

METAL-ORGANIC COMPOUNDS

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**An Inclusion Complex of Uranyl in a
Diazacrown: (Diaza-18-crown-6)²⁺ ·
2CF₃SO₃⁻ and [UO₂(diaza-18-crown-6)]⁺ ·
CF₃SO₃⁻**

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Abstract

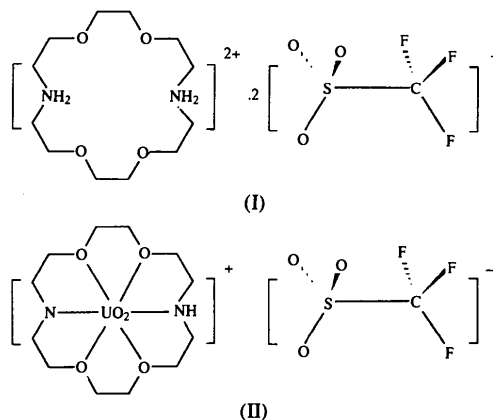
The structures of two compounds involving the macrocycle 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (diaza-18-crown-6, C₁₂H₂₆N₂O₄) are reported. In 1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(trifluoromethanesulfonate), C₁₂H₂₈N₂O₄²⁺ · 2CF₃SO₃⁻, (I), the two N atoms are protonated, resulting in a ring conformation different to that of the neutral crown. The second compound, dioxo[1,4,10,13-tetraoxa-7,16-diazocyclooctadecanido(1-)]uranium trifluoromethanesulfonate, [UO₂(C₁₂H₂₅N₂O₄)]CF₃SO₃⁻, (II), is composed of [UO₂(diaza-18-crown-6)]⁺ cations and CF₃SO₃⁻ anions. The linear uranyl moiety is included into the macrocycle with hexagonal-bipyramidal coordination geometry; one of the N atoms is deprotonated and the two N atoms are thus at different distances from the U atom and have different geometries.

Comment

This work is part of an investigation of inclusion complexes formed between the uranyl ion and macrocycles such as crown ethers (Folcher, Charpin, Costes, Keller & de Villardi, 1979; Navaza, Villain & Charpin, 1984; Deshayes *et al.*, 1994) and azacrowns or coronands (Nierlich, Sabatié, Keller, Lance & Vigner, 1994). The choice of a poorly coordinating solvent-anion pair allows direct uranyl-macrocycle coordination (Fux, Lagrange & Lagrange, 1984; Deshayes *et al.*, 1994). Some solution studies using spectrophotometric methods (Lagrange, Metabanzoulou, Fux & Lagrange, 1989) or EXAFS spectrometry (Deshayes *et al.*, 1994) have shown that the macrocycle diaza-18-crown-6 is able to form an inclusion complex with the uranyl ion. We report

here the structures of two compounds obtained during the course of the investigation of inclusion complexes between uranyl and diaza-18-crown-6 in the solid state.

The synthesis of the two compounds was carried out as described previously (Nierlich *et al.*, 1994), with anhydrous acetonitrile as a solvent and trifluoromethanesulfonate (CF₃SO₃⁻) as a counter ion. Two different crystalline species could be isolated depending on the acidity of the medium and the concentrations of the reagents. Compound (I), [H₂diaza-18-crown-6]²⁺ · 2CF₃SO₃⁻, corresponds to the uncomplexed crown with the two N atoms protonated and two CF₃SO₃⁻ ions as counter ions. Compound (II), [UO₂(diaza-18-crown-6)]⁺ · CF₃SO₃⁻, is an inclusion complex between the uranyl ion and the crown with one aza group deprotonated and one CF₃SO₃⁻ ion per molecule of the complex as a counter ion. The possibility of varying the charge of nitrogen-containing crowns, as illustrated here, makes them more versatile than the corresponding crown ethers.



