(36) A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 221 (1975).
(37) A. Dominicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 1630 (1975).

Contribution from Los Alamos Scientific Laboratory,
University of California, Los Alamos, New Mexico 87545

Synthesis and Structure of the 1:1 Uranyl Nitrate Tetrahydrate–18-Crown-6 Compound, $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-Crown-6). Noncoordination of Uranyl by the Crown Ether

P. G. ELLER* and R. A. PENNEMAN

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The synthesis and crystal structure of $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-crown-6), which forms from the reaction of uranyl nitrate hexahydrate and the cyclic polyether 18-crown-6, are reported. The uranyl group is *not* located within the crown ether group. Rather, the structure consists of neutral $UO_2(NO_3)_2(H_2O)_2$ units and separate crown ether molecules connected by hydrogen bonding through intermediary water molecules. The oxygens of the linear uranyl group are coordinated only to uranium; the eight-coordination of uranium is completed by six equatorial oxygen donors, two from waters and two from symmetrically bidentate nitrates. The uranium and the six equatorial oxygens are coplanar within 0.06 Å. Pertinent distances are U–O(uranyl) = 1.693 (6) Å, U–O(water) = 2.434 (5) Å, U–O(nitrate) = 2.482 (6) and 2.486 (6) Å. The cyclic ether molecule exists in the customary crown conformation with normal distances and angles. Crystal data are as follows: space group $P\bar{1}$, $Z = 1$, $a = 7.526$ (7) Å, $b = 11.27$ (1) Å, $c = 7.802$ (4) Å, $\alpha = 97.51$ (6)°, $\beta = 93.22$ (6)°, $\gamma = 105.95$ (6)°, $R_F = 0.058$ for 2453 diffractometer-collected reflections with $I \geq 3\sigma(I)$.

Introduction

Crown ethers (cyclic polyethers) provide a cavity or cage which can be engineered to accommodate metal ions of different charge and size.[1–6] Resulting complexes are of great synthetic interest since enhanced solubilities and reactivities of ionic materials in nonplar solvents often result. The complexes are also of considerable interest in regard to solvent extraction, isotope separation, and biological transport of metal ions. As a result, the synthesis and characterization of crown ether compounds are the subjects of intense interest in many laboratories.

We have recently turned our attention to the possible utilization of crown ethers as a means of stabilizing unusual oxidation states and geometries in actinide complexes. The chelating ability of crown ethers with respect to alkali and alkaline earth metal ions is well documented, both crystallographically and chemically.[4–6] In contrast, syntheses of only a few lanthanide[7,8] and actinide[9,10] complexes have been reported, and structural verification of polyether complexation to these metals has hitherto been lacking.

In this paper we report the synthesis and structure determination of a 1:1 compound containing uranyl nitrate tetrahydrate and 18-crown-6.[26] While this work was under way, the synthesis of the identical compound by a different method was reported.[9] In that preliminary report, spectroscopic data were interpreted to indicate that the nitrate groups were uncoordinated and the uranyl group lay within the ring of the six crown oxygen atoms. The x-ray structure determination described herein was undertaken to test the hypothesis of crown ether ligation.

Experimental Section

Preparation of $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-crown-6). Excellent crystals of the title compound were prepared in good yield by dissolving 2.70 g (5.4 mmol) of $UO_2(NO_3)_2{\cdot}6H_2O$ and 1.50 g (5.7 mmol) of 18-crown-6 in 90 ml of warm acetonitrile. The solution was allowed to stand overnight at 10 °C, filtered, washed with a few milliliters of acetonitrile, and then vacuum-dried overnight at 25 °C to give 2.64 g (67% yield) of bright yellow needles of the title compound. The x-ray powder pattern, infrared spectrum, and decomposition point of the compound prepared by this method are indistinguishable from material prepared in ethanol.[9]

Anal. Calcd for $UO_{18}N_2C_{12}H_{32}$: C, 19.73; H, 4.42; N, 3.84. Found: C, 20.22; H, 4.08; N, 3.67.

The compound is stable for days at 100 °C under 1 atm of N_2. In an open capillary, the compound melts at 140–147 °C with effervescence to a yellow liquid which resolidifies to a yellow powder by 160 °C and then gradually darkens above 265 °C. From a mixture of neat 18-crown-6 and $UO_2(NO_3)_2{\cdot}6H_2O$ at 150 °C, the compound $UO_3{\cdot}{}^1/_2$(18-crown-6) forms, with properties identical with those of the above yellow powder.

