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Structural Studies of Uranyl Complexes of Diphenyl-dimethylaminosulfonylmethyl Phosphine Oxide and Diisopropyl-tolylsulfinylmethyl Phosphonate Ligands

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Abstract

The molecular structures of the bifunctional ligand, $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ (1), and its coordination complex, $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]_2$ (2), were determined by single crystal X-ray diffraction techniques, and the structural influences on the ligand due to coordination were examined. The ligand 1 crystallizes in the monoclinic space group *Cc*, with $a = 15.982(3)$, $b = 10.003(2)$, $c = 10.245(3)$ Å, $\beta = 99.47(2)^\circ$, $Z = 4$ and $V = 1615.5$ Å^3, $R_F = 2.8\%$ on 1158 unique reflections ($I \geqslant 2\sigma(I)$). Complex 2 is found in the monoclinic space group $P2_1/c$, with $a = 12.680(3)$, $b = 16.149(5)$, $c = 20.204(6)$ Å, $\beta = 107.17(2)$, $Z = 4$ and $V = 3952.7$ Å^3, $R_F = 5.2\%$ on 5060 unique reflections ($I \geqslant 2\sigma(I)$). The complex contains two phosphine oxide ligands bonded to the uranium atom through the phosphoryl oxygen atoms in a *trans* orientation with U–O(P) 2.35(1) Å. The molecular structure for the sulfinylmethylphosphonate complex, $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$ (3), was also determined by single crystal X-ray diffraction techniques, and it crystallized in the monoclinic space group $P2_1/c$, with $a = 10.759(8)$, $b = 13.811(3)$, $c = 17.823(5)$ Å, $\beta = 105.83(3)^\circ$, $Z = 4$ and $V = 2548$ Å^3, $R_F = 10.9\%$ on 1908 unique reflections ($I \geqslant 2\sigma(I)$). The complex shows a single ligand bonded in a bidentate mode to the uranium atom with U–O(P) 2.37(2) Å and U–O(S) 2.36(2) Å.

Introduction

Limited studies of the f-block element coordination chemistry of organosulfoxide, $R_2S(O)$, and organosulfone, $R_2S(O)_2$, ligands have resulted in a number of interesting complexes [1–6] and applications of organosulfoxides in synergistic metal ion solvent extraction schemes [7–11]. Despite favorable coordination characteristics for the monofunctional ligands, little attempt has been made to systematically develop their fundamental coordination chemistry or to combine sulfoxide and sulfone functional groups with other donor centers in bifunctional ligands. Since several classes of bifunctional ligands impart unique coordination and extraction chemistry with f-block elements, we set out to design several routes to bifunctional sulfinyl- and sulfonylmethyl phosphonates and phosphine oxides. We recently reported on general aspects of the synthesis and coordination properties of ligands of the general types $R_2P(O)CH_2S(O)R'$ and $R_2P(O)CH_2S(O)_2R'$ [12], and we describe here results of structural studies of one ligand, $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ (1) and two complexes, $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]$ (2) and $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$ (3), whose syntheses were briefly mentioned in the earlier report.

Experimental

General Information

The ligands, $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ and $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)$, were prepared as described previously [12]. All reactions were carried out under dry nitrogen and dried solvents were employed. Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer and NMR spectra were obtained on Varian FT-80A and JEOL GSX-400 spectrometers. Tetramethylsilane (^1H and ^{13}C) and 85% phosphoric acid (^{31}P) were used as spectral standards.

Preparation of the Complexes

The complexes were prepared in a modified fashion compared to routes described previously [12]. The initial descriptions did not provide crystalline products for the uranyl complexes described

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here; however, the modifications do result in X-ray diffraction quality samples. Spectroscopic and analytical data for the ligands and complexes were provided in the earlier report.

$UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]_2$ (2)

A 2.0 mmol portion of $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in 25 ml anhydrous ethanol, and exactly 4.0 mmol of $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ in 25 ml $CHCl_3$ was added while stirring. After one hour, the solvent and released water were evaporated. The remaining oil was redissolved in 30 ml EtOH, and the solution was refluxed for 2 h and evaporated to dryness. The complex was isolated as a microcrystalline solid and it was found to be analytically pure. Recrystallization from CH_2Cl_2 provided crystals suitable for X-ray analysis.

$UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$ (3)

A 2.0 mmol sample of $UO_2(NO_3)_2 \cdot 6H_2O$ was combined with a 2.0 mmol sample of $(i\text{-}C_3H_7O)P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)$ dissolved in 50 ml of anhydrous ethanol. The solution was refluxed for 2 h and evaporated to dryness. Samples prepared in this fashion were analytically pure. The remaining residue was recrystallized from CH_2Cl_2 and the crystals were suitable for X-ray analysis.

