

Polymeric Chains of Tetranuclear Hydroxo-*o*-phthalatocuprate(II) Units and Silver(I)–Aromatic Interactions in the Crystal Structure of $\text{Ag}[\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{OH})] \cdot 5\text{H}_2\text{O}$

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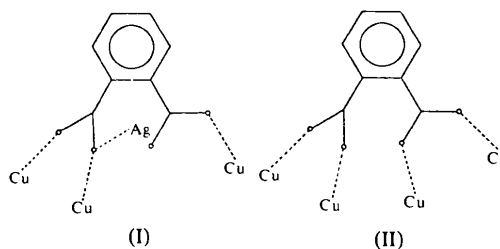
Abstract

The crystal structure of $\text{Ag}[\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{OH})] \cdot 5\text{H}_2\text{O}$, $\text{C}_{16}\text{H}_{19}\text{AgCu}_2\text{O}_9 \cdot 5\text{H}_2\text{O}$, has been determined from diffractometer data by Patterson and Fourier methods and refined to $R = 0.079$ for 2359 counter reflections: $a = 11.388$ (11), $b = 11.772$ (12), $c = 7.875$ (9) Å, $\alpha = 100.3$ (1), $\beta = 80.2$ (1), $\gamma = 102.2$ (1)°, space group $P\bar{1}$, $Z = 2$. The structure consists of centrosymmetric tetranuclear $[\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{OH})]_2^-$ anions (linked in polymeric chains by bridging *o*-phthalate anions), Ag^{I} cations and water molecules. The tetranuclear hydroxo-*o*-phthalatocuprate(II) anions contain two independent Cu atoms linked by triply-bridging hydroxo O atoms and by carboxylate bridges from *o*-phthalate anions. The coordination polyhedron of Cu(1) is a trigonal bipyramid whose equatorial plane is formed by three O atoms from three bridging carboxylates [Cu–O = 2.049 (10), 2.101 (10), 2.233 (12) Å], the axial positions being occupied by an O atom from an OH^- ion [Cu–O = 1.911 (11) Å] and by an O atom from a monodentate carboxylate group [Cu–O = 1.923 (11) Å]. The coordination of Cu(2) is square pyramidal, the basal plane comprising two O atoms from OH^- ions [Cu–O = 1.955 (9), 1.949 (9) Å] and two O atoms from two bridging carboxylates [Cu–O = 1.924 (10), 1.928 (10) Å]. Another O atom from a bridging carboxylate is at the apex of the pyramid [Cu–O = 2.352 (13) Å]. The Ag^{I} ion is linked to this last O atom [Ag–O = 2.264 (12) Å] and to two water molecules [Ag– O_{w} = 2.328 (25), 2.536 (26) Å], and interacts with a benzene C–C bond [Ag–(midpoint of C–C) = 2.431 (16) Å], so that Ag–aromatic complexes, in a distorted tetrahedral configuration, are present.

Introduction

Our previous investigations on the behaviour of the *o*-phthalate (pht) anion as a ligand showed that in the

Cu^{II} complexes pht acts as a mono- or bidentate chelating ligand (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1978*d*) or as a bridge through two or three O atoms from both carboxylate groups (Biagini Cingi, Guastini, Musatti & Nardelli, 1970; Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1977, 1978*a,b,c*) giving rise to different kinds of polymeric chains. In the crystal structure described here two independent bridging pht anions are present: one acts as a tridentate (I) and the other as a tetradentate ligand (II).



The latter is the first example of a pht anion acting as a ligand through all its O atoms; this pht anion is also involved in an aromatic interaction with Ag through a C–C bond.

Experimental

From a solution of phthalic acid, copper(II) carbonate hydroxide and silver nitrate in the molar ratio 2:1:2, a mixture of blue and white crystals separated immediately. After filtration the mother liquor was evaporated to dryness and light-blue crystals were obtained which slowly transformed into the green crystals of the title compound.