As shown in Figs. 1 and 2, the structure of [H₂diaza-18-crown-6]²⁺ · 2CF₃SO₃⁻ consists of macrocyclic cations and CF₃SO₃⁻ ions, the 1:2 ratio indicating that both N atoms of the macrocycle are protonated. The centrosymmetric macrocycle adopts the unusual conformation *g*⁺*g*⁺*g*⁺*g*⁻*g*⁻*g*⁻, different from the configuration *g*⁺*g*⁻*g*⁺*g*⁻*g*⁺*g*⁻ adopted by the neutral macrocycle (Herceg & Weiss, 1972). One of the torsion angles around a C—O bond deviates significantly from that of an *anti* configuration [C(2)—O(1)—C(3)—C(4) -71.1(7)^o]; a similar situation is found for the crown ether 18-crown-6 (Dunitz & Seiler, 1974) and some of its inclusion complexes (Rogers, Rollins, Etzenhouser, Voss & Bauer, 1993), and in the complex [UO₂(18-azacrown-6)]²⁺ · 2CF₃SO₃⁻ (Nierlich *et al.*, 1994). This C—O—C—C torsion angle is located between two

O—C—O torsion angles with the same sign, as has been noted previously (Fyles & Gandour, 1992; Rogers *et al.*, 1993).

The four O atoms and the two N atoms of the macrocycle are in a puckered plane with maximum deviations of ± 0.12 Å. The N(1)⋯N(1ⁱ) distance of 4.687 (8) Å is shorter than in the free neutral macrocycle (5.84 Å; Moras, Metz, Herceg & Weiss, 1972) and both O⋯O distances are longer [O(1)⋯O(1ⁱ) 5.920 (8), O(2)⋯O(2ⁱ) 6.025 (8) Å] than in the neutral macrocycle (5.61–5.67 Å) [symmetry code: (i) $-x, 1-y, -z$]. The crystallographic symmetry is *C_i*, as in the neutral macrocycle (Herceg & Weiss, 1972), but, on the whole, the protonation of the two N atoms induces a more distorted geometry than in the neutral crown. The crystal packing consists of layers of macrocyclic cations and CF₃SO₃⁻ ions, the shortest distances between the cations and the anions being N(1)⋯O(3) and N(1)⋯O(4), both of which are 2.83 (1) Å.

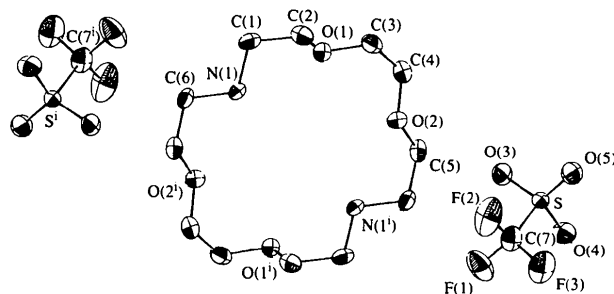


Fig. 1. An ORTEP (Johnson, 1976) view of [H₂diazia-18-crown-6]²⁺·2CF₃SO₃⁻, (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 40% probability level. Symmetry code: (i) $-x, 1-y, -z$.

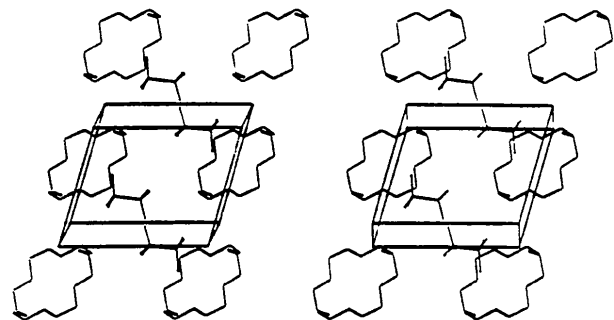


Fig. 2. A stereoview of the crystal packing in (I) viewed along the *a* axis.

The structure of [UO₂(diazia-18-crown-6)]⁺·CF₃SO₃⁻ is shown in Figs. 3 and 4. The symmetry plane contains U, O(3), O(4), N(1), N(2), S, C(7), O(5) and F(2). The uranyl group is hexacoordinated by the four O atoms and two N atoms of the crown, the U atom having a distorted hexagonal-bipyramidal coordination geometry. The uranyl group is

nearly linear [O(3)=U=O(4) 174.54 (4)°], but the U=O distances [1.843 (4)–1.827 (4) Å] are longer than a typical U=O bond length of about 1.75 Å; this is probably due to the imperfect absorption correction (Charpin, Dejean, Folcher, Rigny & Navaza, 1985).