X-ray Diffraction Studies

Room temperature data were collected by variable speed θ–2θ scans on an Enraf Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator. The structures were solved by using standard Patterson and Fourier methods and refined by full matrix least-squares methods using appropriate neutral atom scattering factors and anomalous scattering terms [13]. Refinements included anisotropic thermal parameters for all non-hydrogen atoms and a correction for secondary extinction [14] with compounds 1 and 2. Compound 2 has U atoms in special positions 2(a) and 2(d), and these form a face centered arrangement. Hence reflections with h, k, l all even or all odd are strong, and all other reflections are weak. Approximately twice as many reflections were observed with $I > 2\sigma(I)$ than with $I > 3\sigma(I)$. With so many weak reflections, it was considered appropriate to minimize $\Sigma w(F_o^2 - F_c^2)$ [2]. With compound 3, only U, P and S atoms were refined anisotropically. The Los Alamos Crystal Structure Codes [15] were used for all calculations. Data were corrected for absorption by using the relative intensity of a low angle reflection measured as a function of Ψ (mapped to ϕ) multiplied by a spherical correction that used a radius calculated from the average distance between the three most prominent directions of crystal development. Lattice parameters and data collection information are summarized in Table 1. Atomic coordinates are listed in Tables 2–4, and bond distances and angles are summarized in Tables 5–7. ORTEP drawings with appropriate atomic numbering schemes are given in Figs. 1–3.

Results and Discussion

Previous studies had shown that sulfonylmethylphosphine oxide, $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ (**1**), could be prepared in good yield, as outlined in eqns. (1) and (2) [12]. Subsequent attempts to

$$(C_6H_5)_2PCl + LiCH_2S(O)_2N(CH_3)_2 \xrightarrow{THF} (C_6H_5)_2PCH_2S(O)_2N(CH_3)_2 \tag{1}$$

$$(C_6H_5)_2PCH_2S(O)_2N(CH_3)_2 \xrightarrow[C_6H_6]{KMnO_4/MgSO_4} \underset{\mathbf{1}}{(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2} \tag{2}$$

$$(i\text{-}C_3H_7O)_3P + ClCH_2S(p\text{-}CH_3C_6H_4) \longrightarrow (i\text{-}C_3H_7O)_2P(O)CH_2S(p\text{-}CH_3C_6H_4) + i\text{-}C_3H_7Cl \tag{3}$$

$$(i\text{-}C_3H_7O)_2P(O)CH_2S(p\text{-}CH_3C_6H_4) \xrightarrow[\substack{(CH_3)_2CO \\ H_2O}]{NaIO_4} \underset{\mathbf{4}}{(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)} \tag{4}$$

obtain the corresponding sulfinylmethylphosphine oxide have been unsuccessful as the compound is subject to facile disproportionation. The sulfinylmethyl phosphonate, $(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)$ (**4**), was also prepared as described earlier [12] and as summarized in eqns. (3) and (4). Both ligands were fully characterized by spectroscopic methods. Coordination complexes with uranyl nitrate were prepared, and based upon elemental analyses, the compositions, $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]_2$ (**2**) and $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$ (**3**) were deduced. Infrared spectroscopic data provided some evidence on the structures of the complexes. In particular, **2** showed a phosphoryl stretching frequency in the infrared spectrum at 1161 cm^{-1} and sulfur oxygen stretching frequencies at 1351 and 1145 cm^{-1}. The phosphoryl stretch was shifted down frequency 37 cm^{-1} relative to the free ligand, and this suggested some degree of uranium–phosphoryl oxygen atom donor–acceptor interaction. The SO_2 frequencies, however, were not influenced by coordination, and this suggested that the bi-

