

Influence of the Alkaline Cation on the Structures of Polymeric *o*-Phthalatocuprate(II). II. The Crystal Structures of Disodium Di-*o*-phthalatocuprate(II) Dihydrate and Dipotassium *catena*-Di- μ -(*o*-phthalato)-cuprate(II) Dihydrate

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(I) $\text{Na}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$: monoclinic $P2_1/c$; $a = 11.070$ (10), $b = 6.650$ (8), $c = 12.143$ (11) Å, $\beta = 101.6$ (1)°, $Z = 2$. (II) $\text{K}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$: monoclinic $C2/c$; $a = 12.065$ (15), $b = 21.327$ (16), $c = 7.825$ (9) Å, $\beta = 113.9$ (1)°, $Z = 4$. The structures, determined from diffractometer data by Patterson and Fourier methods, were refined by block-diagonal least squares to $R = 3.5\%$ for (I) and 3.3% for (II). In both compounds Cu is square planar, coordinated by four O atoms from four phthalate groups. In (II) two bridging phthalate anions link adjacent Cu atoms in zigzag polymeric chains. In (I) linear polymeric chains, with Cu atoms bridged by one phthalate group, cross one another in such a way as to form layers parallel to (100). The Na^+ cations occupy the hollows of these layers and are surrounded by six O atoms, five from phthalate ions and one from a water molecule. In (II) the K^+ cations, surrounded by seven O atoms from phthalate ions and water molecules, interpose between adjacent chains. These chains are joined in layers parallel to (101) by the interactions of the K^+ cations with O atoms of phthalate ions and by hydrogen bonds between water molecules and phthalate ions.

Introduction

Our researches on the behaviour as a ligand of the *o*-phthalate anion (pht) showed that in the Cu^{II} complexes pht acts as a bridge through two O atoms from both carboxylate groups, giving rise to different kinds of polymeric chains. With the purpose of determining what influence the alkaline cations exert on these chains we have determined the crystal structures of alkaline *o*-phthalatocuprate(II). In a previous paper (Cingi, Lanfredi, Tiripicchio & Camellini, 1977) we reported the structural results for the Li, Rb and Cs compounds; those for the Na and K compounds are now presented.

Experimental

The compounds of Na (I) and K (II) were prepared by dissolving copper(II) carbonate hydroxide in a solution containing stoichiometric amounts of the alkaline hydrogen *o*-phthalate. By slow evaporation of the solutions, blue elongated prisms were obtained at room temperature.

Preliminary crystal data were determined from rotation and Weissenberg photographs; accurate unit-cell parameters were then obtained by a least-squares procedure applied to the diffractometer measurements of 18 [for (I)] and 16 [for (II)] reflexions, and are listed in Table 1.

Table 1. *Crystal data*

	$\text{Na}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{K}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$
	Monoclinic	Monoclinic
FW	473.82	506.01
Space group	$P2_1/c$	$C2/c$
a (Å)	11.070 (10)	12.065 (15)
b (Å)	6.650 (8)	21.327 (16)
c (Å)	12.143 (11)	7.825 (9)
β (°)	101.6 (1)	113.9 (1)
V (Å ³)	875 (2)	1841 (3)
Z	2	4
D_x, D_m (g cm ⁻³)	1.80, 1.78	1.82, 1.82
$F(000)$	478	1020
μ (Mo $K\alpha$) (cm ⁻¹)	14.09	17.31

Intensity data were collected on a Siemens AED single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation and the ω - 2θ scan technique. Prismatic crystals of dimensions ca $0.10 \times 0.14 \times 0.30$ mm (I) and $0.05 \times 0.10 \times 0.37$ mm (II) were mounted with the [001] and [101] axes, respectively, parallel to the φ axis of the diffractometer. 1546 (I) and 1402 (II) independent reflexions were collected in the ranges $2^\circ < \theta < 25^\circ$ (I) and $3^\circ < \theta < 25^\circ$ (II) and, of these, 1197 (I) and 995 (II), having $I > 2\sigma(I)$, were used in subsequent calculations. A standard reflexion was periodically measured every twenty reflexions for both compounds as a test of crystal and instrument stability. No systematic changes were observed during data

