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(I)

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cis–syn–cis-Dicyclohexano-18-crown-6 Sodium Perrhenate†

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Abstract

The effect of the anion in a crown ether–cation structure is examined by comparing the structure of [{Na(C$_{20}$H$_{36}$O$_6$)}(ReO$_4$)] with one containing the same crown ether and cation, but a different anion. The title compound shows that the crown ether does not form an ideal cavity for sodium, as the Na—O bond lengths vary from 2.470 (4) (O3) to 2.863 (4) Å (O1).
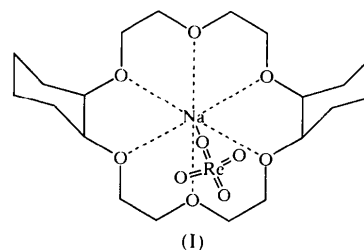
Comment

As part of our current research investigating the role played by the anion in cation-separation processes (Moyer & Bonnesen, 1997), we are interested in examining perturbations of the cation–crown structure when the anion is varied.

Only one structure of the Na$^+$ ion with cis–syn–cis-dicyclohexano-18-crown-6 ether (csc-DC18C6) has been reported. The anion is phenolate, and it forms a 1:2 host–guest complex, with the crown ether adopting a 'highly irregular conformation'. The irregularity is a result of the displacement of two cyclohexano ether O atoms by 1.9 and 2.6 Å out of the plane defined by the four other donors. The phenolate anion is bound to sodium on the crown ether face opposite that of the two bulky cyclohexano groups, and is a bridging group to an uncomplexed ion pair (Fraser *et al.*, 1986).

The structure of the title compound, (I) (Fig. 1), is quite different from the phenolate complex described above. A 1:1 host–guest stoichiometry and a confor-

mation more typical of crown ethers are observed. The Na$^+$ ion is seven-coordinate, with the donor atoms arranged in a capped trigonal prism geometry. The four cyclohexano O-donor atoms (O1, O2, O4 and O5) and sodium are coplanar, with a maximum deviation from this plane of 0.023 (4) Å (O2 and O4). The other two ether O atoms deviate from this plane by 0.929 (5) (O6) and 1.532 (5) Å (O3). Na$^+$ sits in the plane defined by O1, O2, O4 and O5 [deviation 0.012 (3) Å], yet is displaced by 0.111 (3) Å from the calculated centroid of these four O atoms. The Na—O bond distances (Table 1) vary considerably in this structure. A similar variability has been observed previously in sodium–DC18C6 complexes (Fraser *et al.*, 1986; Mercer & Truter, 1973). This consistent variability may be one factor in understanding why the Na$^+$ ion is not extracted as well as the slightly larger K$^+$ ion by DC18C6 (Pedersen & Frensdorff, 1972; Fraser *et al.*, 1986; Hay & Rustad, 1994).
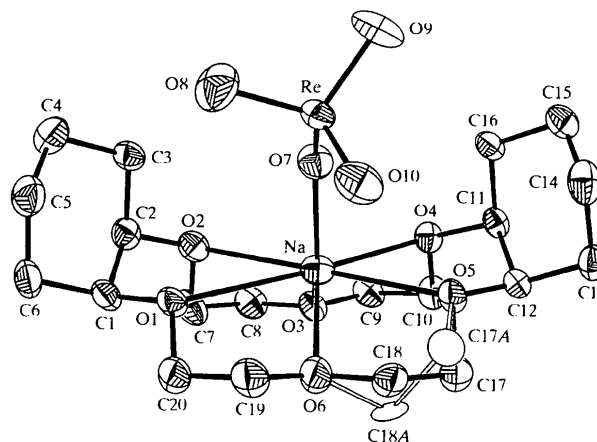

Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. The minor components of disorder are drawn only with a boundary ellipse. H atoms have been omitted for clarity.

The perrhenate anion is bound to sodium through one O atom and is on the same side of the crown ether as the two cyclohexyl groups. The Na—O7 bond distance [2.286 (5) Å] is significantly shorter than the distance of 2.378 (8) Å reported for (15-crown-5)NaReO$_4$ (Weller *et al.*, 1989), the only other structurally characterized

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† Alternative name: (2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane-2κ^6O)-μ-oxo-1:2κ^2O-trioxo-1κ^3O-rheniumsodium.

sodium–perrhenate–crown complex containing an Na—OReO3 bond. This difference may be due to the fact that, in the 15-crown-5 structure, two perrhenate ions are bound to each Na^+ ion, and both bridge two Na^+ ions. Weak hydrogen bonding (Steiner, 1996) is observed in the title compound between activated methylene H atoms and perrhenate O atoms (Table 2).

