Table III. Raman Stretching Frequencies for $OPCl_3$, $OSeCl_2$, and $OSCl_2$ Coordinated to $SbCl_5$ at 77 K and Frequency Shifts ($\Delta\nu$) Due to the Coordination (cm^{-1})[a]

$SbCl_5 \cdot OPCl_3$		$SbCl_5 \cdot OSeCl_2$		$SbCl_5 \cdot OSCl_2$		Assignments (M = P, Se, S)
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	
629 vw	+40	405.5 sh, m	+55	490.5–495 w	+50	$\nu(MCl)_{asym}$
632						
529 w	+40	412.5 vs	+25	515–520 w	+25	$\nu(MCl)_{sym}$
1161 sh	−140	757	−195	1160–1164.5	−165	$\nu(MO)$
		765 w		1075.5 w		

[a] Key: w, weak; m, medium; sh, shoulder; v, very.

are assigned to bending modes (OSbCl) of e symmetry.

The bending vibration $\delta(b_2)$(ClSbCl) can be easily assigned since it is expected to appear near 170 cm^{-1} when allowance is made for correlation between this mode and its corresponding mode $\delta(f_{2g})$(ClSbCl) appearing at 170 cm^{-1} in the Raman spectrum of the $SbCl_6^-$ anion.[13] The Raman spectra of all of the complexes studied present a strong depolarized band at 180 ± 10 cm^{-1} which has been assigned to the b_2 mode.

Ligand Vibration Shifts. $POCl_3$ and $SeOCl_2$ give molecular complexes with $SbCl_5$ and are coordinated through the oxygen atom.[5,6] In the Raman spectra of these adducts, the coordination is shown by the shifts of the symmetric and asymmetric normal modes ν(PCl), ν(SeCl), ν(PO), and ν(SeO) with respect to the spectra of the free oxychlorides[14,15] (Table III). As expected, the ν(PCl) and ν(SeCl) frequencies are increased whereas ν(PO) and ν(SeO) are strongly lowered. As shown by normal-coordinate analysis carried out on some adducts of Lewis acids,[9,16] these latter shifts arise simultaneously from the weakening of the force constants K(M–O) (M = Se, P) and the mechanical coupling generally observed between the M–O and Sb–O oscillators. Comparison between the spectra of free $OSCl_2$[17] and the $SbCl_5 \cdot OSCl_2$ adduct shows the same trend and is in agreement with the expected molecular structure of the complex.

Influence of the Donor Strength of the Ligands. Antimony pentachloride has been used by Gutmann[18] to define the donor strength of various Lewis bases from thermodynamic measurements. From x-ray crystallographic data, Lindqvist[3] and Weiss and Chevrier[2] have shown the relation between the donor strength and the Sb–O bond length in some oxygen donor complexes. From vibrational spectra, it is possible to correlate the position of the ν(SbO) vibration with the donor strength of the ligand; a definite decrease of the corresponding frequency is observed when the donor strength decreases. However, this mode has been shown to be strongly coupled with modes of the ligand by using deuteration (DMSO and DMF) and by carrying out a normal-coordinate analysis in the case of $SbCl_5 \cdot$DMSO.[9] Consequently, there is no simple correlation between the ν(SbO) frequency and the donor strength.

The Sb–Cl modes appear to be more directly related to the donor strength of the ligands. Their frequencies are decreased when the strength of the donors is increased. This trend appears clearly in the case of DMSO and $OSCl_2$ complexes, in which a difference of 10–15 cm^{-1} is observed for the ν(SbCl) stretching modes. The three oxychlorides can by classified in a similar manner. Using the position of the strongest Raman band, the order is as follows: $OSCl_2$ (344 cm^{-1}) < $OPCl_3$ (341 cm^{-1}) < $OSeCl_2$ (329.5 cm^{-1}). Further, it has been possible using these results to propose a molecular structure for $SbCl_5 \cdot OVCl_3$, $OVCl_3$ being a weak donor with a $\nu(a_1)(SbCl_4)$ frequency at 350 cm^{-1}.[19]

Registry No. $SbCl_5 \cdot OSCl_2$, 58298-20-7; $SbCl_5 \cdot OSeCl_2$, 58298-21-8; $SbCl_5 \cdot$DMSO, 23058-09-5; $SbCl_5 \cdot$DMF-h_7, 12075-62-6; $SbCl_5 \cdot$DMF-d_7, 58298-22-9; $SbCl_5 \cdot OP(CH_3)_3$, 37979-80-9; $SbCl_5 \cdot OPCl_3$, 18116-31-9.