Crystal data

$\text{C}_{16}\text{H}_{19}\text{AgCu}_2\text{O}_{14}$, $M_r = 670.3$, triclinic, $a = 11.388$ (11), $b = 11.772$ (12), $c = 7.875$ (9) Å, $\alpha =$

100.3 (1), $\beta = 80.2$ (1), $\gamma = 102.2$ (1)°, $V = 1006$ (2) Å³, $D_c = 2.214$ Mg m⁻³, $Z = 2$, $F(000) = 664$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 3.13$ mm⁻¹; space group $P\bar{1}$ from the structure determination. Cell parameters were determined from photographs and refined from diffractometer data.

Intensity data

Intensities were collected on a Siemens AED single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation and the ω - 2θ scan technique. A thin prismatic crystal ca 0.03 × 0.09 × 0.40 mm was aligned with [001] along the ϕ axis of the diffractometer and all reflections with $2\theta \leq 50^\circ$ were measured. Of 3549 independent reflections, 2359 were used in the analysis [$I > 2\sigma(I)$]. Corrections for Lorentz and polarization effects were made, but no correction for absorption was applied. The absolute scale and the overall temperature factor were obtained by Wilson's method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and refined with *SHELX* (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms was carried out. A ΔF synthesis revealed the positions of the H atoms of the pht anions and of the OH⁻ group. Further cycles were then computed including these H atoms with isotropic thermal parameters. Unit weights were used by analysing the variations of $|\Delta F|$ as a function of $|F_o|$. The final R was 0.079 (observed reflections only). Final atomic coordinates are given in Table 1.* All calculations were carried out on the CYBER 76 computer of the Centro Interuniversitario dell'Italia Nord-Orientale (Bologna) with the financial support of the Università di Parma.

Discussion

In the structure centrosymmetric $[\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{OH})_2]^{2-}$ anions linked in polymeric chains by bridging pht groups, Ag^I ions and water molecules are present (Fig. 1). Bond distances and angles are given in Table 2. The tetranuclear hydroxo-*o*-phthalatocuprate(II) complexes contain two crystallographically independent Cu atoms linked by triply-bridging hydroxo O atoms and by carboxylate bridges from pht anions. The distances $\text{Cu}(2)\text{—Cu}(2^{\text{III}}) = 2.920$ (4), $\text{Cu}(1)\text{—Cu}(2) =$

Table 1. Fractional atomic coordinates ($\times 10^4$, for H $\times 10^3$) with e.s.d.'s

	x	y	z
Ag	-1287 (2)	-1663 (3)	2245 (5)
Cu(1)	4451 (1)	1163 (1)	2387 (2)
Cu(2)	3700 (1)	-452 (1)	5350 (2)
O(11)	3851 (9)	2366 (8)	1616 (13)
O(21)	4583 (14)	1681 (12)	-1018 (16)
O(31)	4748 (11)	2337 (10)	-5103 (14)
O(41)	3076 (9)	1374 (9)	-3849 (16)
O(12)	3779 (8)	-1734 (8)	-1403 (13)
O(22)	2567 (9)	-993 (9)	-2725 (13)
O(32)	2525 (9)	-1240 (9)	3826 (13)
O(42)	2917 (8)	-75 (8)	1720 (12)
O(1)	4907 (8)	-20 (8)	3378 (11)
O _w (2)	2924 (12)	6469 (11)	4317 (19)
O _w (3)	1061 (13)	4588 (14)	4619 (24)
O _w (4)	1535 (14)	2412 (16)	3638 (27)
O _w (5)	8840 (16)	-855 (17)	-286 (34)
O _w (6)	9668 (18)	361 (21)	3633 (39)
C(11)	3742 (12)	3372 (11)	-731 (17)
C(21)	3771 (12)	3324 (12)	-2533 (19)
C(31)	3628 (14)	4322 (13)	-3159 (20)
C(41)	3399 (15)	5313 (13)	-2003 (21)
C(51)	3337 (13)	5336 (12)	-221 (20)
C(61)	3499 (12)	4364 (12)	376 (18)
C(71)	4064 (12)	2382 (12)	-2 (19)
C(81)	3898 (13)	2262 (13)	-3914 (18)
C(12)	1669 (12)	-2103 (11)	-460 (18)
C(22)	1538 (12)	-1907 (11)	1340 (18)
C(32)	579 (12)	-2557 (13)	2293 (20)
C(42)	-270 (14)	-3393 (13)	1427 (23)
C(52)	-137 (14)	-3564 (13)	-353 (20)
C(62)	817 (13)	-2930 (12)	-1307 (19)
C(72)	2777 (13)	-1544 (12)	-1573 (17)
C(82)	2406 (12)	-986 (13)	2344 (19)
H(1)	506 (10)	-41 (10)	244 (15)
H(31)	362 (12)	433 (11)	-436 (17)
H(41)	327 (12)	607 (11)	-246 (17)
H(51)	318 (11)	604 (11)	65 (16)
H(61)	352 (11)	437 (10)	142 (15)
H(32)	38 (11)	-251 (11)	364 (16)
H(42)	-77 (12)	-388 (11)	200 (17)
H(52)	-74 (11)	-403 (11)	-85 (17)
H(62)	90 (11)	-303 (11)	-239 (16)

