

The separation of the 4A and 4E components of the 4T states may be expressed in terms of the first-order trigonal field parameter, v , as $v/2$.⁶ Assuming that the peaks at 13,350 and 14,600 cm^{-1} are the trigonal components of the ${}^4T_{2g}$ term, we may calculate v to be 2500 cm^{-1} . It is not possible to obtain the sign of the trigonal field as all of the transitions in question are vibronically allowed in D_{3d} symmetry. (The shift by the absorption maxima toward the blue region of the spectrum and the accompanying decrease in over-all intensity with decreasing temperature clearly demonstrate the vibronic nature of the intensity mechanism.)

If, however, we look at the absolute value of the trigonal field, $|v|$, we see that the axial distortion in NaCrS_2 ($|v| = 2500$) is much larger than in Cr_2O_3 ($|v| = 700$)⁷ or even in ruby ($|v| = 1425$)⁶ where the Cr^{3+} ion finds itself in a site which is ~ 0.1 Å too small for it.

If only a first-order trigonal field is active, the center of gravity of the ${}^4T_{2g}$ level is maintained and we may calculate a value for Dq . Since the energy of the transition ${}^4A_{2g} \rightarrow {}^4T_{2g}$ is equal to $10Dq$ we find that for NaCrS_2 Dq is 1400 cm^{-1} . Further, if the shoulder at $\sim 18,000$ cm^{-1} is taken as the lower trigonal component of the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition, we may calculate, using the strong-field matrix⁸ for 4T_1 and a value of 18,625 cm^{-1} ($18,000 + (v/4)$) for $E({}^4A_1 \rightarrow {}^4T_1)$, the value of the Racah parameter B to be 440 cm^{-1} . Since the free-ion value, B_0 , for Cr^{3+} is 918 cm^{-1} ,⁹ we may estimate the nephelauxetic ratio β ($B/B_0 = \beta$) for NaCrS_2 to be 0.480, a value which is nearly the same as the $\beta = 0.484$ reported by Companion and Mackin.¹⁰

Using the data of McClure, which were also obtained by single-crystal methods, we find for Cr_2O_3 $B = 503$ cm^{-1} and $\beta = 0.549$. Contrary to Companion and Mackin,¹⁰ we feel this indicates a real difference between the degree of covalence in the Cr-O and Cr-S bonds in Cr_2O_3 and NaCrS_2 .

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Solution Properties of Some Hexafluorides in Anhydrous Hydrogen Fluoride^{1,2}

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A long-standing interest in hexafluorides has been stimulated recently by the most interesting properties

of xenon hexafluoride. Among the more surprising chemical properties of this compound are the extensive solubility in anhydrous hydrogen fluoride and the high electrical conductivity of the resulting solutions.⁴

Among the hexafluorides, xenon hexafluoride is the clear exception. Stable hexafluorides are expected to dissolve in liquid hydrogen fluoride without fluoride ion transfer,⁵ because of the geometrical stabilization of the octahedrally symmetrical compounds. With a few exceptions, however, systematic studies of dilute solutions in hydrogen fluoride have not been reported, even if we include studies of the octahedral hexafluoro anions.^{6,7}

In the present work, the electrical conductivities and Raman spectra of solutions of molybdenum, tungsten, uranium, rhenium, and osmium hexafluorides in hydrogen fluoride were investigated in order to determine the degree of ionization of these compounds in such solutions. The solubilities were also determined.

Hydrogen fluoride absorbs in the infrared and the absorption is quite intense in the region near 600 cm^{-1} where many metal-fluorine vibration bands are observed. But the Raman spectrum can be observed without interference and for the highly symmetrical hexafluoride molecules the Raman spectrum is striking.

Results are presented in Tables I–III.

