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Influence of the Alkaline Cation on the Structures of Polymeric o-Phthalatocuprate(II). I. The Crystal Structures of Dilithium catena-Di-μ-(o-phthalato)-cuprate(II) Tetrahydrate and Dirubidium catena-Di-μ-(o-phthalato)-cuprate(II) Dihydrate

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(I) $Li_2Cu(C_8H_4O_4)_2.4H_2O$: triclinic $P\bar{1}$; $a = 7.823$ (7), $b = 10.935$ (15), $c = 6.514$ (10) Å, $\alpha = 111.8$ (1), $\beta = 112.8$ (1), $\gamma = 87.4$ (1)°, $Z = 1$. (II) $Rb_2Cu(C_8H_4O_4)_2.2H_2O$: monoclinic $C2/c$; $a = 21.919$ (15), $b = 7.827$ (7), $c = 11.191$ (10) Å, $\beta = 101.8$ (3)°, $Z = 4$. The structures, determined from diffractometer data by Patterson and Fourier methods, were refined by block-diagonal least squares to $R = 2.4\%$ for (I) and 6.6% for (II). In both compounds Cu is square-planar, coordinated by four O atoms from four phthalate groups. The phthalate anions bridge adjacent Cu atoms in polymeric chains, which are linear in (I) and zigzag in (II). Coordination of Li is tetrahedral and involves two O atoms from two phthalate groups, belonging to the same chain, and two water molecules. A different behaviour is found for Rb which interposes between two different chains and is surrounded by eight O atoms from four phthalate ions and two water molecules.

Introduction

The o-phthalate (pht) anion can act as a bridge when coordinating to metal atoms through both its carboxylate groups, giving rise to polymeric chains, whose structures are affected by the presence of other ionic or molecular species.

The aim of the present research is to find what influence the alkaline cations, differing in radius and coordination, exert on the polymeric chains formed by pht anions coordinated to Cu^{II}.

Table 1. *Crystal data*

	$Li_2Cu(C_8H_4O_4)_2.4H_2O$, diffractometer data, triclinic	$Rb_2Cu(C_8H_4O_4)_2.2H_2O$, diffractometer data, monoclinic	$Cs_2Cu(C_8H_4O_4)_2.2H_2O$, photographic data, monoclinic
F.W.	477.74	598.78	693.64
Space group	$P\bar{1}$	$C2/c$	$C2/c$
a (Å)	7.823 (7)	21.919 (15)	21.634 (18)
b (Å)	10.935 (15)	7.827 (7)	8.068 (8)
c (Å)	6.514 (10)	11.191 (10)	11.502 (13)
α (°)	111.8 (1)		
β (°)	112.8 (1)	101.8 (3)	97.5 (3)
γ (°)	87.4 (1)		
V (Å^3)	474.2	1879.2	1990.3
Z	1	4	4
D_x, D_m (g cm^{-3})	1.67, 1.67	2.12, 2.12	2.31, 2.27
$F(000)$	243	1164	
μ(Mo $K\alpha$) (cm^{-1})	12.66	67.11	

With this purpose $Li_2Cupht_2.4H_2O$, $Na_2Cupht_2.2H_2O$, $K_2Cupht_2.2H_2O$, $Rb_2Cupht_2.2H_2O$, $Cs_2Cupht_2.2H_2O$ were prepared. From the preliminary X-ray analysis it was found that only the Cs and Rb derivatives are isostructural.

In the present paper the results of the structure analysis of the Li and Rb compounds are compared; the analysis of the Na and K compounds is in progress.

Experimental

The simplest way to prepare the compounds under study is to dissolve copper(II) hydroxocarbonate in a solution containing stoichiometric amounts of the alkaline hydrogen o-phthalate. Deep-blue elongated prismatic, seldom untwinned, crystals were obtained at room temperature by slow evaporation of the solutions. Conventional chemical analyses were in good agreement with the assigned formulae.

Preliminary crystal data were determined from rotation and Weissenberg photographs; those of the Li and Rb compounds were subsequently refined by least squares applied to the diffractometer measurements of 16 and 15 reflexions respectively, and are listed in Table 1.

