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# Crystal and molecular structures of sulfonato complexes of dioxouranium(VI) ion: role of steric effects on coordination structure

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## Abstract

The crystal structures of three sulfonato complexes of uranyl ion are described. All have linear $UO_2$ groups pentagonally coordinated by sulfonato or aquo ligands. In $[(UO_2)(H_2O)(EtSO_3)_2]$ the coordination about $UO_2$ is provided by four O donated by two $EtSO_3^-$ ligands and one O by water: a sulfonate group links the pentagonal bipyramids into chains propagating along the *a* axis. *p*-Toluenesulfonato and mesitylenesulfonato complexes of uranyl ion are monomeric and in each complex two O are donated by monodentate sulfonate and three O by water molecules. The tendencies for complexes with small ligands to form polymeric structures, and for those with bulky ligands to give monomeric structures, which we have observed with carboxylate ligands, seem to extend to sulfonate ligands.

## Introduction

In contrast to the extensive range of uranyl carboxylate complexes which have been detailed in the literature, only one crystal structure of a uranyl sulfonate has so far been reported, namely uranyl methanesulfonate monohydrate [1]. It shows a polymeric pattern like its carboxylate analogue – the uranyl diacetate dihydrates [2]. We considered it worthwhile examining whether the uranyl monosulfonates show the same trends as the uranyl monocarboxylates for which a distinct tendency has been observed to form structures with molecular patterns depending on the ligand size. Thus small acid molecules give rise to polymeric structures, while monomers are observed in uranyl complexes with large carboxylate molecules [3]. We chose for our study a complex with a small sulfonate ion, ethanesulfonate, and two complexes with bulky ions namely 4-methylbenzene sulfonate (*p*-toluene sulfonate) and the 2,4,6-trimethylbenzene sulfonate (mesitylene sulfonate). Only the synthesis of uranyl *ortho*-toluene sulfonate has been reported before [4].

## Experimental

### *Preparation*

Complex **I**, $[(UO_2)(H_2O)(EtSO_3)_2]$, was prepared by reacting a hot aqueous solution of uranyl diacetate with ethanesulfonic acid taken in a molar ratio of 1:2. Well-shaped, yellowish-green single crystals separated out after few days. Their density was determined by flotation to be 2.77(3) g cm$^{-3}$. Complex **II**, $[(UO_2)(H_2O)_3(p\text{-}CH_3C_6H_4SO_3)_2]\cdot 2H_2O$, was synthesized by mixing a hot aqueous solution of 1 mmol of uranyl diacetate with 2 mmol of *p*-toluenesulfonic acid, cf. preparation of uranyl *o*-toluenesulfonate [4]. After a day greenish single crystals could be isolated. Their density was 2.02(3) g cm$^{-3}$ by flotation. Complex **III** was obtained by boiling a mixture of 1 mmol of uranyl diacetate and 2 mmol of trimethylbenzenesulfonic acid each dissolved in 20 cm$^3$ of water. Greenish crystals separated out by slow evaporation. Their density determined by flotation was 1.98(4) g cm$^{-3}$.

### *Crystal structure analysis*

For crystal and experimental data see Table 1. Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å) was used throughout. Reflections were collected at 293 K using a Siemens R3m four-circle diffractometer in $\omega$–$2\theta$ mode. Maximum $2\theta$ was 50° with scan-range $\pm 0.65°$ ($\omega$) around the K$\alpha_1$–K$\alpha_2$ angles, scan speed 5–15° ($\omega$) min$^{-1}$, depending on the intensity of a 2 s pre-scan; backgrounds were

