

A Polymeric Copper(II) Complex with 2,2'-Bipyridine and 1,2-Benzenedicarboxylate(2-)

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Abstract. *catena*-Poly[[aqua(bipyridine- κ^2N,N')copper(II)]- μ_3 -[1,2-benzenedicarboxylato(2-)- $\kappa O:\kappa O':-\kappa O'$]-[(bipyridine- κ^2N,N')copper(II)]- μ -[1,2-benzenedicarboxylato(2-)- $\kappa O:\kappa O'$]] trihydrate, $\{[\text{Cu}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})].3\text{H}_2\text{O}\}_n$, $M_r = 839.76$, monoclinic, $P2_1/n$, $a = 12.902(1)$, $b = 20.561(2)$, $c = 13.558(6)$ Å, $\beta = 109.38(2)^\circ$, $V = 3393(2)$ Å³, $Z = 4$, $D_x = 1.64$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 13.27$ cm⁻¹, $F(000) = 1720$, $T = 292$ K, $R = 0.0364$ for 2834 independent reflections with $I > 2\sigma(I)$. The structure consists of $\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)$ and $\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})$ units linked in polymeric chains by two bridging 1,2-benzenedicarboxylato(2-) anions. The chains are joined by Cu—O interaction forming double chains parallel to the c axis. Pentacoordination of both Cu atoms involves two O atoms from different 1,2-benzenedicarboxylato ions and two N atoms from a 2,2'-bipyridine ligand and at the apical site is another carboxylato O atom for the first Cu atom and the O atom of a water molecule for the second Cu atom. Water molecules which are not bonded to the Cu atom are situated in channels parallel to the b axis.

Introduction. This investigation is a continuation of our studies on the factors governing the choice between different coordination modes of phthalate (1,2-benzenedicarboxylate) ions (Poleti, Stojaković, Prelesnik & Manojlović-Muir, 1990; Prelesnik, Poleti, Stojaković & Herak, 1991).

In the system Cu^{II} ion–2,2'-bipyridine (bpy)–phthalate ion (pht), the existence of two polymorphic modifications is found. Both complexes have the same empirical formula $\text{Cu}(\text{bpy})(\text{pht})\cdot 2\text{H}_2\text{O}$ and

single crystals are grown from an aqueous solution containing $\text{Cu}(\text{NO}_3)_2$, $\text{Na}_2(\text{pht})$ and bpy in an equimolar ratio. The first, recently reported complex (Prelesnik, Poleti, Stojaković & Herak, 1991) is obtained at a pH of approximately 4. The second compound, described here, is obtained at a pH of approximately 2.5.

Experimental. Blue needle-like ($0.09 \times 0.13 \times 0.56$ mm) crystals were obtained by slow evaporation from a dilute aqueous solution containing equimolar amounts of $\text{Cu}(\text{NO}_3)_2$, bpy and sodium phthalate. The solution was slightly acidified (pH approximately 2.5) with several drops of HNO_3 . Cell parameters were obtained by least-squares analysis of the setting angles of 25 reflections with $8 < \theta < 13^\circ$. Intensities were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation, $\omega/2\theta$ scan, $\theta_{\text{max}} = 25^\circ$, scan width = $(0.7 + 0.3\tan\theta)^\circ$, detector aperture = $(2.4 + 0.9\tan\theta)$ mm, variable scan rate, maximum counting time = 60 s. Three standard reflections ($45\bar{4}$, $07\bar{3}$, $54\bar{4}$) measured every 10000 s for intensity control and every 400 reflections for orientation control; no significant variation. 4460 reflections were measured ($h = -15$ to 15 , $k = 0$ to 24 , $l = -16$ to 0), 2834 with $I > 2\sigma(I)$ were used in the refinement ($R_{\text{int}} = 0.0$).

Data were corrected for L_p , but not for absorption. The Cu atoms were located by the Patterson method, and the rest of the non-H atoms by Fourier syntheses and least-squares refinement. H atoms from aromatic rings were placed in calculated positions with fixed coordinates and fixed $U_{\text{iso}} = 0.05$ Å². H atoms of the four water molecules were not found

in difference maps. Anisotropic refinement on F for all non-H atoms (486 parameters, in two blocks) converged to $R = 0.0364$, $wR = 0.0389$, $w = [\sigma^2(F) + 0.015118F^2]^{-1}$, $S = 2.86$ and $(\Delta/\sigma)_{\max} < 0.027$. Final difference map had no features greater than $0.42 \text{ e } \text{Å}^{-3}$ or less than $-0.32 \text{ e } \text{Å}^{-3}$.