Intensities for the Li (I) and Rb (II) compounds were collected on a Siemens AED single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation and the $\omega-2\theta$ scan technique. Elongated prisms $0.25 \times 0.30 \times 0.50$ mm (I) and $0.10 \times 0.10 \times 0.25$ mm (II) were aligned with c along the φ axis of the diffractometer and all the reflexions with $2\theta < 58°$ (I) and $2\theta < 50°$ (II) were measured. Of 2494 (I) and 1650 (II) independent reflexions, 2351 (I) and 1289 (II) having $I \geq 2\sigma(I)$ were used in the structure determinations. Corrections for Lorentz and polarization factors were made but not for absorption. The absolute scale factors and the mean isotropic temperature factors were obtained by Wilson's method. The structures were solved by Patterson and Fourier methods. The refinements were carried out by block-diagonal least squares, first with isotropic, then anisotropic, thermal parameters. The H atoms were located from difference syntheses and refined by

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

	x	y	z
Cu	0	0	0
O(1)	−302 (2)	−1281 (1)	1291 (2)
O(2)	−3252 (2)	−1496 (1)	−1177 (2)
O(3)	−2403 (2)	−793 (1)	4668 (2)
O(4)	−108 (2)	−1507 (1)	7127 (2)
$O_w(1)$	3045 (2)	−1957 (1)	5852 (2)
$O_w(2)$	3798 (2)	−1084 (1)	1795 (2)
C(1)	−2244 (2)	−3053 (2)	723 (3)
C(2)	−1737 (2)	−2976 (2)	3071 (3)
C(3)	−1738 (3)	−4129 (2)	3496 (4)
C(4)	−2302 (4)	−5356 (2)	1584 (4)
C(5)	−2870 (4)	−5425 (2)	−738 (4)
C(6)	−2837 (3)	−4280 (2)	−1178 (3)
C(7)	−1980 (2)	−1855 (2)	233 (3)
C(8)	−1387 (2)	−1650 (2)	5088 (3)
Li	2290 (4)	−1095 (3)	3615 (5)
H(1)	−134 (3)	−409 (2)	518 (4)
H(2)	−230 (3)	−615 (2)	195 (4)
H(3)	−328 (3)	−628 (2)	−209 (4)
H(4)	−325 (3)	−436 (2)	−287 (4)
H(5)	231 (3)	−190 (2)	659 (4)
H(6)	410 (3)	−198 (2)	669 (4)
H(7)	497 (3)	−114 (2)	254 (4)
H(8)	371 (3)	−38 (2)	153 (4)

Table 3. *Thermal parameters* $(Å^2)$ *with e.s.d.'s*

Anisotropic thermal parameters are in the form: $\exp[-0.25 \, (h^2 a^{*2} B_{11} + \cdots + 2klb^* c^* B_{23})]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1·53 (1)	1·73 (1)	0·99 (1)	−0·08 (1)	0·34 (1)	0·61 (1)
O(1)	1·82 (4)	2·33 (5)	1·53 (4)	−0·41 (3)	0·31 (3)	0·94 (4)
O(2)	1·91 (5)	4·00 (6)	2·94 (6)	0·09 (4)	0·33 (4)	2·25 (5)
O(3)	2·10 (5)	1·92 (4)	1·91 (4)	0·44 (4)	0·44 (4)	0·47 (4)
O(4)	2·16 (5)	2·30 (5)	1·36 (4)	0·30 (4)	0·51 (3)	0·71 (4)
$O_w(1)$	2·19 (5)	3·69 (6)	2·47 (5)	0·55 (4)	0·69 (4)	1·59 (5)
$O_w(2)$	2·11 (5)	3·49 (6)	2·84 (6)	0·19 (4)	0·96 (4)	0·93 (5)
C(1)	1·90 (6)	1·83 (6)	1·63 (6)	−0·19 (5)	0·69 (5)	0·49 (5)
C(2)	1·97 (6)	1·71 (6)	1·64 (5)	0·12 (4)	0·78 (5)	0·59 (4)
C(3)	3·58 (8)	2·26 (7)	2·78 (8)	0·43 (6)	1·42 (7)	1·31 (6)
C(4)	5·18 (11)	1·84 (7)	4·39 (10)	0·18 (7)	2·09 (9)	1·23 (7)
C(5)	5·29 (12)	1·81 (7)	3·52 (9)	−0·54 (7)	1·97 (9)	−0·10 (6)
C(6)	3·57 (8)	2·50 (7)	1·96 (7)	−0·68 (6)	1·09 (6)	0·10 (5)
C(7)	1·91 (6)	2·14 (6)	1·28 (5)	−0·08 (5)	0·58 (4)	0·61 (5)
C(8)	1·74 (5)	1·93 (6)	1·44 (5)	0·08 (4)	0·73 (4)	0·67 (4)
Li	2·21 (11)	2·31 (11)	2·07 (11)	0·32 (9)	0·54 (9)	0·85 (9)

