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Solvent-Extraction Complexes of the Uranyl Ion. 1. Crystal and Molecular Structure of Bis(nitrato)bis(tri-*n*-butylphosphine oxide)dioxouranium(VI)

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The complex $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$, made by reacting $UO_2(NO_3)_2 \cdot 6H_2O$ with tri-*n*-butylphosphine oxide, was analyzed by single-crystal X-ray diffraction methods. The monoclinic unit cell has $a = 8.496$ (2) Å, $b = 29.630$ (7) Å, $c = 14.063$ (3) Å, and $\beta = 94.92$ (2)° at 23 °C; the space group is $C2/c$, and $Z = 4$. The structure was determined by the heavy-atom method and refined by least squares. Positions and anisotropic thermal parameters were adjusted for 22 nonhydrogen atoms, while hydrogen atoms were fixed in assumed positions; the agreement factor, R_F, reached 0.043 for 1648 observations ($>3\sigma$). There are discrete molecules in the crystal consisting of uranyl ions surrounded at the equator by six oxygen atoms furnished by two bidentate nitrate ions and two tri-*n*-butylphosphine oxide molecules. Two of the *n*-butyl groups are anti and one is gauche in conformation. The bond between the phosphine oxide and the uranium atom is shorter than the corresponding water to uranium bond in each of two structurally analogous hydrates.

Introduction

Acidic and neutral organophosphorus compounds, alone and in synergistic combinations, have proven to be very effective solvent-extraction reagents for uranium. The extractive properties of these reagents have been extensively investigated,[1,2] but examination of the extraction complexes formed has been less detailed and mainly limited to determination of stoichiometry and analysis of IR and Raman spectra.[3-5] Two such complexes, $UO_2(NO_3)_2(TEP)_2$[6] and $UO_2(TTA)_2$(TOPO),[7] have been structurally characterized, but with rather low precision.

Bis(nitrato)bis(tri-*n*-butylphosphine oxide)dioxouranium(VI) has been prepared by a number of other workers because tri-*n*-butylphosphine oxide (TBPO) was found to be a powerful extractant for U(VI) in nitric acid solutions.[3,8] [This extractant also synergizes the extraction of U(VI) with bis(2-ethylhexyl)phosphoric acid in sulfate solutions.[2]] Solid $UO_2(NO_3)_2(TBPO)_2$ was isolated and its IR and Raman spectra measured. From these it was deduced that the phosphine oxide is directly bonded to the uranium and that the nitrate attachment is bidentate;[3,4] both of these features are confirmed by the present study.

This paper is the first in a series which will report the structures of several of these related extraction complexes for the purpose of comparing them to gain insight into the extraction processes themselves.

Experimental Section

Preparation of Complex. The complex was made by melting together in a water bath at ~65 °C a 1:2 molar ratio of $UO_2(NO_3)_2 \cdot 6H_2O$ and TBPO (Carlisle Chemical Works, Reading, OH). The product was put in a dessicator over H_2SO_4 to remove water, and the solid was again melted and cooled to grow crystals. Good specimens for X-ray study were obtained by removing them from the cooling liquid before all the sample was solidified and blotting off their surface liquid. They are pale yellow, thick platelets, stable in air; mp 65 ± 1 °C.

Table I. Crystal Data and Experimental Methods for $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$

crystal system: monoclinic	$Z = 4$
space group: $C2/c$	mol wt = 830.67
$a = 8.496$ (2) Å	V(cell) = 3526.7 Å^3
$b = 29.630$ (7) Å	$\rho_{calcd} = 1.56$ g cm^{-3}
$c = 14.063$ (3) Å	$\rho_{exptl} = 1.50$ g cm^{-3}
$\beta = 94.92$ (2)°	$\mu = 45.6$ cm^{-1}
$t = 23$ °C	$F(000) = 1656$

12 reflections in 2θ range 35-40° for cell refinement
radiation: Mo Kα_1 ($\lambda = 0.709\,26$ Å); Nb filter
scan: θ-2θ coupled; width: 0.9-1.14° for $2\theta = 2.7$-45°
bkgd: stationary at each end of scan for $^1/_6$ of total scan time
std reflctn: 206, measured hourly
reflctns measd: $+h, +k, \pm l$; total = 2230 (no. $>1\sigma$ = 1984; no. $>3\sigma$ = 1648)

X-ray Diffraction. The monoclinic symmetry of the crystal and the systematic absences indicative of space groups $C2/c$ and Cc were determined from X-ray precession photographs. For determination of accurate unit cell dimensions and measurement of intensities, a computer-controlled Picker four-circle diffractometer was used. These data were obtained from a crystal in the shape of a parallelepiped whose parallel faces were separated by about 0.011, 0.026, and 0.029 cm, respectively. This specimen was sealed in thin-walled glass and mounted with its long dimension parallel to the diffractometer ϕ axis.