Anal. Calcd: N, 0.00; C, 17.23; H, 2.89. Found: N, 0.00; C, 17.34; H, 2.91.

X-Ray Data Collection. Optical examination and precession photographs failed to reveal any symmetry higher than triclinic. A parallelepiped of dimensions 0.06 × 0.08 × 0.14 mm was mounted approximately parallel to the long dimension of the crystal and 12 reflections with 2θ in the range 33–44° were centered using an automated diffractometer and graphite-monochromatized Mo radiation (λ 0.709 30 Å). Least-squares refinement of the setting angles and orientation matrix gave the following cell: $a = 7.526$ (7) Å, $b = 11.27$ (1) Å, $c = 7.802$ (4) Å, $\alpha = 97.51$ (6)°, $\beta = 93.22$ (6)°, $\gamma = 105.95$ (6)°. The unit cell thus chosen contains one formula unit ($\rho_{\text{calcd}} = 1.93$ g cm^{-3}) and the large, medium, and small faces are of the forms {001}, {100}, and {010}, respectively. A data set was collected within the limiting hemisphere $1 \leq 2\theta \leq 60°$ by the θ–2θ scan technique using a Picker FACS-I automated diffractometer equipped with a graphite monochromator (λ 0.709 30 Å). A scan range of 2° plus a θ-dependent dispersion term and background counts of 20 s each were used. Of the 3143 unique reflections examined, 2453 were judged to be above background on the basis that $I \geq 3\sigma(I)$ where $\sigma(I) = [T + B + [0.015(T - B)]^2]^{1/2}$, T being the total count for each scan and B being the estimated background. The intensities of two standard reflections, measured after every 50 reflections, were found to decrease by ca. 8% during data collection, apparently due to crystal decomposition. An appropriate correction was applied using a polynomial determined by least-squares fitting the standard reflection curves. Lorentz and polarization corrections were applied in the usual way. Absorption corrections were applied[11,12] ($\mu = 194.3$ cm^{-1}; transmission coefficients 0.21–0.35). Otherwise, the data collection and reduction were as previously described.[13]

Solution and Refinement of the Structure. The centric space group ($P\bar{1}$) was initially chosen, an assumption supported by the successful refinement of the structure. With one formula unit per cell, the uranyl and crown ether groups each are required to possess $\bar{1}$ symmetry. The uranium atom was placed at the origin, and the carbon, nitrogen, and oxygen atoms were easily located with a difference Fourier synthesis. Neutral atom scattering factors were used for the light atoms and hexavalent scattering factors for uranium.[14] Anomalous dispersion terms were included for uranium.[15] A conventional anisotropic refinement of the 17 nonhydrogen atoms plus an overall scale factor

Table I. Final Atomic Parameters[a]

