Cl(2)—Th(1)—Cl(3)	100.1 (1)	Cl(3)—Th(1)—N(4)	137.5 (2)
Cl(2)—Th(1)—Cl(4)	149.5 (1)	Cl(4)—Th(1)—N(1)	73.0 (2)
Cl(3)—Th(1)—Cl(4)	87.4 (1)	Cl(4)—Th(1)—N(2)	137.4 (2)
Cl(1)—Th(1)—N(1)	74.6 (2)	Cl(4)—Th(1)—N(3)	78.7 (2)
Cl(1)—Th(1)—N(2)	79.1 (2)	Cl(4)—Th(1)—N(4)	75.6 (2)
Cl(1)—Th(1)—N(3)	136.9 (2)	N(1)—Th(1)—N(2)	66.2 (3)
Cl(1)—Th(1)—N(4)	72.5 (2)	N(1)—Th(1)—N(3)	142.0 (2)
Cl(2)—Th(1)—N(1)	137.2 (2)	N(1)—Th(1)—N(4)	128.0 (3)
Cl(2)—Th(1)—N(2)	72.8 (2)	N(2)—Th(1)—N(3)	129.3 (3)
Cl(2)—Th(1)—N(3)	75.5 (2)	N(2)—Th(1)—N(4)	140.9 (2)
Cl(2)—Th(1)—N(4)	79.1 (1)	N(3)—Th(1)—N(4)	65.9 (2)

All non-H atomic displacement parameters were refined anisotropically. Orienting H atoms were located from difference Fourier maps and then the remaining H atoms were generated with ideal geometries (0.96 Å and 109.5°). All were subsequently refined as riding groups with a group displacement parameter. The maximum residual electron density is located 1.2 Å from C(2) and the minimum residual electron density is located 1.0 Å from Th(1). Structural refinements in the other enantiomorph of this non-centrosymmetric space group gave $R = 0.0569$ and $wR = 0.0645$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1990). Molecular graphics: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: BK1289). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 193–195

Metal–α,ω-Dicarboxylate Complexes. I. Aqua(2,2′-bipyridyl-*N*,*N*′)(malonato-*O*,*O*′)copper(II) Monohydrate

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Abstract

The title compound, $[Cu(C_3H_2O_4)(C_{10}H_8N_2)(H_2O)].H_2O$, exists as discrete monomers. The Cu^{II} ion is square pyramidal, with two N atoms of the bipyridyl ligand and two O atoms, one from each of the carboxylates of the folded dibasic acid, providing the base and a water molecule forming a long apical bond [Cu—O5 2.523 (3) Å]. The 'scorpion-like' complex possesses a plane of symmetry bisecting the molecule lengthwise, the non-planarity arising from severe puckering of the six-membered chelate ring of the acid. Hydrogen-bonding interactions between the water molecules and the carboxylate O atoms stabilize the crystal structure.

Comment

In recent years, inorganic solids with novel polymeric networks have found applications in catalysis, separation, magnetism and optics. The extraordinary versatility of α,ω-dicarboxylic acids, forming different types of polymeric species upon coordination, is well known

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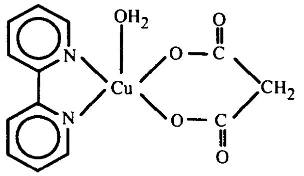
(Michaelides, Kiritsis, Skoulika & Aubry, 1993; Udupa & Krebs, 1980; Karipides, Ault & Reed, 1977; O'Connor & Maslen, 1966). We are interested in the structural frameworks generated by ternary complexes of α,ω-dicarboxylate, with varying chain length and N-donor ligands such as bipyridyl, imidazole and 2-methylimidazole, with Co^{II} and Cu^{II} metal centres, because the acid can act either as a monodentate, a chelating or a bridging ligand. As a result of this, the structure of the title compound, (I), has been determined.