TABLE I
THE SOLUBILITY OF SOME HEXAFLUORIDES IN
ANHYDROUS HYDROGEN FLUORIDE AT ROOM TEMPERATURE

MF ₆	Moles of MF ₆ /1000 g of HF
MoF ₆	1.50
WF ₆	3.14
UF ₆ ^a	0.49
ReF ₆	1.75
OsF ₆ ^b	0.97
XeF ₆ ^c	8.6

^a G. P. Rutledge, R. L. Jarry, and W. Davis, Jr., *J. Phys. Chem.*, **57**, 541 (1953). ^b Value may be affected by reaction with container, see text. ^c Ref 4.

Experimental Section

Materials.—Hydrogen fluoride with a specific conductivity of 10^{-5} – 10^{-6} ohm⁻¹ cm^{-1} at 0° was prepared by fractional distillation as described elsewhere.⁸ Uranium hexafluoride (Oak Ridge National Laboratory) and tungsten and molybdenum hexafluorides (General Chemical Division of Allied Chemical Corp., high purity material) were additionally purified by repeated pumping off of any hydrogen fluoride impurity at -78° .⁹ Rhenium

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Paper presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(3) On leave from Nuclear Institute, "Josef Stefan," Ljubljana, Yugoslavia.

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TABLE II
THE ELECTRICAL CONDUCTIVITY OF SOME MF₆
SOLUTIONS IN ANHYDROUS HYDROGEN FLUORIDE AT 0°

MF ₆	$\kappa_{\text{soln}} \times 10^6$ ohm ⁻¹ cm ⁻¹	$\kappa_{\text{soln}} \times 10^8$ ohm ⁻¹ cm ⁻¹	$\kappa_{\text{soln}}^{\text{cor}} \times 10^5$ ohm ⁻¹ cm ⁻¹	C, M	μ_{soln} , ohm ⁻¹ cm ⁻¹ mole ⁻¹	α , %
MoF ₆	4.56	13.01	8.45	0.8	0.1	0.03
WF ₆	2.59	5.88	3.29	0.09	0.35	0.1
UF ₆	7.25	8.70	1.45	0.003	4.8	1
ReF ₆	3.71	10.97	7.26	0.09	0.7	0.2
OsF ₆ ^a	8.25	62	54	0.06	9	2.3
XeF ₆ ^b			44900	0.75	60	15

^a Value may be affected by reaction with container, see text.

^b Ref 4.

TABLE III
RAMAN BANDS $\Delta\nu$ (CM⁻¹) OF SOME HEXAFLUORIDES IN
ANHYDROUS HYDROGEN FLUORIDE COMPARED WITH THE BANDS
FOUND FOR PURE MATERIALS

		HF soln ^{a,b}	As- signed ^d	Pure gas	MF ₆ liquid		Shift
MoF ₆	ν_1	744	741	741 ^f	736 ^g	741 ^h	+3
	ν_2	651	643	643	641	645	+8
	ν_5	320	(312)		319	322	+8
WF ₆	ν_1	775	(771)		769 ^g	772 ^h	+4
	ν_2	678	(673)		670	672	+5
	ν_5	325	(315)		322	316	+10
UF ₆	ν_1	668	667	666.6 ⁱ	666 ^j		+1
	ν_2	527	535	(535)	524		-8
ReF ₆ ^e	ν_1	756	755	755 ^k	753 ^l		+1
	$\nu_2(\bar{I})$	578	587	(596)	600		-9
	$\nu_5(\bar{I})$	249	248	246			+1
OsF ₆	ν_1	734	(733)		733 ^m		+1

