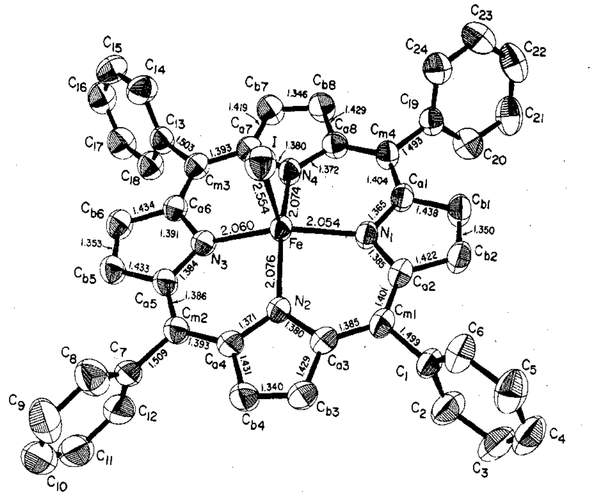

Figure 1. Computer-drawn perspective view of the FeTPPI molecule. The numbering scheme used for the atoms is displayed. The individual bond distances in the coordination group and the porphinato core are shown. Esd's are 0.003 for the distance involving iron and 0.005 Å otherwise.

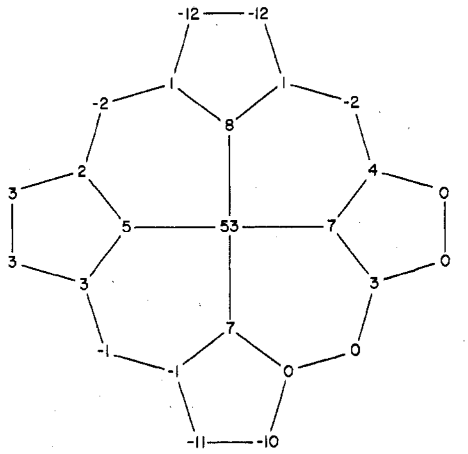

Figure 2. Formal diagram of the porphinato skeleton in FeTPPI illustrating the perpendicular displacements, in units of 0.01 Å, from the mean plane of the core. The orientation of the core is approximately the same as shown in Figure 1.

porphinato nitrogen atoms and away from the iron(III) atom.

Table V summarizes three coordination group parameters for the nine high-spin iron(III) porphyrins of known structure. The parameters are the average Fe–N bond distance and the displacement of the iron(III) atom from the mean plane of the four nitrogen atoms and the mean plane of the core. It is seen that, save for $[FeTPP]_2O$, the average Fe–N bond distance of 2.068 (8) Å agrees to within one esd. Parameters in the coordination groups of the bromo and iodo derivatives of $[FeTPP]^+$ are quite similar; however, the chloro derivative has a substantially smaller displacement of the iron(III) atom (0.39 Å). These differences, however, appear to be related to the conformation of the porphinato core rather than to the anionic axial ligand.

The porphinato core in FeTPPCl has crystallographically required planarity,[2a] and a redetermination of structure[2b] shows that no substantial nonplanarity is obscured by the known disorder. Both $Fe(MesoP)(OCH_3)$ and $Fe(Proto\ IX)SPhNO_2$ have nearly planar porphinato cores; the average displacement of the iron(III) atom is 0.47 (3) Å. The remaining high-spin complexes have substantially less planar cores than the above three complexes; the average value of the iron displacement from the mean plane of the core is 0.54 (1) Å. These conformational differences most probably result from environmental influences rather than the identity of the axial ligand (note the differences between FeTPPCl and Fe(Proto IX)Cl).

Table V. Coordination Group Parameters of Five-Coordinate High-Spin Iron(III) Porphyrins

complex[a]	Fe–N	$\Delta(N_4)$	Δ(core)	ref
$Fe(MesoP)(OCH_3)$	2.073 (6)	0.46	0.49	8
Fe(Proto IX)Cl	2.062 (10)	0.48	0.55	9
FeTPPCl	2.060 (3)	0.39	0.39	2b
FeTPPBr	2.069 (9)	0.49	0.56	1
FeTPPI	2.066 (11)	0.46	0.53	this work
FeTPP(NCS)	2.065 (10)	0.49	0.55	10
$[FeTPP]_2O$	2.087 (8)	0.50	0.54	4
$Fe(Proto\ IX)SPhNO_2$	2.064 (18)	0.43	0.45	11
$[Fe(ODM)]_2O$	2.065 (8)	0.51	0.53	12
av	2.068 (8)	0.47 (4)	0.51 (6)	

[a] Abbreviations: MesoP, mesoporphyrin dianion; Proto IX, protoporphyrin IX dianion; ODM, 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphyrin dianion.