(I)

The Cu^{II} ion in (I) is square pyramidal (Fig. 1), with two N atoms from the bipyridyl ligand and two deprotonated O atoms, one from each carboxylate group of the acid, forming the base and the O atom from the O5 water molecule occupying the apical position. Although the base of the pyramid is planar, the bond angles deviate from the ideal value of 90° (Table 1). The present complex is strictly monomeric, but malonate can form polymeric networks with different metal centres (Ray & Hathaway, 1982; Karipides, Ault & Reed, 1977; Hansson, 1973). The complex molecule has an approximate plane of symmetry passing through atoms Cu1 and O5 bisecting the N1—Cu1—N2 and O1—Cu1—O2 angles.

The Cu—N distances are unequal [Cu—N1 1.962 (3) and Cu—N2 1.995 (3) Å], as are the Cu—O distances [Cu1—O1 1.885 (2) and Cu1—O2 1.932 (2) Å], but the reasons for these distortions are not very obvious. The Cu1—O5 apical bond [2.523 (3) Å] is somewhat longer than the reported values (Chen, Tioh, Zou, Xu & You, 1996). The folded malonate ion forms a six-membered chelate ring having a boat conformation, with the Cu1 and C12 atoms above the mean plane consisting of atoms O1, C11, C13 and O2 by 0.58 and 0.52 Å, respectively. The Cu atom deviates by 0.11 Å from the coordination plane through atoms N1, N2, O1 and O3 towards the apical O5 atom.

The packing down the *b* axis (Fig. 2) shows that the molecules are arranged in bilayers with their longest dimension almost parallel to the *c* axis. There is an extensive hydrogen-bonding network involving the carboxylate group, a coordinated water molecule and a free water molecule present in the lattice (Table 2). The studies of complexes of copper(II) and cobalt(II) metal ions with various N-donor ligands and the higher carboxylic acids are in progress.

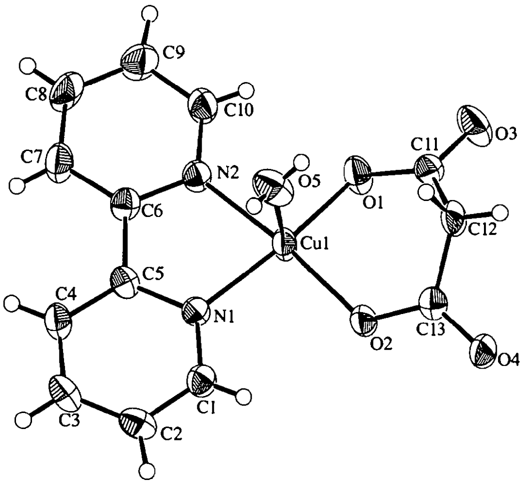


Fig. 1. *ORTEP* (Johnson, 1965) view of the title complex. The water molecule is not shown. Ellipsoids are plotted at the 50% probability level.

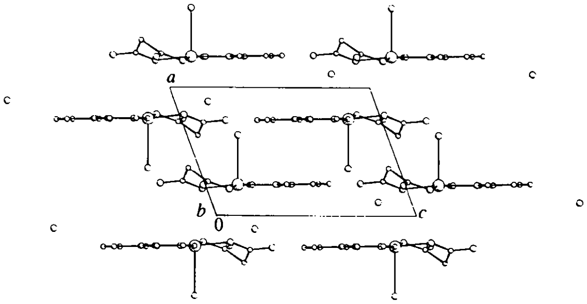


Fig. 2. The packing of molecules viewed down the *b* axis.

Experimental

The title compound was prepared by refluxing basic copper carbonate $[CuCO_3.Cu(OH)_2]$, sodium hydroxide, malonic acid and bipyridyl in the ratio 1:2:1:1 in aqueous media for 45 min. The filtrate was kept at a constant temperature of 295 K and afforded single crystals suitable for crystallographic studies by slow evaporation.