The unit cell dimensions, other crystal data, and the conditions for collecting intensity data are given in Table I.

Structure Determination and Refinement

Data Reduction. The dimensions of the crystal from which intensities were obtained were measured with a microscope, and the six boundary planes were used in a calculation of transmission factors for all reflections.[9] These ranged from 0.40 to 0.63 and were applied to the observed intensities along with Lorentz and polarization corrections and a normalization factor obtained by interpolation between measured values of the reference reflection. This treatment yielded about 2230 relative squared structure factors, F_o^2, of which 1984 were larger than 1σ. The variance of these structure factors, $\sigma^2(F_o^2)$, was taken to be equal to $\sigma_c^2 + (0.05F_o^2)^2$, in which σ_c^2 is attributable to counting statistics and the other contribution represents an estimate of systematic errors of unknown origin.

Structure Determination. The U and P atoms were located by interpreting a Patterson map; and the O, N, and C atoms were found in subsequent electron-density maps whose phases were calculated

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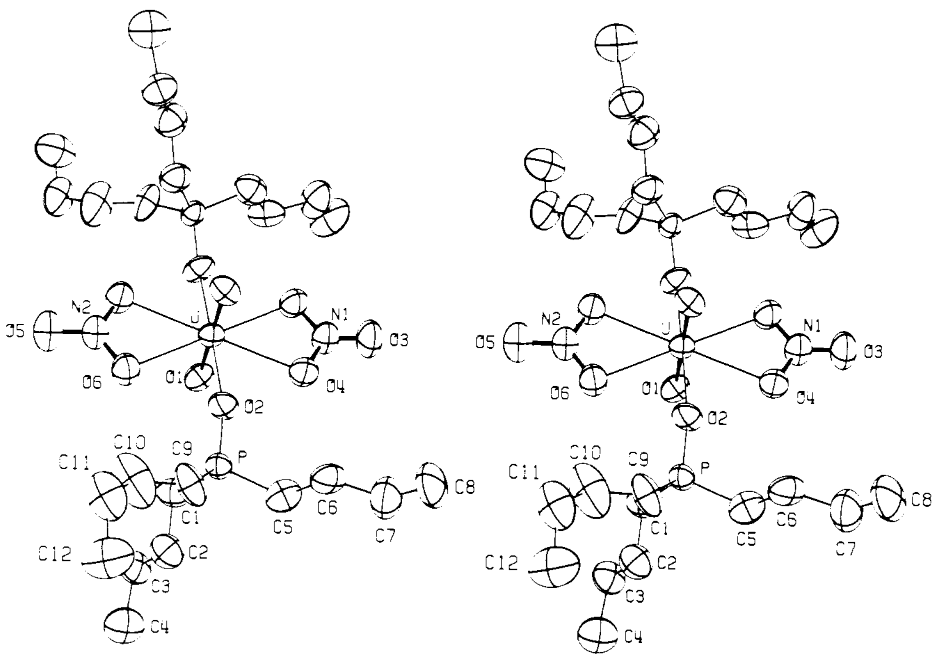

Figure 1. Molecule of $UO_2(NO_3)_2(TBPO)_2$ with the atoms represented by their thermal ellipsoids of 35% probability.

with use of just the U and P atoms. It was assumed that the centrosymmetric space group was correct, and the good quality of the eventual refinement confirms this. Thus the U atoms, two N atoms, and two O atoms were found to be in special positions 4(e) of $C2/c$; and the 17 other nonhydrogen atoms in general positions 8(f). At the last step of refinement, 27 H atoms were included in calculated general positions.