3.164 (6) and $\text{Cu}(1)\text{—Cu}(2^{\text{III}}) = 3.296$ (4) Å are significantly shorter than those found [2.996 (4)–3.347 (5) Å] in a hydroxocopper(II) carboxylate adduct (Little, Yawney & Doedens, 1972), where discrete tetranuclear hydroxo complexes are present. The independent Cu atoms, which are both in a distorted square-pyramidal configuration in the structure described by Little *et al.*, here show two kinds of pentacoordination. Cu(1) is bound to one triply-bridging hydroxo O atom and to four O atoms from four pht anions in a distorted trigonal-bipyramidal configuration, the axial positions being occupied by the hydroxo O(1) and the carboxylic O(11). The Cu—O axial are shorter than the Cu—O equatorial distances. Cu(1) is displaced from the equatorial plane (Table 3) by 0.057 (1) Å towards the apical O(11). Cu(2) is bound to two centrosymmetric

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33948 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°)

(a) The copper coordination polyhedra

Cu(1)—O(11)	1.923 (11)	O(42)—Cu(1)—O(31 ^h)	129.8 (4)	O(22 ^l)—Cu(2)—O(1 ⁱⁱⁱ)	95.6 (4)
Cu(1)—O(31 ^h)	2.233 (12)	O(12 ⁱⁱ)—Cu(1)—O(42)	140.3 (4)	O(1)—Cu(2)—O(1 ⁱⁱⁱ)	83.2 (4)
Cu(1)—O(42)	2.101 (10)	O(12 ⁱⁱ)—Cu(1)—O(31 ^h)	89.6 (4)	O(1)—Cu(2)—O(32)	91.7 (4)
Cu(1)—O(1)	1.911 (11)	O(11)—Cu(1)—O(42)	90.3 (4)	O(32)—Cu(2)—O(22 ^l)	88.5 (4)
Cu(1)—O(12 ⁱⁱ)	2.049 (10)	O(11)—Cu(1)—O(12 ⁱⁱ)	94.5 (4)	O(1)—Cu(2)—O(22 ^l)	175.3 (4)
Cu(2)—O(41 ^h)	2.352 (13)	O(11)—Cu(1)—O(31 ^h)	89.9 (4)	O(32)—Cu(2)—O(1 ⁱⁱⁱ)	165.6 (4)
Cu(2)—O(22 ^l)	1.924 (10)	O(1)—Cu(1)—O(31 ^h)	86.5 (4)	O(41 ^h)—Cu(2)—O(22 ^l)	88.0 (4)
Cu(2)—O(1 ⁱⁱⁱ)	1.949 (9)	O(1)—Cu(1)—O(12 ⁱⁱ)	90.9 (4)	O(41 ^h)—Cu(2)—O(1 ⁱⁱⁱ)	94.2 (4)
Cu(2)—O(32)	1.928 (10)	O(1)—Cu(1)—O(42)	87.8 (4)	O(41 ^h)—Cu(2)—O(1)	96.7 (4)
Cu(2)—O(1)	1.955 (9)	O(11)—Cu(1)—O(1)	173.5 (4)	O(41 ^h)—Cu(2)—O(32)	99.7 (4)