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.0000	0.0000	0.0000	0.0140 (1)	0.00430 (5)	0.0110 (1)	0.0032 (1)	0.0000 (1)	0.002 50 (9)
O1	0.2095 (8)	−0.0000 (5)	−0.0684 (8)	0.020 (1)	0.0066 (6)	0.019 (1)	0.007 (2)	−0.008 (2)	0.002 (2)
O2	0.0510 (9)	0.2173 (5)	−0.0382 (8)	0.028 (2)	0.0043 (5)	0.015 (1)	0.003 (1)	−0.008 (2)	0.003 (1)
O3	0.1189 (9)	0.4374 (5)	0.1613 (8)	0.027 (2)	0.0061 (6)	0.016 (1)	0.011 (2)	0.001 (2)	0.002 (1)
O4	0.1668 (9)	0.1545 (5)	0.2542 (8)	0.028 (2)	0.0054 (6)	0.016 (1)	0.006 (2)	−0.006 (3)	0.003 (1)
N	0.191 (1)	0.0783 (7)	0.351 (1)	0.022 (2)	0.0068 (8)	0.018 (2)	0.007 (2)	−0.009 (3)	−0.005 (2)
O5	0.116 (1)	−0.0361 (6)	0.2876 (8)	0.036 (2)	0.0076 (7)	0.014 (1)	0.006 (2)	−0.011 (3)	0.002 (2)
O6	0.275 (1)	0.1090 (7)	0.4940 (9)	0.045 (2)	0.0119 (9)	0.017 (2)	0.015 (2)	−0.025 (3)	−0.006 (2)
O7	0.2016 (8)	0.4947 (6)	−0.2838 (8)	0.019 (1)	0.0096 (7)	0.015 (1)	0.009 (2)	0.008 (2)	0.003 (2)
O8	−0.1211 (8)	0.2979 (5)	−0.2904 (7)	0.018 (1)	0.0064 (6)	0.012 (1)	0.007 (1)	0.003 (2)	0.004 (1)
O9	−0.3585 (8)	0.3454 (6)	−0.0432 (8)	0.017 (1)	0.0081 (7)	0.017 (1)	0.002 (2)	0.006 (2)	0.004 (2)
C1	0.174 (2)	0.3790 (9)	−0.393 (1)	0.035 (2)	0.009 (1)	0.014 (2)	0.012 (3)	0.011 (4)	0.002 (3)
C2	−0.031 (1)	0.3225 (9)	−0.443 (1)	0.026 (3)	0.010 (1)	0.012 (2)	0.007 (3)	0.011 (4)	0.002 (2)
C3	−0.318 (1)	0.2549 (9)	−0.326 (1)	0.015 (2)	0.009 (1)	0.019 (2)	0.003 (2)	−0.004 (4)	0.001 (1)
C4	−0.399 (1)	0.2305 (9)	−0.161 (1)	0.017 (2)	0.007 (1)	0.023 (3)	−0.002 (2)	0.003 (4)	0.003 (3)
C5	−0.422 (1)	0.323 (1)	0.122 (1)	0.019 (2)	0.013 (1)	0.019 (2)	−0.004 (3)	0.012 (4)	0.006 (3)
C6	−0.398 (1)	0.447 (1)	0.233 (1)	0.016 (2)	0.019 (2)	0.016 (2)	0.007 (3)	0.007 (4)	0.007 (3)

[a] Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

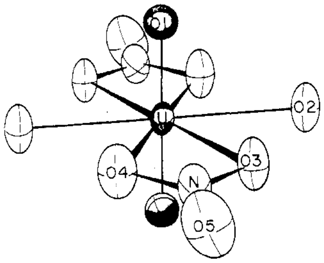

Figure 1. View of the $UO_2(NO_3)_2(H_2O)_2$ unit.

Table II. Selected Distances (Å) and Angles (deg)

A. $UO_2(NO_3)_2(H_2O)_2$ Unit

Distances

U–O1	1.693 (6)	N–O3	1.255 (9)
U–O2	2.434 (5)	N–O4	1.275 (9)
U–O3	2.482 (6)	N–O5	1.213 (9)
U–O4	2.486 (6)		

Angles

O1-U-O2	91.2 (3)	O2-U-O4	115.9 (2)
O1-U-O3	88.0 (3)	O3-U-O4	50.8 (2)
O1-U-O4	87.9 (3)	O3-N-O4	114.7 (7)
O2-U-O3	65.2 (2)	O3-N-O5	123.7 (8)
		O4-N-O5	121.6 (9)

B. 18-Crown-6 Unit

Distances

O7–C1	1.42 (1)	C4–O9	1.43 (1)
C1–C2	1.50 (1)	O9–C5	1.43 (1)
C2–O8	1.42 (1)	C5–C6	1.50 (2)
O8–C3	1.43 (1)	C6–O7′	1.45 (1)
C3–C4	1.48 (1)		

Angles

O7–C1–O2	108.7 (8)	C3–C4–O9	109.5 (8)
C1–C2–O8	108.8 (8)	C4–O9–C5	110.7 (8)
C2–O8–C3	112.0 (7)	O9–C5–C6	108.6 (9)
O8–C3–C4	108.0 (8)	C5–C6–O7′	108.8 (9)

C. Interactions Involving Lattice Water (O6)

Distances

O6–O2	2.654 (8)	O6–O8	3.017 (8)
O6–O7	2.898 (9)	O6–O9	2.906 (9)

and extinction parameter[16,17] was carried out. Methylene hydrogen atoms were inserted in positions of idealized geometry (C–H = 0.95 Å, H–C–H = C–C–H = O–C–H = 109.5°, $B = 6.0$ Å^2) but not refined; no attempt was made to account for the hydrogens attached to the water molecules. In the final refinement the *R* factor was 0.057, the maximum parameter shift was less than 0.06 esd, and the esd in an observation of unit weight was 3.0. A final difference Fourier synthesis contained, as the principal features, peaks of density 1.5 and 1.2 e/Å^3 within 1 Å of the uranium atom. Final atomic parameters are listed in Table I and selected distances and angles are presented in Table II.