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TABLE 1. Lattice parameters

| Compound | **I** | **II** | **III** |
|---|---|---|---|
| Formula | $C_4H_{12}O_9S_2U$ | $C_{14}H_{24}O_{13}S_2U$ | $C_{18}H_{32}O_{13}S_2U$ |
| $M$ | 508.3 | 702.5 | 758.6 |
| System | monoclinic | monoclinic | monoclinic |
| Systematic absence | $h0l$ ($l \neq 2n$) | $h0l$ ($h \neq 2n$) | $h0l$ ($l \neq 2n$) |
| | $0k0$ ($k \neq 2n$) | $0k0$ ($k \neq 2n$) | $0k0$ ($k \neq 2n$) |
| Space group | $P2_1/c$ | $P2_1/a$ | $P2_1/c$ |
| $a$ (Å) | 11.318(7) | 22.068(11) | 8.438(2) |
| $b$ (Å) | 7.973(5) | 8.442(5) | 26.057(9) |
| $c$ (Å) | 12.975(7) | 12.354(6) | 12.077(3) |
| $\beta$ (°) | 90.49(5) | 98.23(4) | 96.05(2) |
| $V$ (Å$^3$) | 1171 | 2277 | 2641 |
| $Z$ | 4 | 4 | 4 |
| $D_c$ (g cm$^{-3}$) | 2.883 | 2.049 | 1.908 |
| $\mu$ (Mo K$\alpha$) (mm$^{-1}$) | 14.25 | 6.88 | 6.35 |
| Index ranges | 0/13; 0/9; −15/15 | 0/26; 0/10; −14/14 | 0/10; 0/31; −14/14 |
| Crystal size (mm) | $0.046 \times 0.17 \times 0.31$ | $0.14 \times 0.42 \times 0.15$ | $0.28 \times 0.12 \times 0.24$ |
| Transmission factor range | 0.11–0.52 | 0.37–0.46 | 0.36–0.52 |
| Reflections unique | 2068 | 4014 | 4675 |
| with $I/\sigma(I) >= 2.0$ | 1785 | 3227 | 3329 |
| $R_{int}$ | 0.039 | 0.042 | 0.032 |
| Parameters refined | 157 | 278 | 320 |
| Weight parameter (g) | 0.0065 | 0.00059 | 0.0010 |
| Shift/$\sigma$ (last cycle) | 0.4 | 0.4 | 0.4 |
| $\delta F_{max}$ (e A$^{-3}$) | 1.5 | 1.9/−0.9 | 1.3/−1.0 |
| Final $R$ | 0.033 | 0.038 | 0.048 |
| Final $R_w$ | 0.053 | 0.047 | 0.055 |
| $S$ (GOF) | 0.62 | 1.38 | 1.12 |

measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections and showed a slight decrease (4–6%) during data collection. The data were rescaled to correct for this. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($17 < 2\theta < 19°$). Reflections were processed using profile analysis in each case and were corrected for Lorentz, polarization and absorption effects (by the Gaussian method); those with ($I/\sigma(I) > 2.0$) were used in the refinement. For each compound the systematic absences define the space group unambiguously. Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found by successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperatures factors, $U = 0.08$ Å$^2$ (0.07 Å$^2$ for **II**). Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid $CH_3$ units, with their initial orientation based on a staggered configuration. Final refinement was on $F$ by least-squares methods. Weighting schemes of the form $w = 1/[\sigma^2(F) + gF^2]$ were used and shown to be satisfactory by a weight analysis. Computing was with SHELXTL PLUS [5] on a DEC Microvax-II. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables (1974) [6].

For crystal **I**, the largest positive and negative peaks on a final Fourier difference synthesis were near the uranium atom. Final atomic coordinates are given in Table 2, selected bond lengths and angles in Table 3.

For crystal **II**, two lattice water molecules were located. H atoms of the water molecules were not

TABLE 2. Atomic coordinates ($\times 10^4$) for uranyl ethanesulfonate monohydrate and isotropic thermal parameters (Å$^2 \times 10^3$) with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| U(1) | 2466.5(2) | 1168.6(4) | 78.3(2) | 21(1)* |
| S(1) | 4528(2) | −2229(2) | 802(2) | 23(1)* |
| S(2) | 632(2) | −2566(2) | 311(2) | 24(1)* |
| O(11) | 2365(5) | 585(8) | −1212(5) | 33(2)* |
| O(12) | 2592(5) | 1761(8) | 1368(5) | 31(2)* |
| O(1) | 5507(5) | −1751(8) | 136(5) | 34(2)* |
| O(2) | 3477(5) | −1339(7) | 470(6) | 34(2)* |
| O(3) | 4351(5) | −4003(7) | 844(6) | 35(2)* |
| O(4) | 1024(4) | −869(7) | 544(5) | 26(2)* |
| O(5) | −637(5) | −2557(8) | 85(5) | 33(2)* |
| O(6) | 1277(5) | −3330(8) | −495(5) | 36(2)* |
| O(7) | 2796(5) | 4106(8) | −366(6) | 37(2)* |
| C(11) | 4867(11) | −1522(13) | 2030(8) | 47(4)* |
| C(12) | 3898(11) | −1809(14) | 2788(9) | 52(4)* |
| C(21) | 837(9) | −3742(9) | 1428(8) | 33(3)* |
| C(22) | 137(15) | −3142(17) | 2337(9) | 69(5)* |