The two U—N distances are slightly different, confirming the deprotonation of one of the N atoms suggested by the 1:1 cation/anion ratio. Furthermore, the geometries around the two N atoms are significantly different; N(2), which has the shorter U—N distance [2.68 (6) Å], is in a nearly planar environment [U—N(2)—C(6) 115 (3), C(6)—N(2)—C(6ⁱ) 120 (5)°], which indicates that it has been deprotonated, while N(1) is slightly further from U [2.74 (6) Å] and is in a distorted tetrahedral environment [U—N(1)—C(1) 111 (3), C(1)—N(1)—C(1ⁱ) 93 (4)°] [symmetry code: (i) $-x, y, z$]. A shorter mean U—N distance [2.60 (1) Å] has been deduced from EXAFS measurements (Deshayes *et al.*, 1994), but in this case the crown was probably not deprotonated; in the inclusion complex between the uranyl ion and 18-azacrown-6 (Nierlich *et al.*, 1994), the mean U—N distance [2.66 (6) Å] is of comparable magnitude. The two O atoms of diaza-18-crown-6 are at equal distances from U [2.71 (3) Å], but this mean distance is longer than is usually reported [2.53 (4) Å (Deshayes *et al.*, 1994); 2.58 (10) Å (Navaza *et al.*, 1984)]. These longer distances may be accounted for by the formation of a covalent bond between U and N(2), reducing the strength of the dative bonds involving U.

The macrocycle adopts the *g⁺g⁻g⁺g⁻g⁺g⁻* conformation (distorted *D_{3d}* sequence), the same as that of free diaza-18-crown-6 (Herceg & Weiss, 1972); this is one of the six more common conformations in 18-crown-6 complexes (Fyles & Gandour, 1992). The same holds true for the K⁺ inclusion complex (which is not deprotonated) (Moras *et al.*, 1972), but not for the Cu²⁺ complex, which adopts the *g⁺g⁺g⁻g⁺g⁺g⁻* conformation and is highly distorted because of the presence of covalent bonding (Herceg & Weiss, 1973). The torsion angles show only slight deviations with respect to the ideal *gauche* and *anti* conformations.

The O atoms and the U atom are coplanar within ± 0.020 Å with N(1) at 0.48 (3) and N(2) at -0.25 (2) Å from this mean plane. The distances N(1)⋯N(2) [5.42 (5) Å] and O(1)⋯O(2ⁱ) [5.42 (3) Å], are shorter than in the free and neutral macrocycle (Moras *et al.*, 1972). The crystal packing consists of alternate layers perpendicular to the *c* axis containing either the complex ions parallel to one another or CF₃SO₃⁻ ions. The shortest distances between the complex and the CF₃SO₃⁻ ions are found between the N atoms and the sulfate O atoms; the two N atoms are not equivalent in this respect as N(2) has one

neighbour, O(5), at 3.10 (4) Å, and N(1) has two, O(6) and O(6'), at 3.6 (1) Å. The distances corresponding to intermolecular contacts are thus longer than in $[\text{H}_2\text{diazia-18-crown-6}]^{2+} \cdot 2\text{CF}_3\text{SO}_3^-$.

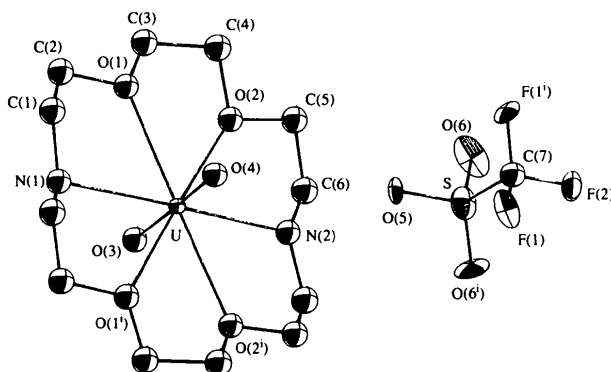


Fig. 3. An ORTEP (Johnson, 1976) view of $[\text{UO}_2(\text{diaza-18-crown-6})]^+ \cdot \text{CF}_3\text{SO}_3^-$, (II), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 40% probability level. Symmetry code: (i) $-x, y, z$.