TABLE 1. X-ray crystallographic data

	1	2	3
Chemical formula	$C_{15}H_{18}NO_3PS$	$C_{30}H_{32}N_4O_{14}P_2S_2U$	$C_{14}H_{23}N_2O_{12}PSU$
Molecular weight	323.35	1040.80	712.41
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Cc	$P2_1/c$	$P2_1/c$
a (Å)	15.982(3)	12.680(3)	10.759(8)
b (Å)	10.003(2)	16.149(5)	13.811(3)
c (Å)	10.245(3)	20.204(6)	17.823(5)
β (°)	99.47(2)	107.17(2)	105.83(3)
V (Å^3)	1615.5	3952.7	2548.0
Z	4	4	4
D_x (g cm^{-3})	1.33	1.75	1.88
$F(000)$	680	1560	1360
λ(Mo Kα_1)	0.70930	0.70930	0.70930
T (°C)	23	23	23
Crystal color	colorless	yellow	yellow
Crystal dimensions (mm)	0.06 × 0.12 × 0.30	0.15 × 0.15 × 0.25	
μ (cm^{-1})	3.0	41.4	62.9
Absorption correction type		empirical psi scan and spherical	
Sphere radius (mm)	0.1	0.1	0.2
Transmission: min., max.	0.87, 1.0	0.42, 0.74	0.048, 0.182
Angle peak width (W)°	1.0	1.2	
$2\theta_{max}$ (°)	50	50	50
Scan type	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
Scan range (°)	1.0 + 0.34 tan θ	1.1 + 0.34 tan θ	0.8 + 0.34 tan θ
Scan rate (° min^{-1})	1.2 to 5.5	1.2 to 5.5	0.8 to 5.5
h, k, l limits	(−18, 18)	(−15, 15)	(0, 10)
	(0, 11)	(0, 19)	(0, 11)
	(−12, 12)	(0, 24)	(−21, 19)
Total reflections collection	2828	7138	4739
No. unique reflections	1417	6926	4483
No. with $I \geq 2\sigma(I)$	1158	5060	1908
R_F equivalent reflections (%)	2.1	2.4	5.9
Standard reflections	400 and 004	$\bar{1}23$ and $\bar{1}\bar{2}3$	400 and 004
		no significant variations	
Weight of F	$(\sigma^2(F) + 0.03F^2)^{-1}$	same	same
Function minimized	$\Sigma w(\Delta F)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(\Delta F)^2$
R_F (I > $n\sigma$(I)) (%)	2.8(2σ)	5.2(2σ)	10.9(2σ)
R_{wF}	2.9	5.8	12.1
R_{wF^2} (all data)		13.9	
GOF	1.3	1.54	4.9
Average Δ/σ	0.01	0.04	0.06
Max. Δ/σ	0.13	0.4	0.71

functional ligand was bonded to uranium only via the phosphoryl donor site. Complex **3** showed a phsophoryl stretching frequency at 1190 cm^{-1} and a sulfur–oxygen stretch at 1000 cm^{-1}. These represent 64 and 50 cm^{-1} coordination shifts with respect to the group frequencies in the free ligand. These data indicated that ligand **4** was probably bonded in a bidentate coordination mode to the uranium atom.

Despite our initial failures to obtain suitable single crystals of **2** and **3**, our inherent interest in the coordination modes displayed by the ligands led us to eventual success. The molecular structure of the ligand **1** and the uranyl complex **2** are shown in Figs. 1 and 2. The uranyl complex is found to contain two independent units (**2a** and **2b**), each with an inversion center, a linear UO_2^{2+} ion bonded to two bidentate nitrate ions and two monodentate sulfonylmethylphosphonate ligands arranged in a *trans* configuration. For the majority, the metrical parameters in the two molecules are identical; however, there are a few that vary beyond three standard deviations, and a few of these warrant brief mention. The uranyl distances, U(1)–O(1) 1.54(2) Å and U(2)–O(8) 1.77(3) Å, are surprisingly different; while the variations in the remaining distances involving uranium are not statistically significant. The U–O(uranyl) distance in molecule **2b**

TABLE 2. Positional parameters for $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ (1)

Atom	*x*	*y*	*z*
P	0.0642(0)	0.0746(0)	0.5413(0)
S	−0.0758(1)	−0.1379(1)	0.5148(1)
N	−0.1527(2)	−0.1790(4)	0.5909(4)
C(1)	0.0787(2)	0.2255(4)	0.6383(4)
C(2)	0.0501(3)	0.3448(5)	0.5794(6)
C(3)	0.0595(4)	0.4627(6)	0.6493(8)
C(4)	0.0987(4)	0.4612(6)	0.7814(7)
C(5)	0.1264(4)	0.3443(6)	0.8394(6)
C(6)	0.1166(3)	0.2267(5)	0.7703(4)
C(7)	0.1591(2)	−0.0246(4)	0.5872(4)
C(8)	0.1665(3)	−0.1310(5)	0.6731(4)
C(9)	0.2443(3)	−0.1962(6)	0.7044(6)
C(10)	0.3118(4)	−0.1577(6)	0.6501(6)
C(11)	0.3047(3)	−0.0523(6)	0.5601(7)
C(12)	0.2284(3)	0.0132(6)	0.5300(5)
C(13)	−0.0233(3)	−0.0026(4)	0.6062(4)
C(14)	−0.2221(4)	0.0854(10)	0.5855(13)
C(15)	−0.1293(5)	−0.2437(8)	0.7205(6)
O(1)	0.0460(2)	0.1052(3)	0.3977(3)
O(2)	−0.0186(2)	−0.2469(3)	0.5239(4)
O(3)	−0.1129(2)	−0.0895(4)	0.3876(3)

