized in terms of the effect of the dipole oriented atmosphere provided by the solvent on the polarizability ellipsoid associated with each Raman band, but no detailed analysis is yet available.

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The Donor Properties of Pyrophosphate Derivatives. V. Complexes of $MoOCl_3$, UO_2^{2+}, and Th^{4+} with Octamethylpyrophosphoramide

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We have previously reported the isolation and characterization of complexes of octamethylpyrophosphoramide (OMPA) with over 30 metal ions.[1-4] The general characteristics of OMPA as a ligand are (1) formation of air-stable complexes with metal ions, (2) coordination as a bidentate ligand through phosphoryl oxygens, (3) enhancement of the maximum coordination number of the metal ion, and (4) essentially electrostatic bonding to metal ions as shown by low *Dq* and β parameters toward Ni(II).

The purpose of the present study was to determine whether OMPA could form stable complexes with oxycations and Th^{4+}.

Experimental Section

Chemicals.—Molybdenum pentachloride was obtained from K and K Laboratories and used without further purification. Both hydrated uranyl perchlorate and hydrated thorium perchlorate were obtained from G. Frederick Smith Chemical Co. Fisher reagent grade acetonitrile and Eastman Organic Spectrograde nitromethane were used as solvents for spectral and conductance studies.

Conductance Measurements.—Molar conductivities of the complexes in both acetonitrile and nitromethane were measured with a Model RC 16B2 conductance bridge manufactured by Industrial Instruments, Inc. A dip type cell with a cell constant of 0.1 cm^{-1} was used.

Spectral Measurements.—Infrared spectra of Nujol mulls and KBr pellets of the complexes were recorded with a Beckman IR-7. Visible and ultraviolet spectra were recorded with a Beckman Model DK-2A.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Complexes. (1) **$MoOCl_3 \cdot OMPA$.**—An alcoholic solution of $MoOCl_3$ was prepared by dissolving 1.1 g (0.0046 mole) of $MoCl_5$ in 30 ml of anhydrous ethanol.[5] Reaction occurs immediately to give a green solution of $MoOCl_3$. Addition of 2.1 g of OMPA (0.007 mole) caused a pale green solid to precipitate from solution. The product was filtered and washed with ether.

Anal. Calcd for $MoOCl_3 \cdot [C_8H_{24}N_4O_3P_2]$: C, 19.9; H, 4.77; N, 11.1. Found: C, 19.3; H, 4.89; N, 11.1.

A Mechrolab osmometer was used to obtain the molecular weight of $MoOCl_3 \cdot OMPA$ in acetonitrile at 37°. Measurements were made for 0.02–0.09 *M* solutions.

Anal. Calcd for $MoOCl_3 \cdot [C_8H_{24}N_4O_3P_2]$: mol wt, 505. Found: mol wt, 470 ± 30.

Molar conductance values of 14 and 7 $cm^2\ ohm^{-1}\ mole^{-1}$ were obtained at 23° for 1×10^{-3} *M* solutions of $MoOCl_3 \cdot OMPA$ in nitromethane and acetonitrile, respectively.

(2) **$UO_2(ClO_4)_2 \cdot 3OMPA$.**—One gram (0.002 mole) of $UO_2(ClO_4)_2 \cdot 4H_2O$ was dehydrated with 5 ml of 2,2-dimethoxypropane for 1 hr. Three grams (0.01 mole) of OMPA was added to the resulting solution. Some precipitation occurred about 1 min after adding OMPA. Anhydrous ether was added to precipitate additional product. An 80% yield (2.1 g) of $UO_2(ClO_4)_2 \cdot 3OMPA$ was obtained.

Anal. Calcd for $UO_2[C_8H_{24}N_4O_3P_2]_3(ClO_4)_2$: C, 21.7; H, 5.42; N, 12.6. Found: C, 22.0; H, 5.61; N, 12.5.

A molar conductance value of 162 $cm^2\ ohm^{-1}\ mole^{-1}$ was obtained for a 9.6×10^{-4} *M* solution of $UO_2(ClO_4)_2 \cdot 3OMPA$ in nitromethane at 23°.

(3) **$Th(ClO_4)_4 \cdot 4OMPA$.**—Hydrated $Th(ClO_4)_4 \cdot 6H_2O$ (0.74 g, 0.001 mole) was dissolved in 10 ml of acetone. A 5:1 ratio of OMPA (1.43 g) was added to the solution. A white solid precipitated from solution when anhydrous ether was added. The product was washed several times with ether and dried under vacuum for 2 hr at room temperature. A 97% yield was obtained.

Anal. Calcd for $Th[C_8H_{24}O_3P_2]_4(ClO_4)_4$: C, 21.6; H, 5.41; N, 12.6. Found: C, 21.7; H, 5.75; N, 12.3.

The molar conductance was measured at 23° for a 8.89×10^{-4} *M* nitromethane solution and found to be 315 $cm^2\ ohm^{-1}\ mole^{-1}$.

Results and Discussion

$MoOCl_3 \cdot OMPA$.—The complex is a nonelectrolyte and monomeric in acetonitrile (Experimental Section). The ultraviolet and visible absorption peaks for $MoOCl_3 \cdot OMPA$ (Table I) are similar to those reported for other adducts of $MoOCl_3$.[6,7] On the basis of spectral assignments made by previous workers for the MoO^{3+} ion,[8,9] the bands for $MoOCl_3 \cdot OMPA$ at 13,700 and 19,000 cm^{-1} have been assigned as the transitions

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TABLE I

ULTRAVIOLET AND VISIBLE SPECTRAL DATA IN ACETONITRILE

Compound	λ_{max}, mμ (cm^{-1})	ϵ
$MoOCl_3 \cdot OMPA$	240 (41,700)	4870
	306 (32,700)	2900
	447 (22,400)	43
	732 (13,650)	21

$^2B_2 \rightarrow {}^2E(1)$ and $^2B_2 \rightarrow {}^2B_1$. The bands at 32,700 and 41,700 cm^{-1} are charge-transfer bands, as indicated by their high molar absorptivities.