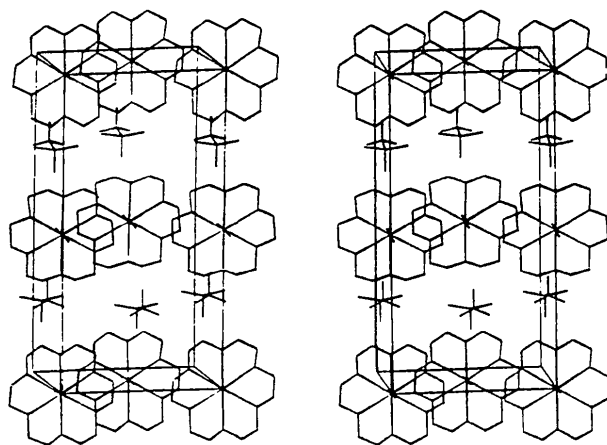


Fig. 4. A stereoview of the crystal packing in (II) viewed along the b axis.

Experimental

Compound (I)

Crystal data

$\text{C}_{12}\text{H}_{28}\text{N}_2\text{O}_4^{2+} \cdot 2\text{CF}_3\text{SO}_3^-$

$M_r = 562.51$

Triclinic

$P\bar{1}$

$a = 8.036$ (3) Å

$b = 8.267$ (2) Å

$c = 10.104$ (3) Å

$\alpha = 73.88$ (2)°

$\beta = 87.31$ (3)°

$\gamma = 78.33$ (3)°

$V = 631$ (1) Å³

$Z = 1$

$D_x = 1.479$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 8-12^\circ$

$\mu = 0.29$ mm⁻¹

$T = 290$ K

Irregular

$0.40 \times 0.40 \times 0.25$ mm

Light yellow

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)

1676 measured reflections

1565 independent reflections

1229 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.013$

$\theta_{\text{max}} = 22^\circ$

$h = -8 \rightarrow 8$

$k = -8 \rightarrow 8$

$l = -10 \rightarrow 0$

3 standard reflections

frequency: 60 min

intensity decay: 1.7%

Refinement

Refinement on F

$R = 0.056$

$wR = 0.057$

$S = 0.88$

1229 reflections

154 parameters

H-atoms included using a

riding model (C—H 0.95, N—H 1.05 Å, $B = 6$ Å²)

Unit weights applied

$\Delta\rho_{\text{max}} = 0.32$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (I)

	x	y	z	B_{eq}
S	0.2240 (2)	0.1776 (2)	0.2329 (1)	3.54 (3)
F(1)	0.0892 (6)	0.2501 (7)	0.4529 (4)	10.3 (2)
F(2)	0.2171 (7)	-0.0068 (7)	0.4853 (5)	11.5 (2)
F(3)	0.3612 (6)	0.1860 (7)	0.4572 (4)	10.7 (1)
O(1)	-0.1172 (5)	0.7931 (5)	0.1182 (4)	4.67 (9)
O(2)	-0.3286 (5)	0.5389 (5)	0.1550 (4)	4.75 (9)
O(3)	0.0649 (5)	0.1369 (5)	0.2087 (4)	5.3 (1)
O(4)	0.2365 (6)	0.3526 (5)	0.1813 (4)	6.4 (1)
O(5)	0.3691 (5)	0.0601 (5)	0.2091 (5)	6.2 (1)
N(1)	0.1854 (5)	0.6863 (5)	-0.0030 (4)	3.5 (1)
C(1)	0.1774 (7)	0.7731 (7)	0.1085 (6)	4.7 (1)
C(2)	0.0298 (8)	0.7390 (8)	0.2024 (6)	5.2 (2)
C(3)	-0.2754 (8)	0.7916 (7)	0.1906 (6)	5.7 (2)
C(4)	-0.3116 (8)	0.6238 (8)	0.2573 (6)	5.9 (2)
C(5)	-0.3275 (7)	0.3611 (7)	0.2141 (6)	5.0 (2)
C(6)	0.3299 (7)	0.7169 (7)	-0.0972 (6)	4.7 (1)
C(7)	0.2238 (9)	0.1482 (9)	0.4152 (7)	6.4 (2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

Table 2. Selected geometric parameters (Å, °) for (I)