All calculations were performed on an IBM AT-compatible PC using *SHELXS86* (Sheldrick, 1986), *SHELX76* (Sheldrick, 1976), *CRYSTAN* (Burzlaff, Böhme & Gomm, 1977), *CSU* (Vicković, 1986) and *ORTEP* (Johnson, 1976). Scattering factors were from Cromer & Mann (1968), f' and f'' values from Cromer & Liberman (1970).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* and selected bond distances and angles in Table 2. The atomic numbering scheme and a view of the repeating unit are shown in Fig. 1.

The crystal structure consists of $[-\{\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)\} - \text{C}_8\text{H}_4\text{O}_4 - \{\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})\} - \text{C}_8\text{H}_4\text{O}_4 -]$ repeating units and three water molecules in general positions. These water molecules are situated in channels parallel to the b axis and they are hydrogen bonded to each other and to O atoms of the carboxylate [O...O distances are from 2.722 (6) to 2.854 (7) Å].

Two chemically and crystallographically independent phthalate anions act as bridging ligands (Fig. 1). One phthalate anion behaves as a bidentate ligand bridging two Cu atoms through O atoms from both carboxylate groups. The other phthalate anion acts as a tridentate ligand bridging three Cu atoms, one of which belongs to an adjacent, centrosymmetrically related chain. Owing to these Cu(1)—O(1') bonds, the single chains are linked in double chains running along c (Fig. 2).

The coordination polyhedron around each Cu atom is approximately a square pyramid formed by two O atoms from two different phthalate ions and two N atoms from a 2,2'-bipyridine ligand in the basal positions. The coordination sphere around the Cu(1) atom is completed by the carboxylate O(1') atom of the phthalate anion belonging to the adjacent chain. The apex of the pyramid around the Cu(2) atom is occupied by the O(W1) atom of a water molecule. Both Cu atoms have two longer Cu...O contacts: Cu(1)...O(4) 3.319 (5), Cu(1)...O(6) 3.083 (4), Cu(2)...O(1) 3.257 (4) and Cu(2)...O(8) 2.833 (6) Å.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55907 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1021]

Table 1. *Positional* ($\times 10^4$, Cu $\times 10^5$) and *equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) with *e.s.d.'s* in parentheses