Starred items: equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

TABLE 3. Selected bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses for uranyl ethanesulfonate monohydrate[a]

| | | | |
|---|---|---|---|
| U(1)–O(11) | 1.741(6) | U(1)–O(12) | 1.743(6) |
| U(1)–O(2) | 2.357(6) | U(1)–O(4) | 2.385(5) |
| U(1)–O(7) | 2.441(7) | U(1)–O(1a) | 2.359(6) |
| U(1)–O(5a) | 2.356(6) | S(1)–O(1) | 1.461(6) |
| S(1)–O(2) | 1.448(6) | S(1)–O(3) | 1.430(6) |
| S(1)–C(11) | 1.730(11) | S(2)–O(4) | 1.455(6) |
| S(2)–O(5) | 1.463(6) | S(2)–O(6) | 1.418(7) |
| S(2)–C(21) | 1.740(10) | O(1)–U(1a) | 2.359(6) |
| O(5)–U(1b) | 2.356(6) | | |
| O(11)–U(1)–O(12) | 179.1(3) | O(2)–U(1)–O(4) | 72.5(2) |
| O(2)–U(1)–O(1a) | 73.8(2) | O(7)–U(1)–O(1a) | 68.5(2) |
| O(4)–U(1)–O(5a) | 74.9(2) | O(7)–U(1)–O(5a) | 70.3(2) |
| S(1)–O(1)–U(1a) | 149.7(4) | U(1)–O(2)–S(1) | 151.2(4) |
| U(1)–O(4)–S(2) | 142.1(4) | S(2)–O(5)–U(1b) | 151.7(4) |

Hydrogen bonds (Å) (e.s.d. 0.01 Å)

| Atom (1) | Atom (2) | | Distance |
|---|---|---|---|
| O(7) | O(3) | $x$, $1+y$, $z$ | 2.79 |
| O(7) | O(6) | $x$, $1+y$, $z$ | 2.68 |

[a] O(1a) at $1-x$, $-y$, $-z$ from O(1); O(5a) at $-x$, $-y$, $-z$ from O(5).

included. Final refinement included a secondary extinction parameter of 0.00032(4). The only significant peak on the final difference synthesis was a diffraction ripple of the U atom, located at the position $x_U$, $1/2+y_U$, $z_U$. Table 4 lists final atomic coordinates, and Table 5 gives selected bond lengths and angles.

For **III**, two lattice water molecules were located. Some water protons were visible on difference Fourier syntheses, but they were not consistently identifiable and were not included in refinement. The largest positive peak on a final difference Fourier synthesis (height 1.3 e Å$^{-3}$) was a possible lattice water proton. Table 6 lists final atomic coordinates, and Table 7 gives selected bond lengths and angles.

