Crystal structure of (2,2′-dipyridylamine)(carbonato)copper(II) trihydrate, $Cu(CO_3)(C_{10}H_9N_3) \cdot 3H_2O$

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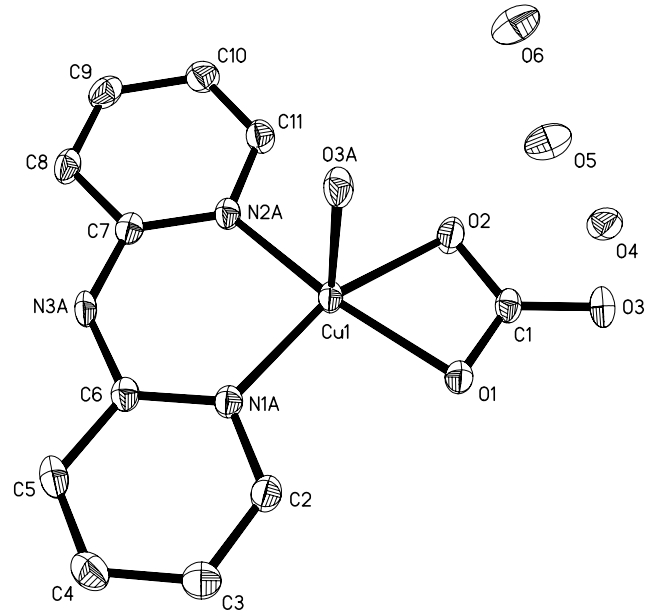
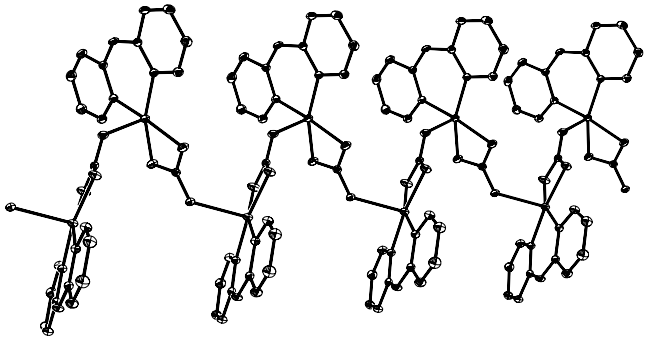
Received August 29, 2007, accepted and available on-line December 31, 2007; CCDC no. 1267/2176





Abstract

$C_{11}H_{15}CuN_3O_6$, monoclinic, $P12_1/c1$ (no. 14), a = 11.245(1) Å, b = 7.1554(7) Å, c = 17.339(2) Å, β = 101.106(1)°, V = 1369.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.030, $wR_{ref}(F^2)$ = 0.080, T = 273 K.

Source of material

A mixture of $CuCO_3$ (0.5 mmol), $Cu(OH)_2 \cdot H_2O$ (0.5 mmol), isophthalate (1 mmol) and 2,2′-dipyridylamine (1 mmol) was stirred into 15 mL aqueous solution. The reaction mixture was heated on a water bath for 10 h at 70 °C, and then filtered. The blue crystal was separated from the mother liquor by slow evaporation at room temperature after 3 weeks.

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Discussion

The design and construction of metal-organic coordination polymers is of current interest in the fields of supramolecular chemistry and crystal engineering. Major reasons for this interest arise from their intriguing variety of topologies and structural diversity [1-5]. However, only very recently have attempts been made to combine both coordination bonds and weaker non-covalent forces such as hydrogen bonding and π-π contacts to crystal engineer organic-inorganic materials. In this regard, the dicarboxylic acids are good candidate as bridging ligands for designing new organic-inorganic hybrid materials as it may participate in both types of interaction as well as their diverse coordination modes [6-10]. On the other hand, in spite of polycyclic aromatic ligands such as 2,2-bipyridine and 1,10-phenanthroline frequently being used in combination with dicarboxylates and leading to novel architectures where they facilitate supramolecular self-assembly through aromatic-aromatic (π-π and C···H) interactions, studies on 2,2′-dipyridylamine (Hdpa) with dicarboxylates are less reported [11]. Considering dpa may provide potential supramolecular recognition sites for noncovalent interactions to form higher dimensionality along with interesting magnetic properties.