	B		B		B
H(1)	3·3 (4)	H(4)	3·1 (4)	H(7)	4·0 (5)
H(2)	3·2 (4)	H(5)	3·9 (5)	H(8)	5·0 (6)
H(3)	3·6 (5)	H(6)	3·7 (5)		

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

	x	y	z
Cu	0	3718 (2)	2500
Rb	4472 (1)	2906 (1)	3976 (1)
O(1)	657 (3)	3424 (9)	−1436 (6)
O(2)	733 (3)	6244 (8)	−1154 (6)
O(3)	535 (3)	3786 (10)	1338 (6)
O(4)	1010 (4)	1321 (10)	1916 (7)
O_w	656 (4)	15 (10)	4012 (7)
C(1)	1525 (4)	4486 (12)	27 (8)
C(2)	1562 (4)	3390 (12)	1019 (9)
C(3)	2149 (5)	3007 (14)	1726 (9)
C(4)	2676 (5)	3798 (14)	1466 (10)
C(5)	2632 (5)	4890 (15)	480 (10)
C(6)	2047 (4)	5252 (14)	−238 (9)
C(7)	916 (4)	4726 (13)	−916 (8)
C(8)	994 (4)	2730 (13)	1443 (8)
H(1)	219 (5)	218 (15)	247 (10)
H(2)	302 (5)	369 (15)	202 (10)
H(3)	301 (6)	547 (17)	26 (11)
H(4)	201 (6)	604 (18)	−98 (12)
H(5)	77 (5)	88 (14)	435 (9)
H(6)	88 (6)	6 (19)	314 (12)

least squares with isotropic thermal parameters. Unit weights were assumed. At the end of the refinement R was 0·024 for (I) and 0·066 for (II).

Final atomic coordinates and thermal parameters are given in Tables 2 and 3 for (I), and 4 and 5 for (II).*

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* A list of observed and calculated structure factors is available from the authors on request, and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32084 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

All calculations were performed on a CDC-6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna).

Discussion of the results

Both structures consist of polymeric chains of *o*-phthalatocuprate complexes, alkali metal cations and water molecules. Bond distances and angles are given in Tables 6 and 7. The conformation of the pht anion is the same in both compounds (Fig. 1), the carboxylate groups being rotated around the C—C bonds on the same side and by nearly the same angles with respect to the benzene ring [the angles the planes through C(1)-C(7)O(1)O(2) and C(2)C(8)O(3)O(4) form with the benzene plane are 58·1 and 40·0 in (I) and 57·7 and 37·8° in (II)] in such a way as to determine the lowest interaction between O(1) and O(3) [O(1)···O(3) = 3·11 in (I) and 3·18 Å in (II)]. The reciprocal orientation of the carboxylate groups is also such as to allow a bridging behaviour when the pht anions coordinate to Cu^{II}, the atoms involved in coordination being O(1) and O(4) or O(2) and O(3). This behaviour corresponds to the two ways of bridging observed in (I) and (II) respectively.

In (I) two Cu atoms are bridged by two pht anions through O(1) and O(4), to form a linear polymeric chain running along [001] (Fig. 2). In (II) bridging involves O(2) and O(3) [Fig. 3(a) and (b)] and the complexes are linked in polymeric chains which now are zigzag, the adjacent monomers being related by the *c* glide.