Crystal data

$[Cu(C_3H_2O_4)(C_{10}H_8N_2)-(H_2O)].H_2O$
$M_r = 357.80$
Triclinic
$P\overline{1}$
$a = 7.138\ (3)$ Å
$b = 10.148\ (4)$ Å
$c = 10.686\ (2)$ Å
$\alpha = 105.81\ (3)°$
$\beta = 104.54\ (2)°$
$\gamma = 105.30\ (3)°$
$V = 673.5\ (4)$ Å^3
$Z = 2$
$D_x = 1.764$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10–12°$
$\mu = 1.655$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.32 × 0.12 × 0.08 mm
Blue-green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1955 measured reflections
1955 independent reflections
1831 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 23.5°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0382$
$wR(F^2) = 0.1066$
$S = 1.046$
1951 reflections
256 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0921P)^2 + 0.1003P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.011$

$\Delta\rho_{\max} = 0.617$ e Å^{-3}
$\Delta\rho_{\min} = -1.162$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.019 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O1	1.885 (2)	O2—C13	1.271 (3)
Cu1—O2	1.932 (2)	O3—C11	1.192 (4)
Cu1—N1	1.962 (3)	O4—C13	1.223 (4)
Cu1—N2	1.995 (3)	C11—C12	1.506 (4)
Cu1—O5	2.523 (3)	C12—C13	1.481 (4)
O1—C11	1.286 (4)		
O1—Cu1—O2	92.13 (10)	C11—O1—Cu1	124.0 (2)
O1—Cu1—N1	169.00 (9)	C13—O2—Cu1	124.3 (2)
O2—Cu1—N1	95.78 (9)	O3—C11—O1	122.1 (3)
O1—Cu1—N2	91.51 (10)	O3—C11—C12	119.9 (3)
O2—Cu1—N2	172.70 (9)	O1—C11—C12	118.1 (3)
N1—Cu1—N2	79.81 (10)	C13—C12—C11	116.2 (2)
O1—Cu1—O5	100.46 (11)	O4—C13—O2	124.1 (3)
O2—Cu1—O5	95.12 (10)	O4—C13—C12	118.3 (3)
N1—Cu1—O5	86.45 (10)	O2—C13—C12	117.5 (3)
N2—Cu1—O5	90.44 (10)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots$*A*	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*	H—*D*$\cdots$*A*
O6—H61$\cdots$O1^{i}	2.13 (4)	2.850 (4)	173 (4)	5 (3)
O6—H62$\cdots$O3^{ii}	2.10 (4)	2.737 (4)	169 (4)	8 (3)
O5—H52$\cdots$O4^{iii}	2.12 (5)	2.743 (4)	154 (6)	19 (4)
O5—H51$\cdots$O6^{iv}	2.08 (4)	2.811 (4)	170 (4)	7 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, y, 1+z$; (iii) $1-x, -y, -z$; (iv) $1-x, 1-y, 1-z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

The authors wish to dedicate this paper to the memory of the late Dr K. Venkatasubramanian, who pioneered the X-ray crystallographic work in this laboratory. We wish to acknowledge Professor P. Natarajan, Director of the Institute, for his encouragement.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: DE1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 195–197

Luminescent Tris(3-ethyl-1,5-diaza-3-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]-decane-*P*)gold(I) Tetraiodide Trihydrate, [(EtTPA)$_3$Au]I$_4$.3H$_2$O

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Abstract

The title complex, [Au(C$_8$H$_{17}$N$_3$P)$_3$]I$_4$.3H$_2$O, has the complex cation lying with its Au and associated I atom on a crystallographic threefold axis. The AuP$_3$ moiety has distorted trigonal-planar geometry [the Au atom is 0.336 (3) Å from the P$_3$ plane], with Au—P 2.334 (3), Au$\cdots$I 2.9129 (12) Å and P—Au—P 117.97 (3)°. The asymmetric unit also has one iodide ion and one water molecule in general positions, with O$\cdots$I distances [3.516 (2) and 3.576 (2) Å] consistent with O—H$\cdots$I hydrogen bonding.

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