Description of the Structure

The structure of $UO_2(NO_3)_2(H_2O)_2 \cdot 2H_2O \cdot$(18-crown-6) consists of neutral $UO_2(NO_3)_2(H_2O)_2$ molecules and 18-crown-6 molecules connected into infinite chains via hydrogen bonding through intermediary water molecules. Thus, the crown molecules are not bound directly to the uranyl group as others have suggested.[9,10]

The geometry at the uranyl group is depicted in Figure 1 and a stereoview of the overall structure is presented in Figure 2. The linear uranyl group occupies a crystallographic inversion center and exhibits characteristic coordination, forming an angle of 86.6° with the least-squares equatorial plane containing the six donor atoms. The six equatorial ligand atoms, which are coplanar within 0.06 Å and alternate above and below the UO_6 least-squares plane, are afforded by two water molecules (U–O = 2.434 (5) Å) and by two symmetrically bidentate nitrate groups (U–O = 2.482 (6) and 2.486 (6) Å). These parameters may be compared with values found

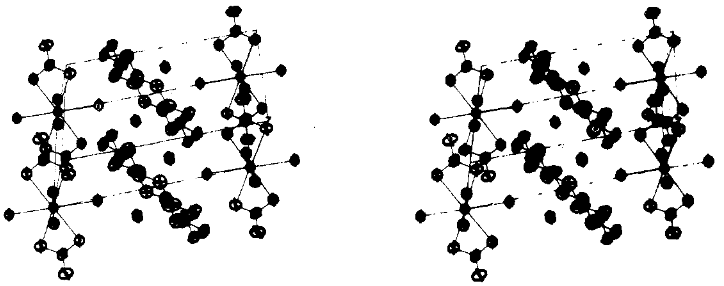

Figure 2. Stereoview of the structure ($\bar{1}01$ direction). Hydrogen atoms are omitted for clarity and ellipsoids are drawn at the 50% probability level.

for uranyl nitrate hexahydrate, which displays the same neutral coordination unit, $UO_2(NO_3)_2(H_2O)_2$.[18,19] A neutron diffraction study[19] of that structure indicated the U–O(nitrate) distances to be 2.504 (5) and 2.547 (6) Å and the U–O(H_2O) distance to be 2.397 (3) Å. An x-ray diffraction study[18] of lower accuracy indicated the parameters to be 2.44 and 2.50 Å [U–O(nitrate)] and 2.38 Å [U–O(H_2O)]. Within the present structure, the pattern of angles within the equatorial plane is reasonable for symmetrically bidentate nitrate groups and is in satisfactory agreement with the values reported for uranyl nitrate hexahydrate.[18,19]

In $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-crown-6), the uranyl oxygen is not involved in bonding to any atom other than uranium. The U–O distance, 1.693 (6) Å, falls at the lower end of the range of observed uranyl U–O distances, as expected since the uranyl oxygens are not further coordinated. Short uranyl U–O bonds (~1.7 Å) and longer equatorial bonds (~2.5 Å) are found in UO_2F_2, UO_2CO_3, and $NaUO_2(OAc)_3$,[20–22] which also contain "free uranyl". Correlations of uranyl bond distance data with bond strength were first made by Zachariasen[20] and are the subject of a recent review.[23] These studies show that U–O bonds range from 1.7 Å (free uranyl) to 2.1 Å, where in this latter extreme differences in U–O bond orders have disappeared. For the secondary uranium–oxygen bonds and a "bond strength" of 0.33, Zachariasen[20] predicted U–O distances of 2.48 Å, being in agreement with our value for the U–O(nitrate) distances and being only slightly longer than our $U{-}OH_2$ distance (2.434 (5) Å).