TABLE 4. Atomic coordinates ($\times 10^4$) and temperatures factors (Å$^2 \times 10^3$) for uranyl 4-methylbenzene sulfonate pentahydrate with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| U | 1086.3(1) | 6734.5(3) | 4254.5(2) | 35(1)* |
| S(1) | 564.5(9) | 3261.5(23) | 2769.0(16) | 39(1)* |
| S(2) | 2454.1(10) | 6542.5(28) | 2997.9(20) | 50(1)* |
| O(1) | 1033(3) | 8346(6) | 3363(5) | 50(2)* |
| O(2) | 1124(3) | 5149(7) | 5179(4) | 51(2)* |
| O(3) | −34(3) | 6408(7) | 3913(6) | 56(2)* |
| O(4) | 616(3) | 8368(6) | 5502(5) | 51(2)* |
| O(5) | 1903(3) | 7976(8) | 5431(6) | 62(2)* |
| O(11) | 789(3) | 4909(7) | 2783(4) | 43(2)* |
| O(12) | −58(3) | 3236(7) | 2985(5) | 53(2)* |
| O(13) | 958(3) | 2267(8) | 3467(5) | 57(2)* |
| O(21) | 1993(3) | 5899(7) | 3629(5) | 55(2)* |
| O(22) | 2525(4) | 8221(8) | 3145(7) | 80(3)* |
| O(23) | 3012(3) | 5633(9) | 3254(5) | 69(3)* |
| C(11) | 566(4) | 2600(10) | 1420(6) | 40(3)* |
| C(12) | 150(5) | 3038(13) | 589(8) | 73(4)* |
| C(13) | 151(6) | 2505(16) | −440(8) | 80(5)* |
| C(14) | 585(6) | 1455(12) | −671(7) | 63(4)* |
| C(15) | 1009(7) | 1037(19) | 140(9) | 116(6)* |
| C(16) | 1015(6) | 1564(15) | 1219(9) | 98(6)* |
| C(17) | 586(7) | 802(17) | −1815(8) | 89(5)* |
| C(21) | 2161(5) | 6159(14) | 1643(8) | 60(4)* |
| C(22) | 1772(12) | 7063(26) | 1075(15) | 190(12)* |
| C(23) | 1537(9) | 6711(24) | −6(13) | 153(10)* |
| C(24) | 1710(6) | 5706(25) | −593(11) | 114(7)* |
| C(25) | 2057(13) | 4589(31) | 53(15) | 205(15)* |
| C(26) | 2272(11) | 4833(24) | 1153(14) | 182(12)* |
| C(27) | 1493(7) | 5491(37) | −1746(11) | 183(12)* |
| O(001) | 871(3) | 1461(6) | 5588(5) | 45(2)* |
| O(002) | 2186(4) | 1186(11) | 3722(9) | 124(5)* |

Starred items: equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

## Discussion

The common feature of all three uranyl sulfonates is the presence of pentagonal bipyramids as the coordination polyhedron around the U atom, however complex **I** exhibits a polymeric molecular pattern, while compounds **II** and **III** are monomers. Dimensions are summarized in Table 8. In all three complexes, the $UO_2$ groups are close to linear with U–O distances in the range 1.742–1.753 Å. The equatorial distances to coordinated acid oxygen atoms are slightly shorter than those to water molecules, ranges 2.35–2.39 and 2.37–2.46 Å, respectively. The distances in **III** are generally slightly longer than those in **I** and **II**, indicative of slightly increased steric effects from the bulky mesityl group. The sulfonato groups are tetrahedral with typical S–O and S–C distances, the S–O(bonded) being longer than S–O(free), as expected. Other ligand dimensions are also normal.

In the $[UO_2(H_2O)(C_2H_5SO_3)_2]$ complex, the adjacent bipyramids are bridged by two bidentate sulfonate groups giving rise to infinite chains propagating along the *a* axis (see Figs. 1 and 2). The equatorial coordination around the U atom consists thus of four sulfonato-oxygen atoms each of them belonging to a different anion. The fifth oxygen is donated by the water molecule. The O–U–O angles within this equatorial plane are in the range 68.5(2)–74.9(2)° indicating a fairly regular pentagonal arrangement. The maximum deviation from the mean equatorial plane is shown by the water oxygen ±(0.06 Å). The $[UO_2(H_2O)(C_2H_5SO_3)_2]_n$ chains are connected by hydrogen bonds to form sheets (Fig. 2) parallel to the *ab* plane. The interactions between adjacent sheets seem to be fairly weak, possibly of van der Waals character. It is interesting to note that the bidentate sulfonate groups are also bridging in uranyl methanesulfonate monohydrate [1]; however, in **I** the