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Fluorosulfates of the Lanthanide Elements

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Fluorosulfates of scandium, yttrium, and most of the lanthanide elements in oxidation state III have been prepared by the action of peroxydisulfuryl difluoride upon anhydrous carbonates of the metals. When oxides of Nd, Sm, and Eu were used in place of carbonates, only part of the solid reacted.

Experimental Section

Synthesis. Peroxydisulfuryl difluoride, $S_2O_6F_2$, was prepared by allowing sulfur trioxide to react with fluorine.[1] Carbonates of the metals were produced by dissolving the appropriate oxide in dilute nitric acid and adding sodium bicarbonate to give a precipitate. The solid was washed with water followed by methanol. It was powdered in a mortar and dried for several hours at 110 °C. Oxides of metals used in these preparations were of a quality in which at least 99.9% of the rare earth element was the one desired.

In a typical preparation, about 1 mmol of a freshly prepared carbonate was placed in a Pyrex glass bulb which could be attached to a vacuum line by a ground joint and later closed by a Fischer and Porter Lab Crest valve having a Teflon stem. The vessel was held at about 70 °C and evacuated until it reached constant weight. It was then cooled to −183 °C, and peroxydisulfuryl difluoride, $S_2O_6F_2$, was added in sufficient amount to be present in excess for the reaction. When the vessel stood at room temperature or somewhat higher for about 15 h the following reaction occurred

$$M_2(CO_3)_3 + 3S_2O_6F_2 \rightarrow 2M(SO_3F)_3 + 3CO_2 + 1.5O_2$$

Table I. Data of Lanthanide Fluorosulfate Preparations

Starting material	Wt of starting material, g	Product	Wt of product expected, g	Wt of product found, g
Nd_2O_3	0.0605	$Nd(SO_3F)_3$[a]	0.1585	0.1382
Sm_2O_3	0.0869	$Sm(SO_3F)_3$[a]	0.2230	0.1801
Eu_2O_3	0.0988	$Eu(SO_3F)_3$[a]	0.2521	0.1502
$Sc_2(CO_3)_3$	0.0895	$Sc(SO_3F)_3$	0.2267	0.2235
$Y_2(CO_3)_3$	0.0960	$Y(SO_3F)_3$	0.2087	0.2092
$La_2(CO_3)_3$	0.0919	$La(SO_3F)_3$	0.1750	0.1754
$Pr_2(CO_3)_3$	0.0200	$Pr(SO_3F)_3$	0.0386	0.0385
$Nd_2(CO_3)_3$	0.0608	$Nd(SO_3F)_3$	0.1145	0.1153
$Sm_2(CO_3)_3$	0.0655	$Sm(SO_3F)_3$	0.1218	0.1175
$Eu_2(CO_3)_3$	0.0646	$Eu(SO_3F)_3$	0.1200	0.1159
$Gd_2(CO_3)_3$	0.1004	$Gd(SO_3F)_3$	0.1845	0.1923
$Tb_2(CO_3)_3$	0.1242	$Tb(SO_3F)_3$	0.2276	0.2343
$Dy_2(CO_3)_3$	0.1643	$Dy(SO_3F)_3$	0.3031	0.2989
$Ho_2(CO_3)_3$	0.0994	$Ho(SO_3F)_3$	0.1800	0.1786
$Er_2(CO_3)_3$	0.1893	$Er(SO_3F)_3$	0.3416	0.3360
$Tm_2(CO_3)_3$	0.1715	$Tm(SO_3F)_3$	0.3087	0.3170
$Yb_2(CO_3)_3$	0.1346	$Yb(SO_3F)_3$	0.2406	0.2462
$Lu_2(CO_3)_3$	0.1133	$Lu(SO_3F)_3$	0.2029	0.2068

[a] Not obtained pure by this reaction (see text).