TABLE 3. Positional parameters for $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]_2$ (2)

Atom	*x*	*y*	*z*
Molecule 2a			
U(1)	0.0000(0)	0.0000(0)	0.0000(0)
O(1)	0.0868(7)	0.0674(7)	−0.0101(4)
O(2)	−0.0275(7)	0.0768(6)	0.0925(4)
P(1)	−0.0148(3)	0.1107(3)	0.1635(2)
C(1)	−0.0710(12)	0.2124(10)	0.1626(9)
C(2)	−0.0467(16)	0.2609(12)	0.2187(10)
C(3)	−0.0993(19)	0.3395(14)	0.2146(11)
C(4)	−0.1834(21)	0.3580(15)	0.1575(16)
C(5)	−0.2114(18)	0.3106(15)	0.0989(11)
C(6)	−0.1605(13)	0.2317(12)	0.1023(8)
C(7)	−0.0881(13)	0.0411(11)	0.2047(7)
C(8)	−0.1262(18)	−0.0350(13)	0.1733(9)
C(9)	−0.1764(16)	−0.0840(11)	0.2109(10)
C(10)	−0.1903(17)	−0.0630(15)	0.2754(12)
C(11)	−0.1457(22)	0.0103(16)	0.3050(11)
C(12)	−0.0917(19)	0.0670(14)	0.2723(10)
C(13)	0.1303(10)	0.1052(9)	0.2172(6)
S(1)	0.2278(4)	0.1612(3)	0.1876(2)
O(3)	0.2055(11)	0.2456(8)	0.1860(8)
O(4)	0.2350(11)	0.1193(9)	0.1263(6)
N(1)	0.3507(11)	0.1352(12)	0.2429(7)
C(14)	0.3975(19)	0.0514(12)	0.2400(14)
C(15)	0.3681(14)	0.1730(16)	0.3103(10)
N(2)	−0.1817(13)	0.0885(10)	−0.0980(8)
O(5)	−0.1648(8)	0.0928(7)	−0.0350(5)
O(6)	−0.1158(9)	0.0480(7)	−0.1183(5)
O(7)	−0.2585(11)	0.1247(9)	−0.1372(7)
Molecule 2b			
U(2)	0.5000(0)	0.0000(0)	0.5000(0)
O(8)	0.5965(8)	0.0203(7)	0.5814(5)
O(9)	0.4304(9)	0.1355(7)	0.4971(5)
P(2)	0.3930(3)	0.2127(3)	0.5237(2)
C(16)	0.4080(12)	0.3079(12)	0.4772(7)
C(17)	0.4990(16)	0.3015(15)	0.4461(9)
C(18)	0.5079(23)	0.3807(18)	0.4106(12)
C(19)	0.4473(25)	0.4514(16)	0.4153(11)
C(20)	0.3700(20)	0.4505(15)	0.4525(13)
C(21)	0.3435(15)	0.3785(13)	0.4807(9)
C(22)	0.4728(14)	0.2335(13)	0.6144(8)
C(23)	0.4603(16)	0.1710(12)	0.6620(8)
C(24)	0.5309(24)	0.1841(16)	0.7342(12)
C(25)	0.6057(21)	0.2530(18)	0.7476(12)
C(26)	0.6099(18)	0.3124(15)	0.6976(12)
C(27)	0.5437(16)	0.3016(15)	0.6312(11)
C(28)	0.2516(10)	0.2040(10)	0.5232(7)
S(2)	0.1585(5)	0.1709(5)	0.4394(3)
O(10)	0.1856(13)	0.0901(11)	0.4288(10)
O(11)	0.1563(12)	0.2343(14)	0.3913(7)
N(3)	0.0397(11)	0.1658(12)	0.4497(8)
C(29)	−0.0232(18)	0.2447(12)	0.4518(14)
C(30)	0.0196(19)	0.1057(14)	0.5035(13)
N(4)	0.6607(13)	0.0602(13)	0.4317(9)
O(12)	0.6009(9)	0.1063(8)	0.4522(6)
O(13)	0.6473(14)	−0.0159(9)	0.4407(9)
O(14)	0.7309(12)	0.0871(10)	0.4098(8)

Type II extinction parameter 5.5(10) × 10^{-8} cm.

is typical of uranyl distances, and it may be compared directly with the distance in $UO_2(NO_3)_2[(C_4H_9O)_3P(O)]_2$, 1.742(7) Å [16]. The origin of the anomalous short distance in molecule **2a** is not obvious.