(b) The silver coordination polyhedron

Ag—O(41 ^{iv})	2.264 (12)	O(41 ^{iv})—Ag—O _w (5 ^v)	106.1 (6)	O _w (5 ^v)—Ag—C(42)	106.9 (6)
Ag—O _w (5 ^v)	2.328 (25)	O(41 ^{iv})—Ag—O _w (6 ^v)	88.3 (6)	O _w (5 ^v)—Ag—O _w (6 ^v)	87.3 (9)
Ag—O _w (6 ^v)	2.536 (26)	O(41 ^{iv})—Ag—C(32)	141.7 (5)	O _w (6 ^v)—Ag—C(32)	93.4 (6)
Ag—C(32)	2.571 (15)	O(41 ^{iv})—Ag—C(42)	133.2 (5)	O _w (6 ^v)—Ag—C(42)	125.3 (6)
Ag—C(42)	2.486 (18)	O _w (5 ^v)—Ag—C(32)	112.2 (6)		

(c) The phthalate anions

C(11)—C(21)	1.405 (20)	C(82)—O(42)	1.248 (18)	C(61)—C(51)—H(51)	119 (7)
C(21)—C(31)	1.402 (22)	C(32)—H(32)	1.04 (12)	C(51)—C(61)—H(61)	121 (9)
C(31)—C(41)	1.388 (23)	C(42)—H(42)	0.85 (13)	C(11)—C(61)—H(61)	116 (9)
C(41)—C(51)	1.389 (22)	C(52)—H(52)	0.88 (13)	C(62)—C(12)—C(22)	119.8 (1.3)
C(51)—C(61)	1.370 (21)	C(62)—H(62)	0.83 (12)	C(62)—C(12)—C(72)	117.3 (1.2)
C(11)—C(61)	1.375 (20)			C(22)—C(12)—C(72)	122.6 (1.2)
C(11)—C(71)	1.521 (20)	C(61)—C(11)—C(21)	119.4 (1.3)	C(12)—C(22)—C(32)	120.1 (1.3)
C(71)—O(11)	1.259 (18)	C(61)—C(11)—C(71)	119.6 (1.2)	C(12)—C(22)—C(82)	122.4 (1.2)
C(71)—O(21)	1.216 (20)	C(21)—C(11)—C(71)	121.0 (1.2)	C(32)—C(22)—C(82)	117.4 (1.3)
C(21)—C(81)	1.518 (21)	C(11)—C(21)—C(31)	118.8 (1.3)	C(22)—C(32)—C(42)	119.6 (1.4)
C(81)—O(31)	1.227 (18)	C(11)—C(21)—C(81)	126.2 (1.3)	C(32)—C(42)—C(52)	119.5 (1.5)
C(81)—O(41)	1.249 (19)	C(31)—C(21)—C(81)	115.0 (1.3)	C(42)—C(52)—C(62)	121.2 (1.5)
C(31)—H(31)	0.95 (13)	C(21)—C(31)—C(41)	120.2 (1.4)	C(12)—C(62)—C(52)	119.8 (1.4)
C(41)—H(41)	1.06 (14)	C(31)—C(41)—C(51)	120.4 (1.5)	C(12)—C(72)—O(12)	118.2 (1.2)
C(51)—H(51)	1.00 (13)	C(41)—C(51)—C(61)	119.0 (1.4)	C(12)—C(72)—O(22)	115.4 (1.2)
C(61)—H(61)	0.83 (12)	C(11)—C(61)—C(51)	122.2 (1.3)	O(12)—C(72)—O(22)	126.1 (1.3)
C(12)—C(22)	1.382 (20)	C(11)—C(71)—O(11)	119.0 (1.2)	C(22)—C(82)—O(32)	114.0 (1.3)
C(22)—C(32)	1.384 (20)	C(11)—C(71)—O(21)	117.5 (1.3)	C(22)—C(82)—O(42)	119.6 (1.3)
C(32)—C(42)	1.397 (22)	O(11)—C(71)—O(21)	123.3 (1.4)	O(32)—C(82)—O(42)	126.4 (1.3)
C(42)—C(52)	1.367 (23)	C(21)—C(81)—O(31)	119.1 (1.4)	C(22)—C(32)—H(32)	128 (7)
C(52)—C(62)	1.372 (22)	C(21)—C(81)—O(41)	117.8 (1.3)	C(42)—C(32)—H(32)	122 (7)
C(12)—C(62)	1.387 (20)	O(31)—C(81)—O(41)	122.9 (1.4)	C(32)—C(42)—H(42)	119 (9)
C(12)—C(72)	1.507 (20)	C(21)—C(31)—H(31)	122 (8)	C(52)—C(42)—H(42)	120 (9)
C(72)—O(12)	1.241 (17)	C(41)—C(31)—H(31)	118 (8)	C(42)—C(52)—H(52)	117 (8)
C(72)—O(22)	1.285 (18)	C(31)—C(41)—H(41)	121 (7)	C(62)—C(52)—H(52)	121 (9)
C(22)—C(82)	1.511 (20)	C(51)—C(41)—H(41)	119 (7)	C(52)—C(62)—H(62)	121 (9)
C(82)—O(32)	1.291 (18)	C(41)—C(51)—H(51)	123 (7)	C(12)—C(62)—H(62)	119 (9)