collection. After corrections for Lorentz and polarization effects, the absolute scales and the overall temperature factors were determined by Wilson's method. No corrections for absorption were made because of the low value of μr . Both structures were solved by the heavy-atom technique. The refinements were carried out by block-diagonal least squares, first with isotropic, then with anisotropic thermal parameters. The H atoms were located from a ΔF map and refined by least squares with isotropic thermal

parameters. Unit weights were chosen at each stage of the refinement after analysing the variation of $|\Delta F|$ with respect to $|F|$. At the end of the refinements R was 0.035 for (I) and 0.033 for (II).*

Final atomic coordinates are given in Tables 2 and 3 for (I) and (II) respectively.

Atomic scattering factors of Cromer & Mann (1968) were used for non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for H.

All calculations were performed on a CYBER 76 computer of the Centro di Calcolo Elettronico Inter-universitario dell'Italia Nord-Orientale (Bologna).

Table 2. Fractional atomic coordinates for (I) ($\times 10^4$ for Cu, Na, O, C; $\times 10^3$ for H) with e.s.d.'s

	x	y	z
Cu	0	0	0
Na	928 (2)	3489 (3)	2020 (2)
O(1)	-1098 (3)	1948 (5)	527 (3)
O(2)	-1941 (3)	-850 (5)	1032 (3)
O(3)	-698 (3)	2123 (5)	2998 (3)
O(4)	-1165 (3)	5148 (5)	3581 (2)
O _w	1670 (4)	4121 (6)	428 (3)
C(1)	-2906 (4)	2248 (7)	1288 (4)
C(2)	-2672 (4)	3509 (7)	2218 (4)
C(3)	-3639 (4)	4637 (8)	2483 (4)
C(4)	-4817 (4)	4504 (8)	1837 (4)
C(5)	-5045 (4)	3269 (8)	901 (4)
C(6)	-4084 (4)	2138 (8)	621 (4)
C(7)	-1907 (4)	999 (7)	933 (4)
C(8)	-1417 (4)	3553 (7)	2977 (4)
H(1)	-342 (4)	569 (8)	318 (4)
H(2)	551 (4)	541 (8)	209 (4)
H(3)	-588 (4)	320 (7)	43 (4)
H(4)	-427 (4)	124 (7)	-13 (4)
H(5)	179 (4)	331 (8)	-5 (4)
H(6)	144 (4)	514 (8)	6 (4)

Table 3. Fractional atomic coordinates for (II) ($\times 10^4$ for Cu, K, O, C; $\times 10^3$ for H) with e.s.d.'s

	x	y	z
Cu	0	2349 (1)	2500
K	3338 (1)	1967 (1)	2690 (2)
O(1)	4070 (3)	3123 (2)	4254 (4)
O(2)	3763 (3)	3336 (2)	6778 (4)
O(3)	1260 (3)	2972 (2)	3073 (5)
O(4)	567 (4)	3350 (2)	165 (5)
O _w	3508 (4)	3202 (2)	510 (5)
C(1)	2905 (4)	4031 (2)	4196 (6)
C(2)	1824 (5)	4007 (2)	2640 (6)
C(3)	1244 (6)	4560 (3)	1787 (8)
C(4)	1798 (6)	5135 (3)	2520 (9)
C(5)	2868 (6)	5163 (3)	4014 (9)
C(6)	3456 (5)	4608 (2)	4877 (8)
C(7)	3606 (4)	3454 (2)	5114 (6)
C(8)	1158 (5)	3401 (2)	1846 (7)
H(1)	32 (5)	458 (3)	71 (7)
H(2)	127 (5)	553 (3)	180 (8)
H(3)	348 (5)	553 (3)	465 (8)
H(4)	438 (5)	464 (2)	602 (7)
H(5)	357 (6)	328 (3)	149 (9)
H(6)	429 (5)	315 (3)	39 (8)