The U–O(phosphoryl) distances, 2.36(1) and 2.38(2) Å, are typical and may be compared with the related distance in $UO_2(NO_3)_2[(C_4H_9O)_3PO]_2$, 2.347(6) Å. The bond distance does not particularly parallel the relatively small phosphoryl coordination shift found in the infrared spectrum of **2**. The distances and angles in the sulfonylamide group also show some variation upon comparison of the two independent molecules of **2**, and some thermal parameters in this group are larger than those in the rest of the molecule. Further, comparable parameters in the sulfonylamide fragment of the free ligand vary unexpectedly, for example, S–O(2) 1.416(3) Å, S–O(3) 1.425(3) Å, N–C(14) 1.446(8) Å, N–C(15) 1.469(7) Å. Nonetheless, comparisons between the free ligand **1** and complex **2** are appropriate. The P=O bond distance in **1**, 1.484(3) Å, falls within a range (1.38–1.56 Å, av. 1.46 Å) encountered in many phosphoryl compounds [17], and it is identical to the distance in $(C_6H_5)_3P(O)$ [18] 1.46 Å. This

TABLE 4. Positional parameters for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$ (3)

Atom	*x*	*y*	*z*
U	0.9285(1)	0.2214(1)	0.0546(1)
P	1.0740(10)	0.1888(8)	−0.1085(6)
S	0.7993(13)	0.1520(13)	−0.1409(9)
O(1)	0.871(3)	0.326(2)	0.005(2)
O(2)	0.978(3)	0.108(2)	0.109(1)
O(3)	1.068(2)	0.196(2)	−0.026(1)
O(4)	1.078(4)	0.284(3)	−0.149(2)
O(5)	1.197(3)	0.125(2)	−0.113(2)
O(6)	0.818(2)	0.139(2)	−0.060(1)
O(7)	1.152(3)	0.286(2)	0.102(2)
O(8)	1.224(5)	0.360(3)	0.211(2)
O(9)	1.030(3)	0.308(2)	0.178(1)
O(10)	0.807(3)	0.257(2)	0.154(2)
O(11)	0.620(5)	0.212(3)	0.142(2)
O(12)	0.697(3)	0.182(2)	0.044(2)
N(1)	1.138(5)	0.325(4)	0.164(3)
N(2)	0.708(4)	0.221(3)	0.109(2)
C(1)	1.080(8)	0.387(6)	−0.114(4)
C(2)	1.181(11)	0.432(8)	−0.122(5)
C(3)	0.996(11)	0.427(9)	−0.187(6)
C(4)	0.943(3)	0.124(2)	−0.170(2)
C(5)	0.690(4)	0.054(3)	−0.196(2)
C(6)	0.603(4)	0.095(3)	−0.260(2)
C(7)	0.517(4)	0.034(4)	−0.308(2)
C(8)	0.530(5)	−0.062(4)	−0.282(2)
C(9)	0.613(5)	−0.101(4)	−0.219(2)
C(10)	0.698(4)	−0.037(3)	−0.168(2)
C(11)	0.413(7)	−0.126(6)	−0.334(4)
C(12)	1.347(10)	0.149(8)	−0.079(6)
C(13)	1.390(7)	0.054(6)	−0.117(4)
C(14)	1.360(10)	0.127(8)	−0.012(6)

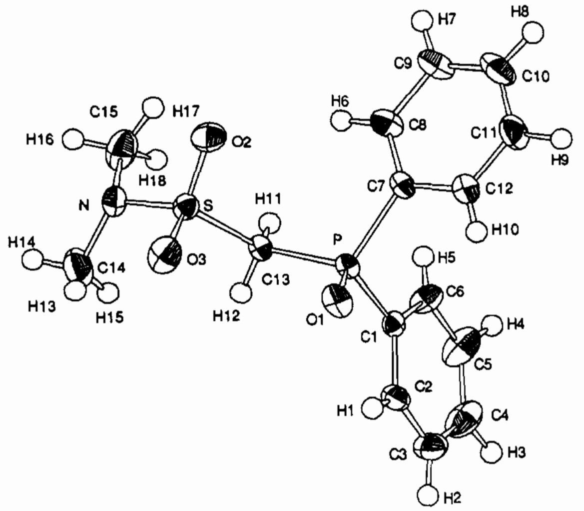

Fig. 1. Molecular structure and atom labeling scheme for $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$.