Refinement. The coordinates and anisotropic thermal parameters of all 22 nonhydrogen atoms in the asymmetric unit were adjusted by the method of least squares. For this refinement, the 1648 values of F_o^2 which were larger than $3\sigma(F_o^2)$ were used as observations with each weighted as $w = 1/\sigma^2(F_o^2)$. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, where F_c is the calculated structure factor. Scattering factors of the neutral atoms[10] were used, and, for uranium, anomalous dispersion corrections were included and adjusted in the refinement. Values of $\Delta F' = -10.9$ (6) and $\Delta F'' = 11.0$ (7) were obtained; these are close to the theoretical values.[11]

After all other atoms had ceased to move in the refinement, H atoms were included, with the assumption that they were tetrahedrally disposed about the C atoms at 1-Å distance; the rotational positions of the terminal methyl H atoms were obtained by use of difference Fourier maps. Each H atom was given an isotropic thermal parameter equivalent to the average motion of the C atom to which it is attached. With the H atom parameters all fixed, a final cycle of refinement was carried out.

Convergence of the refinement was smooth and the agreement index, $R = \sum||F_o| - |F_c||/\sum|F_o|$, was 0.043; σ_1 was 1.32. The weighted index, R_w, was 0.061. The atomic coordinates after refinement are listed in Table II, and the anisotropic thermal parameters, U_{ij}, are given in Table III. The H atom parameters and a listing of structure amplitudes on an absolute scale are available as supplementary material.

Description and Discussion of the Structure

There are discrete molecules of the complex in the crystal. One of these is shown in Figure 1. It has a twofold symmetry axis through O(3), N(1), U, N(2), and O(5) with a center of symmetry at the U atom. The linear UO_2^{2+} ion is surrounded at its equator by six O atoms provided by two bidentate NO_3^- ions and two neutral TBPO molecules. The complex molecules are packed loosely together in the crystal, which is soft and low melting. The packing is illustrated by Figure 2. In Table IV are listed the bond distances and angles which are relevant to a discussion of the structure.

Table II. Atomic Coordinates and Standard Deviations

atom	10^4x	10^4y	10^4z
U	0	3504.2 (3)	2500
P	3497 (3)	3559 (1)	4228 (2)
O(1)	921 (9)	3504 (3)	1440 (5)
O(2)	2545 (8)	3512 (3)	3294 (5)
O(3)	0	2079 (5)	2500
O(4)	1025 (10)	2726 (3)	2963 (6)
O(5)	0	4916 (5)	2500
O(6)	1030 (10)	4282 (3)	2976 (6)
N(1)	0	2482 (6)	2500
N(2)	0	4513 (6)	2500
C(1)	2279 (15)	3825 (5)	5103 (9)
C(2)	3016 (18)	3876 (5)	6078 (10)
C(3)	1899 (16)	4066 (5)	6764 (10)
C(4)	2687 (18)	4159 (6)	7733 (11)
C(5)	4056 (17)	3016 (5)	4657 (10)
C(6)	5097 (15)	2757 (6)	4022 (9)
C(7)	5401 (21)	2267 (6)	4304 (13)
C(8)	6441 (23)	2018 (7)	3770 (14)
C(9)	5151 (16)	3893 (5)	4132 (10)
C(10)	5088 (26)	4353 (7)	4078 (13)
C(11)	6581 (21)	4641 (6)	3942 (13)
C(12)	7827 (24)	4656 (7)	4697 (13)

When the best least-squares plane is drawn among the six equatorial O atoms, the deviations from it are as follows: O(2), ±0.123 Å; O(4), ±0.132 Å; O(6), ±0.145 Å. The UO_2^{2+} ion is perpendicular to this plane within one standard deviation.

The shape of the $UO_2(NO_3)_2(TBPO)_2$ molecule is very similar to that of $UO_2(NO_3)_2(TEP)_2$,[6] $UO_2(NO_3)_2{\cdot}2H_2O$,[12] $UO_2(NO_3)_2{\cdot}6H_2O$,[13] and $UO_2(NO_3)_2(TPAO)_2$[14a] (TPAO =

