

formation. The Mo—O(water) distance, for example, is appreciably longer at 2.337 (3) Å. The distances between the Mo and the terminal O atoms [1.704 (3) and 1.695 (3) Å] are in good agreement with those in bis( $\mu$ -ethoxycarbonylimido)-bis[( $\eta$ -cyclopentadienyl)oxomolybdenum] and  $\mu$ -ethoxycarbonylimido- $\mu$ -oxo-bis[( $\eta$ -cyclopentadienyl)oxomolybdenum] (Korswagen, Weidenhammer & Ziegler, 1979) and show that the bonds have at least partial double-bond character.

The atoms of the five-membered chelate ring are coplanar within 0.030 (4) Å whereas those of the six-membered ring deviate more appreciably from planarity [maximum displacement 0.235 (3) Å for O(4)]. The angle between these two planes is 7.2 (1)°. The bite angles of the five- and six-membered chelate rings differ significantly, introducing a considerable distortion into the octahedron. The other two six-membered rings are planar to within  $\pm 0.01$  Å and are almost parallel to each other [dihedral angle 13.9 (1)°].

The N—N distance [1.403 (4) Å] is intermediate between single- and double-bond lengths indicating that the azo group is involved in resonance. The C—N bond lengths [1.295 (5) and 1.315 (4) Å] and C(8)—C(9) length [1.469 (6) Å] also suggest delocalization. The strained structure of the rings resulting from the steric conditions for complex formation, evident from some distorted angles, may influence both the resonance and the bond lengths.

Fig. 2 shows the contents of the unit cell projected on the (100) plane. The closest intermolecular non-H atom contact is O(1)⋯C(4) ( $x + \frac{1}{2}$ ,  $-y + \frac{1}{2}$ ,  $z + \frac{1}{2}$ ),

3.308 (5) Å. The shortest intermolecular O⋯H distance [O(1)⋯H(4) ( $x + \frac{1}{2}$ ,  $-y + \frac{1}{2}$ ,  $z + \frac{1}{2}$ ), 2.304 (3) Å] is too long to be considered a hydrogen-bonding interaction (Hamilton & Ibers, 1968). The packing of the molecules is thus determined by van der Waals forces. The molecules are packed in layers, but are displaced with respect to one another to relieve short intermolecular contacts, so that packing forces are unlikely to influence the geometry of the molecule to any appreciable extent.

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## Structure of Aquacarbonato(di-2-pyridylamine)copper(II) Dihydrate

PERVAIZ AKHTER, PAUL FITZSIMMONS AND BRIAN HATHAWAY\*

*Chemistry Department, University College, Cork, Ireland*

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**Abstract.** (I) [Cu(CO<sub>3</sub>)(H<sub>2</sub>O)(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)]<sub>2</sub>.2H<sub>2</sub>O,  $M_r = 348.79$ , monoclinic,  $P2_1/c$ ,  $Z = 4$ ,  $a = 9.345$  (3),  $b = 20.158$  (5),  $c = 7.812$  (2) Å,  $\beta = 107.27$  (4)°,  $V = 1405.25$  Å<sup>3</sup>,  $D_m(\text{floatation}) = 1.66$  (5),  $D_x = 1.648$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 153.7$  mm<sup>-1</sup>,  $T = 298$  K,  $F(000) = 716$ .  $R = 0.044$  for 1898 unique reflections. The CuN<sub>2</sub>O<sub>2</sub>O' chromophore involves a distorted square based pyramidal structure, with nearly symmetrically bonded biden-

tate di-2-pyridylamine (dpyam) and carbonate groups, in the basal plane, from which the Cu atom is displaced 0.328 (4) Å towards the apical O(4) atom [Cu—O(4) = 2.202 (3) Å]. The dpyam ligand has a bite angle of 92.2 (1)° at the Cu atom and the [CO<sub>3</sub>]<sup>2-</sup> anion one of 66.5 (1)°. The dihedral angle between the mean planes of the dpyam and the carbonate ligands is 50.3°.