Table 5. *Thermal parameters* (Å^2) *with e.s.d.'s*

Anisotropic thermal parameters are in the form: $\exp[-0·25\,(h^2a^{*2}B_{11} + \cdots + 2klb^*c^*B_{23})]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1·15 (6)	1·03 (6)	1·01 (6)	0	0·37 (5)	0
Rb	3·08 (4)	2·16 (4)	2·19 (4)	0·26 (4)	0·89 (3)	0·02 (4)
O(1)	2·58 (31)	1·60 (30)	1·57 (29)	−0·18 (25)	−0·37 (24)	0·01 (24)
O(2)	1·91 (27)	1·08 (26)	1·68 (27)	0·41 (24)	0·27 (22)	−0·07 (23)
O(3)	1·72 (27)	2·47 (32)	2·08 (29)	0·73 (26)	0·74 (23)	0·51 (26)
O(4)	3·67 (37)	1·65 (31)	2·59 (33)	−0·04 (29)	1·23 (28)	0·23 (27)
O_w	5·02 (44)	1·53 (30)	2·83 (35)	−0·12 (31)	1·57 (32)	−0·16 (28)
C(1)	1·77 (39)	1·03 (37)	1·55 (38)	0·13 (32)	0·60 (30)	−0·51 (31)
C(2)	1·52 (37)	1·29 (39)	1·70 (38)	0·46 (31)	0·65 (30)	0·08 (31)
C(3)	1·76 (40)	2·22 (46)	2·18 (42)	0·52 (39)	−0·06 (33)	−0·82 (39)
C(4)	1·64 (41)	2·14 (47)	3·01 (49)	0·68 (37)	0·14 (35)	−1·07 (41)
C(5)	2·35 (45)	2·64 (51)	2·89 (49)	−0·51 (41)	0·43 (37)	−0·39 (43)
C(6)	1·34 (37)	2·13 (45)	2·49 (45)	−0·50 (35)	0·65 (33)	−0·18 (38)
C(7)	1·32 (35)	1·69 (40)	0·98 (34)	−0·07 (32)	0·11 (27)	0·32 (31)
C(8)	2·00 (38)	1·48 (38)	0·90 (33)	−0·61 (34)	0·37 (29)	0·15 (32)

	B		B		B
H(1)	2·99 (2·54)	H(3)	4·36 (3·11)	H(5)	2·32 (2·32)
H(2)	2·65 (2·42)	H(4)	5·14 (3·47)	H(6)	5·12 (3·44)

Table 6. *Bond distances* (Å) *and angles* (°) *in the lithium compound*

(a) In the coordination polyhedron

Cu—O(1)	1·942 (3)	Cu—O(2)	2·770 (4)
Cu—O(4^i)	1·955 (3)	Cu—O(3^i)	3·033 (4)
O(1)—Cu—O(4^i)	87·4 (1)	O(4^i)—Cu—O(3^i)	47·3 (1)
O(1)—Cu—O(2)	52·3 (1)	O(2)—Cu—O(3^i)	70·8 (1)
O(1)—Cu—O(3^i)	113·7 (1)	O(2)—Cu—O(4^i)	78·7 (1)

(b) In the phthalate anion

C(1)—C(2)	1·392 (4)	C(1)—C(7)	1·497 (4)
C(2)—C(3)	1·386 (4)	C(7)—O(1)	1·284 (3)
C(3)—C(4)	1·390 (4)	C(7)—O(2)	1·230 (3)
C(4)—C(5)	1·373 (4)	C(2)—C(8)	1·499 (4)
C(5)—C(6)	1·386 (4)	C(8)—O(4)	1·273 (3)
C(1)—C(6)	1·388 (4)	C(8)—O(3)	1·241 (3)
C(3)—H(1)	1·00 (3)	C(5)—H(3)	0·97 (2)
C(4)—H(2)	0·98 (3)	C(6)—H(4)	0·99 (3)