$(\text{H}_2\text{diazia-18-crown-6})^{2+}$			
N(1)—C(1)	1.487 (7)	O(1)—C(2)	1.410 (7)
O(1)—C(3)	1.438 (7)	O(2)—C(4)	1.426 (7)
O(2)—C(5)	1.423 (7)	C(1)—C(2)	1.506 (8)
C(3)—C(4)	1.445 (9)	C(5)—C(6')	1.497 (8)
C(6)—N(1)—C(1)	112.6 (4)	N(1)—C(1)—C(2)	111.2 (5)
C(1)—C(2)—O(1)	106.6 (5)	C(2)—O(1)—C(3)	115.3 (5)
O(1)—C(3)—C(4)	115.7 (6)	C(3)—C(4)—O(2)	109.1 (6)
C(4)—O(2)—C(5)	111.8 (5)	O(2)—C(5)—C(6')	107.0 (5)
C(5')—C(6)—N(1)	111.4 (5)		
CF_3SO_3^-			
S—O(3)	1.435 (4)	S—O(4)	1.418 (4)
S—O(5)	1.416 (4)	S—C(7)	1.790 (8)
C(7)—F(1)	1.340 (9)	C(7)—F(2)	1.291 (9)
C(7)—F(3)	1.325 (8)		

O(3)—S—O(4)	115.9 (3)	O(3)—S—O(5)	114.5 (3)	O(6)	-0.111 (2)	-0.247 (3)	0.261 (2)	17.2 (9)
O(4)—S—O(5)	114.4 (3)	O(3)—S—C(7)	102.8 (3)	N(1)	0	-0.011 (4)	-0.1254 (9)	2.8 (2)
O(4)—S—C(7)	102.1 (4)	O(5)—S—C(7)	104.7 (4)	N(2)	0	0.037 (3)	0.122 (1)	2.8
F(1)—C(7)—F(2)	106.3 (7)	F(1)—C(7)—F(3)	107.0 (7)	C(1)	-0.101 (2)	-0.121 (3)	-0.151 (1)	3.4 (2)
F(2)—C(7)—F(3)	107.1 (7)	S—C(7)—F(1)	111.1 (5)	C(2)	-0.210 (2)	-0.049 (2)	-0.1280 (9)	3.4 (2)
S—C(7)—F(2)	113.2 (6)	S—C(7)—F(3)	111.7 (6)	C(3)	-0.315 (2)	0.010 (4)	-0.0310 (8)	3.4 (2)
Symmetry code: (i) -x, 1 - y, -z.				C(4)	-0.312 (2)	-0.041 (2)	0.0361 (9)	3.4
				C(5)	-0.212 (2)	-0.001 (4)	0.1222 (8)	3.4
				C(6)	-0.108 (2)	0.086 (2)	0.148 (1)	3.4
				C(7)	0	-0.499 (5)	0.261 (1)	4.8 (7)

Compound (II)*Crystal data*[UO₂(C₁₂H₂₅N₂O₄)]-
CF₃SO₃*M_r* = 680.44

Orthorhombic

*Cmc*2₁*a* = 11.386 (4) Å*b* = 8.601 (2) Å*c* = 21.858 (7) Å*V* = 2141 (2) Å³*Z* = 4*D_x* = 2.11 Mg m⁻³Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 8–12°

μ = 7.352 mm⁻¹*T* = 290 K

Platelet

0.40 × 0.35 × 0.12 mm

Light yellow

*Data collection*Enraf–Nonius CAD-4
diffractometer

ω/2θ scans

Absorption correction:

ψ scans (North, Phillips
& Mathews, 1968)*T_{min}* = 0.362, *T_{max}* =
1.00

1204 measured reflections

1026 independent reflections

650 observed reflections
[*I* > 3σ(*I*)]*R_{int}* = 0.011θ_{max} = 25°*h* = 0 → 13*k* = 0 → 10*l* = -26 → 0

3 standard reflections

frequency: 60 min

intensity decay: 2%

*Refinement*Refinement on *F**R* = 0.029ω*R* = 0.036*S* = 6.10

650 reflections

83 parameters

H atoms included using
a riding model (C—H
0.95 Å, *B* = 6 Å²)

Unit weights applied

(Δ/σ)_{max} = 0.07Δρ_{max} = 0.77 e Å⁻³Δρ_{min} = -1.50 e Å⁻³

Atomic scattering factors

and anomalous-dispersion

terms from *International**Tables for X-ray**Crystallography* (1974,

Vol. IV)