**Introduction.** From a preparative solution, methanol/water, containing Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O, KPF<sub>6</sub>, NaHCO<sub>3</sub>

\* To whom correspondence should be addressed.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Cu	0.70366 (5)	0.41583 (2)	0.66194 (6)	0.0261 (3)
N(1)	0.8549 (3)	0.4864 (2)	0.6899 (4)	0.028 (2)
C(1)	0.8082 (5)	0.5450 (2)	0.6054 (6)	0.035 (2)
C(2)	0.9022 (6)	0.5946 (2)	0.5940 (7)	0.042 (3)
C(3)	1.0566 (6)	0.5851 (2)	0.6752 (7)	0.045 (3)
C(4)	1.1061 (5)	0.5269 (2)	0.7617 (6)	0.038 (2)
C(5)	1.0006 (4)	0.4778 (2)	0.7683 (5)	0.028 (2)
N(3)	1.0561 (4)	0.4183 (2)	0.8547 (5)	0.033 (2)
C(6)	0.9824 (4)	0.3674 (2)	0.9128 (5)	0.027 (2)
C(7)	1.0705 (5)	0.3193 (2)	1.0230 (6)	0.035 (2)
C(8)	1.0049 (6)	0.2686 (2)	1.0856 (7)	0.044 (3)
C(9)	0.8494 (5)	0.2655 (2)	1.0417 (6)	0.039 (2)
C(10)	0.7687 (4)	0.3143 (2)	0.9298 (6)	0.035 (2)
N(2)	0.8336 (4)	0.3645 (2)	0.8635 (4)	0.030 (2)
C(11)	0.5298 (4)	0.3717 (2)	0.3988 (6)	0.030 (2)
O(1)	0.5689 (3)	0.3419 (1)	0.5533 (4)	0.034 (2)
O(2)	0.5909 (3)	0.4306 (1)	0.4043 (4)	0.033 (1)
O(3)	0.4401 (4)	0.3477 (2)	0.2616 (4)	0.041 (2)
O(4)	0.5666 (3)	0.4692 (1)	0.8029 (4)	0.039 (2)
O(5)	0.3679 (3)	0.3916 (2)	0.9202 (4)	0.039 (2)
O(6)	0.3671 (3)	0.2849 (2)	0.7069 (5)	0.047 (2)

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

Cu—N(1)	1.970 (3)	Cu—O(4)	2.202 (3)
Cu—N(2)	1.972 (3)	C(11)—O(1)	1.299 (5)
Cu—O(1)	1.974 (3)	C(11)—O(2)	1.313 (5)
Cu—O(2)	1.998 (3)	C(11)—O(3)	1.246 (5)
N(1)—Cu—N(2)	92.2 (1)	O(4)—Cu—N(2)	99.7 (1)
O(1)—Cu—N(1)	159.7 (1)	O(4)—Cu—O(1)	101.1 (1)
O(1)—Cu—N(2)	96.3 (1)	O(4)—Cu—O(2)	102.7 (1)
O(2)—Cu—N(1)	98.7 (1)	O(1)—C(11)—O(2)	112.9 (4)
O(2)—Cu—N(2)	153.9 (1)	O(1)—C(11)—O(3)	123.5 (4)
O(2)—Cu—O(1)	66.5 (1)	O(2)—C(11)—O(3)	123.6 (4)
O(4)—Cu—N(1)	95.6 (1)		

and dpyam, a mixture of blue plates (I) and needles (II) was obtained. Analysis showed that both sets of crystals had the same composition,  $[\text{Cu}(\text{dpyam})(\text{CO}_3)] \cdot 3\text{H}_2\text{O}$ . Found for (I): C, 38.33; H, 3.45; N, 12.18%; calculated for  $\text{C}_{11}\text{H}_{15}\text{CuN}_3\text{O}_6$ : C, 37.88; H, 3.33; N, 12.05%. As the colours of the crystals of (I) and (II) and the spectroscopic properties suggest different copper(II) environments, the crystal structure of the plate-shaped crystals has been determined for comparison with the known structure of the blue needles (Sletten, 1984).