C(6)—C(1)—C(2)	119·5 (6)	C(4)—C(5)—C(6)	120·3 (6)
C(6)—C(1)—C(7)	119·2 (5)	C(1)—C(6)—C(5)	120·3 (6)
C(2)—C(1)—C(7)	121·0 (5)	C(1)—C(7)—O(1)	114·7 (5)
C(1)—C(2)—C(3)	119·7 (6)	C(1)—C(7)—O(2)	122·4 (5)
C(1)—C(2)—C(8)	119·9 (6)	O(1)—C(7)—O(2)	122·8 (5)
C(3)—C(2)—C(8)	120·2 (5)	C(2)—C(8)—O(4)	117·2 (5)
C(2)—C(3)—C(4)	120·4 (6)	C(2)—C(8)—O(3)	117·7 (5)
C(3)—C(4)—C(5)	119·8 (6)	O(4)—C(8)—O(3)	125·1 (5)
C(2)—C(3)—H(1)	121 (4)	C(4)—C(5)—H(3)	120 (3)
C(4)—C(3)—H(1)	119 (3)	C(6)—C(5)—H(3)	119 (3)
C(3)—C(4)—H(2)	118 (3)	C(5)—C(6)—H(4)	118 (3)
C(5)—C(4)—H(2)	122 (4)	C(1)—C(6)—H(4)	121 (3)

(c) Around the lithium cation

Li—O$_w$(1)	1·911 (6)	Li—O(1)	1·971 (4)
Li—O$_w$(2)	1·971 (5)	Li—O(3^{iii})	1·935 (5)
O(1)—Li—O$_w$(1)	123·1 (2)	O$_w$(1)—Li—O$_w$(2)	120·4 (2)
O(1)—Li—O$_w$(2)	103·9 (2)	O$_w$(1)—Li—O(3^{iii})	109·6 (2)
O(1)—Li—O(3^{iii})	94·6 (2)	O$_w$(2)—Li—O(3^{iii})	99·9 (2)

(d) In the water molecules

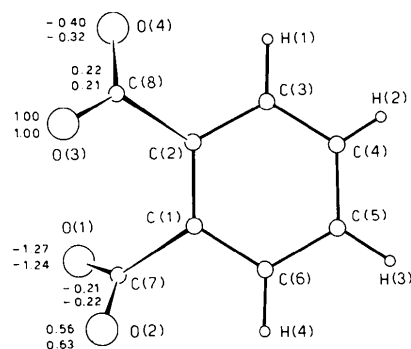|			
O$_w$(1)—H(5)	0·87 (3)	O$_w$(2)—H(7)	0·87 (2)
O$_w$(1)—H(6)	0·80 (2)	O$_w$(2)—H(8)	0·84 (3)
H(5)—O$_w$(1)—H(6)	111·3 (6)	H(7)—O$_w$(2)—H(8)	108·4 (5)

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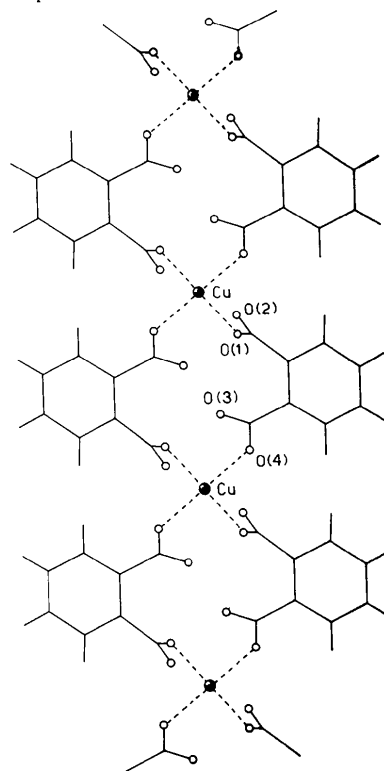

Fig. 2. Projection of a chain in the Li compound on the plane (100).

Table 6 (*cont.*)

(e) Hydrogen bonds

O$_w$(1)—H(5) · · · O(4)	2·863 (4)	O(4)—O$_w$(1)—H(5)	18 (1)
H(5) · · · O(4)	2·05 (3)	O(4)—H(5)—O$_w$(1)	155 (2)
O$_w$(2)—H(7) · · · O(3^{iv})	2·792 (5)	O(3^{iv})—O$_w$(2)—H(7)	10 (2)
H(7) · · · O(3^{iv})	1·94 (2)	O(3^{iv})—H(7)—O$_w$(2)	165 (2)
O$_w$(1)—H(6) · · · O(2^v)	2·734 (5)	O(2^v)—O$_w$(1)—H(6)	12 (2)
H(6) · · · O(2^v)	1·96 (2)	O(2^v)—H(6)—O$_w$(1)	163 (2)
O$_w$(2)—H(8) · · · O(2^{ii})	2·981 (5)	O(2^{ii})—O$_w$(2)—H(8)	6 (2)
H(8) · · · O(2^{ii})	2·15 (2)	O(2^{ii})—H(8)—O$_w$(2)	172 (2)