TABLE 5. Selected bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses for uranyl 4-methylbenzene sulfonate pentahydrate

| | | | |
|---|---|---|---|
| U–O(1) | 1.744(6) | U–O(2) | 1.753(6) |
| U–O(3) | 2.464(6) | U–O(4) | 2.410(6) |
| U–O(5) | 2.389(6) | U–O(11) | 2.402(5) |
| S(1)–O(11) | 1.476(6) | S(1)–O(12) | 1.437(7) |
| S(1)–O(13) | 1.410(6) | S(1)–C(11) | 1.758(8) |
| U–O(21) | 2.355(6) | S(2)–O(21) | 1.471(7) |
| S(2)–O(22) | 1.434(7) | S(2)–O(23) | 1.446(7) |
| S(2)–C(21) | 1.736(10) | | |
| O(1)–U–O(2) | 178.0(3) | O(11)–U–O(21) | 73.2(2) |
| O(11)–U–O(3) | 68.9(2) | O(3)–U–O(4) | 70.1(2) |
| O(4)–U–O(5) | 73.5(2) | O(5)–U–O(21) | 74.2(2) |
| U–O(11)–S(1) | 131.9(3) | U–O(21)–S(2) | 138.4(4) |

Hydrogen bonds (Å) (e.s.d. 0.01 Å)

| Atom (1) | Atom (2) | | Distance |
|---|---|---|---|
| O(001)($H_2O$) | O(3) | $-x, 1-y, 1-z$ | 2.712 |
| | O(4) | $x, y, z$ | 2.670 |
| | O(13) | $x, y, z$ | 2.740 |
| | O(23) | $1/2-x, y-1/2, 1-z$ | 2.766 |
| O(002)($H_2O$) | O(5) | $1/2-x, y-1/2, 1-z$ | 2.611 |
| | O(22) | $x, y-1, z$ | 2.737 |
| | O(13) | $x, y, z$ | 2.834 |
| O(4) | O(12) | $-x, 1-y, 1-z$ | 2.740 |
| O(5) | O(23) | $1/2-x, 1/2+y, 1-z$ | 2.775 |

oxygens coordinated by the $UO_2$ moiety in the equatorial plane are donated by four different sulfonate groups, producing the layer structure shown in Fig. 3. It bears a close resemblance to that observed in crystals of uranyl diformate monohydrate [7]. On the other hand in the structure of the uranyl diacetate dihydrate [2], one acetate ion links adjacent bipyramids to form chains, while the other is chelated to the $UO_2$ ion by its bidentate carboxylic group. In contrast, the carboxylate analogue of the title compound I, uranyl propanecarboxylate $NH_4[UO_2(C_2H_5COO)_3]$ [8], is monomeric with hexagonal coordination around $UO_2$.

Complexes **II** and **III** are both monomeric. In each case two of the five coordinated oxygens are contributed by the two monodentate sulfonate anions and three water molecules. U–O distances fall in the normal range, see Tables 6 and 7. Despite the small difference in the shape and dimensions of the ligand molecules, the structural patterns of the complexes are not the same. In complex **II** the oxygens donated to the coordination equatorial plane by the sulfonate groups are neighbours (see Fig. 4) making the monomer fairly compact and yielding the packing shown in Fig. 5. In contrast, the oxygens contributed by the sulfonate groups to the coordination pentagon of complex **III** are separated by an oxygen of a water molecule (Fig. 6). The shape of the monomer is thus elongated. Its molecules are packed in columns parallel to the *c* axis (Fig. 7).