Discussion of the results

In both compounds, polymeric chains of square-planar *o*-phthalatocuprate(II) complexes, alkali-metal cations and water molecules are present. Bond distances and angles are given in Tables 4 and 5. Fig. 1 shows that the conformation of the pht anion is almost the same in both compounds, with the carboxylate groups rotated around the C—C bonds on the same side with respect to the benzene ring. The angles formed by the planes through C(1)C(7)O(1)O(2) and C(2)C(8)O(3)O(4) with the benzene plane are of a different order of magnitude [70.4 and 23.8 in (I) and 68.0 and 35.7° in (II)]. In the Li and Rb compounds also the carboxylate groups are rotated on the same side, but by nearly the same angles. The reciprocal orientations of the carboxylate groups are mainly due to the necessity of reducing

* Lists of structure factors and thermal parameters are available from the authors and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33011 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

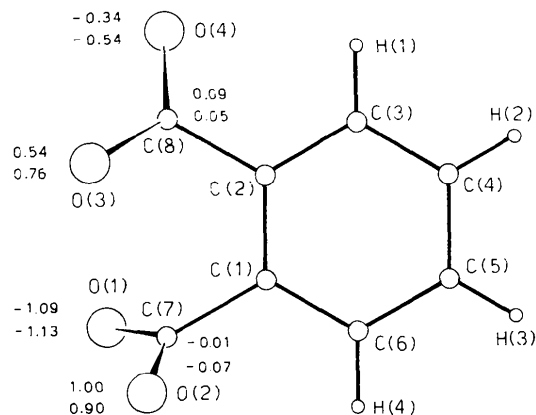


Fig. 1. Conformation of the phthalate anion in the two compounds. Displacements (in Å) of the atoms of the carboxylate groups in the Na and K compounds with respect to the benzene plane are also reported.

the interaction between O(1) and O(3) [O(1)···O(3) = 2.95 in (I) and 3.15 Å in (II)] and are such as to allow a bridging behaviour of the pht anion through O(1) and O(4), as found in (I), or through O(2) and O(3), as

found in (II). Since the distance O(1)···O(4) [4.29 in (I) and 4.17 Å in (II)] is longer than O(2)···O(3) [3.19 in (I) and 3.32 Å in (II)], the distance between two bridged Cu atoms is longer in (I) [6.92 Å] than in (II) [5.74 Å].

An analogous situation was found in the Li and Rb compounds: in the first, pht bridges through O(1) and O(4) and the Cu···Cu distance is 6.51 Å; in the

Table 4. Bond distances (Å) and angles (°) in the sodium compound

(a) In the coordination polyhedron			
Cu—O(1)	1.969 (4)	Cu—O(3 ^l)	3.068 (4)
Cu—O(4 ^l)	1.936 (3)	Cu—O(2)	2.755 (5)

O(1)—Cu—O(2)	53.0 (1)	O(3 ^l)—Cu—O(4 ^{ll})	46.4 (1)
O(1)—Cu—O(3 ^{ll})	103.1 (1)	O(1)—Cu—O(4 ^l)	88.8 (2)
O(1)—Cu—O(4 ^{ll})	91.2 (2)	O(2)—Cu—O(3 ^{ll})	66.9 (1)
O(1)—Cu—O(3 ^v)	76.9 (1)	O(3 ^{ll})—Cu—O(4 ^l)	133.6 (1)
O(2)—Cu—O(3 ^l)	113.2 (1)	O(2)—Cu—O(4 ^{ll})	92.7 (1)
O(2)—Cu—O(4 ^l)	87.3 (1)		

(b) In the phthalate anion

C(1)—C(2)	1.388 (7)	C(1)—C(7)	1.513 (7)
C(2)—C(3)	1.397 (7)	C(7)—O(1)	1.273 (6)
C(3)—C(4)	1.383 (7)	C(7)—O(2)	1.237 (6)
C(4)—C(5)	1.384 (7)	C(2)—C(8)	1.505 (7)
C(5)—C(6)	1.399 (7)	C(8)—O(3)	1.237 (6)
C(1)—C(6)	1.392 (7)	C(8)—O(4)	1.288 (6)
C(3)—H(1)	1.09 (5)	C(5)—H(3)	0.99 (5)
C(4)—H(2)	1.07 (5)	C(6)—H(4)	1.07 (5)