TABLE 5. Selected bond distances (Å) and angles (°) for $(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2$ (1)

Distances			
P–C(1)	1.801(4)	C(2)–C(3)	1.375(8)
P–C(7)	1.809(4)	C(3)–C(4)	1.395(9)
P–C(13)	1.816(4)	C(4)–C(5)	1.353(9)
P–O(1)	1.484(3)	C(5)–C(6)	1.369(7)
S–C(13)	1.776(4)	C(6)–C(1)	1.388(6)
S–N	1.614(4)	C(7)–C(8)	1.374(6)
S–O(2)	1.416(3)	C(8)–C(9)	1.395(6)
S–O(3)	1.425(3)	C(9)–C(10)	1.348(8)
N–C(14)	1.446(8)	C(10)–C(11)	1.393(8)
N–C(15)	1.469(7)	C(11)–C(12)	1.373(7)
C(1)–C(2)	1.381(6)	C(12)–C(7)	1.389(6)
Angles			
C(1)–P–C(7)	106.8(2)	P–C(1)–C(6)	122.7(3)
C(1)–P–C(13)	101.1(2)	P–C(13)–S	117.1(2)
C(1)–P–O(1)	111.1(2)	C(2)–C(1)–C(6)	118.6(4)
C(7)–P–C(13)	109.6(2)	C(1)–C(2)–C(3)	120.9(5)
C(7)–P–O(1)	113.0(2)	C(2)–C(3)–C(4)	119.3(6)
C(13)–P–O(1)	114.5(2)	C(3)–C(4)–C(5)	119.8(6)
N–S–C(13)	105.7(2)	C(4)–C(5)–C(6)	121.0(6)
N–S–O(2)	107.8(2)	C(5)–C(6)–C(1)	120.4(5)
N–S–O(3)	107.0(2)	P–C(7)–C(8)	124.9(3)
C(13)–S–O(2)	108.0(2)	P–C(7)–C(12)	115.8(3)
C(13)–S–O(3)	108.3(2)	C(8)–C(7)–C(12)	119.4(4)
O(2)–S–O(3)	119.3(2)	C(7)–C(8)–C(9)	119.3(5)
S–N–C(14)	117.2(5)	C(8)–C(9)–C(10)	121.0(6)
S–N–C(15)	116.6(4)	C(9)–C(10)–C(11)	120.4(5)
C(14)–N–C(15)	113.6(7)	C(10)–C(11)–C(12)	118.9(5)
P–C(1)–C(2)	118.7(3)	C(11)–C(12)–C(7)	121.1(5)

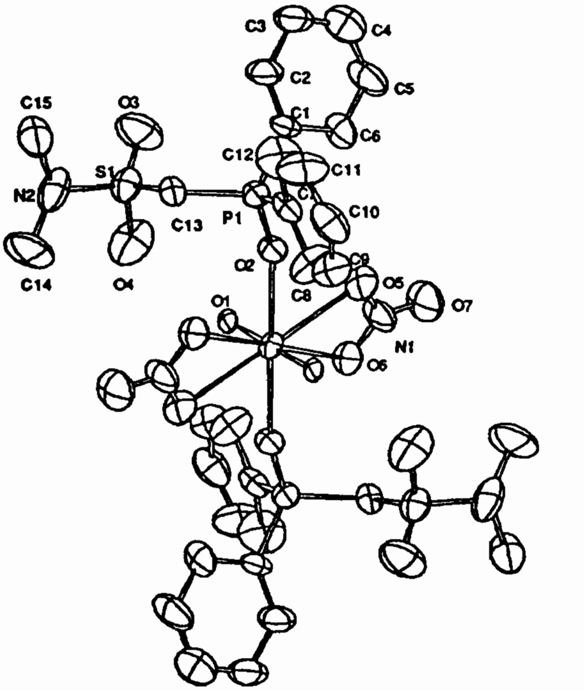

Fig. 2. Molecular structure and atom labeling scheme for $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]_2$.

TABLE 6. Selected bond distances (Å) and angles (°) for $UO_2(NO_3)_2[(C_6H_5)_2P(O)CH_2S(O)_2N(CH_3)_2]_2$ (2)

