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## Structure of a 1 : 2 Complex of Sodium Perchlorate and 1,4,7,10-Tetraoxacyclododecane (12-Crown-4)

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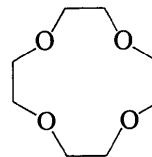
**Abstract.** Na(C<sub>8</sub>H<sub>16</sub>O<sub>4</sub>)<sub>2</sub>ClO<sub>4</sub>, monoclinic,  $P2_1/a$ ,  $a = 15.420$  (8),  $b = 15.245$  (10),  $c = 9.650$  (5) Å,  $\beta = 92.13$  (4)°,  $V = 2267$  (4) Å<sup>3</sup>.  $D_c = 1.391$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo } K\alpha) = 1.972$  cm<sup>-1</sup>. Final  $R_1 = 0.0712$  for 1401 reflections with  $F_o > 3\sigma(F_o)$ . The sodium ion forms a sandwich structure with two 12-crown-4 rings. The eightfold coordination about the sodium ion may be described as slightly distorted rectangular antiprismatic with the heteroatoms being planar to within  $\pm 0.01$  Å. The perchlorate group is not bonded to any other atoms and is disordered.

**Introduction.** Since the early 1960's there has been an upsurge of interest in the coordination complexes of macrocyclic compounds which may serve as models for certain naturally occurring bioinorganic systems. Macrocycles display an unusual affinity for the alkali- and alkaline-earth-metal ions, and, indeed, the tendency for the oxygen atoms of crown ethers to coordinate to these species significantly exceeds their tendency to coordinate with transition-metal ions (Hughes, Hal-tiwanger, Pierpont, Hampton & Blackmer, 1980).

It has been found that the configuration of a macrocyclic complex depends on the relative sizes of the complexed ion and the cavity. If the cavity is significantly larger than the ion, the ligand wraps around the ion forming a three-dimensional structure. If

the cavity is only slightly larger, the macrocycle will tend to pucker so that all of the heteroatoms are coordinated. When the size of the hole is commensurate with the size of the metal ion, the coordination geometry will be planar. In cases where the cavity is smaller than the ion, the macrocycle retains its planar configuration, but the metal ion remains outside the plane of the ligand, and a sandwich structure is noted.

The formation of 1 : 2 'sandwich' compounds of Na<sup>+</sup> with 12-crown-4



has been confirmed by crystallographic studies which describe structures containing several water molecules within the crystal lattice (van Remoortere & Boer, 1974; Boer, Neuman, van Remoortere & Steiner, 1974). Although not complexed to the metal ion, the water molecules were found to form a hydrogen-bonded network that interacted with the anion. In contrast, this investigation describes an anhydrous species and reveals that the aqueous array is not necessary for the stability of the crystal, and seems to have little effect on the stability of the metal-crown complexation as evidenced by the Na–O bond distances.

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Crystals were prepared by A. J. Smetana and provided by Professor A. I. Popov. The 0.08 × 0.20 × 0.59 mm colorless crystal was mounted on a glass fiber along the normal to (110) and was found by the precession technique to exhibit the systematic extinctions  $0k0, k = 2n + 1; h0l, h = 2n + 1$ . Data were collected ( $\mp h, +k, +l$ ) with Mo radiation on a Picker FACS-I diffractometer by the  $\theta$ - $2\theta$  scan mode, with  $2\theta \leq 50^\circ$ . 4027 unique reflections were measured; of these, 1401 had values of  $F > 3\sigma(F)$ .

Initial structural details were obtained from *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and solution and refinement were effected with the entire system of Zalkin's programs (*MAGPIK, ABSORB, INCOR, ORDER2, FORDAP, LESQ, DISMAT, DISTAN, HFINDR, LSPLAN*) (A. Zalkin, Univ. of California), and with *ORFLS* (Busing, Martin & Levy, 1978), which was used to refine the multiplicities of the partially occupied anionic positions. The Na<sup>+</sup>-dicrown unit and the perchlorate moiety were input into *MULTAN*. The set chosen as a basis for initial positioning of the atoms had the highest combined figure of merit, 2.8811.

After refinement of the 23 atomic positions determined by *MULTAN*, the remaining positions were identified from difference maps. Hydrogen positions were postulated by *HFINDR* and were not refined; hydrogen thermal parameters were refined isotropically. All other atomic positions were refined anisotropically.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) as were the real and imaginary dispersion correction terms. An anomalous scattering factor of zero was assumed for hydrogen. An *ORTEP* (Johnson, 1976) drawing of the sodium-dicrown unit is illustrated in Fig. 1.