It is noteworthy that even though differences in transmission coefficients are not unusually large for this crystal, a refinement prior to application of the absorption corrections gave a significantly longer U–O distance, 1.750 (6) Å, than the final U–O distance, 1.693 (6) Å, although no other molecular parameters differed so drastically. A final trial refinement using neutral atom scattering factors for uranium, as well as one in which the 2θ cutoff limit was set at 40°, gave U–O distances within two esd's of the shorter value. It is also pertinent that uranyl U–O distances reported for the two determinations of $UO_2(NO_3)_2(H_2O)_2{\cdot}4H_2O$ differ significantly (1.749 (7) and 1.770 (7) Å for the neutron diffraction study[19] and 1.85 and 1.87 Å for the less accurate x-ray diffraction study[18]). A neutron diffraction study of $UO_2(NO_3)_2{\cdot}2H_2O$ reveals uranyl–oxygen distances of 1.763 (5) and 1.754 (4) Å.[24]

The coordinated water molecule (O2) is connected by a moderately strong hydrogen bond (O–O = 2.654 (8) Å) to a lattice water molecule (O6). Oxygen O6 is in turn situated almost symmetrically above half of the crown ether at distances suggestive of weak hydrogen-bonding interactions (O6–O(crown) = 2.898 (9), 3.017 (8), and 2.906 (9) Å). Since the crown molecule occupies a crystallographic inversion center, this pattern of O6–O(crown) distances is repeated on the other half of the crown molecule to give a trans bicapped arrangement.

The ether molecule itself has the customary crown conformation with normal internal distances and angles.[4–6] The ring is slightly puckered, the six oxygen atoms being alternately 0.23 Å above and below the six-atom least-squares plane. The carbon atoms also are alternately above and below this plane, at distances of 0.23–0.37 Å. Distances from the ring center to oxygens are 4 at 2.76 (1) Å and 2 at 2.90 (1) Å.

Discussion

This study shows conclusively that in the compound $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-crown-6) no direct uranyl–crown ether bonding obtains. This result is in opposition to the view recently proposed[9,10] that UO_2^{2+} is inserted in the crown, yielding directly bonded $[UO_2(\text{18-crown6})]^{2+}$ cations. The present structure determination was carried out using material isolated from acetonitrile, whereas the previous synthesis used ethanol; nevertheless, the x-ray powder patterns, infrared mull spectra, and decomposition temperatures are indistinguishable for products from the two preparations.

The previous structure assignment was based largely on infrared and electronic spectral data. The infrared bands previously reported[9] are very similar to those we observe and generally correspond (with small shifts) to a superposition of the spectra of $UO_2(NO_3)_2{\cdot}6H_2O$ and 18-crown-6. However, the assignment of a medium strong infrared-active band at 1030 cm^{-1} to "symmetric" ν_{NO_3} is clearly incompatible with D_{3h} symmetry of unbound nitrate ions but consistent with the bidentate ligation observed in the crystal structure. Bidentate nitrates provide the correct U–O–U "bite" for a planar or near-planar UO_6 configuration. The observed minor shifts in the crown ether bands are attributable to slight conformational changes, including those due to the hydrogen bonding.[1,6,9]

If a direct uranyl–18-crown-6 interaction occurred in the present compound, then one might also expect interactions with the related compounds, dibenzo-18-crown-6 and dicyclohexyl-18-crown-6. These two compounds have hole diameters and donor properties virtually identical with those of 18-crown-6 but are sufficiently different topologically to disrupt the hydrogen-bonding arrangement observed in the present compound. However, under conditions similar to those used to prepare $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-crown-6), we were unable to isolate compounds containing these crown ethers. We find that the polyether 15-crown-5, whose "bite" may be better suited for equatorial uranyl complexation, does form a 1:1 crystalline hydrated uranyl nitrate compound; however, its infrared spectrum is very similar to that of $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-crown-6), and, hence, uranyl–crown ether ligation probably is also absent in this compound.

Conclusions

This study has served once again to emphasize that the highly charged actinide ions display striking preference for polar oxygen ligands as in H_2O and NO_3^-. The presence of such ligands present an unfavorable competition with respect to crown ether ligation. Hence, the utilization of anhydrous conditions and nonpolar solvents will probably favor formation of uranyl–crown ether complexes. This study further shows that caution must be exercised in assigning structures of complexes containing crown ethers solely on the basis of spectroscopic and composition data, especially in view of the ability of metal–crown ether compounds to contain clathrated and hydrogen-bonded crown ethers.[4–6,25,27]

Note Added in Proof. Harman et al.[28] have just reported the first structure of an authentic lanthanide crown ether complex, neutral $[La(\text{dicyclohexyl-18-crown-6})(NO_3)_3]$.

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Registry No. $UO_2(NO_3)_2(H_2O)_2{\cdot}2H_2O{\cdot}$(18-crown-6), 59752-72-6.