(d) The hydroxyl group

O(1)—H(1)	0.81 (12)
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(e) Probable hydrogen bonds

O _w (4)—O(11)	2.845 (20)	O _w (4)—O _w (6 ^v)	2.860 (30)	O _w (5)—O _w (4 ⁱⁱ)	2.972 (32)	O _w (3)—O _w (3 ^{ix})	2.726 (22)
O _w (2)—O _w (3)	2.737 (21)	O _w (2)—O(32 ^{vi})	2.929 (20)	O _w (2)—O(31 ^{viii})	2.839 (19)	O _w (6)—O _w (6 ^{ix})	2.722 (39)
O _w (3)—O _w (4)	2.680 (27)	O _w (5)—O(42 ^h)	2.935 (23)	O _w (5)—O _w (6 ^{viii})	2.963 (37)		

(f) Symmetry code

(i)	$x, y, 1 + z$	(iv)	$-x, -y, -z$	(vii)	$1 - x, 1 - y, -z$	(ix)	$-x, 1 - y, 1 - z$
(ii)	$1 - x, -y, -z$	(v)	$-1 + x, y, z$	(viii)	$2 - x, -y, -z$	(x)	$2 - x, -y, 1 - z$
(iii)	$1 - x, -y, 1 - z$	(vi)	$x, 1 + y, z$				

hydroxo O atoms and to three O atoms from three phthalate groups in a distorted square-pyramidal arrangement. The apex of the pyramid is occupied by O(41^h) at a distance [2.352 (13) Å] in good agreement with those generally found for this type of coordination. The four

atoms forming the base of the pyramid show a small tetrahedral distortion, as can be seen from their displacements (Table 3) from the mean plane through them. The Cu atom is displaced by 0.155 (1) Å towards the apex of the pyramid.

Table 3. *Least-squares planes*

Equations of the least-squares planes are in the form $AX + BY + CZ = D$, where X , Y and Z are coordinates in Å referred to orthogonal axes and are obtained from fractional coordinates by applying the matrix: $\|a \sin \gamma, 0, -c \sin \alpha \cos \beta^* \| a \cos \gamma, b, c \cos \alpha \| 0, c \sin \alpha \sin \beta^* \|$. Deviations (Å) of relevant atoms from the planes are in square brackets.