Experimental

Dicyclohexano-18-crown-6 was obtained from commercial sources and separated into its component isomers following a published procedure (Izatt et al., 1975). Crystals were obtained by slow evaporation of a 2-propanol solution containing equimolar amounts of $NaReO_4$ and csc-DC18C6.

Crystal data

[NaReO4(C20H36O6)]	Mo $K\alpha$ radiation
$M_r = 645.70$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 9.224\,(2)$ Å	$\theta = 10.6\text{–}16.3°$
$b = 27.735\,(6)$ Å	$\mu = 4.96$ mm^{-1}
$c = 10.497\,(3)$ Å	$T = 163$ K
$\beta = 112.42\,(1)°$	Plate
$V = 2482.4\,(11)$ Å^3	$0.47 \times 0.34 \times 0.20$ mm
$Z = 4$	Colourless
$D_x = 1.73$ Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractometer	$R_{int} = 0.030$
ω scans	$\theta_{max} = 26°$
Absorption correction:	$h = -11 \to 0$
ψ scans (Siemens, 1995)	$k = 0 \to 34$
$T_{min} = 0.194$, $T_{max} = 0.378$	$l = -11 \to 12$
5163 measured reflections	3 standard reflections
4861 independent reflections	frequency: 120 min
3854 reflections with	intensity decay: 11.3%
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R(F) = 0.035$	$\Delta\rho_{max} = 1.92$ e Å^{-3}
$wR(F^2) = 0.086$	$\Delta\rho_{min} = -0.81$ e Å^{-3}
$S = 1.16$	Extinction correction: none
4856 reflections	Scattering factors from Inter-
307 parameters	national Tables for X-ray
H atoms not refined	Crystallography (Vol. IV)
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 4.5183P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (Å, °)

Re—O7	1.723 (4)	Na—O3	2.470 (4)
Re—O8	1.718 (5)	Na—O4	2.603 (4)
Re—O9	1.711 (5)	Na—O5	2.624 (4)
Re—O10	1.706 (5)	Na—O6	2.545 (5)
Na—O1	2.863 (4)	Na—O7	2.286 (5)
Na—O2	2.673 (5)		

O10—Re—O9	109.7 (2)	O3—Na—O5	112.6 (2)
O10—Re—O8	109.2 (3)	O6—Na—O5	65.41 (14)
O9—Re—O8	109.3 (3)	O4—Na—O5	63.19 (13)
O10—Re—O7	109.6 (2)	O7—Na—O2	97.4 (2)
O9—Re—O7	110.1 (2)	O3—Na—O2	64.50 (13)
O8—Re—O7	108.9 (2)	O6—Na—O2	116.4 (2)
Re—O7—Na	148.9 (3)	O4—Na—O2	114.22 (14)
O7—Na—O3	143.2 (2)	O5—Na—O2	177.0 (2)
O7—Na—O6	97.1 (2)	O7—Na—O1	82.1 (2)
O3—Na—O6	119.5 (2)	O3—Na—O1	110.61 (15)
O7—Na—O4	98.8 (2)	O6—Na—O1	61.92 (13)
O3—Na—O4	65.01 (13)	O4—Na—O1	173.62 (14)
O6—Na—O4	124.0 (2)	O5—Na—O1	123.19 (14)
O7—Na—O5	84.6 (2)	O2—Na—O1	59.42 (13)
O1—C1—C2—O2	53.2 (6)	O4—C11—C12—O5	−51.9 (6)
O2—C7—C8—O3	62.3 (6)	O5—C17—C18—O6	67.3 (7)
O3—C9—C10—O4	−61.2 (6)	O6—C19—C20—O1	−64.2 (7)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C17—H17B$\cdots$O8^i	0.99	2.40	3.271 (11)	146
C18—H18B$\cdots$O10	0.99	2.53	3.456 (10)	156
C20—H20B$\cdots$O10^{ii}	0.99	2.47	3.454 (8)	172

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, -y, 2 - z$.