$$U_{\text{eq}} = (1/3)\sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Cu(1)	1560 (10)	5580 (3)	18300 (10)	30.5 (2)
Cu(2)	9670 (10)	15880 (3)	67270 (10)	31.3 (2)
O(1)	576 (3)	497 (2)	8310 (3)	35 (1)
O(2)	1852 (3)	1118 (2)	7978 (3)	35 (1)
O(3)	1152 (3)	300 (2)	1107 (3)	38 (1)
O(4)	1707 (3)	1228 (2)	581 (3)	40 (1)
O(5)	1236 (3)	243 (2)	3119 (3)	38 (1)
O(6)	1865 (4)	1229 (2)	3704 (3)	44 (1)
O(7)	1507 (3)	1011 (2)	5870 (3)	34 (1)
O(8)	3042 (4)	1591 (2)	6436 (3)	46 (1)
O(W1)	-730 (3)	1110 (2)	6417 (3)	45 (1)
O(W2)	1232 (4)	2016 (2)	1987 (3)	57 (2)
O(W3)	2367 (4)	3134 (3)	1262 (5)	78 (2)
O(W4)	243 (5)	3242 (3)	1466 (5)	78 (2)
N(1)	-859 (4)	874 (2)	2562 (4)	34 (1)
N(2)	-880 (4)	1078 (2)	671 (4)	30 (1)
N(3)	283 (4)	2213 (2)	5561 (4)	31 (1)
N(4)	476 (4)	2286 (2)	7517 (4)	35 (1)
C(1)	1546 (5)	667 (3)	8455 (4)	28 (1)
C(2)	2450 (4)	291 (3)	9245 (4)	27 (1)
C(3)	3181 (5)	-60 (3)	8904 (5)	38 (2)
C(4)	3933 (5)	-481 (3)	9586 (5)	42 (2)
C(5)	3960 (5)	-545 (3)	10601 (5)	47 (2)
C(6)	3227 (5)	-185 (3)	10952 (5)	39 (2)
C(7)	2469 (4)	229 (3)	10280 (4)	27 (1)
C(8)	1709 (5)	625 (3)	683 (4)	32 (1)
C(9)	1882 (5)	626 (3)	3764 (4)	32 (1)
C(10)	2759 (4)	300 (3)	4657 (4)	27 (1)
C(11)	3270 (5)	-247 (3)	4438 (5)	36 (2)
C(12)	4133 (5)	-544 (3)	5216 (5)	42 (2)
C(13)	4477 (5)	-279 (3)	6222 (5)	43 (2)
C(14)	3976 (5)	272 (3)	6427 (5)	35 (2)
C(15)	3108 (4)	562 (3)	5665 (4)	29 (2)
C(16)	2517 (5)	1106 (3)	6004 (4)	32 (2)
C(17)	-892 (5)	658 (3)	3484 (5)	47 (2)
C(18)	-1654 (6)	907 (4)	3911 (6)	56 (2)
C(19)	-2381 (6)	1374 (4)	3392 (6)	59 (2)
C(20)	-2345 (6)	1595 (4)	2447 (6)	53 (2)
C(21)	-1586 (5)	1325 (3)	2033 (5)	37 (2)
C(22)	-1561 (5)	1464 (3)	973 (5)	34 (2)
C(23)	-2218 (5)	1923 (3)	315 (6)	53 (2)
C(24)	-2205 (6)	1951 (4)	-700 (6)	60 (2)
C(25)	-1561 (6)	1534 (4)	-1036 (5)	49 (2)
C(26)	-887 (5)	1114 (3)	-321 (5)	36 (2)
C(27)	317 (5)	2165 (3)	4578 (5)	38 (2)
C(28)	-285 (5)	2580 (3)	3791 (5)	43 (2)
C(29)	-943 (6)	3044 (3)	4002 (5)	46 (2)
C(30)	-971 (5)	3100 (3)	5014 (5)	45 (2)
C(31)	-335 (5)	2683 (3)	5776 (4)	33 (1)
C(32)	-247 (5)	2714 (3)	6905 (5)	36 (2)
C(33)	-856 (5)	3143 (3)	7273 (5)	42 (2)
C(34)	-683 (6)	3139 (3)	8336 (6)	49 (2)
C(35)	89 (6)	2717 (3)	8982 (5)	49 (2)
C(36)	660 (6)	2293 (3)	8539 (5)	44 (2)

The Cu—O and Cu—N distances in the basal planes as well as the corresponding angles (Table 2) are in good agreement with values found in related Cu complexes (Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980; Krstanović, Karanović, Stojaković & Golič, 1982; Krstanović, Karanović & Stojaković, 1985; Prelesnik, Poleti, Stojaković & Herak, 1991). As expected, the apical Cu(1)—O(1') and Cu(2)—O(W1) distances are significantly longer than the basal Cu—O bonds. The Cu(1) and Cu(2) atoms are displaced from the basal plane toward the apex of the pyramid by 0.123 (6) and 0.143 (6) Å, respectively. The angle between the [N(1),N(2),O(3),O(5)] and [N(3),N(4),O(2),O(7)] basal planes is 29.31 (7)°.

Bond lengths and angles in the bpy ligands are normal for this compound (Merritt & Schroeder,