**Experimental.** The unit-cell data (25 reflections,  $\theta$  3–25°) and intensities were collected on a Philips PW 1100 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. Reflections with  $3.0 < \theta < 25^\circ$  in one quadrant were examined in the  $\omega$ - $2\theta$  scan mode, with a constant scan speed of  $0.05^\circ \text{ s}^{-1}$ , and a variable scan width of  $(0.7 + 0.1 \tan \theta)^\circ$ . 1958 observed reflections were collected of which 1898 were unique [ $I > 2.5\sigma I$ ;  $-10 < h < 10$ ,  $0 < k < 23$ ,  $0 < l < 9$ ]. Lorentz and polarization corrections were applied, but no correction was made for absorption.

The structure was solved by the *SHELX76* direct methods (Sheldrick, 1976) and difference Fourier techniques and refined (191 parameters, 9.94 observations/parameter) by least-squares minimization of  $\sum w(|F_o| - |F_c|)^2$ , with anisotropic temperature factors on all the non-H atoms. The positions of the H atoms were calculated geometrically and 'floated' on the adjacent C, N and O atoms, assuming C—H, N—H and O—H distances of 1.08 Å, and a fixed temperature factor of  $0.07 \text{ \AA}^2$ . Maximum shift/e.s.d. was  $< 0.001$ , with a refined weighting scheme,  $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$  with  $k = 1.00$  and  $g = 0.004272$ .  $R = 0.044$  and  $wR = 0.051$ . The maximum and minimum residual electron densities were 0.73 and  $-0.86 \text{ e \AA}^{-3}$ . Complex neutral atomic scattering factors were employed and those for Cu were taken from Cromer & Waber (1974). All calculations were carried out with *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1979), *CHEM-X* (Davies, 1980) and *PUBTAB* (Henrick, 1980) on the UCC mainframe IBM 4341 and VAX 11/780 computers. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.\* Selected bond lengths and angles are given in Table 2, and Fig. 1 shows the molecular structure of (I), and the atom-numbering scheme used.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53363 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

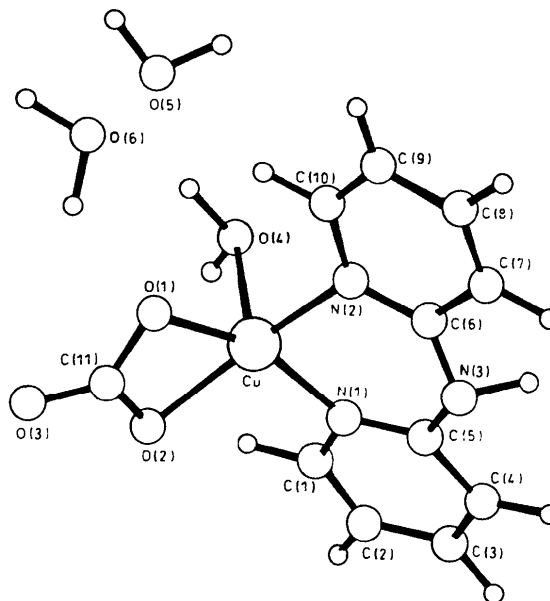


Fig. 1. The molecular structure of  $[\text{Cu}(\text{dpyam})(\text{CO}_3)(\text{OH}_2)] \cdot 2\text{H}_2\text{O}$ , and the atom-numbering scheme used, viewed approximately down the  $c$  axis.