C(6)—C(1)—C(2)	120.3 (4)	C(4)—C(5)—C(6)	119.8 (4)
C(6)—C(1)—C(7)	117.3 (4)	C(1)—C(6)—C(5)	120.0 (5)
C(2)—C(1)—C(7)	122.4 (4)	C(1)—C(7)—O(1)	116.7 (4)
C(1)—C(2)—C(3)	119.0 (5)	C(1)—C(7)—O(2)	118.7 (4)
C(1)—C(2)—C(8)	120.5 (4)	O(1)—C(7)—O(2)	124.6 (4)
C(3)—C(2)—C(8)	120.3 (4)	C(2)—C(8)—O(3)	120.6 (4)
C(2)—C(3)—C(4)	120.9 (5)	C(2)—C(8)—O(4)	115.6 (4)
C(3)—C(4)—C(5)	120.0 (4)	O(3)—C(8)—O(4)	123.8 (4)
C(2)—C(3)—H(1)	118 (2)	C(4)—C(5)—H(3)	120 (3)
C(4)—C(3)—H(1)	121 (2)	C(6)—C(5)—H(3)	120 (3)
C(3)—C(4)—H(2)	117 (3)	C(5)—C(6)—H(4)	119 (2)
C(5)—C(4)—H(2)	123 (3)	C(1)—C(6)—H(4)	121 (2)

(c) Around the sodium cation

Na—O(1)	2.781 (5)	Na—O(2 ^{lll})	2.445 (5)
Na—O(3)	2.517 (5)	Na—O(3 ^{lll})	2.430 (5)
Na—O _w	2.286 (5)	Na—O(4 ^{ll})	2.370 (5)

O(1)—Na—O(3)	67.4 (1)	O(1)—Na—O(4 ^{ll})	65.1 (1)
O(1)—Na—O _w	84.1 (2)	O(3)—Na—O _w	151.4 (2)
O(1)—Na—O(2 ^{lll})	148.2 (1)	O(3)—Na—O(3 ^{lll})	80.8 (1)
O(1)—Na—O(3 ^{lll})	106.9 (1)	O(3)—Na—O(3 ^{lll})	106.2 (1)
O _w —Na—O(2 ^{lll})	127.7 (2)	O(3)—Na—O(4 ^{ll})	86.6 (1)
O _w —Na—O(3 ^{lll})	82.2 (2)	O _w —Na—O(4 ^{ll})	80.3 (1)
O(2 ^{lll})—Na—O(3 ^{lll})	81.8 (1)	O(2 ^{lll})—Na—O(4 ^{ll})	114.1 (1)
O(3 ^{lll})—Na—O(4 ^{ll})	161.4 (2)		

(d) In the water molecule

O _w —H(5)	0.82 (5)	H(5)—O _w —H(6)	103 (5)
O _w —H(6)	0.82 (5)		

(e) Hydrogen bonds

O _w —H(5)···O(2 ^v)	2.860 (6)	O(2 ^v)—O _w —H(5)	9 (4)
H(5)···O(2 ^v)	2.05 (5)	O(2 ^v)—H(5)—O _w	168 (5)
O _w —H(6)···O(1 ^{lv})	2.878 (6)	O(1 ^{lv})—O _w —H(6)	10 (3)
H(6)···O(1 ^{lv})	2.07 (5)	O(1 ^{lv})—H(6)—O _w	166 (5)

Asymmetric units

- (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$
 (ii) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$
 (iii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$
 (iv) $-x, 1 - y, -z$
 (v) $-x, -y, -z$
 (vi) $x, \frac{1}{2} - y, \frac{1}{2} + z$

Table 5. Bond distances (Å) and angles (°) in the potassium compound

(a) In the coordination polyhedron			
Cu—O(3)	1.930 (5)	Cu—O(2 ^l)	1.999 (5)
Cu—O(4)	3.062 (5)	Cu—O(1 ^l)	2.533 (5)