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Registry No. FeTPPI, 25482-28-4.

Supplementary Material Available: Tables II and III, bond distances and angles in FeTPPI, and a listing of structure factor amplitudes (×10) (31 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of Di-*n*-propylammonium Ethoxybis(di-*n*-propylmonothiocarbamato)dioxouranate(VI), a Mixed-Chelate Alkoxide of Uranium

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Although many reports involving the uranyl ion UO_2^{2+} have appeared in the chemical literature, most concern the chemistry of the simple salts (and adducts of these compounds)[2] and complexes which exhibit uranyl–oxygen and uranyl–nitrogen linkages.[3] The chemistry of the common organic chelating species such as tropolonates,[4] β-diketonates,[5] and Schiff bases[6]

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has been described, and much attention has also been focused on the structural aspects[3] of such compounds. Photochemical studies[7] and the use of the uranyl ion (in the form of complex species of the type $UO_2F_5^{3-}$, for example) in studies of the binding of heavy metals to proteins[8] have also been reported.

Uranyl complexes involving heavier donor atoms in group 5A (such as phosphorus and arsenic) and group 6A (such as sulfur and selenium), however, are not so well-known. The UO_2^{2+} ion is considered to be a "hard" acid[9] and thus does not easily form simple acceptor–donor adducts with the heavy congeners of nitrogen and oxygen and, as a result, virtually all uranyl–sulfur compounds found in the research literature involve sulfur as the sulfide[2] or some other anionic form such as the thiocarbamate involved in this investigation.

The present report details the synthesis and structural study of one of the members of a new set of compounds[10] of the type $[R_2NH_2]^+[UO_2(R_2NCOS)_2OR']^-$ (the uranyl thiocarbamate alkoxides), where R = *n*-C_3H_7 and R′ = C_2H_5 in this case. These compounds represent (1) the first air- and moisture-stable class of actinide alkoxides, (2) the first actinide alkoxide existing in conjunction with a chelating anion, and (3) the first UO_5S_2 metal center. Consequently, since these compounds also possess the uranium–oxygen bond in three separate environments in the same molecule, they are of considerable structural interest.

Experimental Section

The title compound was prepared by bubbling carbonyl sulfide (Matheson, 97.5% purity) through a solution of di-*n*-proylamine (Eastman, reagent grade) in absolute ethanol at 0 °C for 5–10 min followed by the addition of a saturated, ethanolic solution of $UO_2Cl_2 \cdot 3H_2O$ (Alfa Products) with stirring. The bright yellow complex that precipitated from solution was filtered on a Büchner funnel, washed with several portions of cold diethyl ether, and allowed to dry in the open air. Anal. Calcd for $[(n\text{-}C_3H_7)_2NH_2]^+[UO_2((n\text{-}C_3H_7)_2NCOS)_2OC_2H_5]^-$: C, 35.83; H, 6.65; N, 5.70; S, 8.70. Found: C, 35.72; H, 6.52; N, 5.71; S, 8.34.

A small yellow crystal, approximately 0.14 × 0.11 × 0.08 mm in size, was glued to a glass fiber and examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Cu X-ray tube ($\lambda(K\alpha_1)$ 1.540 56 Å). ω scans of several low-angle reflections showed peaks with half-widths of 0.1°. The space group is *C*2/*c*. The setting angles of 12 manually centered reflections ($91° < 2\theta < 95°$) were used to determine the least-squares analysis of the following cell parameters: $a = 23.217$ (7) Å, $b = 15.238$ (3) Å, $c = 19.567$ (6) Å, $\beta = 109.50$ (4)°, and $V = 6525$ Å^3. For $Z = 8$ and a molecular weight of 713.8 the calculated density is 1.45 g cm^{-3}.

Intensity data were collected using the θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each peak was scanned 0.7° before the $K\alpha_1$ peak to 0.7° after the $K\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range. The temperature during the data collection was 22 ± 1 °C. Three standard reflections were measured every 200th scan. A total of 8674 scans were performed, but the last 3245 were deleted because of the severity of the crystal decomposition and lack of consistency among the standard reflections. The 5071 scans, excluding the standard reflections, resulted in 4046 unique data of which 2815 had $I > 3\sigma$. An absorption correction ($\mu = 165$ cm^{-1}) was applied[11] which ranged from 2.4 to 4.4. The crystal decay factor based on the variations of the three standard reflections ranged from 1.0 to 2.1. This large variation was alleviated to some extent by the averaging of equivalent reflections but remains one of the limiting factors in the accuracy of the data.