TABLE 6. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for uranyl 2,4,6-trimethylbenzenesulfonate trihydrate with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| U(1) | 1783.6(5) | 219.4(2) | 2275.6(3) | 33(1)* |
| S(1) | 2687.6(32) | 1005.6(10) | −4.6(21) | 35(1)* |
| S(2) | 3739.3(44) | −790.4(13) | 3994.0(29) | 59(1)* |
| O(1) | 2247(9) | −165(3) | 1157(6) | 47(3)* |
| O(2) | 1299(9) | 596(3) | 3387(6) | 48(3)* |
| O(3) | 4527(9) | 417(3) | 2869(6) | 46(3)* |
| O(4) | −505(9) | −289(3) | 2451(6) | 47(3)* |
| O(5) | −540(9) | 579(3) | 1130(6) | 54(3)* |
| O(11) | 2573(9) | 935(3) | 1201(6) | 40(2)* |
| O(12) | 4034(10) | 738(3) | −350(7) | 55(3)* |
| O(13) | 1211(9) | 851(3) | −623(6) | 49(3)* |
| O(21) | 2565(12) | −445(4) | 3562(9) | 84(4)* |
| O(22) | 5001(13) | −800(4) | 3272(11) | 106(6)* |
| O(23) | 4354(17) | −687(4) | 5074(8) | 107(5)* |
| C(11) | 2934(12) | 1672(4) | −203(8) | 33(3)* |
| C(12) | 3713(14) | 1970(5) | 644(10) | 47(4)* |
| C(13) | 3698(15) | 2494(5) | 520(10) | 53(4)* |
| C(14) | 2977(16) | 2730(5) | −400(12) | 58(5)* |
| C(15) | 2300(16) | 2425(5) | −1276(11) | 57(5)* |
| C(16) | 2295(13) | 1897(4) | −1196(10) | 43(4)* |
| C(17) | 4611(17) | 1761(5) | 1678(11) | 67(5)* |
| C(18) | 2869(22) | 3304(5) | −505(14) | 82(7)* |
| C(19) | 1649(17) | 1592(5) | −2218(10) | 59(5)* |
| C(21) | 2810(14) | −1406(5) | 3937(10) | 48(4)* |
| C(22) | 2124(16) | −1590(6) | 4864(11) | 62(5)* |
| C(23) | 1457(16) | −2069(6) | 4835(12) | 69(6)* |
| C(24) | 1553(15) | −2387(5) | 3891(13) | 59(5)* |
| C(25) | 2169(14) | −2192(5) | 3008(11) | 56(5)* |
| C(26) | 2796(14) | −1709(5) | 3007(11) | 52(5)* |
| C(27) | 1948(22) | −1260(8) | 5919(14) | 107(9)* |
| C(28) | 851(19) | −2927(6) | 3922(15) | 83(7)* |
| C(29) | 3449(21) | −1537(7) | 1938(12) | 86(7)* |
| O(001) | 6349(9) | 276(3) | 1187(6) | 49(3)* |
| O(002) | 2110(15) | 365(5) | 5894(10) | 108(4) |

Starred items: equivalent isotropic *U* defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

In both **II** and **III**, the sulfonate groups act as monodentate ligands. The tetrahedral geometry prohibits in both cases more than one oxygen from taking part in coordinating to a single $UO_2$, in contrast to the flat, more flexible carboxylate group which is usually bidentate. The fairly large size of the $RSO_3^-$ tetrahedron introduces strains in the equatorial plane so that the maximum number of coordinated oxygens is five; in the majority of uranyl complexes with aromatic carboxylates, these are bidentate, allowing hexagonal coordination in the equatorial plane.

An extensive network of hydrogen bonds operates in both compounds. In complex **II** two water molecules are located between the monomers with distances of 2.61–2.83 Å between the water oxygen atoms and the oxygen atoms coordinated to the uranium (see Table 6 and Fig. 5). In the structure of complex **III**, hydrophobic interactions take place between the columns

TABLE 7. Selected bond lengths (Å) and bond angles (°) for uranyl 2,4,6-trimethylbenzenesulfonate trihydrate with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| O(4) | O(13) | $-x,\ -y,\ -z$ | 2.67 |
| U(1)–O(1) | 1.759(8) | U(1)–O(2) | 1.746(8) |
| U(1)–O(3) | 2.406(7) | U(1)–O(4) | 2.370(8) |
| U(1)–O(5) | 2.462(7) | U(1)–O(11) | 2.406(7) |
| U(1)–O(21) | 2.373(10) | S(1)–O(11) | 1.481(7) |
| S(1)–O(12) | 1.432(9) | S(1)–O(13) | 1.440(8) |
| S(1)–C(11) | 1.768(10) | S(2)–O(21) | 1.398(10) |
| S(2)–O(22) | 1.445(13) | S(2)–O(23) | 1.379(10) |
| S(2)–C(21) | 1.784(13) | | |
| O(1)–U(1)–O(2) | 179.2(4) | O(4)–U(1)–O(5) | 69.8(3) |
| O(2)–U(1)–O(3) | 86.9(3) | O(3)–U(1)–O(21) | 76.7(3) |
| O(3)–U(1)–O(11) | 71.5(2) | U(1)–O(21)–S(2) | 148.3(7) |
| O(5)–U(1)–O(11) | 69.6(3) | U(1)–O(11)–S(1) | 132.6(4) |
| O(4)–U(1)–O(21) | 72.9(3) | | |