Table 3. Fractional atomic coordinates and equivalent
isotropic displacement parameters (Å²) for (II)*B_{eq}* = (4/3)Σ_iΣ_jβ_{ij}*a_i*·*a_j* for U, S, F(1), F(2), O(5) and O(6);*B_{iso}* for all others.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}/B_{iso}</i>
U	0	0.0009 (4)	0	1.91 (1)
S	0	-0.2946 (9)	0.247 (1)	6.5 (2)
F(1)	0.096 (2)	-0.569 (2)	0.243 (2)	12.4 (5)
F(2)	0	-0.507 (5)	0.3224 (9)	7.5 (6)
O(1)	-0.209 (1)	-0.032 (1)	-0.0576 (6)	2.7 (1)
O(2)	-0.205 (1)	0.034 (1)	0.0622 (6)	2.7
O(3)	0	-0.212 (2)	0.008 (9)	2.9 (2)
O(4)	0	0.210 (2)	-0.016 (9)	2.9
O(5)	0	-0.297 (3)	0.175 (1)	7.3 (8)

Table 4. Selected geometric parameters (Å, °) for (II)

U environment			
U—O(3)	1.84 (4)	U—O(4)	1.83 (4)
U—N(1)	2.74 (6)	U—N(2)	2.68 (6)
U—O(1)	2.71 (3)	U—O(2)	2.71 (3)
O(3)—U—O(4)	174.54 (4)	O(1)—U—O(1 ¹)	123 (1)
O(2)—U—O(2 ¹)	118 (1)	N(1)—U—N(2)	176 (2)
N(1)—U—O(1)	62.1 (5)	O(1)—U—O(2)	59.2 (3)
O(2)—U—N(2)	59.3 (5)		
(Diaza-18-crown-6) ⁻			
N(1)—C(1)	1.59 (5)	N(2)—C(6)	1.42 (4)
O(1)—C(2)	1.55 (4)	O(1)—C(3)	1.38 (4)
O(2)—C(4)	1.50 (4)	O(2)—C(5)	1.35 (4)
C(1)—C(2)	1.48 (5)	C(3)—C(4)	1.53 (2)
C(5)—C(6)	1.50 (5)		
C(1)—N(1)—C(1 ¹)	93 (4)	N(1)—C(1)—C(2)	104 (3)
C(1)—C(2)—O(1)	112 (3)	C(2)—O(1)—C(3)	116 (3)
O(1)—C(3)—C(4)	108 (3)	C(3)—C(4)—O(2)	105 (3)
C(4)—O(2)—C(5)	103 (3)	O(2)—C(5)—C(6)	102 (3)
C(5)—C(6)—N(2)	113 (3)	C(6)—N(2)—C(6 ¹)	120 (5)
CF ₃ SO ₃ ⁻			
S—O(5)	1.58 (5)	S—O(6)	1.37 (3)
S—C(7)	1.78 (6)	C(7)—F(1)	1.31 (3)
C(7)—F(2)	1.34 (4)		
O(5)—S—O(6)	103 (3)	O(5)—S—C(7)	99 (2)
O(6)—S—C(7)	105 (2)	O(6)—S—O(6 ¹)	136 (5)
F(1)—C(7)—F(2)	106 (4)	F(1)—C(7)—F(1 ¹)	114 (5)
F(1)—C(7)—S	114 (3)	F(2)—C(7)—S	103 (4)

Symmetry code: (i) -x, y, z.

Table 5. Torsion angles (°)

(H ₂ diaza-18-crown-6) ²⁺ .2CF ₃ SO ₃ ⁻ , (I)	
C(6)—N(1)—C(1)—C(2)	-179.8 (4)
C(1)—C(2)—O(1)—C(3)	-172.4 (5)
O(1)—C(3)—C(4)—O(2)	-64.0 (7)
C(4)—O(2)—C(5)—C(6 ¹)	-174.9 (4)
C(5 ¹)—C(6)—N(1)—C(1)	-175.8 (3)
N(1)—C(1)—C(2)—O(1)	-56.1 (6)
C(2)—O(1)—C(3)—C(4)	-71.1 (7)
C(3)—C(4)—O(2)—C(5)	167.3 (5)
O(2)—C(5)—C(6 ¹)—N(1 ¹)	56.5 (4)

Symmetry code: (i) -x, 1 - y, -z.

