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Bis(acetato- κ^2O,O')(di-2-pyridyl- κN -amine)copper(II) Dihydrate

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Abstract

The copper(II) ion in the title complex, [Cu(C₂H₃O₂)₂-(C₁₀H₉N₃)]·2H₂O, is coordinated unsymmetrically to each of the two bidentate acetate ligands and to the N atoms of the di-2-pyridylamine (dpyam) ligand. The copper(II) ion is surrounded by a distorted square-based arrangement of the two dpyam pyridyl N atoms at dis-

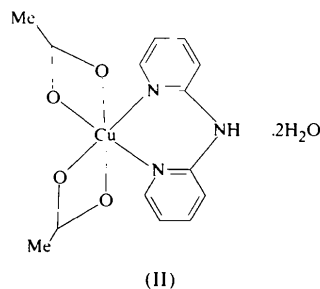
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tances of 1.974 (2) and 1.995 (2) Å, and by two acetate O atoms at distances of 1.965 (1) and 1.967 (1) Å. The second O atom from each acetate group is involved in weak coordination in the tetragonal positions, at longer Cu—O distances of 2.482 (2) and 2.690 (2) Å, completing the six-coordination. The overall geometry at the copper(II) ion is best described as distorted octahedral with elongated axial bonds.

Comment

The local molecular stereochemistries of the [Cu(chelate)(OXO)(OYO)] complexes, where chelate is ethylenediamine (en) or 2,2'-bipyridyl (bipy), and OXO and OYO are oxyanions, were characterized by electron-spin resonance (ESR) and electronic spectra (Procter *et al.*, 1972). Mononuclear or polynuclear complexes with axially elongated octahedral stereochemistries were suggested from this stoichiometry. In order to investigate this postulation, the crystal structures of complexes containing the di-2-pyridylamine (dpyam) and other related chelate ligands have been reported. The complexes [Cu(tmen)(NO₃)₂], where tmen is *N,N,N',N'*-tetramethylethylenediamine (Pavkovic & Miller, 1977), [Cu(DMAEP)(NO₃)₂], where DMAEP is 2-(2-dimethylaminoethyl)pyridine (Lewis & Hodgson, 1973), [Cu(bipy)(NO₂)₂] (Stephens, 1969) and [Cu(dpyam)(CH₃CO₂)₂].H₂O [(I); Munoz *et al.*, 1993] are mononuclear, whereas a polynuclear chain structure is known to exist for the corresponding complexes [Cu(dpyam)(CH₃CO₂)(ClO₄)]·H₂O (Ray *et al.*, 1982), [Cu(dpyam)(CH₃CO₂)(NO₃)] (Aduldecha & Hathaway, 1991) and [Cu(dpyam)(CH₃CH₂CO₂)(NO₃)] (Youngme *et al.*, 1998). In a search for additional examples containing this type of stoichiometry with the dpyam chelate ligand, the crystal structure of [Cu(dpyam)(CH₃CO₂)₂].2H₂O, (II), has been determined and compared with the known structures of relevant complexes.



The crystal structure of (II) is composed of discrete monomeric molecules with an irregular (4+2) coordination polyhedron about copper. This arrangement consists of two dpyam N atoms and two acetate O atoms forming a tetrahedrally distorted square base. A second O atom from each acetate group then occupies the tetragonal position above and below the CuN₂O₂ basal

plane at longer distances of 2.482 (2) and 2.690 (2) Å, *i.e.* the two axial bonds of the octahedral geometry are elongated, which is quite typical and expected for Cu^{II} in view of Jahn–Teller effects (Hathaway, 1987). The acetate groups are bent towards the Cu atom to occupy the fifth and sixth (axial) coordination sites, with O2—Cu—O4 angles of 148.25 (6)°. The basal bond angles about copper are all close to 90°. However, the basal atoms depart significantly from coplanarity, having a slight tetrahedral twist of the equatorial plane, as is evident from the dihedral angle of 34.38 (5)° between the N1—Cu—N3 and O1—Cu—O3 planes, and the high value of the mean deviation [± 0.424 (1) Å] from the plane defined by atoms N1, N3, O1 and O3. Thus, the geometry at the copper(II) ion is best described as distorted octahedral with elongated axial positions. The Cu atom deviates significantly from the mean planes formed by the acetate groups [0.1548 (3) and 0.2846 (3) Å]; the pyridine rings in the dpyam ligand are individually essentially planar and these planes form a dihedral angle of 25.70 (6)°.