Table II. Data from the Analysis of Lanthanide Fluorosulfates

Compd	% M		% S		% F	
	Calcd	Found	Calcd	Found	Calcd	Found
$Sc(SO_3F)_3$	13.0	12.9	28.0	28.1	17.1	15.9
$Y(SO_3F)_3$	23.1	23.4	24.8	24.7	14.7	13.6
$La(SO_3F)_3$	31.9	31.5	22.0	21.3	13.1	12.7
$Nd(SO_3F)_3$	32.7	32.3	21.8	21.9	12.9	12.6
$Sm(SO_3F)_3$	33.6	33.3	21.5	21.5	12.7	12.6
$Eu(SO_3F)_3$	33.9	35.4	21.4	21.6	12.7	12.0
$Gd(SO_3F)_3$	34.6	35.0	21.5	21.6	12.6	12.0
$Tb(SO_3F)_3$	34.7	34.9	21.1	20.8	12.5	11.7
$Dy(SO_3F)_3$	35.3	36.9	20.9	20.4	12.4	11.7
$Ho(SO_3F)_3$	35.7	36.0	20.8	20.2	12.3	11.5
$Er(SO_3F)_3$	35.9	35.0	20.6	20.0	12.3	11.9
$Tm(SO_3F)_3$	36.3	37.4	20.5	19.8	12.2	11.8
$Yb(SO_3F)_3$	36.8	36.9	20.4	22.4	12.1	12.1
$Lu(SO_3F)_3$	37.1	37.4	20.4	20.4	12.0	12.3

After the reaction had gone to completion, the vessel was pumped to constant weight under dynamic vacuum. The carbonates of lanthanum, praseodymium, and neodymium as prepared for this work required a reaction temperature of about 60 °C and a period of 5–10 days. Cerium carbonate gave a Ce(IV) compound which is discussed elsewhere.[2] Table I gives data regarding the preparations.

Oxides of only three of the rare earth elements, Nd, Sm, and Eu, gave indications of reacting extensively with $S_2O_6F_2$. Results obtained for these are included in Table I. Raman spectra indicated the products to be mixtures of fluorosulfate with oxide. Complete reaction of these oxides was not obtained even at 75 °C with a reaction period up to 17 days.

Analysis. For each salt, with the exception of $Pr(SO_3F)_3$, M, S, and F were determined, and the results are shown in Table II.

Properties. The various fluorosulfates had the colors characteristic of the metals in the III oxidation state. All of the salts were soluble in water or in dimethyl sulfoxide. They also dissolved, but to a much smaller extent, in formamide. They appeared to be essentially insoluble in fluorosulfuric acid, acetonitrile or *N,N*-dimethylformamide.

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Registry No. $Sc(SO_3F)_3$, 58438-33-8; $Y(SO_3F)_3$, 58438-34-9; $La(SO_3F)_3$, 58438-35-0; $Pr(SO_3F)_3$, 58438-36-1; $Nd(SO_3F)_3$, 58438-37-2; $Sm(SO_3F)_3$, 58438-38-3; $Eu(SO_3F)_3$, 58438-39-4; $Gd(SO_3F)_3$, 58438-40-7; $Tb(SO_3F)_3$, 58438-41-8; $Dy(SO_3F)_3$, 58438-42-9; $Ho(SO_3F)_3$, 58438-43-0; $Er(SO_3F)_3$, 58438-44-1; $Tm(SO_3F)_3$, 58438-45-2; $Yb(SO_3F)_3$, 58438-46-3; $Lu(SO_3F)_3$, 58438-47-4; $S_2O_6F_2$, 13709-32-5.

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Reactions of $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$ with Pyridine[1]

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The dinuclear complexes of molybdenum,[2,3] tungsten,[4] and rhenium[2b,3,5,6a] halides undergo a variety of reactions with various heteroatom-containing ligands. Although they are frequently accompanied by geometric rearrangement and/or reduction of the metal to a lower oxidation state, in general these reactions occur with retention of the dinuclear framework. This paper describes the study of the extended reactions of several dinuclear complexes of molybdenum with pyridine as well as certain related spectroscopic observations about the products.