The structure was refined in sections: each ring with its hydrogen atoms was treated separately and the

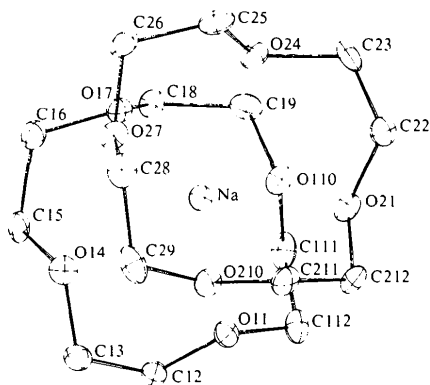


Fig. 1. The sodium-dicrown unit illustrating the 50% probability ellipsoids and the atom labeling scheme. H atoms are designated by the number of the carbon atom to which they are attached.

Table 1. Positional parameters for Na(12-crown-4)<sub>2</sub>ClO<sub>4</sub>

(A) Sodium and dicrown non-hydrogen atoms

	x	y	z	$B_{eq}^*$ ( $\text{\AA}^2$ )
Na	0.0127 (3)	0.2478 (5)	0.4924 (5)	4.1
O(11)	0.0369 (3)	0.1040 (4)	0.3812 (6)	5.0
C(12)	-0.038 (1)	0.062 (3)	0.326 (9)	6.5
C(13)	-0.115 (1)	0.081 (1)	0.410 (2)	6.3
O(14)	-0.1294 (4)	0.1717 (4)	0.4251 (6)	5.8
C(15)	-0.1755 (9)	0.212 (1)	0.310 (2)	5.6
C(16)	-0.160 (1)	0.308 (1)	0.321 (2)	5.7
O(17)	-0.0727 (3)	0.3328 (4)	0.3160 (6)	4.8
C(18)	-0.042 (1)	0.335 (1)	0.182 (1)	5.0
C(19)	0.056 (1)	0.332 (1)	0.195 (2)	5.8
O(110)	0.0905 (3)	0.2591 (4)	0.2724 (6)	5.3
C(111)	0.093 (1)	0.183 (1)	0.193 (2)	6.7
C(112)	0.107 (1)	0.108 (1)	0.295 (2)	6.0
O(21)	0.1637 (4)	0.2406 (4)	0.5922 (6)	5.4
C(22)	0.2006 (7)	0.3208 (8)	0.648 (1)	5.8
C(23)	0.1659 (7)	0.3954 (9)	0.561 (1)	6.7
O(24)	0.0689 (4)	0.3965 (4)	0.5549 (6)	5.5
C(25)	0.0322 (9)	0.4349 (9)	0.669 (1)	6.5
C(26)	-0.0626 (8)	0.4131 (9)	0.674 (1)	6.5
O(27)	-0.0742 (3)	0.3190 (4)	0.6756 (5)	5.3
C(28)	-0.0638 (8)	0.287 (1)	0.811 (1)	6.6
C(29)	-0.0533 (8)	0.189 (1)	0.794 (1)	7.4
O(210)	0.0220 (4)	0.1680 (4)	0.7157 (5)	5.3
C(211)	0.1018 (7)	0.1719 (9)	0.790 (1)	6.2
C(212)	0.1703 (7)	0.170 (1)	0.686 (1)	5.7

(B) Perchlorate atoms

	x	y	z	Multiplicity	$B_{eq}^*$ ( $\text{\AA}^2$ )
Cl	0.2477 (4)	0.4705 (2)	0.0033 (8)	1	7.7
O(31)	0.3396 (8)	0.474 (1)	0.007 (2)	0.716 (4)	11.4
O(32)	0.24 (2)	0.49 (2)	-0.14 (3)	0.486 (3)	11.8
O(33)	0.179 (5)	0.484 (4)	0.049 (8)	0.404 (3)	34.6
O(34)	0.236 (1)	0.486 (1)	0.149 (2)	0.791 (4)	12.1
O(35)	0.243 (2)	0.557 (2)	-0.042 (3)	0.542 (4)	22.4
O(36)	0.237 (1)	0.3779 (7)	-0.012 (2)	0.783 (5)	12.3
O(37)	0.160 (3)	0.467 (3)	-0.042 (5)	0.309 (2)	10.3

\* Equivalent isotropic thermal parameters are given for non-hydrogen atoms. These are calculated as  $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$ .

perchlorate moiety was refined either independently or with one ring at a time.