	A	B	C	D
Plane I: O(42), O(31 ^l), O(12 ^{ll})				
	-0.3518	0.8676	-0.3514	-2.5665
[O(42) 0, O(31 ^l) 0, O(12 ^{ll}) 0, Cu(1) 0.057 (1), O(11) 1.977 (10), O(1) -1.851 (10)]				
Plane II: O(1), O(32), O(22 ^l), O(1 ^{lll})				
	0.2562	-0.9504	-0.1764	2.6998
[O(1) -0.068 (10), O(32) 0.084 (11), O(22 ^l) -0.082 (11), O(1 ^{lll}) 0.066 (10), Cu(2) -0.155 (1), O(41 ^l) -2.497 (11)]				
Plane III: C(11), C(21), C(31), C(41), C(51), C(61)				
	0.9834	0.1691	-0.0654	4.5759
[C(11) 0.017 (14), C(21) -0.018 (14), C(31) 0.011 (16), C(41) 0.002 (17), C(51) -0.004 (15), C(61) -0.008 (14), C(71) 0.181 (14), C(81) -0.138 (15), O(11) 0.004 (10), O(21) 0.558 (16), O(31) 0.736 (12), O(41) -1.180 (10)]				
Plane IV: C(11), C(71), O(11), O(21)				
	-0.9196	-0.3717	-0.1272	-4.8599
[C(11) -0.006 (14), C(71) 0.022 (14), O(11) -0.005 (10), O(21) -0.011 (16)]				
Plane V: C(21), C(81), O(31), O(41)				
	-0.6072	0.5731	-0.5504	0.6022
[C(21) 0.010 (14), C(81) -0.026 (15), O(31) 0.008 (12), O(41) 0.007 (11)]				
Plane VI: C(12), C(22), C(32), C(42), C(52), C(62)				
	0.5480	-0.8361	-0.0241	3.3439
[C(12) 0.008 (14), C(22) -0.008 (14), C(32) 0.004 (15), C(42) 0.002 (16), C(52) -0.003 (16), C(62) -0.003 (15), C(72) 0.181 (15), C(82) -0.052 (15), O(12) 1.207 (10), O(22) -0.714 (11), O(32) 0.528 (11), O(42) -0.633 (10)]				
Plane VII: C(12), C(72), O(12), O(22)				
	-0.1977	-0.7186	-0.6667	1.8856
[C(12) 0.013 (14), C(72) -0.032 (14), O(12) 0.009 (10), O(22) 0.010 (11)]				
Plane VIII: C(22), C(82), O(32), O(42)				
	0.7042	-0.5525	-0.4459	2.3989
[C(22) -0.002 (14), C(82) 0.005 (15), O(32) -0.001 (10), O(42) -0.001 (9)]				
Plane IX: Cu(1), Cu(2), Cu(1 ^{lll}), Cu(2 ^{lll})				
	0.0087	-0.7296	-0.6839	-1.1797
[Cu(1) 0, Cu(2) 0, Cu(1 ^{lll}) 0, Cu(2 ^{lll}) 0]				

Of the two independent pht anions, one acts as a tetradentate and the other as a tridentate ligand; in the latter, one O atom bridges two different metal atoms (Cu and Ag). Four pht anions, two for each type, join the tetranuclear complexes into polymeric chains running along [001], adjacent complexes being related by *c*. Strong centrosymmetric hydrogen bonds which the OH⁻ groups form with the uncoordinated O(21)

[O(1)···O(21^{ll}) = 2.535 (17), H(1)···O(21^{ll}) = 1.78 (12) Å, O(1)–H(1)–O(21^{ll}) = 155 (7)°] complete the linkage of the tetranuclear hydroxocuprate(II) in polymeric chains. The environment of the OH⁻ group is distorted tetrahedral: Cu(1)–O(1)–Cu(2) = 109.9 (5), Cu(1)–O(1)–Cu(2^{lll}) = 117.3 (5), Cu(2)–O(1)–Cu(2^{lll}) = 96.8 (4), O(21^{ll})–O(1)–Cu(1) = 110.3 (5), O(21^{ll})–O(1)–Cu(2) = 116.8 (5), O(21^{ll})–O(1)–Cu(2^{lll}) = 105.3 (5)°. In both independent pht anions the carboxylate groups are rotated around their C–C bonds on the same side with respect to the benzene ring as in all the compounds where pht acts as a bridging ligand. The dihedral angles they form are: C(11)C(71)O(11)O(21) = 16.5 and C(21)C(81)–O(31)O(41) = 62.3° in the tridentate pht group, and C(12)C(72)O(12)O(22) = 59.4 and C(22)C(82)–O(32)O(42) = 30.8° in the tetradentate pht group. The less rotated (16.5°) carboxylate group is monodentate and involved in a strong hydrogen bond with the OH⁻ group. The benzene planes of the tri- and tetradentate pht anions form an angle of 66.5° and the angles they form with the plane through the metal atoms of the tetranuclear complex are 86.0 and 50.9° respectively.