A three-dimensional Patterson calculation showed the uranium atom position, and subsequent least-squares refinements and Fourier calculations revealed all of the atoms in the structure. Least-squares refinements in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized converged rapidly to the final structure. The expressions that were used in proccessing the data and estimating weights are given in the supplementary material; the "ignorance factor", *p*, was set to 0.05. Scattering factors from Doyle and Turner[12] were used, and anomalous dispersion corrections[13] were applied. Anisotropic thermal parameters were applied only to the uranium atom. Hydrogen atoms were included at calculated positions of 0.95 ± 0.01 Å from the carbon or nitrogen atoms to which they are bonded, but they were not refined.

Table I. Positional and Thermal Parameters with Estimated Deviations[a] for the Nonhydrogen Atoms

atom	*x*	*y*	*z*	*B*, Å^2
U	0.14583 (2)	0.04975 (3)	0.11598 (3)	*b*
S(1)	0.1140 (2)	0.1771 (3)	0.2058 (2)	6.84 (9)
S(2)	0.1487 (2)	−0.0406 (3)	0.2455 (2)	7.49 (9)
O(1)	0.1272 (4)	0.2011 (6)	0.0813 (5)	6.2 (2)
O(2)	0.1693 (4)	−0.1029 (6)	0.1325 (5)	6.3 (2)
O(3)	0.1575 (4)	0.0261 (5)	0.0112 (5)	5.8 (2)
O(4)	0.0662 (4)	0.0272 (5)	0.0706 (5)	5.6 (2)
O(5)	0.2244 (4)	0.0738 (6)	0.1556 (5)	6.0 (2)
N(1)	0.1128 (6)	0.327 (1)	0.1335 (8)	8.6 (3)
N(2)	0.1924 (6)	−0.199 (1)	0.2265 (8)	8.5 (3)
N(3)	−0.0501 (5)	0.0136 (8)	0.0911 (6)	6.2 (3)
C(1)	0.1168 (6)	0.238 (1)	0.1340 (8)	6.6 (3)
C(2)	0.1711 (6)	−0.120 (1)	0.1962 (8)	6.1 (3)
C(3)	0.2105 (9)	0.020 (1)	−0.012 (1)	9.9 (5)
C(4)	0.234 (2)	−0.079 (2)	−0.007 (2)	19.1 (11)
C(5)	0.1232 (9)	0.378 (1)	0.073 (1)	9.7 (5)
C(6)	0.062 (1)	0.389 (2)	0.016 (1)	11.9 (6)
C(7)	0.074 (1)	0.450 (2)	−0.046 (2)	14.4 (8)
C(8)	0.0935 (9)	0.378 (1)	0.190 (1)	9.9 (5)
C(9)	0.150 (1)	0.411 (2)	0.237 (1)	11.6 (6)
C(10)	0.126 (1)	0.469 (2)	0.294 (1)	13.1 (7)
C(11)	0.2161 (8)	−0.257 (1)	0.186 (1)	9.3 (5)
C(12)	0.181 (2)	−0.337 (3)	0.159 (2)	19.6 (12)
C(13)	0.130 (2)	−0.334 (3)	0.114 (2)	22.4 (15)
C(14)	0.213 (1)	−0.214 (1)	0.308 (1)	11.1 (6)
C(15)	0.162 (1)	−0.252 (2)	0.313 (1)	13.3 (7)
C(16)	0.186 (1)	−0.267 (2)	0.407 (1)	14.3 (7)
C(17)	−0.0326 (7)	−0.063 (1)	0.1415 (8)	6.8 (3)
C(18)	−0.0239 (7)	−0.147 (1)	0.1014 (9)	8.4 (4)
C(19)	−0.002 (1)	−0.223 (2)	0.152 (1)	12.5 (6)
C(20)	−0.0556 (7)	0.096 (1)	0.128 (1)	8.3 (4)
C(21)	−0.0639 (8)	0.169 (1)	0.073 (1)	9.4 (5)
C(22)	−0.074 (1)	0.261 (2)	0.107 (1)	14.4 (7)

[a] Here and in the following tables the number in parentheses is the estimated standard deviation for the least significant figures.
[b] The anisotropic temperature factor for *U* has the form $\exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^* + \ldots))$, with $B_{11} = 4.43$ (2), $B_{22} = 4.71$ (3), $B_{33} = 5.00$ (3), $B_{12} = -0.31$ (2), $B_{13} = 1.43$ (2), and $B_{23} = -0.08$ (2).