Hydrogen bonds (Å) (e.s.d. 0.01 Å)

| Atom (1) | Atom (2) | | Distance |
|---|---|---|---|
| O(001)($H_2O$) | O(3) | $x,\ y,\ z$ | 2.70 |
| | O(5) | $x+1,\ y,\ z$ | 2.75 |
| | O(12) | $x,\ y,\ z$ | 2.82 |
| O(002)($H_2O$) | O(4) | $-x,\ -y,\ 1-z$ | 2.54 |
| | O(22) | $1-x,\ -y,\ 1-z$ | 2.78 |
| O(3) | O(23) | $1-x,\ -y,\ 1-z$ | 2.66 |

TABLE 8. Comparative dimensions in **I**–**III** (Å and °)

| Compound | **I** | **II** | **III** |
|---|---|---|---|
| Sulfonate | ethyl | tolyl | mesityl |
| U–O(uranyl) | 1.742(6) | 1.748(6) | 1.753(8) |
| U–O–U | 179.1(3) | 178.0(3) | 179.2(4) |
| U–O(acid) | 2.346(6) | 2.378(10) | 2.390(7) |
| U–O(water) | 2.441(7) | 2.389–2.464 | 2.370–2.462 |
| U–O–S | 142.1–151.7 | 131.9–138.4 | 132.6–148.3 |
| S–O(bonded) | 1.456(6) | 1.473(3) | 1.439(10) |
| S–O(free) | 1.424(6) | 1.432(7) | 1.424(10) |
| S–C | 1.735(10) | 1.747(10) | 1.776(12) |

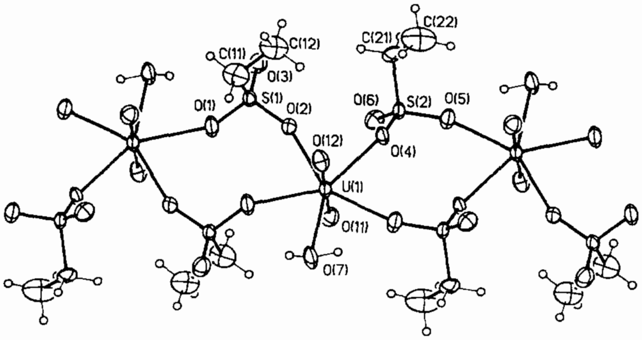

Fig. 1. [$UO_2(H_2O)(C_2H_5SO_3)_2$] complex, showing atomic numbering.

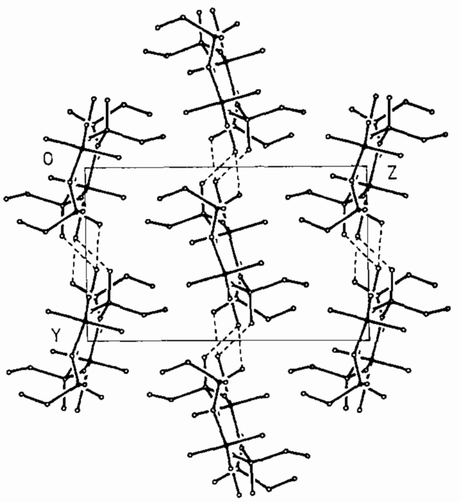

Fig. 2. Packing of complex **I** viewed along *a* axis.

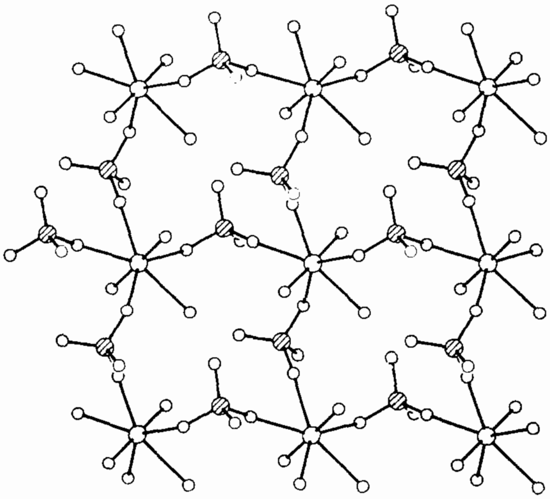

Fig. 3. Molecular pattern of [$UO_2(H_2O)(CH_3SO_3)_2$].