The Ag ion shares an O atom with Cu(2) and completes its coordination sphere with two water molecules and a contact with the C(32)–C(42) bond [the distance between Ag and the midpoint of the bond is 2.431 (16) Å] of the benzene ring of the tetradentate pht from an adjacent chain. The configuration around Ag (Fig. 2) is distorted tetrahedral [the angles involving the midpoint (C_{mid}) of C(32)–C(42) are: O_w(5^v)–Ag–C_{mid} = 110.4 (8), O_w(6^v)–Ag–C_{mid} = 109.1 (6) and O(41^{lv})–Ag–C_{mid} = 139.9 (5)°]. This Ag complex shows the usual asymmetric Ag–C interaction which is a common feature [with the exception of naphthalene-tetrakis(silver perchlorate) tetrahydrate] (Griffith & Amma, 1974) of the Ag–aromatic complexes, independently of the stereochemistry, the nature of the aromatic

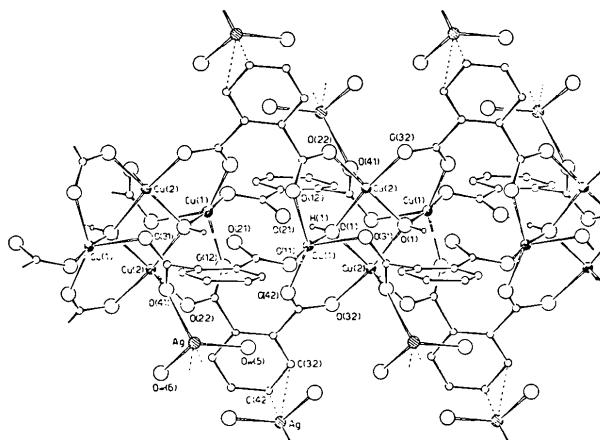


Fig. 1. Polymeric chains of $[\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)(\text{OH})]_2^-$ tetranuclear complexes and their linkage with the Ag ions.

compound, and the counter ions. This asymmetry is reflected both in the distances [$\text{Ag}-\text{C}(42) = 2.486$ (18), $\text{Ag}-\text{C}(32) = 2.571$ (15) Å] and in the angles [$\text{Ag}-\text{C}(42)-\text{C}(32) = 77.4$ (9), $\text{Ag}-\text{C}(32)-\text{C}(42) = 70.6$ (9)°]. Packing is determined by the Ag-C interactions and by hydrogen bonds involving the water molecules and the O atoms from pht anions of different chains.

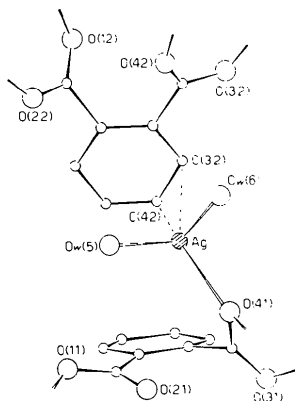


Fig. 2. Coordination around the Ag atom.

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Calcium Binding to α -Amino Acids: The Crystal Structure of Calcium Di-L-glutamate Tetrahydrate

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Abstract

Crystals of calcium di-L-glutamate tetrahydrate $\text{Ca}(\text{C}_5\text{H}_8\text{NO}_4)_2 \cdot 4\text{H}_2\text{O}$ are tetragonal, space group $P4_32_12$, with $a = 7.5624$ (1), $c = 29.0771$ (9) Å, and four formula weights per unit cell. A trial structure was obtained by Patterson and Fourier techniques and was refined by full-matrix least-squares calculations using absorption-corrected, $\text{Cu K}\alpha$, diffractometer data. The later stages of refinement were based on an octant of data, and anomalous-dispersion effects were used to establish the proper enantiomorph. The final R index is 0.032 both for the octant of 1632 reflections and for the half-octant of 893 unique data. The Ca ion lies on a crystallographic twofold axis and is coordinated to two

α -carboxyl groups and two γ -carboxyl groups from glutamate ions, and to two water molecules. Each of the glutamate carboxyl groups contributes a single O atom to the Ca coordination polyhedron and serves as a unidentate ligand. The sixfold coordination polyhedron has distorted octahedral geometry.

Introduction

Ca ions are involved in a variety of biological processes, many of which are mediated by calcium-protein complexes. Crystallographic, spectroscopic, and chemical data all indicate that glutamate and aspartate residues are particularly common compo-