Supplementary Material Available: List of F_o and F_c values (23 pages). Ordering information is given on any current masthead page.

References and Notes

(1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967); *ibid*, **92**, 386(1970); C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **16**, 11 (1972).

(2) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).

(3) E. P. Kyba, M. G. Siegel, L. R. Sousa, G. D. Y. Sogah, and D. J. Cram, *J. Am. Chem. Soc.*, **95**, 2691, 2692 (1973).

(4) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).

(5) M. R. Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973).

(6) B. E. Jepson and R. DeWitt, *J. Inorg. Nucl. Chem.*, **38**, 1175 (1976).
(7) A. Cassol, A. Seminaro, and G. DePaoli, *Inorg. Nucl. Chem. Lett.*, **9**, 1163 (1973).
(8) P. R. Heckley and R. B. King, *Proc. Rare Earth Res. Conf., 10th*, **1**, 311 (1973).
(9) R. M. Costes, G. Folcher, N. Keller, P. Plurien, and P. Rigny, *Inorg. Nucl. Chem. Lett.*, **11**, 469 (1975).
(10) R. M. Costes, G. Folcher, P. Plurien, and P. Rigny, *Inorg. Nucl. Chem. Lett.*, **12**, 13 (1976).
(11) J. de Meulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).
(12) L. K. Templeton and D. H. Templeton, Abstracts, American Crystallographic Association Summer Meeting, Storrs, Conn., June 1973, No. E10.
(13) R. R. Ryan and B. I. Swanson, *Inorg. Chem.*, **13**, 1681 (1974).
(14) D. T. Cromer, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1976.
(15) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(16) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967).
(17) A. C. Larson, *Acta Crystallogr.*, **23**, 664 (1967).
(18) D. Hall, A. D. Rae, and T. N. Waters, *Acta Crystallogr.*, **19**, 389 (1965).
(19) J. C. Taylor and M. A. Mueller, *Acta Crystallogr.*, **19**, 536 (1965).
(20) W. H. Zachariasen, *Acta Crystallogr.*, **7**, 795 (1954); H. A. Plettinger, *ibid.*, **12**, 526 (1959), revised in 4th International Transplutonium Element Symposium Proceedings of the Baden-Baden Conference, North Holland Publishing Co., Amsterdam, 1976.
(21) H. R. Hoekstra, *Inorg. Chem.*, *2*, 492 (1963).
(22) L. H. Jones, *Spectrochim. Acta*, **10**, 395 (1958); **15**, 409 (1959).
(23) B. W. Veal, D. J. Lam, W. T. Carnall, and H. R. Hoekstra, *Phys. Rev., B*, **12**, 5651 (1975).
(24) N. Kent Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, **10**, 323 (1971).
(25) D. Bright and M. R. Truter, *Nature (London)*, **225**, 176 (1970).
(26) Here and elsewhere in this paper, the trivial name "18-crown-6" will be used for the cyclic polyether 1,4,7,10,13,16-hexaoxacyclooctadecane.
(27) In a meeting with the French authors,[9,10] they agreed that the $\nu_{NO_3^-}$ bands occur in a region complicated by the presence of other bands, making alternate interpretations possible. Further, they noted that their preparation of a dihydrate compound directly from the tetrahydrate is readily explicable on the basis of our structure for the latter, in which there are two lattice waters not bound to uranyl.
(28) M. E. Harman, F. A. Hart, M. B. Hursthouse, G. P. Moss, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 396 (1976).

Contribution from the Los Alamos Scientific Laboratory,
University of California, Los Alamos, New Mexico 87545

"Bent" vs. Coplanar M–SO_2 Coordination. The Structure of the Sulfur Dioxide Adduct, $Pt(PPh_3)_3(SO_2)\cdot 0.7SO_2$[1]