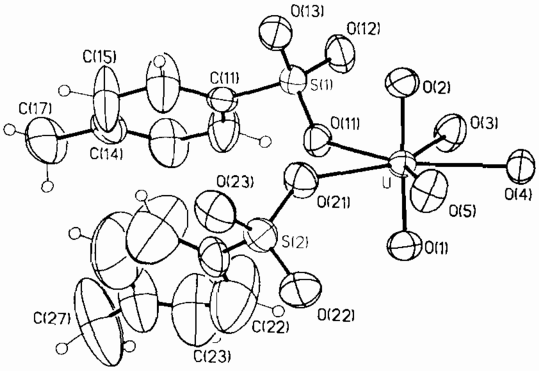

Fig. 4. [$UO_2(H_2O)_3(CH_3C_6H_4SO_3)_2 \cdot 2H_2O$], showing atomic numbering.

and hydrogen bonds are formed along the columns, with O...O distances in the range 2.54–2.82 Å (see Table 7 and Fig. 7). The polymeric structure of uranyl

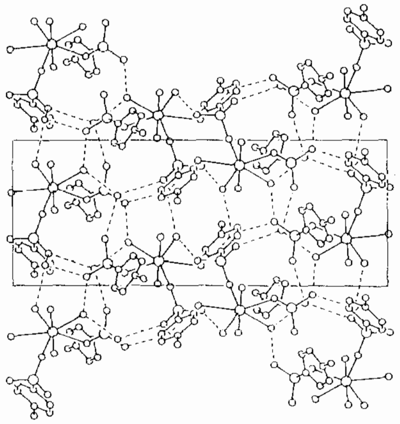

Fig. 5. Packing of complex **II** viewed along *c* axis.

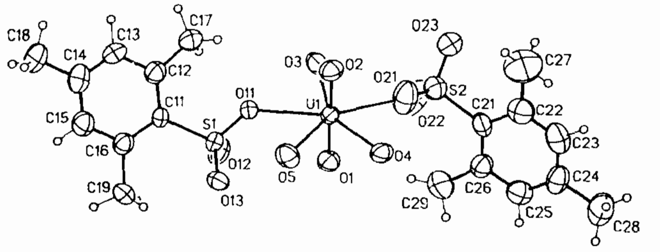

Fig. 6. $[UO_2(H_2O)_3[(CH_3)_3C_6H_2SO_3]_2]$, showing atomic numbering.

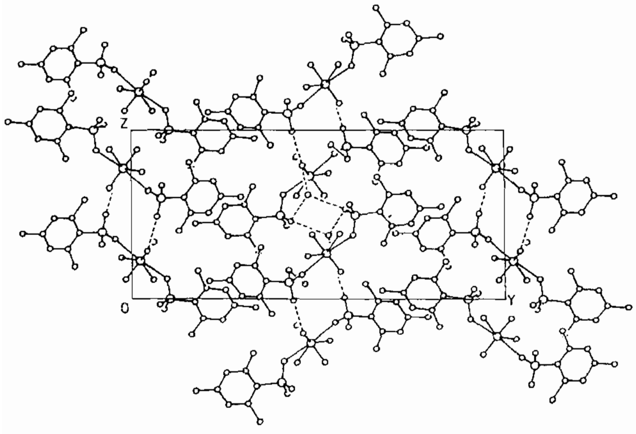

Fig. 7. Packing of complex **III** viewed along *a* axis.

ethanesulfonate and the monomeric structures of complexes **II** and **III** conform to the general feature of uranyl complexes with monobasic carboxylates, i.e. that steric factors play a significant role in determining the molecular layout. Thus small ligands prefer to form polymeric structures with pentagonal bipyramids as the coordination polyhedron of the U atom, while monomeric structures dominate in uranyl complexes with aromatic carboxylates.

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