Anisotropic displacement parameters were used for all non-H atoms. H atoms were placed in calculated positions, were refined using a riding model, and each was given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the C atom to which it is attached. Two ethylene crown C atoms (C17 and C18) were disordered over two sites (80:20). All equivalent 1,1- and 1,3-distances involving only the disordered atoms, O5 and O6, were restrained to be equal. Additionally, the U^{ij} components of bonded disordered atoms or disordered atoms within 0.7 Å of each other were restrained to be similar. Despite the restraints, atom C18A exhibits unusual anisotropic displacement parameters. Five peaks in the final difference map with electron density greater than 1 e Å^{-3} are located ~ 1 Å from the Re atom.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: XCAD4 (Harms, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL (Siemens, 1995). Software used to prepare material for publication: PLATON (Spek, 1998).

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Racemic Phase of Diaquabis(5-oxoprolinato)zinc(II)†

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Abstract

The title compound, diaquabis(5-oxopyrrolidine-2-carboxylato-O^2)zinc(II), [Zn(C$_5$H$_6$NO$_3$)$_2$(H$_2$O)$_2$], consists of a two-dimensional net of molecules parallel to the ($\bar{1}$01) plane linked by hydrogen bonds, with every Zn^{2+} ion displaying a distorted tetrahedral coordination. The main difference between the two 5-oxoprolinate ligands is in the conformation of the five-membered ring, with one having an envelope form and the other a planar twisted form.

Comment

The structures of 5-oxoproline in the racemic form and L-form (Pattabhi & Venkatesan, 1974; Taira & Watson,

1977; van Zoeren *et al.*, 1978), and the structure of L-diaquabis(5-oxoprolinato)zinc(II) (Rodier *et al.*, 1990) have been reported previously. In this paper, the racemic form, (I), of the Zn derivative is reported.

(I)
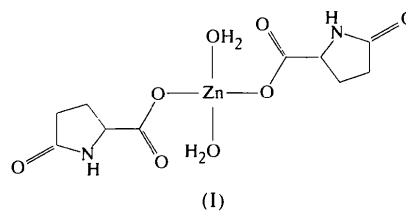
L-Pyroglutamates (also termed 'L-pidolates') are used in human therapeutics as well resorbed vectors of trace elements. Because they are chiral, it has to be ensured that there are no racemates in the solid dosage forms. In order to establish the structural differences between the two forms, an X-ray study was carried out.

There is a non-crystallographic pseudo-twofold axis parallel to the *b* axis, displaced from the origin by $0.63a + 0.37c$ (on the Zn atom). The greatest deviation between pseudo-equivalent sites is 0.34(2) Å for the N1/N1' pair of atoms. The structure consists of Zn^{2+} ions tetrahedrally coordinated by two water molecules and two O atoms of two 5-oxoprolinate ligands. The steric hindrance between these two ligands produces an O1—Zn—O1' bond angle of 132.2(2)° and a shortening of the O(water)—Zn—O(water) bond angle to 99.4(2)°. For both ligands, the CC(O)OZn moiety is planar [largest deviation from the mean plane defined by the five atoms is 0.016(4) Å for O1 and 0.017(6) Å for Zn in the unprimed and primed ligands, respectively].

The main difference between the two ligands is in the conformation of the five-membered ring, which has an envelope form with the C5' atom out of the plane defined by the remaining four atoms in the primed ligand, and a planar twisted form on the C2—C5 bond in the unprimed ligand. This produces a widening of C3—C4—C5 [106.4(5)°], which is 104.3(4)° in the primed ligand and 104.3(1)° in the L-derivative (Rodier *et al.*, 1990), and C5—C2—N1 [104.4(5)°], which is 102.6(5)° in the primed ligand and 102.9(1)° in the L-derivative.

The structure consists of layers of molecules parallel to the ($\bar{1}$01) plane linked by hydrogen bonds. Different layers are displaced along the *c* axis and the molecules are twisted around the *b* axis with respect to the position of the L-derivative. This explains the similarity of the *b* axes of the two structures [5.893(13) and 5.888(3) Å]. The stress produced by the hydrogen-bond interactions produces a shortening of the Zn—O1'—C1' angle [112.9(4)° *versus* 114.1(4)° for the unprimed ligand and 115.0(6)° for the L-derivative] and the O2—C1—C2—N1 torsion angle [5.7(8)° for the primed ligand, 9.9(8)° for the unprimed ligand and −11.7(2)° for the L-derivative].