The discrepancy indices for 2739 data where $F^2 > 3\sigma$ and $25° < 2\theta < 110°$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.044$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.054$$

R for all 4046 data is 0.069. The error in an observation of unit weight is 1.29. In the last cycle no parameter changed more than 0.17σ. The largest peak in the final difference Fourier was 1.4 e/Å^3 and is a ripple near the uranium atom.

Results and Discussion

Atomic parameters, hydrogen positional parameters, distances, and angles are listed in Tables I–IV. Figure 1 shows an ORTEP view of the nonhydrogen atoms and the numbering scheme used for the atoms in the tables.

The uranium atom is heptacoordinate and is at the center of a pentagonal bipyramid consisting of two sulfur atoms and five oxygen atoms (see Figure 1). The overall molecular structure of the title compound is remarkably similar to that of diethylammonium ethoxybis(diethylmonothiocarbamato)dioxouranate(VI),[10] which has ethyl groups in place of *n*-propyl groups. In each compound two formula units form a hydrogen-bonded dimer about a crystallographic center of symmetry. These dimers pack in the two crystal lattices with different symmetry, yet corresponding bond distances and angles (excepting the alkyl groups) are in close agreement for the two structures. This consistency indicates that we are observing a structure which is characteristic of the complex and not one which is dominated by molecular packing effects

Table II. Estimated Hydrogen Positional Parameters[a]

	x	*y*	*z*
H(1)	0.2425	0.0568	0.0182
H(2)	0.1995	0.0398	−0.0616
H(3)	0.2032	−0.1162	−0.0376
H(4)	0.2461	−0.0992	0.0422
H(5)	0.2699	−0.0817	−0.0228
H(6)	0.1505	0.3458	0.0546
H(7)	0.1408	0.434	0.0906
H(8)	0.0344	0.4166	0.0355
H(9)	0.0464	0.3327	−0.004
H(10)	0.1023	0.4217	−0.065
H(11)	0.0903	0.5057	−0.0254
H(12)	0.0359	0.4593	−0.0846
H(13)	0.075	0.3402	0.216
H(14)	0.0659	0.425	0.1683
H(15)	0.1697	0.4484	0.2115
H(16)	0.1774	0.3656	0.2612
H(17)	0.1055	0.4304	0.3174
H(18)	0.0977	0.5133	0.2677
H(19)	0.1600	0.4961	0.3297
H(20)	0.2563	−0.2742	0.216
H(21)	0.2188	−0.2255	0.1445
H(22)	0.1774	−0.3664	0.2008
H(23)	0.2055	−0.3721	0.1383
H(24)	0.1321	−0.3060	0.0711
H(25)	0.104	−0.3002	0.1336
H(26)	0.1143	−0.3920	0.1033
H(27)	0.2223	−0.160	0.3351
H(28)	0.2478	−0.2524	0.3244
H(29)	0.1536	−0.3069	0.2873
H(30)	0.1273	−0.2143	0.2960
H(31)	0.1953	−0.211	0.4303
H(32)	0.2215	−0.3036	0.4216
H(33)	0.1537	−0.2945	0.4194
H(34)	−0.0637	−0.0735	0.1627
H(35)	0.0053	−0.0494	0.1792
H(36)	0.0059	−0.135	0.0782
H(37)	−0.0621	−0.1617	0.0655
H(38)	−0.0317	−0.2356	0.1756
H(39)	0.0363	−0.2088	0.1884
H(40)	0.0026	−0.2737	0.1255
H(41)	−0.0187	0.1056	0.1684
H(42)	−0.0897	0.094	0.1448
H(43)	−0.0987	0.1570	0.0315
H(44)	−0.028	0.1733	0.0592
H(45)	−0.0389	0.2737	0.1492
H(46)	−0.1097	0.2574	0.1215
H(47)	−0.0791	0.3066	0.072
H(48)	−0.0891	−0.0007	0.0543
H(49)	−0.0119	0.0180	0.084

[a] Isotropic temperature parameters assigned were $B = 10.0$ Å^2 for atoms H(1)–H(47) and $B = 8.0$ Å^2 for H(48) and H(49).