Molecule 2a		Molecule 2b	
Distances			
U(1)–O(1)	1.54(2)	U(2)–O(8)	1.77(3)
U(1)–O(2)	2.36(1)	U(2)–O(9)	2.38(2)
U(1)–O(5)	2.46(2)	U(2)–O(12)	2.46(3)
U(1)–O(6)	2.53(3)	U(2)–O(13)	2.53(3)
P(1)–O(2)	1.50(1)	P(2)–O(9)	1.47(2)
P(1)–C(1)	1.78(2)	P(2)–C(16)	1.81(3)
P(1)–C(7)	1.79(3)	P(2)–C(22)	1.83(3)
P(1)–C(13)	1.88(3)	P(2)–C(28)	1.77(2)
S(1)–C(13)	1.76(2)	S(2)–C(28)	1.84(3)
S(1)–O(3)	1.39(2)	S(2)–O(10)	1.39(2)
S(1)–O(4)	1.45(2)	S(2)–O(11)	1.40(3)
S(1)–N(1)	1.65(3)	S(2)–N(3)	1.56(3)
N(1)–C(14)	1.46(4)	N(3)–C(29)	1.50(4)
N(1)–C(15)	1.48(3)	N(3)–C(30)	1.57(4)
N(2)–O(5)	1.25(3)	N(4)–O(12)	1.20(3)
N(2)–O(6)	1.19(3)	N(4)–O(13)	1.26(3)
N(2)–O(7)	1.26(3)	N(4)–O(14)	1.18(3)
C–C(ring)	1.40(3) av.	C–C(ring)	1.42(3) av.
Angles			
C(1)–P(1)–C(7)	109(1)	C(16)–P(2)–C(22)	104(1)
C(1)–P(1)–C(13)	112(1)	C(16)–P(2)–C(28)	110(1)
C(10–P(1)–O(2)	113(1)	C(16)–P(2)–O(9)	114(1)
C(7)–P(1)–C(13)	104(1)	C(22)–P(2)–C(28)	106(1)
C(7)–P(1)–O(2)	107(1)	C(22)–P(2)–O(9)	112(1)
C(13)–P(1)–O(2	111(1)	C(28)–P(2)–O(9)	110(1)
C(13)–S(1)–O(3)	109(1)	C(28)–S(2)–O(10)	105(1)
C(13)–S(1)–O(4)	106(1)	C(28)–S(2)–O(11)	108(2)
C(13)–S(1)–N(1)	104(1)	C(28)–S(2)–N(3)	107(1)
O(3)–S(1)–O(4)	120(1)	O(10)–S(2)–O(11)	125(2)
O(3)–S(1)–N(1)	116(1)	O(10)–S(2)–N(3)	108(2)
O(4)–S(1)–N(1)	100(1)	O(11)–S(2)–N(3)	103(2)
S(1)–N(1)–C(14)	121(3)	S(2)–N(3)–C(29)	120(3)
S(1)–N(1)–C(15)	112(2)	S(2)–N(3)–C(30)	121(3)
C(14)–N(1)–C(15)	118(3)	C(29)–N(3)–C(30)	103(3)
C(2)–C(1)–P(1)	122(2)	C(17)–C(16)–P(2)	115(3)
P(1)–C(13)–S(1)	116(1)	P(2)–C(28)–S(2)	114(1)
O(5)–N(2)–O(6)	118(2)	O(12)–N(4)–O(13)	115(3)
O(5)–N(2)–O(7)	117(3)	O(12)–N(4)–O(14)	123(4)
O(6)–N(2)–O(7)	125(3)	O(13)–N(4)–O(14)	121(4)

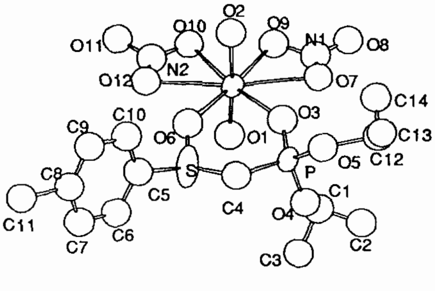

Fig. 3. Molecular structure and atom labeling scheme for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$.

bond length does not significantly lengthen upon coordination with UO_2^{2+}, 1.50(1) and 1.47 Å. The P–C(13) and C(13)–S distances in the ligand are normal, and there is little change upon coordination except for S(2)–C(28) in molecule 2, 1.84(3) Å, which is long and the difference borders on the 3σ significance test. Finally, the uranyl nitrate interactions, U–O(N) av. 2.51 Å, are typical and fall within a range of distances of related $UO_2(NO_3)_2 \cdot L_2$ complexes [12].