Experimental Section

General Data. Pyridine (Matheson Coleman and Bell) was distilled from calcium hydride under a nitrogen atmosphere prior to use. Molybdenum hexacarbonyl and molybdenum(III) chloride (Climax Molybdenum) were used without further purification. Optical spectra were recorded using a Cary Model 14 spectrophotometer. Infrared spectra (>400 cm^{-1}) were obtained on a Perkin-Elmer Model 225 grating spectrophotometer employing either KBr disks or Nujol mulls supported on polyethylene plates. Frequencies are precise to ±1 cm^{-1}. Raman spectra were recorded on a Cary Model 82 laser Raman spectrometer equipped with a rotating sample cell similar to that described elsewhere.[6b] Unless otherwise noted, a slit width of 3 cm^{-1} and a scan rate equal to the ratio of the slit width to time constant were employed. Excitation was provided by Coherent Radiation Laboratory Model 52 argon and kryton ion lasers. Reported frequencies are precise to ±1 cm^{-1}. Far-infrared spectra (<400 cm^{-1}) were recorded on a Beckman Fourier Model FS-720 spectrophotometer employing Nujol mulls supported on polyethylene plates. Frequencies are precise to ±0.5 cm^{-1}.

Raman intensities were determined by adding a known amount of internal standard ($KReO_4$ or KNO_2) to a predetermined quantity of the desired complex admixed with an inert substrate (KBr). The resulting mixture was homogenized in a Spex Wig-L-Bug for 3–5 min. A polar planimeter was used to determine the intensity of each band of interest by integrating the area under each envelope and comparing it to the area of a selected band in the internal standard. All intensities were corrected for phototube response.

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Tricesium 1,1,1,2,2,2-Hexachloro-μ-hydrido-di-μ-chloro-dimolybdenum(III),[7] $Cs_3Mo_2Cl_8H$, **tricesium 1,1,1,2,2,2-hexabromo-μ-hydrido-di-μ-bromo-dimolybdenum(III),** $Cs_3Mo_2Br_8H$, **tricesium enneachlorodimolybdenum,[7]** $Cs_3Mo_2Cl_9$, ***mer*-trichlorotris(pyridine)molybdenum(III),[8]** *mer*-$MoCl_3(py)_3$, **tetrachloro-[2] and tetrabromotetrakis(pyridine)dimolybdenum(II),[2a]** $Mo_2Cl_4(py)_4$ **and** $Mo_2Br_4(py)_4$, **and tetrapotassium octachlorodimolybdenum(II),[9]** $K_4Mo_2Cl_8$, were prepared according to literature procedures.

Preparation of Tricesium Enneabromodimolybdenum(III), $Cs_3Mo_2Br_9$. $Cs_3Mo_2Br_8H$ (1.0 g, 0.81 mmol) was placed in a 200-ml beaker along with a Teflon-coated stirrer bar. Deoxygenated hydrobromic acid (75 ml, 48%) was added and the mixture stirred under nitrogen until dissolution was completed. Two platinum electrodes, each measuring ~10 cm^2 in area, were then inserted into the solution, and, with continuous stirring and maintaining a steady stream of nitrogen through the solution, the mixture was electrolyzed for 2 min at 4.0 ± 0.5 A.[10] The red precipitate, which began forming almost immediately, was collected by suction filtration, washed with 50 ml of distilled water, 50 ml of absolute ethanol, and finally 50 ml of anhydrous ether, and dried in vacuo. The isolated yield of tricesium enneabromodimolybdenum was 65%. Anal. Calcd for $Cs_3Mo_2Br_9$: Br, 55.04. Found: Br, 55.08.

Reaction of $Cs_3Mo_2Cl_8H$ **with Pyridine.** Tricesium 1,1,1,2,2,2-hexachloro-μ-hydrido-di-μ-chloro-dimolybdenum(III) (1.5 g, 1.2 mmol) was placed in a 12-in. × 0.5-in. (i.d.) Fischer-Porter combustion tube. Pyridine (20 ml) and a Teflon-coated stirring bar were added and the vessel was tightly sealed with a Teflon-lined cap and placed