The Mo═O stretching frequency appears at 990 cm^{-1} in $MoOCl_3 \cdot OMPA$, which is slightly higher than Mo═O stretching frequencies previously reported.[6] These include 965 cm^{-1} for $[MoOCl_5]^{2-}$, 979 cm^{-1} for $MoOCl_3 \cdot bipy$, 967 cm^{-1} for $MoOCl_3 \cdot 2(C_6H_5)_3PO$, and 980 cm^{-1} for $MoOCl_3 \cdot 2CH_3CN$. The decrease in the P═O stretching frequency and the increase in the P—N stretching frequencies are support for coordination of molybdenum with the phosphoryl oxygens. In conclusion, the experimental evidence supports the presence of six-coordinate molybdenum in a molecular complex in which $[Mo{=}O]^{3+}$ is attached to three chlorides and two phosphoryl oxygens.

$UO_2(ClO_4)_2 \cdot 3OMPA$.—At present, there is general agreement that UO_2^{2+} can form complexes with four, five, and six donor sites.[10] The molar conductance of $UO_2(ClO_4)_2 \cdot 3OMPA$ in nitromethane is in the range expected for 2:1 electrolytes.[11] The shifts in the P═O and P—N stretching frequencies (Table II) are in the direction expected for formation of chelate rings through the phosphoryl oxygens. It was not possible to assign a U═O stretching frequency since this occurs in the same region as P—N$_1$ (900–1000 cm^{-1}). On the basis of these experimental data, a likely structure for $UO_2(ClO_4)_2 \cdot 3OMPA$ is one in which the phosphoryl oxygens from the OMPA molecules form chelate rings in the equatorial positions around $[O{=}U{=}O]^{2+}$. This would give a structure similar to that found for $NaUO_2(C_2H_3O_2)_3$[12] except that the chelate rings involving OMPA molecules would be puckered.

TABLE II

INFRARED SPECTRAL ASSIGNMENTS (CM^{-1})[a]

Band	OMPA	$Th(ClO_4)_4 \cdot$ 4OMPA[b]	$UO_2(ClO_4)_2 \cdot$ 3OMPA[c]	$MoOCl_3 \cdot$ OMPA[c]
P═O	1238 s	1140 s	1160 s, 1185 sh	1188 s
P—N$_1$	988 s	995 s	1000 s	1018 m
P—N$_2$	756 w	790, 765 w	795 w, 770 m, 775 m	795 w
P—O—P	915 s	905 s	920 s	910 s
Metal—O	...	...	...	990 s
ClO_4^-	...	1090 s	1090 s	...

[a] Intensities of bands: s, strong; m, medium; w, weak; sh, shoulder. [b] KBr pellet. [c] Nujol mull.

$Th(ClO_4)_4 \cdot 4OMPA$.—The elemental analysis, infrared spectral data, and conductivity measurements support the assignment of a coordination number of eight to Th^{4+}. The decrease in the P═O stretching frequency (98 cm^{-1}) as well as the increase in P—N$_1$ and P—N$_2$ stretching frequencies are support for coordination of the Th^{4+} to the phosphoryl oxygens of OMPA.

The acetylacetonate (acac) complex of Th^{4+}, Th(acac)$_4$, has an Archimedian antiprismatic structure.[13] The ability of OMPA to coordinate as a bidentate ligand and the similarity in stoichiometry and ring size in the systems $Th(ClO_4)_2 \cdot 4OMPA$ and Th(acac)$_4$ lead us to predict an Archimedian antiprismatic structure for $Th(ClO_4)_4 \cdot 4OMPA$.

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The Preparation and Electrical Properties of Niobium Selenide and Tungsten Selenide[1]

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Revolinsky, *et al.*,[2] have shown that $NbSe_2$ has both a hexagonal two-layer structure of the NbS_2 type and a four-layer structure of a new structure type. The structures are composed of trigonal prismatic $NbSe_2$ slabs.

The anions are arranged as two parallel close-packed sheets with the metal atoms occupying trigonal prismatic sites. The arrangement of the cations with respect to each other is that of a close-packed hexagonal layer. The $NbSe_2$ slabs can be stacked in a number of different ways with one, two, three, four, or six $NbSe_2$ layer sequences being the usual arrangements. Figure 1a illustrates the two-layer sequence for $NbSe_2$. For both the two-layer (ϵ) and the four-layer (ζ) structures, the coordination within the "molecular" slabs is trigonal prismatic.

Beerntsen, *et al.*,[3] have shown that the two-layer $NbSe_2$ structure is superconducting. The high-temperature four-layer modification was also superconducting. Revolinsky, *et al.*,[2] reported that the superconducting transition temperature for the two-layer phase was 7°K.

Brixner[4] has described the preparation, structure, and thermoelectric properties of WSe_2. WSe_2 is a rather well-behaved semiconductor with a relatively low electrical conductivity (increasing with temperature) and a high Seebeck coefficient. Figure 1b shows a two-layer sequence for WSe_2. Both WSe_2 and $NbSe_2$ crystallize in the D_{6h}^4-P6/mmc space group and have exactly the same anion packing. It can be seen from Figure 1 that only the cation arrangement differs.

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