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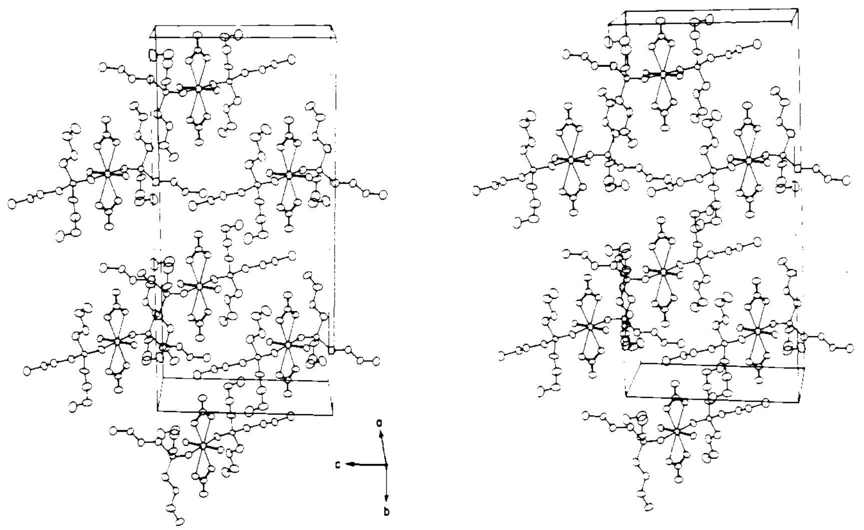

Figure 2. Stereoscopic view of the unit cell of $UO_2(NO_3)_2(TBPO)_2$ and some of its neighboring molecules.

Table III. Anisotropic Thermal Parameters[a] (Å^2)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0.0431 (4)[b]	0.0710 (5)	0.0638 (5)	0	−0.0012 (2)	0
P	0.056 (2)	0.065 (2)	0.072 (2)	−0.001 (2)	−0.005 (1)	−0.006 (2)
O(1)	0.079 (5)	0.091 (6)	0.082 (5)	−0.003 (5)	0.010 (4)	−0.016 (5)
O(2)	0.057 (4)	0.097 (6)	0.097 (5)	0.013 (5)	−0.024 (4)	−0.024 (5)
O(3)	0.127 (12)	0.067 (10)	0.155 (13)	0	0.006 (9)	0
O(4)	0.092 (6)	0.084 (7)	0.108 (7)	−0.002 (5)	−0.026 (5)	−0.004 (5)
O(5)	0.131 (12)	0.084 (11)	0.152 (13)	0	0.019 (9)	0
O(6)	0.077 (6)	0.077 (6)	0.115 (7)	0.003 (5)	−0.008 (5)	−0.005 (5)
N(1)	0.063 (10)	0.078 (13)	0.112 (13)	0	0.004 (9)	0
N(2)	0.081 (12)	0.069 (13)	0.107 (12)	0	0.016 (9)	0
C(1)	0.082 (9)	0.111 (12)	0.094 (9)	−0.015 (8)	−0.009 (7)	−0.006 (8)
C(2)	0.113 (11)	0.114 (13)	0.106 (11)	−0.005 (10)	0.017 (9)	−0.010 (9)
C(3)	0.101 (10)	0.114 (12)	0.091 (10)	0.009 (9)	0.024 (8)	−0.019 (8)
C(4)	0.108 (12)	0.169 (17)	0.126 (13)	0.001 (11)	0.012 (10)	−0.005 (11)
C(5)	0.100 (11)	0.124 (13)	0.110 (11)	0.007 (9)	−0.002 (9)	0.011 (9)
C(6)	0.071 (8)	0.148 (15)	0.089 (9)	0.040 (9)	−0.006 (7)	−0.012 (9)
C(7)	0.130 (14)	0.102 (14)	0.193 (18)	0.025 (11)	−0.015 (13)	−0.019 (12)
C(8)	0.153 (16)	0.144 (17)	0.196 (18)	0.065 (13)	−0.002 (13)	−0.070 (14)
C(9)	0.093 (10)	0.088 (11)	0.142 (12)	−0.032 (9)	0.047 (8)	−0.042 (10)
C(10)	0.217 (21)	0.145 (18)	0.172 (17)	−0.086 (16)	0.120 (15)	−0.034 (14)
C(11)	0.134 (14)	0.121 (14)	0.152 (15)	−0.045 (12)	0.065 (12)	−0.013 (11)
C(12)	0.148 (16)	0.205 (23)	0.132 (15)	−0.011 (15)	−0.005 (13)	0.025 (14)

[a] The U_{ij} values listed are for the temperature factor $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] Least-squares standard deviations of the last one or two digits are given in parentheses.