[UO₂(C₁₂H₂₅N₂O₄)]⁺.CF₃SO₃⁻, (II)

C(1 ¹)—N(1)—C(1)—C(2)	175 (1)
C(1)—C(2)—O(1)—C(3)	-169 (2)
O(1)—C(3)—C(4)—O(2)	56 (2)
C(4)—O(2)—C(5)—C(6)	-176 (2)
C(5)—C(6)—N(2)—C(6 ¹)	-169 (2)
N(1)—C(1)—C(2)—O(1)	-57 (2)
C(2)—O(1)—C(3)—C(4)	158 (2)
C(3)—C(4)—O(2)—C(5)	174 (2)
O(2)—C(5)—C(6)—N(2)	-60 (2)

Symmetry code: (i) -x, y, z.

Data collection was performed using *CAD-4 Software* (Enraf–Nonius, 1989). Lorentz–polarization corrections were applied to both sets of data. The S atom in (I) was located by the heavy-atom method and the remaining part of the structure by subsequent difference Fourier syntheses. The structure was refined by a full-matrix least-squares method with anisotropic displacement parameters for all non-H atoms. The U atom in (II) was located by the heavy-atom method and the remaining part of the structure by subsequent difference Fourier syntheses. The structure was refined by a full-matrix least-squares method with anisotropic displacement parameters for U and the atoms of the trifluoromethanesulfonate moiety (except C). Due to the pseudo-centrosymmetry of the macrocycle, strong correlations were present between atoms that would be equivalent in the centrosymmetric space group *Cmcm*. This could only be overcome by fixing constraints of equality on the corresponding displacement parameters. The two enantiomorphs were checked but gave the same results. All calculations were performed on a VAX4200 computer. Programs used: *MolEN* (Fair, 1990) and *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: PA1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

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Two Lasalocid Sodium Salts

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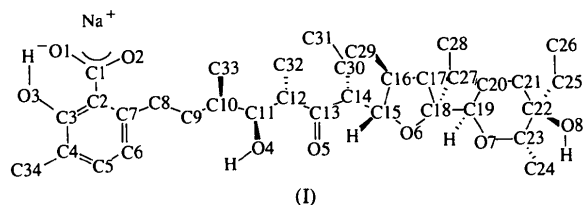
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Abstract

The structures of two new forms of lasalocid sodium salt, sodium 6-[7*R*-{5*S*-ethyl-5-(5*R*-ethyltetrahydro-5-hydroxy-6*S*-methyl-2*H*-pyran-2*R*-yl)tetrahydro-3*S*-methyl-2*S*-furanyl}-4*S*-hydroxy-3*R*,5*S*-dimethyl-6-oxononyl]-2-hydroxy-3-methylbenzoate (A), Na⁺.C₃₄H₅₃O₈⁻, and sodium 6-[7*R*-{5*S*-ethyl-5-(5*R*-ethyltetrahydro-5-hydroxy-6*S*-methyl-2*H*-pyran-2*R*-yl)tetrahydro-3*S*-methyl-2*S*-furanyl}-4*S*-hydroxy-3*R*,5*S*-dimethyl-6-oxononyl]-2-hydroxy-3-methylbenzoate diethyl ether solvate (B), Na⁺.C₃₄H₅₃O₈⁻.C₄H₁₀O, are reported. Form A exists as a 'head-to-head' dimer, while form B is a 'head-to-tail' dimer. Sodium is coordinated to six O atoms from the lasalocid anion in both forms, but the coordination spheres differ. Form A contains a bridging carbonyl O atom, but, remarkably, the carboxylate group does not coordinate to the sodium ion. In form B, the carbonyl O atom does not bridge but there is a direct carboxylate–sodium interaction.

Comment

The structures of sodium salts of lasalocid and a derivative have been known for almost two decades (Schmidt, Wang & Paul, 1974; Smith, Duax & Fortier, 1978). Two new forms (A and B) were obtained as we attempted to prepare other lasalocid complexes using the sodium salt as a starting material.



In both structures, the lasalocid anion adopts the usual circular intramolecularly hydrogen-bonded conformation with interactions involving O1 and O3, O2 and O4, and O8 and the carboxylate group. Both compounds A and B occur as dimers. In the 'head-to-head' dimer of A (Fig. 1), the dimeric nature derives from a crystallographic twofold symmetry transformation, whereas in the 'head-to-tail' dimer of B (Fig. 2), the dimeric complex is formed by two crystallographically independent