O(3)—Cu—O(2 ^l)	90.6 (2)	O(4)—Cu—O(2 ^{lll})	131.5 (1)
O(3)—Cu—O(3 ^{ll})	93.0 (2)	O(4)—Cu—O(2 ^l)	110.1 (2)
O(2 ^l)—Cu—O(2 ^{lll})	86.1 (2)	O(4)—Cu—O(3)	46.6 (1)
O(3)—Cu—O(2 ^{lll})	175.0 (2)	O(3)—Cu—O(4 ^{ll})	74.1 (2)
O(3)—Cu—O(1 ^l)	93.1 (2)	O(4)—Cu—O(4 ^{ll})	91.6 (1)
O(3)—Cu—O(1 ^{lll})	119.6 (2)	O(1 ^l)—Cu—O(1 ^{lll})	133.2 (2)
O(2 ^l)—Cu—O(1 ^l)	56.6 (1)	O(4)—Cu—O(1 ^{lll})	78.1 (1)
O(2 ^{lll})—Cu—O(1 ^l)	88.3 (1)	O(4)—Cu—O(1 ^l)	139.5 (1)

(b) In the phthalate anion

C(1)—C(2)	1.378 (7)	C(1)—C(7)	1.501 (6)
C(2)—C(3)	1.396 (8)	C(7)—O(1)	1.253 (6)
C(3)—C(4)	1.403 (9)	C(7)—O(2)	1.263 (6)
C(4)—C(5)	1.347 (10)	C(2)—C(8)	1.516 (7)
C(5)—C(6)	1.404 (8)	C(8)—O(3)	1.296 (6)
C(1)—C(6)	1.398 (7)	C(8)—O(4)	1.221 (6)
C(3)—H(1)	1.09 (6)	C(5)—H(3)	1.05 (5)
C(4)—H(2)	1.07 (6)	C(6)—H(4)	1.11 (6)

C(2)—C(1)—C(6)	120.2 (4)	C(4)—C(5)—C(6)	120.0 (6)
C(2)—C(1)—C(7)	122.7 (4)	C(1)—C(6)—C(5)	119.3 (5)
C(6)—C(1)—C(7)	116.8 (4)	C(1)—C(7)—O(1)	119.5 (4)
C(1)—C(2)—C(3)	120.2 (5)	C(1)—C(7)—O(2)	118.5 (4)
C(1)—C(2)—C(8)	123.3 (4)	O(1)—C(7)—O(2)	121.9 (4)
C(3)—C(2)—C(8)	116.4 (5)	C(2)—C(8)—O(3)	115.0 (4)
C(2)—C(3)—C(4)	118.7 (6)	C(2)—C(8)—O(4)	119.9 (4)
C(3)—C(4)—C(5)	121.6 (6)	O(3)—C(8)—O(4)	125.1 (5)
C(2)—C(3)—H(1)	124 (3)	C(4)—C(5)—H(3)	133 (3)
C(4)—C(3)—H(1)	117 (3)	C(6)—C(5)—H(3)	106 (3)
C(3)—C(4)—H(2)	113 (3)	C(5)—C(6)—H(4)	119 (2)
C(5)—C(4)—H(2)	125 (3)	C(1)—C(6)—H(4)	122 (2)

(c) Around the potassium cation

K—O(1)	2.735 (5)	K—O _w	3.190 (5)
K—O _w ^{lv}	2.616 (5)	K—O(3 ^l)	3.153 (6)
K—O(4 ^v)	2.687 (6)	K—O(4 ^{lv})	3.096 (6)
K—O(2 ^l)	2.806 (7)		

(d) In the water molecule

O _w —H(5)	0.76 (7)	H(5)—O _w —H(6)	114 (7)
O _w —H(6)	0.99 (7)		

(e) Hydrogen bonds

O _w —H(6)···O(1 ^{vl})	2.857 (9)	O _w —H(6)···O(1 ^{vl})	166 (5)
H(6)···O(1 ^{vl})	1.88 (7)	H(6)—O _w ···O(1 ^{vl})	9 (3)