Asymmetric units: (i) x, y, $z-1$; (ii) $-x$, $-y$, $-z$; (iii) $-x$, $-y$, $1-z$; (iv) $1+x$, y, z; (v) $1 + x, y, 1 + z$.

The distance between two bridged Cu atoms is longer in (I), 6·51, than in (II), 5·94 Å, mainly as a consequence of the fact that O(1)···O(4) [3·85 in (I) and 4·02 Å in (II)] is longer than O(2)···O(3) [3·38 in (I) and 3·49 Å in (II)].

Table 7. *Bond distances (Å) and angles (°) in the rubidium compound*

(a) In the coordination polyhedron

Cu—O(3)	1·922 (9)	Cu—O(2^i)	1·965 (9)
Cu—O(4)	3·072 (9)	Cu—O(1^i)	2·792 (8)
O(3)—Cu—O(2^i)	89·8 (3)	O(4)—Cu—O(2^{iii})	70·2 (2)
O(3)—Cu—O(2^{iii})	90·1 (3)	O(4)—Cu—O(2^i)	111·0 (2)
O(3)—Cu—O(3^{ii})	176·8 (3)	O(4)—Cu—O(3)	46·1 (3)
O(2^i)—Cu—O(2^{iii})	178·3 (3)	O(3)—Cu—O(4^{ii})	136·6 (3)
O(3)—Cu—O(1^i)	91·3 (3)	O(4)—Cu—O(4^{ii})	104·7 (2)
O(3)—Cu—O(1^{iii})	86·2 (3)	O(1^i)—Cu—O(1^{iii})	73·5 (2)
O(2^i)—Cu—O(1^i)	52·5 (2)	O(4)—Cu—O(1^{iii})	104·4 (2)
O(2^{iii})—Cu—O(1^i)	125·8 (2)	O(4)—Cu—O(1^i)	136·9 (2)

(b) In the phthalate anion

C(1)—C(2)	1·392 (14)	C(1)—C(7)	1·534 (12)
C(2)—C(3)	1·398 (14)	C(7)—O(1)	1·251 (12)
C(3)—C(4)	1·393 (16)	C(7)—O(2)	1·265 (12)
C(4)—C(5)	1·383 (16)	C(2)—C(8)	1·511 (14)
C(5)—C(6)	1·396 (14)	C(8)—O(3)	1·289 (12)
C(1)—C(6)	1·377 (14)	C(8)—O(4)	1·221 (13)
C(3)—H(1)	1·04 (11)	C(5)—H(3)	1·02 (14)
C(4)—H(2)	0·88 (10)	C(6)—H(4)	1·02 (14)
C(2)—C(1)—C(6)	121·6 (9)	C(4)—C(5)—C(6)	119·4 (10)
C(2)—C(1)—C(7)	121·6 (8)	C(1)—C(6)—C(5)	119·6 (9)
C(6)—C(1)—C(7)	116·3 (8)	C(1)—C(7)—O(1)	117·9 (8)
C(1)—C(2)—C(3)	118·7 (9)	C(1)—C(7)—O(2)	117·0 (8)
C(1)—C(2)—C(8)	122·9 (8)	O(1)—C(7)—O(2)	125·0 (8)
C(3)—C(2)—C(8)	118·1 (9)	C(2)—C(8)—O(3)	115·5 (8)
C(2)—C(3)—C(4)	119·5 (9)	C(2)—C(8)—O(4)	119·5 (9)
C(3)—C(4)—C(5)	121·0 (10)	O(3)—C(8)—O(4)	124·9 (9)
C(2)—C(3)—H(1)	120 (6)	C(4)—C(5)—H(3)	123 (7)
C(4)—C(3)—H(1)	120 (6)	C(6)—C(5)—H(3)	118 (7)
C(3)—C(4)—H(2)	116 (7)	C(5)—C(6)—H(4)	120 (8)
C(5)—C(4)—H(2)	122 (7)	C(1)—C(6)—H(4)	120 (8)