**Discussion.** The structure of (I) (Fig. 1) consists of a neutral [Cu(dpyam)(CO<sub>3</sub>)(OH<sub>2</sub>)] unit and two uncoordinated water molecules, in general positions in the unit cell. The local molecular structure of the copper(II) ion involves a distorted square-based pyramidal CuN<sub>2</sub>O<sub>2</sub>O' chromophore. The dpyam ligand bonds symmetrically in-the-plane with Cu—N distances of 1.970 (3) and 1.972 (3) Å, and an N(1)—Cu—N(2) dpyam bite angle of 92.2 (1)°. The carbonate group also bonds nearly symmetrically in-the-plane, with Cu—O distances of 1.974 (3) and 1.988 (3) Å, and an O(1)—Cu—O(2) bite angle of 66.5 (1)°. A water molecule occupies the apical position of the CuN<sub>2</sub>O<sub>2</sub>O' chromophore, with a longer Cu—O(4) distance of 2.202 (3) Å, to give a tetragonality,  $T^5$ , of 0.899 (Procter, Hathaway & Nicholls, 1968). The four in-plane ligand atoms, N(1), N(2), O(1) and O(2) are reasonably planar (r.m.s.d. = 0.047 Å), but with a slight tetrahedral twist. The Cu atom lies 0.328 (4) Å above this plane, towards the apical water molecule, O(4) (Hathaway, 1987*b*), giving *trans* in-plane N—Cu—O angles of 159.7 (1) and 153.9 (1)°, respectively, and resulting in a carbonate and dpyam roof-top dihedral angle of 50.3 (5)°. There are no unusual bond lengths or bond angles in the dpyam ligand (Ray & Hathaway, 1978). The separate pyridine rings are planar, (r.m.s.d. 0.004 and 0.010 Å, respectively) and the dihedral angle is 11.9 (6)°. The carbonate anion is essentially planar, with the C—O distances of the coordinated O atoms significantly longer, 1.299 (5) and 1.313 (5) Å, respectively, than that of the uncoordinated oxygen, O(3), 1.246 (5) Å. The O(1)—C(11)—O(2) angle, 112.9 (4)°, is significantly less than the remaining O—C—O angles of 123.5 (4) and 123.6 (4)°, respectively. The water molecules in the unit cell are involved in a number of H bonds in the range 2.70–2.78 Å to each other and to the carbonate anion.

The structure of (I) has a CuN<sub>2</sub>O<sub>2</sub>O' chromophore comparable to that of the blue needles of [Cu(dpyam)(O<sub>2</sub>CO)]·3H<sub>2</sub>O, (II) (Sletten, 1984). Both have a square-based pyramidal structure with in-plane coordination of a dpyam ligand and a bidentate carbonate anion. However they differ in respect of the nature of the fifth ligand; in (I) this involves a water molecule while in (II) the third oxygen of the carbonate anion, O(3), is involved as the fifth ligand. Consequently, while the carbonate in (I) is one coordinate to a single Cu atom, as a bidentate chelate ligand, in (II) the carbonate is two coordinate, bridging between two separate Cu atoms, as a bidentate chelate ligand to the first Cu atom and as a monodentate ligand to the second (Hathaway, 1987*a*). In (II) as the in-plane ligands are more coplanar, the Cu atom is lifted out of the plane by only 0.141 Å and the out-of-plane Cu—O distance is correspondingly

longer, 2.295 (5) Å. Consequently, the tetragonality,  $T^5$ , of (I) and (II) are 0.899 and 0.861, respectively and the dihedral angles between the in-plane ligands are significantly different, 50.3 and 5.3°, respectively.

**Spectroscopic properties.** The significant crystallographic differences between (I) and (II) are not reflected in their colour, both are blue and their electronic spectra involve single broad bands at 15 000 and 15 600 cm<sup>-1</sup>, respectively, with a poorly resolved shoulder at 11 500 cm<sup>-1</sup> in (I). This difference is consistent with the higher tetragonality,  $T^5$ , in (I) than (II). The infrared spectrum of (I) shows strong bands at 1570 and 1310 cm<sup>-1</sup> arising from the splitting of the C—O anti-symmetric stretching mode ( $\nu_3$ ) of the free carbonate anion, when its symmetry is lowered from  $D_{3h}$  to  $C_{2v}$  in bidentate coordination to the Cu atom (Nakamoto, 1978; Hathaway, 1987*b*).

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