The asymmetric unit of the title complex comprises one Cu^{2+} cation, one carbonate dianion and one 2,2′-dipyridylamine molecule (figure, top). The Cu(II) ion is five-coordinated (CuN_2O_3) and the coordination polyhedron can be described as a distorted square pyramid. The equatorial plane is formed by N1, N2 from 2,2′-dipyridylamine and O1, O2 from carbonate. The bond lengths of Cu—N1, Cu1—N2, Cu1—O1 and Cu1—O2 are 1.972(2) Å, 1.979(2) Å, 1.976(2) Å and 1.988(2) Å, respectively. The axial position is occupied by the O atom from another carbonate ligand with the Cu1—O1 distance of 1.987(2) Å. Carbonate adopts two types of coordinated modes: monodentate and chelated coordination. Adjacent Cu atoms are connected by the carbonate ligands with a separation of 5.468 Å to form a one-dimensional chain. These chains are decorated with 2,2′-dipyridylamine ligands alternating at the two sides and the pyridine rings of 2,2′-dipyridylamine at each side of the zigzag chain are arranged in a nearly parallel fashion with an inter-ring distance of 7.155 Å. The adjacent chains are stacked along [100] by π-π stacking interactions through the intercalation of the lateral pyridine rings in a zipper-like way into a two-dimensional layer (figure, bottom). Their interfacial (inter-pyridine plane) distance of 3.668 Å indicates relatively strong π-π aromatic stacking interactions which plays an important role in molecular aggregation. In addition, three crystallographically unique free water molecules are observed in the asymmetric unit which form a water tape associated by O–H···O hydrogen bonds. These bonds provide novel structural aspects of water and new insights into water with implications in biological environment.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.19 × 0.25 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.27 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7748, 3056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2260
$N(param)_{refined}$:	190
Programs:	SHELXS-97 [12], SHELXL-97 [13]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(4WA)	4*e*	0.6706	0.1561	0.2068	0.094
H(4WB)	4*e*	0.7650	0.0321	0.2228	0.094
H(5WA)	4*e*	0.6066	0.5232	0.2073	0.102
H(5WB)	4*e*	0.7237	0.4605	0.2183	0.102
H(6WA)	4*e*	0.5789	0.8459	0.2034	0.112
H(6WB)	4*e*	0.4675	0.7968	0.2179	0.112
H(3)	4*e*	0.9528	0.8558	–0.0976	0.039
H(2)	4*e*	0.7135	0.7341	0.1129	0.041
H(3A)	4*e*	0.5455	0.8172	0.0246	0.051
H(4)	4*e*	0.5637	0.9001	–0.1025	0.052
H(5)	4*e*	0.7524	0.8937	–0.1360	0.048
H(8)	4*e*	1.1425	0.7968	–0.1116	0.042
H(9)	4*e*	1.3348	0.7021	–0.0558	0.047
H(10)	4*e*	1.3741	0.5968	0.0750	0.046
H(11)	4*e*	1.2196	0.5879	0.1419	0.042

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*e*	0.96874(2)	0.68095(4)	0.12852(1)	0.0295(2)	0.0341(2)	0.0202(2)	0.0007(1)	0.0070(1)	0.0045(1)
O(1)	4*e*	0.8730(1)	0.5971(2)	0.20647(9)	0.0300(9)	0.051(1)	0.0282(9)	0.0016(7)	0.0070(7)	0.0110(8)
O(2)	4*e*	1.0648(1)	0.5457(3)	0.21986(9)	0.0345(9)	0.058(1)	0.0318(9)	0.0076(8)	0.0115(7)	0.0182(8)
O(3)	4*e*	0.9716(2)	0.4679(2)	0.31889(9)	0.051(1)	0.0321(9)	0.0230(8)	0.0049(8)	0.0110(7)	0.0037(7)
O(4)	4*e*	0.6917(2)	0.0455(3)	0.2044(1)	0.046(1)	0.072(2)	0.069(1)	–0.005(1)	0.009(1)	–0.018(1)
O(5)	4*e*	0.6524(2)	0.4323(3)	0.2190(1)	0.048(1)	0.059(1)	0.104(2)	–0.008(1)	0.030(1)	0.008(1)
O(6)	4*e*	0.5263(2)	0.7632(3)	0.1988(1)	0.052(1)	0.067(1)	0.112(2)	–0.000(1)	0.033(1)	–0.010(1)
N(1)	4*e*	0.8344(2)	0.7603(3)	0.0445(1)	0.032(1)	0.029(1)	0.0232(9)	–0.0011(8)	0.0069(8)	0.0011(8)
N(2)	4*e*	1.0888(2)	0.6869(2)	0.0591(1)	0.032(1)	0.028(1)	0.0220(9)	–0.0004(8)	0.0068(7)	0.0012(8)
N(3)	4*e*	0.9547(2)	0.8088(3)	–0.0517(1)	0.039(1)	0.041(1)	0.0185(9)	0.0001(9)	0.0064(8)	0.0072(8)
C(1)	4*e*	0.9699(2)	0.5332(3)	0.2513(1)	0.038(1)	0.025(1)	0.022(1)	–0.0017(9)	0.009(1)	–0.0026(9)
C(2)	4*e*	0.7217(2)	0.7661(3)	0.0622(1)	0.035(1)	0.038(1)	0.031(1)	0.002(1)	0.012(1)	0.006(1)
C(3)	4*e*	0.6208(2)	0.8160(4)	0.0099(2)	0.035(1)	0.050(2)	0.044(2)	0.005(1)	0.008(1)	0.004(1)
C(4)	4*e*	0.6316(2)	0.8651(4)	–0.0657(2)	0.037(1)	0.050(2)	0.041(2)	0.009(1)	–0.001(1)	0.008(1)
C(5)	4*e*	0.7434(2)	0.8615(4)	–0.0855(1)	0.051(2)	0.041(2)	0.026(1)	0.002(1)	0.003(1)	0.009(1)
C(6)	4*e*	0.8442(2)	0.8092(3)	–0.0293(1)	0.036(1)	0.026(1)	0.023(1)	–0.001(1)	0.0065(9)	–0.0004(9)
C(7)	4*e*	1.0676(2)	0.7485(3)	–0.0158(1)	0.035(1)	0.023(1)	0.027(1)	–0.0028(9)	0.0083(9)	–0.0024(9)
C(8)	4*e*	1.1594(2)	0.7546(3)	–0.0599(1)	0.044(1)	0.039(1)	0.025(1)	–0.005(1)	0.014(1)	0.002(1)
C(9)	4*e*	1.2732(2)	0.6985(3)	–0.0270(2)	0.038(1)	0.044(2)	0.041(1)	–0.006(1)	0.020(1)	–0.004(1)
C(10)	4*e*	1.2968(2)	0.6351(3)	0.0510(2)	0.032(1)	0.043(2)	0.039(1)	0.001(1)	0.009(1)	–0.001(1)
C(11)	4*e*	1.2039(2)	0.6312(3)	0.0904(1)	0.039(1)	0.040(1)	0.027(1)	0.002(1)	0.007(1)	0.001(1)

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