(c) Around the rubidium cation

Rb—O$_w^v$	2·838 (9)	Rb—O(1^{viii})	2·986 (7)
Rb—O(s^x)	2·878 (8)	Rb—O$_w^{vi}$	3·069 (9)
Rb—O(1^{ix})	2·921 (8)	Rb—O(3^x)	3·244 (8)
Rb—O(4^{vii})	2·971 (8)	Rb—O (3^{ix})	3·413 (11)

(d) In the water molecule

O$_w$—H(5)	0·81 (11)	H(5)—O$_w$—H(6)	106 (10)
O$_w$—H(6)	1·18 (14)		

(e) Hydrogen bonds

O$_w$—H(5)···O(1^{iv})	2·738 (11)	O$_w$—H(5)—O(1^{iv})	127 (9)
H(5)···O(1^{iv})	2·17 (11)	H(5)—O$_w$—O(1^{iv})	39 (7)
O$_w$—H(6)···O(4)	2·810 (13)	O$_w$—H(6)—O(4)	145 (11)
H(6)···O(4)	1·76 (14)	H(6)—O$_w$—O(4)	21 (7)

Asymmetric units: (i) $-x$, $1-y$, z; (ii) $-x$, y, $\frac{1}{2}-z$; (iii) x, $1-y$, $\frac{1}{2}+z$; (iv) x, $-y$, $\frac{1}{2}+z$; (v) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$; (vi) $\frac{1}{2}+x$, $\frac{1}{2}+y$, z; (vii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (viii) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$; (ix) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (x) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$.
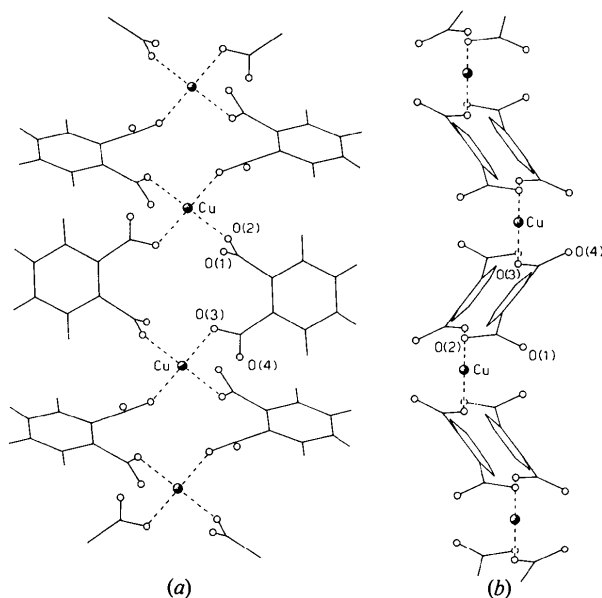

(a)   (b)

Fig. 3. Two different projections of a chain in the Rb compound (a) along the perpendicular, contained in the plane (100), to the line joining two adjacent Cu atoms, (b) on the plane (100).
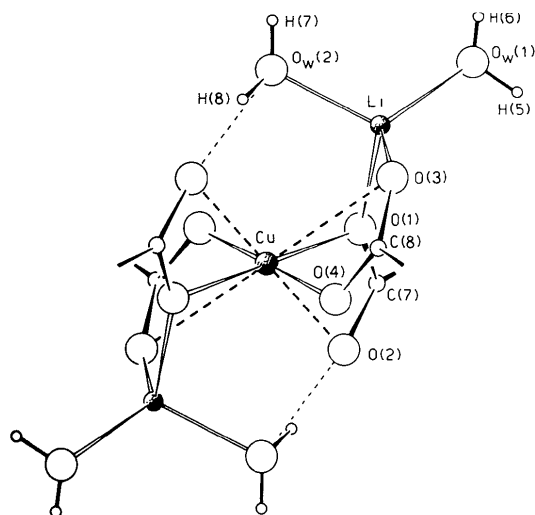

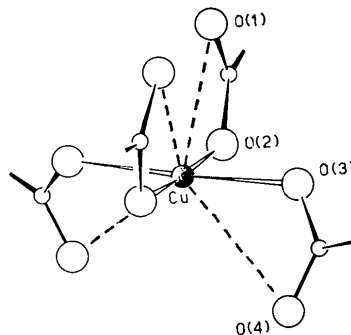Fig. 4. Coordination around the Cu and the Li atoms in the Li compound.