Table III. Distances (Å)

U–O(1)	2.40 (1)	C(17)–N(3)	1.49 (2)
–O(2)	2.39 (1)	C(20)–N(3)	1.47 (2)
–O(3)	2.19 (1)	C(3)–C(4)	1.61 (4)
–O(4)	1.80 (1)	C(5)–C(6)	1.49 (3)
–O(5)	1.77 (1)	C(6)–C(7)	1.62 (3)
–S(1)	2.877 (4)	C(8)–C(9)	1.42 (3)
–S(2)	2.865 (4)	C(9)–C(10)	1.67 (3)
S(1)–C(1)	1.70 (2)	C(11)–C(12)	1.46 (4)
S(2)–C(2)	1.73 (2)	C(12)–C(13)	1.22 (5)
O(1)–C(1)	1.26 (2)	C(14)–C(15)	1.35 (3)
O(2)–C(2)	1.26 (2)	C(15)–C(16)	1.74 (3)
O(3)–C(3)	1.45 (2)	C(17)–C(18)	1.55 (2)
N(1)–C(1)	1.37 (2)	C(18)–C(19)	1.50 (3)
N(2)–C(2)	1.35 (2)	C(20)–C(21)	1.51 (3)
C(5)–N(1)	1.50 (2)	C(21)–C(22)	1.60 (3)
C(8)–N(1)	1.54 (2)	N(3)–O(3)[a]	2.70 (2)
C(11)–N(2)	1.43 (2)	N(3)–O(4)	2.87 (2)
C(14)–N(2)	1.53 (3)		

[a] At position $-x, -y, -z$.

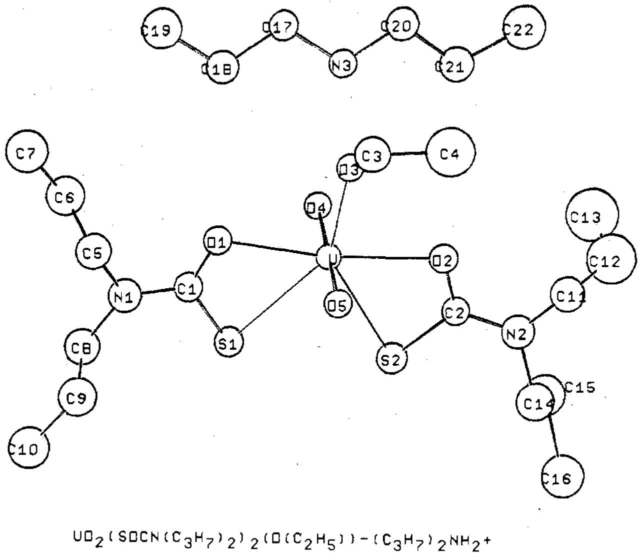

Figure 1. ORTEP view of the structure.

Table IV. Selected Angles (deg)

O(4)–U–O(5)	176.6 (4)	O(2)–U–S(2)	58.3 (2)
O(4)–U–O(1)	89.2 (4)	S(2)–U–S(1)	73.6 (2)
–O(2)	91.8 (4)	S(1)–U–O(1)	57.7 (3)
–O(3)	86.2 (4)	O(1)–C(1)–S(1)	120 (1)
–S(1)	90.0 (3)	O(2)–C(2)–S(2)	119 (1)
–S(2)	93.6 (3)	C(1)–N(1)–C(5)	119 (2)
O(5)–U–O(1)	89.3 (4)	C(1)–N(1)–C(8)	122 (2)
–O(2)	89.3 (4)	C(5)–N(1)–C(8)	118 (2)
–O(3)	90.7 (4)	C(2)–N(2)–C(11)	118 (2)
–S(1)	91.7 (3)	C(2)–N(2)–C(14)	122 (2)
–S(2)	89.7 (3)	C(11)–N(2)–C(14)	117 (2)
O(1)–U–O(3)	87.7 (3)	O(3)[a]–N(3)–O(4)	126 (1)
O(3)–U–O(2)	82.7 (3)		

[a] Atom at $-x, -y, -z$.

or subject to excessive error. On the other hand, the alkyl groups are poorly defined with some large thermal parameters and some bond lengths which clearly are in error.

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Registry No. $[(n\text{-}C_3H_7)_2NH_2]^+[UO_2((n\text{-}C_3H_7)_2NCOS)_2OC_2H_5]^-$, 68890-41-5.

Supplementary Material Available: Data processing formulas and the listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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