Table IV. Interatomic Distances and Bond Angles with Standard Deviations

atoms	dist, Å	atoms	angle, deg
U–O(1)	1.742 (7)	O(4)–N(1)–O(4)	110 (2)
U–O(2)	2.347 (6)	O(4)–N(1)–O(3)	124.7 (8)
U–O(4)	2.530 (8)	O(6)–N(2)–O(6)	114 (2)
U–O(6)	2.535 (8)	O(6)–N(2)–O(5)	123.0 (8)
P–O(2)	1.489 (7)	U–O(2)–P	146.0 (5)
P–C(1)	1.85 (2)	C(1)–P–O(2)	109.5 (5)
P–C(5)	1.77 (2)	C(5)–P–O(2)	109.0 (6)
P–C(9)	1.73 (2)	C(9)–P–O(2)	111.5 (7)
N(1)–O(3)	1.19 (2)	C(1)–P–C(5)	108.1 (7)
N(1)–O(4)	1.27 (1)	C(1)–P–C(9)	108.1 (6)
N(2)–O(5)	1.19 (2)	C(5)–P–C(9)	110.6 (8)
N(2)–O(6)	1.26 (1)	P–C(1)–C(2)	117 (1)
C(1)–C(2)	1.47 (2)	C(1)–C(2)–C(3)	113 (2)
C(2)–C(3)	1.52 (2)	C(2)–C(3)–C(4)	113 (1)
C(3)–C(4)	1.49 (2)	P–C(5)–C(6)	114 (1)
C(5)–C(6)	1.52 (2)	C(5)–C(6)–C(7)	115 (2)
C(6)–C(7)	1.52 (2)	C(6)–C(7)–C(8)	117 (2)
C(7)–C(8)	1.42 (2)	P–C(9)–C(10)	123 (2)
C(9)–C(10)	1.36 (2)	C(9)–C(10)–C(11)	122 (2)
C(10)–C(11)	1.56 (2)	C(10)–C(11)–C(12)	119 (2)
C(11)–C(12)	1.44 (3)		

triphenylarsine oxide), especially in the attachment of the various species to the U atom. It is therefore of interest to compare these structures in detail. In each complex (excluding the first one, which was not determined accurately), the geometry of the planar NO_3^- ions and their bond distances to the U atom are quantitatively the same within the experimental errors. The O–N–O angle for the O atoms bonded to the U atom is reduced from 120° to 112–115°, and these N–O bonds are elongated relative to the N–O bond to each terminal O atom. As for the monodentate ligands, however, the U–O distances to TBPO and TPAO are 2.35 and 2.36 Å, while the U to H_2O distances are 2.40, 2.45, and 2.46 Å. The longer (and weaker) bond to H_2O is in agreement with the observation that the phosphine (and arsine) oxides readily replace H_2O to form the extraction complex, even in aqueous media. The P═O—U bond length found here is equal to the average value of this bond found in several recent determinations[14a-d,g,i] of related structures.

The PO_4 group is tetrahedral (average of six angles is 109.3°), and the P═O bond length is in good agreement with the average value found in similar U(VI) and U(IV) complexes with trimethylphosphine oxide and triphenylphosphine oxide.[14a-i] While the P-C bonds range in length from 1.73 to 1.85 Å, similar variations were found in the other compounds and probably are sterically induced.

In each TBPO molecule in the crystal, two butyl groups are anti in conformation and one is gauche. The torsion angles,[15] viewing the butyl groups from the P atom along the middle C-C bond, are as follows: $\angle$[C(1), C(2), C(3), C(4)] = −175 (1)°; $\angle$[C(5), C(6), C(7), C(8)] = −176(2)°; $\angle$[C(9), C(10), C(11), C(12)] = −67(3)°. The anti conformation in alkanes is of slightly lower energy;[16] in gaseous butane there is about a 3:2 mixture of anti and gauche forms at room temperature.[17] Mixtures of the two butyl conformations have also been observed in the solid, for example, in the tetrabutylammonium ion.[18] The C-C bond lengths found here scatter considerably, but there average is 1.48 Å. This appears foreshortened because of the large thermal motions which these atoms are executing; the root-mean-square amplitudes range from about 0.3 Å near the P atom to about 0.45 Å at the ends of the chains. If a correction for thermal motion is applied,[19] with the assumption that each atom rides on the next more central one, the average bond length increases to 1.51 Å, this agrees better with the values found in structures in which the C positions can be more precisely determined. the C-C-C angles in the three butyl groups average 114.3, 115.3, and 121.3°, respectively. In free butane, these are found to be 112.6°.[17]