^a The concentrations of the HF solutions: MoF₆, 1.50 molal; WF₆, 1.95 molal; UF₆, 0.57 molal; ReF₆, 1.38 molal; OsF₆, 0.65 molal. ^b The estimated uncertainty in the frequencies is ± 0.5 cm⁻¹ for ν_1 and $\pm 1-2$ cm⁻¹ for ν_2 and ν_5 . The ν_2 of ReF₆, which is broadened and depressed because of the Jahn-Teller distortion (ref c), is somewhat more uncertain (± 5 cm⁻¹, see Figure 1). ^c B. Weinstock and G. L. Goodman, *Advan. Chem. Phys.*, **9**, 169 (1965). ^d Values assigned for the gas by Weinstock and Goodman (ref c). Values in brackets were obtained from combination bands. ^e The spectrum is affected by a dynamic Jahn-Teller distortion (ref c). ^f H. H. Claassen, H. Selig, and J. G. Malm, *J. Chem. Phys.*, **37**, 2880 (1962). ^g K. N. Tanner and A. B. F. Duncan, *J. Am. Chem. Soc.*, **73**, 1164 (1951). ^h T. G. Burke, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **20**, 447 (1952). ⁱ H. H. Claassen, B. Weinstock, and J. G. Malm, *ibid.*, **25**, 426 (1956). ^j H. H. Claassen, unpublished observation, quoted in ref c. ^k H. H. Claassen, J. G. Malm, and H. Selig, *J. Chem. Phys.*, **36**, 2890 (1962). ^l J. Gaunt, *Trans. Faraday Soc.*, **50**, 209 (1954). ^m B. Weinstock, H. H. Claassen, and J. G. Malm, *J. Chem. Phys.*, **32**, 181 (1960).

and osmium hexafluorides were prepared by high-pressure fluorination of the metals with fluorine¹⁰ and purified as mentioned above.

The purity of the hexafluorides was checked by looking for foreign bands in the infrared spectra of their vapors. A 10-cm nickel cell with silver chloride windows and a Beckman IR-12 spectrometer were used for this purpose.

Apparatus and Procedure.—All of the solutions used in this work were prepared on a vacuum line with all critical parts fabricated from polychlorotrifluoroethylene (Kel-F).¹¹

The mixing tubes were fabricated from 3/8 in. o.d., 0.060 in. wall Kel-F extruded tubing. The tubes were hot pinched to-

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gether at one end and at the other end flare connected to the adapter attached to an all-Kel-F valve.¹¹ For the electrical conductivity measurements, Kel-F low-conductivity cells (cell constant about 0.04 cm⁻¹) with bright platinum electrodes¹¹ and a conventional conductivity bridge (Industrial Instruments Inc., Model RC-18) were used. The conductivities were measured at 0°. It should be mentioned here that these hexafluorides slowly react with Kel-F causing a time dependence of the conductivity data. The rate of reduction of these oxidizing hexafluorides by Kel-F surfaces varies somewhat depending on the method of preparation. Well-seasoned extruded tubing appears to be best; molded tubes are somewhat more reactive. To what extent these effects are due to lower molecular weight fragments, impurities, or slow reaction with the bulk phase itself is not understood. In practice the change in conductivity with time for most solutions is rather slow (<2%/hr), and a simple extrapolation back to zero time is feasible. However, in the case of the most reactive of the investigated hexafluorides, osmium hexafluoride, the reaction with the Kel-F seems to be rather fast (~20%/hr). That is probably the cause for the high electrical conductivity of its solution and also makes the solubility data for this compound unreliable.

The Raman cell (total volume 7 ml) was a sapphire tube (3/8 in. o.d., 4 in. long) fitted at one end with a sapphire window and at the other end with an all-Kel-F extension and valve. The parts were assembled with the aid of Teflon Swagelok fittings. The Raman measurements were made with a Cary Model 81 Raman spectrometer. Sapphire by itself shows a few Raman bands which have to be taken into account in the evaluation of the spectra. Concentrations of the solutions were determined by weight.

Note that the specific conductivities of the solutions are very low, especially when corrected for the specific conductivity of the hydrogen fluoride batch used in the experiment. As noted above, there is some uncertainty in the value for osmium hexafluoride.

As shown in Table III, the Raman spectra of the hexafluoride solutions in anhydrous hydrogen fluoride fit the pattern established for the octahedral molecule found in the gas and liquid.

The principal symmetric vibration ν_1 for each of hexafluoride solutions appears to be slightly shifted to higher frequency for the solution as compared with the pure gas or liquid. Similar shifts were observed for the other two Raman-active vibrations, ν_2 and ν_5 . These bands, however, are usually broader and less intense than the central symmetrical breathing vibration. Both for the pure substance and for the solution, the band centers can only be determined with some uncertainty and it is difficult to establish a clear trend in their relative values (Figure 1).