In the crystal, the H atoms of one of the water molecules (O5) link inversion-related pairs of molecules at (x, y, z) and $(-x, 1-y, 1-z)$ through O—H...O hydrogen bonding involving the acetate O2 and O3 atoms. These pairs are linked to form an infinite chain along the *c*-axis direction by the second water molecule (O6) through O—H...O hydrogen bonding involving the acetate O4 and the water O5 atoms. The N—H group interlinks these chains by forming N—H...O hydrogen bonds with O6. Details of the hydrogen bonding are given in Table 2.

The arrangement around the Cu atom in (II) is comparable to the situations observed in the related complexes [Cu(tmen)(NO₃)₂] (Pavkovic & Miller, 1977),

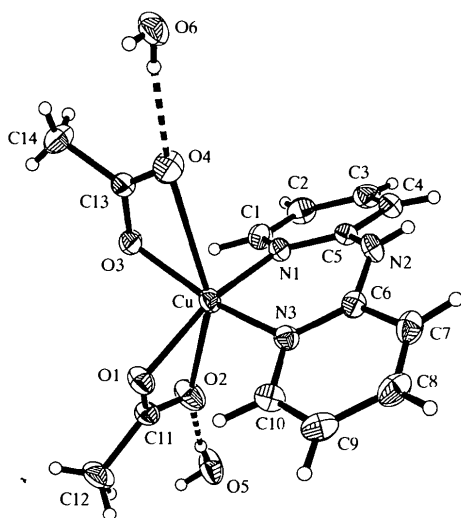


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

[Cu(DMAEP)(NO₃)₂] (Lewis & Hodgson, 1973) and [Cu(bipy)(NO₂)₂] (Stephens, 1969). These complexes display tetragonally elongated octahedral geometry of the CuN₂O₂O'O' chromophore, with long off-axis coordination of the second O atom from each nitrito or nitrate ligand in the axial positions. There is a close similarity between dihydrate (II) and monohydrate (I) of the same material. The structure of (I) has a CuN₂O₂O'O' chromophore very comparable to that of (II). All bond lengths and angles in both complexes (except the hydrogen bonds) are very similar. The local molecular geometry of (I) and (II) can be considered as basically five-coordinate (4+1) or six-coordinate, with a long off-axis Cu—O4 bond giving a (4+1+1') structure. However, the arrangement around the Cu atom in (II) differs from the arrangements observed in the related polynuclear complexes, *i.e.* [Cu(dpyam)(CH₃CO₂)(ClO₄)]·H₂O (Ray *et al.*, 1982), [Cu(dpyam)(CH₃CO₂)(NO₃)] (Aduldecha & Hathaway, 1991) and [Cu(dpyam)(CH₃CH₂CO₂)(NO₃)] (Youngme *et al.*, 1998), with respect of the coordination nature of the oxyanions in the complexes. In (II), both acetate groups coordinate to a single Cu atom as a bidentate chelate ligand, while in this group of complexes, the perchlorate or nitrate group bridges between two Cu atoms. The latter complexes involve the near symmetrically bonded dpyam ligand, an oxygen bonding in the plane and a second bridging semi-coordinate oxyanion completing the six-coordination in the axial positions.

Experimental

The title complex was prepared by adding a boiling solution containing Cu(O₂CCH₃)₂·H₂O (0.73 g, 2.0 mmol) in water (40 ml) to a warm solution of dpyam (0.35 g, 2.0 mmol) in ethanol (60 ml). Complex (II) was obtained as blue–green crystals on slow evaporation of the solvent.