Crystals have also been prepared by reacting $UO_2(NO_3)_2 \cdot 6H_2O$ with di-*n*-butylphosphoric acid (HDBP) and by a mixture of HDBP and TBPO. Analysis of these structures is in progress, and the results should make possibe a comparison of the roles enacted by the acidic, neutral, and combined extractants in complexing U(VI).

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Registry No. $UO_2(NO_3)_2(TBPO)_2$, 78821-60-0; $UO_2(NO_3)_2$, 36478-76-9.

Supplementary Material Available: A listing of observed and calculated structure amplitudes and a table of H atom parameters (7 pages). Ordering formation is given on any current masthead page.

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Gas-Phase Structures of $(CF_3)_2S{=}O$, $(CF_3)_2S{=}NCl$, and $(CF_3)_2SF_2$. An Electron Diffraction Study

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The gas-phase structures of $(CF_3)_2S{=}O$, $(CF_3)_2S{=}NCl$, and $(CF_3)_2SF_2$, which have been determined via electron diffraction studies, reveal some interesting effects when compared with the totally fluorinated analogues. The S=O bond lengths and the XSX angles in $X_2S{=}O$ molecules increase with decreasing electronegativity of X (X = F 1.415_9 Å, 92.7_9 (0_4)°; X = CF_3 1.469 (4) Å, 94.2 (8)°). The increase in the XSX angle in $X_2S{=}NCl$ is even more enhanced (X = F 89.3 (6)°; X = CF_3 99.4 (9)°). The geometries of the S=NCl groups in $F_2S{=}NCl$ and $(CF_3)_2S{=}NCl$ are remarkably different with S=N and N-Cl shorter in $(CF_3)_2S{=}NCl$ (1.434 (8) Å, 1.676 (8) Å) than in $F_2S{=}NCl$ (1.477 (9) Å, 1.723 (4) Å) and with a larger S=NCl bond angle (138.2 (3.8)° vs. 120.0 (6)°) in $(CF_3)_2S{=}NCl$. The decrease of the equatorial bond angle from 101.5 (5)° in SF_4 to 97.3 (8)° in $(CF_3)_2SF_2$ is incompatible with the VSEPR model.

Introduction

Bis(*F*-alkyl)sulfur(IV) compounds are extremely interesting materials because of their chemical properties and because of the geometry at the sulfur center. Their syntheses and reaction chemistry have been examined in some detail.[2a] Earlier workers have suggested that the two fluorine atoms bonded to sulfur in $(R_f)_2SF_2$ undergo rapid exchange between axial and equatorial sites, and thus the ^{19}F NMR chemical shift observed is an average value.[2b] However, our infrared spectral studies support axial positions for these fluorine atoms in the gas-phase spectrum of $(CF_3)_2SF_2$.[3] The Raman study suggests an axial configuration for this molecule in the liquid phase. Unfortunately, no gas-phase ^{19}F NMR spectral data are available. In the present electron diffraction study, the axial positions of the S-F bonds are confirmed for the gas-phase molecule.

The isoelectronic molecules $(CF_3)_2S{=}O$ and $(CF_3)_2S{=}NCl$ differ markedly in stability due largely to the presence of the labile chlorine atom bonded to nitrogen in the latter. On the basis of Raman studies, the symmetry of $(CF_3)_2S{=}O$ is C_s.[4] The present study shows that a surprising difference in the geometries of the S=NCl groups in $F_2S{=}NCl$[5] and $(CF_3)_2S{=}NCl$ exists. It now has been possible to determine the structures of $(CF_3)_2SF_2$, $(CF_3)_2S{=}O$, and $(CF_3)_2S{=}NCl$ and

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(1) (a) Universität Tübingen. (b) University of Idaho.
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