The molecular structure of the sulfinylmethylphosphonate complex, 3, is shown in Fig. 3. The

TABLE 7. Selected bond distances (Å) and angles (°) for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]$ (3)

Distances			
U–O(1)	1.72(3)	N(1)–O(7)	1.27(4)
U–O(2)	1.84(3)	N(1)–O(8)	1.17(5)
U–O(3)	2.37(2)	N(1)–O(9)	1.28(5)
U–O(6)	2.36(2)	N(2)–O(10)	1.25(4)
U–O(7)	2.48(3)	N(2)–O(11)	1.26(5)
U–O(9)	2.48(3)	N(2)–O(12)	1.24(4)
U–O(10)	2.52(3)	O(4)–C(1)	1.56(7)
U–O(12)	2.51(3)	O(5)–C(12)	1.59(9)
P–O(3)	1.49(2)	C(1)–C(2)	1.29(11)
P–O(4)	1.51(4)	C(1)–C(3)	1.47(11)
P–O(5)	1.61(3)	C(12)–C(13)	1.60(10)
P–C(4)	1.78(3)	C(12)–C(14)	1.20(10)
S–O(6)	1.40(2)	C(8)–C(11)	1.61(7)
S–C(4)	1.81(3)	C–C(ring)	1.38(6) av.
S–C(5)	1.89(4)		
Angles			
O(3)–P–O(4)	116(2)	C(2)–C(1)–O(4)	109(8)
O(3)–P–O(5)	110(1)	C(3)–C(1)–O(4)	93(7)
O(3)–P–C(4)	114(1)	C(2)–C(1)–C(3)	93(8)
O(4)–P–O(5)	109(2)	C(13)–C(12)–O(5)	93(7)
O(4)–P–C(4)	105(2)	C(14)–C(12)–O(5)	99(9)
O(5)–P–C(4)	102(2)	C(13)–C(12)–C(14)	104(10)
C(4)–S–O(6)	112(2)	S–C(5)–C(6)	109(3)
C(4)–S–C(5)	99(2)	S–C(5)–C(10)	120(3)
O(6)–S–C(5)	110(2)	O(7)–N(1)–O(8)	123(5)
P–C(4)–S	108(2)	O(7)–N(1)–O(9)	114(5)
U–O(3)–P	144(1)	O(8)–N(1)–O(9)	121(5)
U–O(6)–S	136(2)	O(10)–N(2)–O(11)	110(4)
C(1)–O(4)–P	127(4)	O(10)–N(2)–O(12)	128(5)
C(12)–O(5)–P	129(5)	O(11)–N(2)–O(12)	120(5)

quality of the data only allowed for anisotropic refinement of the U, P and S positions. The structure contains a linear UO_2^{2+} group bonded to two bidentate nitrate ions and a bidentate sulfinylmethylphosphonate ligand. The U–O(uranyl) distances, 1.72(3) and 1.84(3) Å, are comparable with uranyl distances in related complexes. The U–O(P) distance, 2.37(2) Å, also compares well with the distance in 2 and other related complexes. The U–O(6)-(sulfinyl) distance, 2.36(2) Å, suggests that the SO–U and PO–U interactions are comparable in strength. Unfortunately, the P=O and S=O distances for the uncoordinated ligand are not available for comparison; however, the P=O and S=O bond distances in 3, 1.49(2) and 1.40(2) Å, can be compared with the related distances in the complex $Gd(NO_3)_3$-$[(i\text{-}C_3H_7O)_2P(O)CH_2S(O)(p\text{-}CH_3C_6H_4)]\cdot H_2O$ (4) [12]: P=O, 1.475(5) Å and S=O, 1.506(5) Å. The ligand in 4 is also bonded in a bidentate fashion. The S=O bond distance in 3 is unexpectedly short, and it is shorter than S=O distances in free ligands $(C_6H_5)_2SO$ 1.489(5) Å [19] and $[(CH_3)_2N]_2SO$ 1.480(9) Å [20]. The average UO_2^{2+}–nitrate oxygen atom distance, 2.50 Å, is identical to that found in complex 2.

From inspection of Table 1, it is clear that the quality of the refinement for 3 is significantly lower than that for 1 and 2, as evidenced by the high values of *R* and *GOF*. We attribute this to poor crystal quality, as indicated also by the high value of R_F for equivalent reflections and the low ratio of observed to unique reflections. Data were collected on the best of several crystals. In spite of the marginal nature of the final metrical parameters, the overall architectural features are no doubt correct, and the structure establishes the important bidenticity of the ligand.

The structures presented here confirm the tentative structural conclusions based upon the spectroscopic data for 2 and 3, and they provide additional evidence for the nature of the interactions between uranyl ions and bifunctional ligands and sulfinylmethylphosphonates and sulfonylmethylphosphine oxides. The structure of 3 also affirms our previous finding illustrated by a Gd(III) complex that the sulfinylmethylphosphonate 4 is capable of forming bidentate complexes with hard metal centers including UO_2^{2+}. The structure of 2 suggests that sulfonylmethylphosphine oxides and the phosphonate analog will probably only select a monodentate coordination geometry.

Supplementary Material

Observed and calculated structure factors, hydrogen atom positional parameters and anisotropic thermal parameters are available from the authors upon request.

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