P. GARY ELLER, R. R. RYAN,* and DAVID C. MOODY

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An x-ray structure determination of the compound $Pt(PPh_3)_3(SO_2)\cdot 0.7SO_2$ conclusively demonstrates the presence of a pyramidal Pt–SO_2 moiety, in contrast to conclusions reached earlier for a disordered benzene solvate form of the same compound. The Pt–SO_2 geometry in the present compound is characteristic of that found in other well-defined structures containing nonplanar M–SO_2 groups, with a long Pt–S bond of 2.368 (3) Å and Pt–S–O angles of 107.4 (3) and 106.7 (3)°. In other details, the geometry of the pseudotetrahedral coordination unit agrees with the earlier study, with P–Pt–P angles and P–Pt–S angles in the ranges 115.51 (9)–120.91 (9) and 93.3 (1)–99.6 (1)°, respectively. These results are evaluated in light of a recently proposed bonding scheme for M–SO_2 complexes, and compared with pseudotetrahedral complexes containing linear M–NO groups. Cell data: space group $P\bar{1}$, $Z = 2$, $a = 13.723$ (6), $b = 14.325$ (7), $c = 12.626$ (7) Å, $\alpha = 111.18$ (4), $\beta = 90.58$ (4), $\gamma = 91.86$ (3), $\rho_{calcd} = 1.51$ g/cm^3, $R = 0.037$, and $R_w = 0.043$ for 3868 diffractometer-collected reflections with $I \geq 2\sigma(I)$.

Introduction

Crystal structure analyses have been reported for seven complexes in which a sulfur dioxide molecule is attached directly to a transition metal.[2-7] Two cases are square-pyramidal d^8 Vaska-type adducts, $[M(PPh_3)_2(CO)Cl(SO_2)]$, where M = Rh and Ir, which are characterized by long M–S bonds (Rh–S = 2.45 Å, Ir–S = 2.49 Å) and by distinctly nonplanar, or "bent", M–SO_2 moieties (M–S–O = 104–108°).[2] Recently the formally pentacoordinate complex $Rh(\pi\text{-}C_5H_5)(C_2H_4)(SO_2)$ was shown to contain a coplanar Rh–SO_2 moiety with a short Rh–S distance of 2.096 (2) Å.[3] Two other well-defined examples of coplanar M–SO_2 moieties with short M–S distances are afforded by the d^6 hexacoordinate complexes $[Ru(NH_3)_4Cl(SO_2)]Cl$,[4] with Ru–S = 2.07 Å, and $Mn(\pi\text{-}C_5H_5)(CO)_2(SO_2)$,[5] with Mn–S = 2.05 Å. The other two structurally characterized M–SO_2 complexes are the tetracoordinate platinum–phosphine complexes $Pt(PPh_3)_2(SO_2)_2$, shown unambiguously in a previous paper[6] to contain two bent Pt–SO_2 groups with long Pt–S bonds of 2.391 (2) and 2.464 (2) Å, and $Pt(PPh_3)_3(SO_2)\cdot {}^3/_2C_6H_6$,[7] previously claimed to contain a *coplanar* Pt–SO_2 moiety with a *long* Pt–S bond, 2.40 Å. This latter result seemed highly unusual and provoked a reexamination of that structure.

The benzene solvate of $Pt(PPh_3)_3(SO_2)$ crystallizes in a hexagonal cell with space group restraints requiring the molecule to possess threefold symmetry, and hence a threefold disorder of the oxygen atoms in the Pt–SO_2 group is demanded. Clearly, selection of a disordered *bent* model would be equally acceptable on the basis of the reported crystallographic results and, in fact, such a selection gives a reasonable "bent" M–SO_2 geometry. Indeed, we find that using a bent Pt–SO_2 model in which a *single* oxygen atom is refined (hence redundant, or overlapping, oxygen positions are generated by the threefold operator for the two oxygen atoms of the SO_2 group), refinement proceeds to convergence with a reasonable pyramidal M–SO_2 geometry. However, our attempts to repeat the reported refinement with a coplanar M–SO_2 group led to divergence and totally unrealistic thermal parameters for the oxygen atoms.

Further, Fourier syntheses revealed a triangle of oxygen peaks about the threefold axis, consistent with the above bent M–SO_2 model but clearly inconsistent with a coplanar M–SO_2 model (for which a hexagon of oxygen peaks should be observed). We invariably obtained these results, using either the reported structure factors or a low temperature (−78 °C) data set collected by us, and using several different least-squares codes. These results and the implications from the structure of $Pt(PPh_3)_2(SO_2)_2$[6] clearly favor the bent Pt–SO_2 model for $Pt(PPh_3)_3(SO_2)$. To dispel any question of the correctness of this interpretation, we have solved the structure of the SO_2-solvated, triclinic form of this compound. The coordination unit in this structure is well-ordered and unambiguously contains a bent M–SO_2 moiety, with geometry characteristic of the previously observed bent M–SO_2 structures.

The importance of this structure lies in its relevance to a proposed bonding model for M–SO_2 complexes,[8] to previous