Refinement of the perchlorate moiety was complicated by apparent disorder. *MULTAN* initially indicated seven atomic positions around the chlorine atom at distances which ranged from 1.14 to 1.83  $\text{\AA}$ . Under anisotropic refinement, one fully occupied chlorine atom position was established with seven partially occupied oxygen positions and a residual surrounding it, positions which were close to those postulated by *MULTAN*. In the final refinement, the unrestrained overall oxygen occupancy summed to 4.03. Chemical evidence for the presence of alternate anions could not be found.

Positional parameters with associated e.s.d.'s are listed in Table 1.\*

The discrepancy index,  $R_1 = (\sum |F_o - F_c|) / \sum F_o = 0.0712$  for 1401 data with  $F > 3\sigma(F)$ , and  $R_2 = \{\sum (w|F_o - F_c|^2) / \sum wF_o^2\}^{1/2} = 0.0756$ .

The final difference Fourier map indicates one peak ( $1.48 \text{ e } \text{\AA}^{-3}$ ) about  $1 \text{ \AA}$  from the chlorine atom position.

**Discussion.** Bond distances for the C—C atoms varied from  $1.48 (1)$  to  $1.52 (2) \text{ \AA}$ , with a mean value of  $1.50 (1) \text{ \AA}$ , while those for the C—O atoms varied from  $1.39 (2)$  to  $1.49 (2) \text{ \AA}$ , with an average value of  $1.42 (3) \text{ \AA}$ . The crown ring angles varied from  $105 (7)$  to  $116 (3)^\circ$ , with an average value of  $111 (3)^\circ$ . The coordination about the sodium ion may be described as that of a slightly distorted rectangular antiprism. Sodium—oxygen distances range from  $2.474 (8)$  to  $2.543 (8)$  and average  $2.49 (5) \text{ \AA}$ , in good agreement with the calculated distance of  $2.54 \text{ \AA}$  based upon coordination numbers of 8 and 3 for sodium and oxygen, respectively (Shannon, 1976).

The oxygen—oxygen distances (*s* edges) in the two parallel planes of the antiprism average  $2.79 (3) \text{ \AA}$ , while the oxygen—oxygen distances between the planes (*l* edges) range from  $3.26 (2)$  to  $3.581 (8) \text{ \AA}$ , and average  $3.41 (11) \text{ \AA}$ . The *l/s* edge ratio is 1.22, in excellent agreement with that reported (van Remoortere & Boer, 1974), but significantly different from that of the Hoard—Silverton model calculated value of 1.06 (Hoard & Silverton, 1963). The *l*-edge oxygen—sodium—oxygen angles vary from  $82.1 (4)$  to  $91.1 (3)^\circ$  and average  $86.4 (3.3)^\circ$ ; the intraplanar oxygen—sodium—oxygen angles vary from  $66.8 (6)$  to  $68.8 (5)^\circ$ , and average  $68.0 (7)^\circ$ , also in excellent agreement with reported values (van Remoortere & Boer, 1974). The close agreement between the distances and angles reported herein for an anhydrous complex perchlorate with those reported for a hydrated chloride (van Remoortere & Boer, 1974) indicates that the hydrate

\* Lists of structure factor amplitudes, anisotropic thermal parameters, hydrogen-atom parameters and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36704 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

network has no effect on the coordination about the sodium ion.

Displacements of the heteroatoms from planarity for both rings are  $\pm 0.01 \text{ \AA}$ . The Na<sup>+</sup> ion is centered between the planes at a distance of  $1.53 (1) \text{ \AA}$  from each.

The perchlorate groups form a layer with all chlorine atoms restricted to the region  $z = \pm 0.0033$ . The sodium—dicrown units form another layer, with the sodium ions located at  $z = 0.5 \pm 0.0076$ . Thus, each ion is approximately centered in a rectangular parallelepiped of counter ions. The *x* and *y* dimensions of the coordination polyhedron are approximately equal, reflective of approximately equal *x* and *y* dimensions of the cell. There does not appear to be any significant interaction between the perchlorate ions and either the sodium ions or the dicrown unit as a whole. The perchlorate moiety is assumed to occupy semi-random positions in the structure, positions which are approximated by the partial occupancy of the perchlorate oxygen atoms.

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