Crystal data

[Cu(C₂H₃O₂)₂(C₁₀H₉N₃)]·
2H₂O
M_r = 388.86
Triclinic
P $\bar{1}$
a = 7.3161 (5) Å
b = 10.9267 (14) Å
c = 11.2045 (10) Å
 α = 83.479 (9)°
 β = 76.746 (8)°
 γ = 73.386 (7)°
V = 834.33 (14) Å³
Z = 2
D_x = 1.548 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
Cell parameters from 39
reflections
 θ = 5.33–12.58°
 μ = 1.344 mm⁻¹
T = 293 (2) K
Parallelepiped
0.68 × 0.66 × 0.48 mm
Blue

Data collection

Siemens *P4* diffractometer
 $\theta/2\theta$ scans

*R*_{int} = 0.013
 θ_{max} = 27.50°

Absorption correction: $h = -1 \rightarrow 9$
 empirical ψ scans $k = -13 \rightarrow 14$
 (XSCANS; Siemens, 1994) $l = -14 \rightarrow 14$
 $T_{\min} = 0.378$, $T_{\max} = 0.525$ 3 standard reflections
 4743 measured reflections every 97 reflections
 3843 independent reflections intensity decay: <3%
 3514 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} = 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.030$ $\Delta\rho_{\max} = 0.280 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.085$ $\Delta\rho_{\min} = -0.471 \text{ e } \text{\AA}^{-3}$
 $S = 1.071$ Extinction correction: none
 3843 reflections Scattering factors from
 293 parameters *International Tables for*
 All H atoms refined *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0505P)^2]$
 $+ 0.1566P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu—O1	1.9654 (14)	Cu—O4	2.690 (2)
Cu—O3	1.9669 (14)	O1—C11	1.267 (2)
Cu—N1	1.9742 (15)	O2—C11	1.239 (3)
Cu—N3	1.995 (2)	O3—C13	1.279 (2)
Cu—O2	2.4824 (15)	O4—C13	1.233 (2)
O1—Cu—O3	89.15 (6)	N1—Cu—O2	96.90 (6)
O1—Cu—N1	154.42 (6)	N3—Cu—O2	106.41 (6)
O3—Cu—N1	93.99 (6)	O1—Cu—O4	114.89 (6)
O1—Cu—N3	94.46 (6)	O3—Cu—O4	53.50 (5)
O3—Cu—N3	156.92 (6)	N1—Cu—O4	86.84 (6)
N1—Cu—N3	92.50 (6)	N3—Cu—O4	104.90 (5)
O1—Cu—O2	57.53 (5)	O2—Cu—O4	148.25 (6)
O3—Cu—O2	94.76 (6)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O5—H1O5...O2	0.78 (3)	2.01 (3)	2.778 (3)	169 (3)
O5—H2O5...O3 ⁱ	0.76 (3)	2.11 (3)	2.845 (3)	164 (4)
O6—H1O6...O5 ⁱⁱ	0.76 (4)	2.04 (4)	2.798 (4)	174 (3)
O6—H2O6...O4	0.80 (3)	2.02 (3)	2.801 (3)	167 (3)
N2—H1N2...O6 ⁱⁱⁱ	0.77 (2)	2.02 (2)	2.784 (3)	174 (2)

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

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93 and PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1235). Services for accessing these data are described at the back of the journal.

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Metal Alkoxycarboxylate Complexes. I. Poly[aquabis(methoxyacetato)(nitrato)-neodymium(III)]

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Abstract

The title compound, [Nd(O₂CCH₂OCH₃)₂(NO₃)(H₂O)]_n, contains nine-coordinate Nd atoms in which the carboxylate ligands chelate to one metal atom and each bridges to a second metal atom, resulting in the formation of pleated sheets. The Nd—O distances range from 2.375 (4) to 2.629 (4) Å.

Comment

The discovery that lanthanide metal salts of 2-[2-(2-methoxyethoxy)ethoxy]acetate (MEEA) are room-temperature liquids (Apblett, Long *et al.*, 1994; Apblett *et al.*, 1995) has prompted an investigation of the structural chemistry of simpler alkoxycarboxylates so that the resulting structural and spectroscopic characterizations of these solid complexes can be used