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

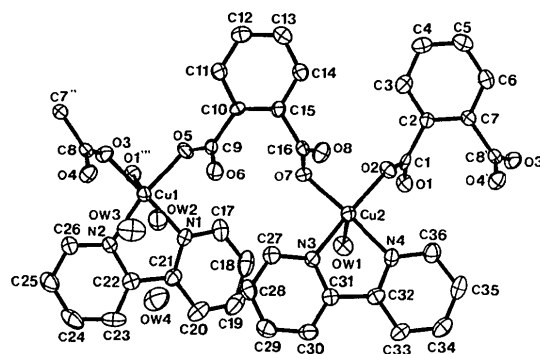
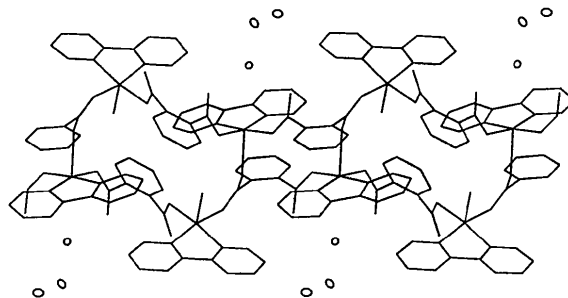
Coordination polyhedra			
Cu(1)—O(3)	1.931 (5)	Cu(2)—O(2)	1.957 (4)
Cu(1)—O(5)	1.949 (4)	Cu(2)—O(7)	1.944 (5)
Cu(1)—N(1)	1.996 (6)	Cu(2)—N(3)	2.001 (5)
Cu(1)—N(2)	2.001 (4)	Cu(2)—N(4)	2.015 (5)
Cu(1)—O(1)'	2.348 (4)	Cu(2)—O(W1)	2.308 (4)
O(1)'—Cu(1)—O(3)	91.3 (5)	O(2)—Cu(2)—O(7)	89.7 (2)
O(1)'—Cu(1)—O(5)	85.1 (2)	O(2)—Cu(2)—O(W1)	101.1 (2)
O(1)'—Cu(1)—N(1)	91.6 (2)	O(2)—Cu(2)—N(3)	168.4 (2)
O(1)'—Cu(1)—N(2)	106.5 (2)	O(2)—Cu(2)—N(4)	95.0 (2)
O(3)—Cu(1)—O(5)	88.0 (2)	O(7)—Cu(2)—O(W1)	97.9 (2)
O(3)—Cu(1)—N(1)	177.0 (2)	O(7)—Cu(2)—N(3)	94.1 (2)
O(3)—Cu(1)—N(2)	97.6 (2)	O(7)—Cu(2)—N(4)	172.2 (2)
O(5)—Cu(1)—N(1)	93.1 (2)	O(W1)—Cu(2)—N(3)	89.2 (2)
O(5)—Cu(1)—N(2)	166.9 (2)	O(W1)—Cu(2)—N(4)	87.3 (2)
N(1)—Cu(1)—N(2)	80.7 (2)	N(3)—Cu(2)—N(4)	80.1 (2)
Carboxylato groups			
O(1)—C(1)	1.251 (8)	O(5)—C(9)	1.263 (7)
O(2)—C(1)	1.266 (8)	O(6)—C(9)	1.242 (7)
O(3)—C(8)	1.252 (8)	O(7)—C(16)	1.270 (8)
O(4)—C(8)	1.247 (7)	O(8)—C(16)	1.238 (7)
O(3)—C(8)—O(4)	126.9 (6)	O(1)—C(1)—O(2)	126.1 (6)
O(5)—C(9)—O(6)	125.7 (6)	O(7)—C(16)—O(8)	124.5 (6)

Symmetry code: (i) $-x, -y, 1-z$.

1956; Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980). No C or N atom is more than 0.028 Å from the mean plane of its pyridine ring. In one bpy ligand [N(3),N(4),C(27)···C(36)] the dihedral angle between the pyridine rings is 6.1 (2)°. The corresponding angle in the second bpy ligand [N(1),N(2),C(17)···C(26)] is 13.8 (2)°. This angle is relatively large, but does not exceed values found previously (Anderson, 1972; Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980). The angle between the two unique bpy ligands is 12.73 (7)°.

The phthalate anions feature no unusual bond lengths and angles (Krstanović, Karanović & Stojaković, 1985; Prelesnik, Poleti, Stojaković & Herak, 1991). The benzene rings are planar in both anions. In the first, the tridentate phthalate ligand, both carboxylato groups, [O(1),O(2),C(1),C(2)] and [O(3'),O(4'),C(7),C(8')], have their plane tilted to the same side of the benzene ring plane by 60.1 (2) and 54.5 (2)°, respectively. Similarly, in the second, the bidentate phthalate ligand, these angles are 39.7 (2)° for the first [O(5),O(6),C(9),C(10)] and 57.9 (2)° for the second [(O(7),O(8),C(15),C(16))] carboxylato group.

The crystal and molecular structure of the other, already noted, Cu(pht)(bpy).2H₂O polymorph is completely different (Prelesnik, Poleti, Stojaković & Herak, 1991). This polymorph consists of dimeric centrosymmetric units and crystal water molecules, *i.e.* its formula should be written as [Cu₂(pht)₂(bpy)₂].4H₂O. The phthalate ion plays a combined chelate and bridging role. The chelate action should be regarded as a primary one, while dimerization is achieved through longer Cu—O(carboxylato) bonds by the bridging action of phthalate ions.

Fig. 1. Perspective view of the repeating unit with the numbering scheme. H atoms are omitted for clarity. Symmetry code: (') $x, y, 1+z$; (") $x, y, -1+z$; (""') $-x, -y, 1-z$.Fig. 2. Connection between polymeric chains running along the c axis. The c axis is horizontal (right to left).

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