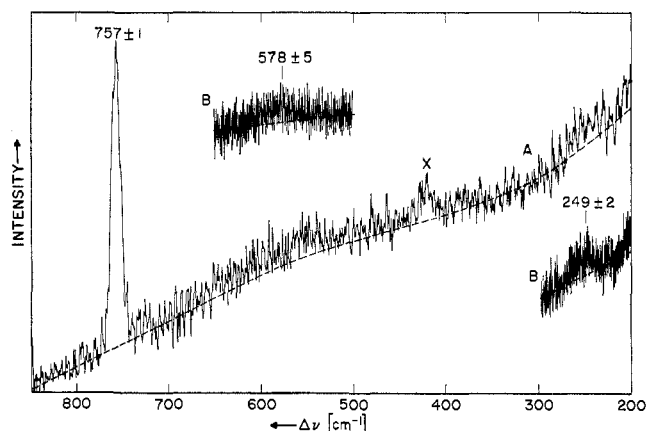


Figure 1.—Raman spectrum of ReF₆-HF 1.4 m solution: X, band due to the sample tube; A, scanning speed 0.25 cm⁻¹/sec; B, scanning speed 0.05 cm⁻¹/sec.

The effect of the shift from pure gas to solution in such solvents as hydrogen fluorides has never been adequately studied. A theory explaining the frequency shifts due to solvent effects

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 Octamethylpyrophosphoramidate

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We have previously reported the isolation and characterization of complexes of octamethylpyrophosphoramidate (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 oxyanions 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) $\text{MoOCl}_3 \cdot \text{OMPA}$.—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 $\text{MoOCl}_3 \cdot [\text{C}_8\text{H}_{24}\text{N}_4\text{O}_3\text{P}_2]$: 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 $\text{MoOCl}_3 \cdot \text{OMPA}$ in acetonitrile at 37° . Measurements were made for 0.02–0.09 M solutions.

Anal. Calcd for $\text{MoOCl}_3 \cdot [\text{C}_8\text{H}_{24}\text{N}_4\text{O}_3\text{P}_2]$: mol wt, 505. Found: mol wt, 470 ± 30 .

Molar conductance values of 14 and $7 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ were obtained at 23° for $1 \times 10^{-3} M$ solutions of $\text{MoOCl}_3 \cdot \text{OMPA}$ in nitromethane and acetonitrile, respectively.

(2) $\text{UO}_2(\text{ClO}_4)_2 \cdot 3\text{OMPA}$.—One gram (0.002 mole) of $\text{UO}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ 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 $\text{UO}_2(\text{ClO}_4)_2 \cdot 3\text{OMPA}$ was obtained.

Anal. Calcd for $\text{UO}_2[\text{C}_8\text{H}_{24}\text{N}_4\text{O}_3\text{P}_2]_3(\text{ClO}_4)_2$: C, 21.7; H, 5.42; N, 12.6. Found: C, 22.0; H, 5.61; N, 12.5.

A molar conductance value of $162 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ was obtained for a $9.6 \times 10^{-4} M$ solution of $\text{UO}_2(\text{ClO}_4)_2 \cdot 3\text{OMPA}$ in nitromethane at 23° .

(3) $\text{Th}(\text{ClO}_4)_4 \cdot 4\text{OMPA}$.—Hydrated $\text{Th}(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ (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 $\text{Th}[\text{C}_8\text{H}_{24}\text{O}_3\text{P}_2]_4(\text{ClO}_4)_4$: 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 $8.89 \times 10^{-4} M$ nitromethane solution and found to be $315 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$.

Results and Discussion

$\text{MoOCl}_3 \cdot \text{OMPA}$.—The complex is a nonelectrolyte and monomeric in acetonitrile (Experimental Section). The ultraviolet and visible absorption peaks for $\text{MoOCl}_3 \cdot \text{OMPA}$ (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 $\text{MoOCl}_3 \cdot \text{OMPA}$ at 13,700 and $19,000 \text{ cm}^{-1}$ have been assigned as the transitions

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