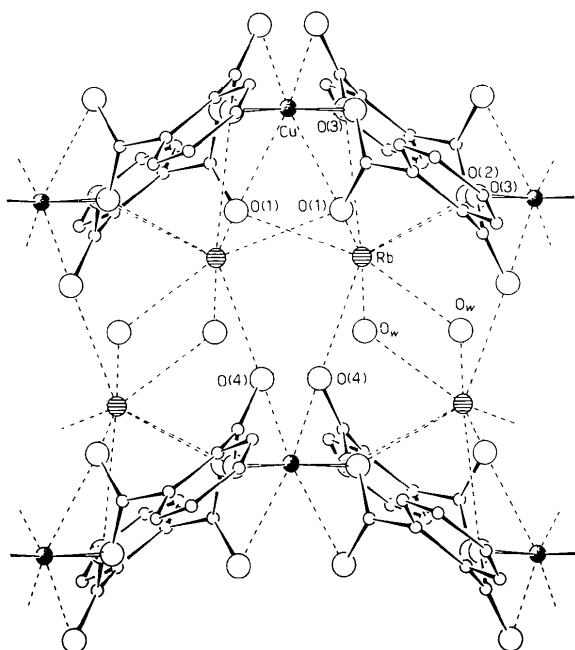Fig. 5. Coordination around the Cu atom in the Rb compound.

Fig. 6. Projection along a of the structure of the Rb compound. The role of the Rb cations and of the water molecules in joining together the chains in layers is shown.

In (I) the Cu atom, which lies on a centre of symmetry, is surrounded by four O atoms belonging to four pht groups in a nearly perfect square-planar arrangement (Fig. 4).

In (II) Cu lies on a binary axis and coordination is also square-planar, but more distorted (Fig. 5).

In both compounds the Cu atoms also form four longer contacts [2·770 and 3·033 in (I), 2·792 and 3·072 Å in (II)] involving uncoordinated O atoms of carboxylate groups, and so the coordination number rises to eight and the coordination polyhedron assumes the form of an irregular square-antiprism in (I) and a distorted dodecahedron in (II).

The O atoms involved in these long Cu···O contacts are displaced by ~40° from the apical octahedral sites because of the restricting geometry of the carboxylate group.

A similar situation was found in CaCu-$(CH_3COO)_4.6H_2O$, which contains four Cu···O contacts of 2·79 Å (Langs & Hare, 1967). The polarized single-crystal electronic spectra of this compound have been interpreted by Billing, Hathaway & Nicholls (1970) assuming that the long-bonded O atoms are involved in a weak 'semi-coordination' interaction. These authors point out that filled sp^2 orbitals of the long-bonded O atoms are properly situated to interact with the Cu d_{z^2} orbital and that the p_z orbitals of the same O atoms may also in principle be involved in weak π-bonding with the d_{xz} and d_{yz} orbitals of the Cu atom.

The Li cation is small enough to approach a chain and to form two bonds with two O atoms belonging to two pht of the same chain. Coordination is completed to tetrahedral by two water molecules (Fig. 4). Bond distances and angles agree well with those found in lithium hydrogen phthalate dihydrate (Gonschorek & Küppers, 1975). The water molecules are important in packing because of the hydrogen bonds they form with carboxylate groups of adjacent chains.

The bigger size of the Rb cation is responsible for the more extensive coordination of this ion, which is surrounded by eight O atoms belonging to pht anions from two adjacent chains and to water molecules, the six nearest at distances in the range 2·838–3·069 Å and two others at 3·244 and 3·413 Å. These interactions, together with hydrogen bonds between the water molecules and O atoms of pht anions, join the chains in layers parallel to (100) (Fig. 6). The packing of these layers is determined by normal van der Waals contacts.

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