Asymmetric units

- (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
 (ii) $-x, y, \frac{1}{2} - z$
 (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
 (iv) $\frac{1}{2} - x, \frac{1}{2} - y, -z$
 (v) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
 (vi) $1 - x, y, \frac{1}{2} - z$

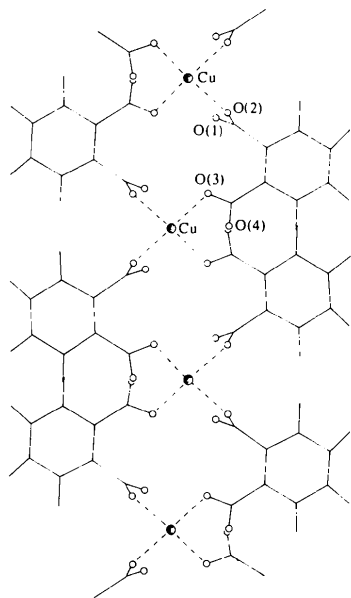


Fig. 2. Projection of a chain on the plane $(\bar{1}01)$ in the K compound.

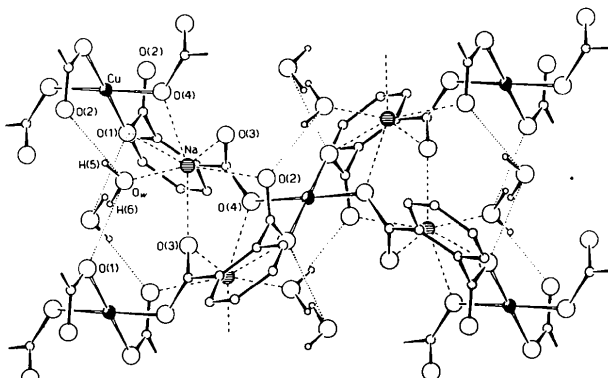


Fig. 3. Projection along a of the structure of the Na compound.

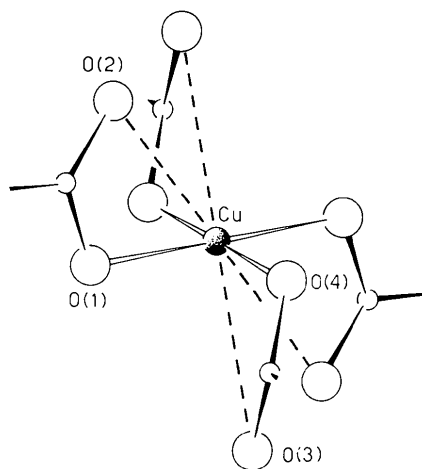


Fig. 4. Coordination around the Cu atom in the Na compound.

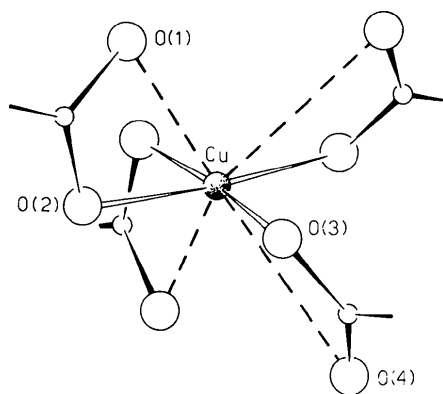


Fig. 5. Coordination around the Cu atom in the K compound.

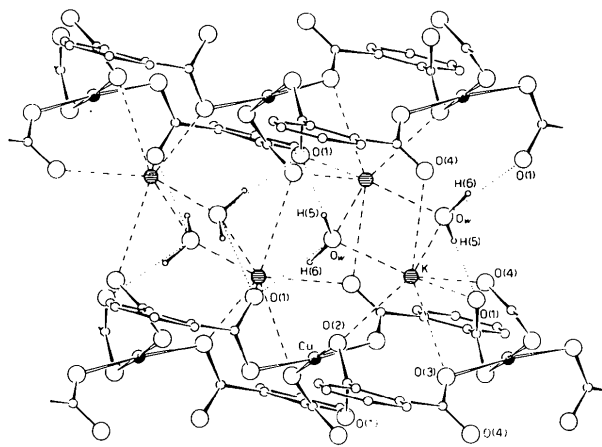


Fig. 6. Clinographic projection of the structure of the K compound.

second, pht bridges through O(2) and O(3) and $\text{Cu} \cdots \text{Cu}$ decreases to 5.94 Å.

In (II) the complexes, linked by double pht bridges, form zigzag polymeric chains running along $[101]$, the direction of the crystal elongation (Fig. 2). In (I) linear polymeric chains, with one pht bridging two adjacent Cu atoms, running parallel to $[011]$ and $[0\bar{1}1]$, cross one another so that layers parallel to (100) are formed (Fig. 3). Zigzag chains are also present in the Rb compound, and linear chains in the Li compound, although determined by double pht bridges.

In both compounds, Cu atoms, lying on a centre of symmetry in (I) and on a binary axis in (II), are in a square-planar arrangement determined by four O atoms belonging to four pht ligands (Figs. 4 and 5). Cu atoms also form four longer contacts [2.775 and 3.068 Å in (I), 2.533 and 3.062 Å in (II)] with uncoordinated O atoms of carboxylate groups, so that the coordination number rises to eight, as already found in the Li and Rb compounds.

In (I) the Na⁺ cations are small enough to insert in the hollows of the crossed polymeric chains. These cations are surrounded by six O atoms, five from pht anions and one from a water molecule (Fig. 3), with Na–O distances in the range 2.286–2.781 Å.

In (II) the K⁺ cations interpose between adjacent chains (Fig. 6) and are surrounded by seven O atoms (at distances in the range 2.616–3.190 Å) belonging to pht anions and to water molecules. K–O interactions together with hydrogen bonds between water molecules and pht anions join the chains in layers parallel to (101).

Packing of the layers in both compounds is determined by normal van der Waals contacts.

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The Crystal and Molecular Structure of 4-Nitrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecane. RbSCN, C₁₇H₂₃O₈N₂SRb

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The crystal and molecular structure of the title compound (4-nitrobenzo-18-crown-6.RbSCN) has been determined from 1935 observed three-dimensional data measured on a Syntex P2₁ single-crystal automated diffractometer. The unit cell is monoclinic with $a = 13.222$ (3), $b = 8.179$ (2), $c = 21.150$ (4) Å, $\beta = 110.54$ (1)°, $V = 2142$ (1) Å³ and contains four formula units. The space group is $P2_1/c$. The crystal structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The final R value is 0.056.

Introduction

One of the important properties of macrocyclic polyethers is their ability to form complexes with various inorganic cations by means of ion–dipole interactions between the cation and electronegative O atoms arranged symmetrically in the macro-ring.

In recent years, a number of papers have been published reporting structures of the above type containing 1,4,7,10,13,16-hexaoxacyclooctadecane (Bright & Truter, 1970; Bush & Truter, 1971; Dunitz, Dobler, Seiler & Phizackerley, 1974; Goldberg, 1975; Hašek, Hlavatá & Huml, 1977; Mallinson, 1975).

Dunitz *et al.* (1974) showed that the six O atoms in 1,4,7,10,13,16-hexaoxacyclooctadecane formed, for the K⁺ cation, an almost regular planar hexagon having a side length of approximately 2.81 Å. For cations with a higher van der Waals radius the O hexagon remains almost without change, and the cation moves away from the mean O plane.

In the case of the Na⁺ cation the hexagon of O atoms is greatly deformed. One of the O atoms deviates from the mean plane of the other five by some 1.95 Å.

In an attempt to elucidate the pronounced effect of substituents in an 18-membered ring on selectivity towards various cations (Petránek & Ryba, 1974), work was started in order to solve a number of structures containing 1,4,7,10,13,16-hexaoxacyclooctadecane with various substituents (Hašek & Huml, 1975; Hašek, Hlavatá & Huml, 1977). In this paper we present the crystal and molecular structure of the complex 4-nitrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecane.RbSCN.

Experimental

The crystals used in the measurements were prepared by Petránek & Ryba (1974). They were yellow, in the