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### Chloro(di-2-pyridyl- $\kappa$ N-amine)(propionato- $\kappa^2$ O,O')copper(II) monohydrate

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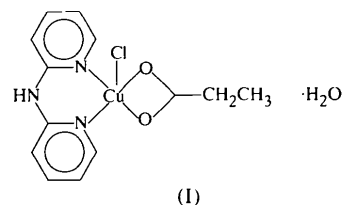
#### Abstract

In the title compound, [CuCl(C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>)(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)]·H<sub>2</sub>O, the CuN<sub>2</sub>O<sub>2</sub>Cl chromophore involves a distorted square-based pyramidal structure, with nearly symmetrically bonded bidentate di-2-pyridylamine and propionate groups in the basal plane, and a Cl atom at the apex. The Cu atom is displaced from the basal plane towards the apical Cl atom by 0.304 (1) Å.

#### Comment

Di-2-pyridylamine (dpyam) and similar ligands (rigid or semi-rigid) are well known for their stabilizing effect on the five-coordination state of copper(II) (Harrison & Hathaway, 1980). The five-coordination copper(II) complexes usually show a stereochemistry ranging from a slightly distorted trigonal-bipyramidal to a distorted square-pyramidal arrangement (Greiner *et al.*, 1994; Harrison *et al.*, 1981; Nagle *et al.*, 1990). A structural pathway from a regular trigonal-bipyramidal [ $\tau = 1.0$ ;  $\tau = (\beta - \alpha)/60$ , where  $\alpha$  and  $\beta$  are basal angles (Addison *et al.*, 1984)] to a regular square-based pyramidal ( $\tau = 0.0$ ) stereochemistry has been suggested for these complexes (Hathaway, 1984, 1987; Murphy *et al.*, 1998). The inherent flexibility of the copper(II) coordination sphere and the dpyam ligand along with the non-stereospecific nature of the rather large spherical halide ion led to our interest in these complexes. Herewith we report the structure of the title compound, (I), a five-

coordination complex where a chloride ion is present along with the dpyam ligand.



The asymmetric unit of (I) consists of a neutral [Cu(dpyam)(O<sub>2</sub>CCH<sub>2</sub>CH<sub>3</sub>)Cl] unit and an uncoordinated water molecule. The copper(II) ion involves a distorted square-based pyramidal CuN<sub>2</sub>O<sub>2</sub>Cl chromophore. The dpyam ligand bonds symmetrically in the plane with Cu—N distances of 1.970 (2) and 1.972 (2) Å, and a bite angle of 93.95 (6)°, which is in the range normally observed for the coordinated dpyam ligand (Ray & Hathaway, 1978). The propionate group also bonds nearly symmetrically in the plane, with C—O distances of 2.012 (2) and 2.049 (1) Å, and an O1—Cu1—O2 bite angle of 64.14 (6)°. A chloride anion then occupies the apical position of the CuN<sub>2</sub>O<sub>2</sub>Cl chromophore, with a longer Cu—Cl distance of 2.489 (1) Å. The ligand atoms which are involved in the coordination (N1, N2, O1 and O2) are coplanar and the Cu atom lies 0.304 (1) Å above this plane, towards the apical Cl atom, giving identical *trans* in-plane N—Cu—O angles of 156.84 (7)°. A zero  $\tau$  value  $\{[(N1—Cu1—O2) - (N2—Cu1—O1)]/60\}$  indicates that (I) is consistent with a nearly regular square-based pyramidal stereochemistry (Addison *et al.*, 1984; Murphy *et al.*, 1998). The N1—Cu1—N2 and O1—Cu1—O2 planes make a dihedral angle of 23.24 (7)°.

There are no unusual bond lengths or angles in the dpyam ligand. The pyridine rings are planar and they form a dihedral angle of 2.37 (7)°. Atoms O1, O2, C11 and C12 of the propionate group are essentially coplanar, and the dihedral angle between this plane and the mean plane through the dpyam ligand is 16.6 (1)°; the

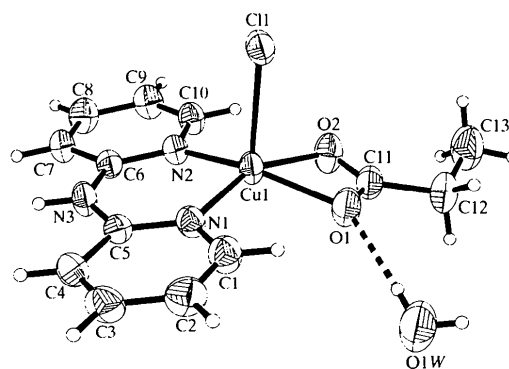


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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O1—C11—O2 angle of 117.7 (2)° deviates significantly from the other angles around C11.

In the solid state, the inversion-related molecules which are stacked along the *a* axis are linked by an N3—H3A···Cl1(1 - *x*, -*y*, -*z*) hydrogen bond to form a dimeric pair. Along the *c* direction, the dimeric pairs are interlinked by the water molecule through O1W—H2W···O1 and O1W—H1W···Cl1(-*x*, -*y*, -1 - *z*) hydrogen bonds (Table 2).

The structure of (I) has a CuN<sub>2</sub>O<sub>2</sub>Cl chromophore comparable to those of the mono(dpyam) complexes [Cu(dpyam)(CO<sub>3</sub>)(OH<sub>2</sub>)·2H<sub>2</sub>O ( $\tau = 0.10$ ), [Cu(dpyam)(CO<sub>3</sub>)·3H<sub>2</sub>O, [Cu(dpyam)(OH<sub>2</sub>)<sub>2</sub>F]·3H<sub>2</sub>O ( $\tau = 0.15$ ) and [Cu(dpyam)Cl(NO<sub>3</sub>)·0.5H<sub>2</sub>O ( $\tau = 0.27$ )] (Akhter *et al.*, 1991; Mathews & Manohar, 1991; Jacobson & Jensen, 1981; Sletten, 1984), and the bis(dpyam) complex [Cu(dpyam)<sub>2</sub>(NCO)<sub>2</sub>][SO<sub>4</sub>·2(dpyam)·H<sub>2</sub>O ( $\tau = 0.31$ )] (Akhter & Hathaway, 1991). The distortions of these complexes suggest the chromophores involve a square-pyramidal structure, distorted towards a trigonal-bipyramidal stereochemistry with different percentage of trigonal distortion. This type of distortion is also observed in the dimeric dpyam complexes [Cu<sub>2</sub>(OH)<sub>2</sub>(OH<sub>2</sub>)(dpyam)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O, [Cu<sub>2</sub>(OH)<sub>2</sub>(F<sub>2</sub>BF<sub>3</sub>)<sub>2</sub>(dpyam)<sub>2</sub>], [Cu<sub>2</sub>(OH)<sub>2</sub>(ONO<sub>2</sub>)<sub>2</sub>(dpyam)<sub>2</sub>], [Cu<sub>2</sub>(OH)<sub>2</sub>(O<sub>2</sub>CH)<sub>4</sub>(dpyam)<sub>2</sub>]·H<sub>2</sub>O and [Cu<sub>2</sub>(dpyam)<sub>2</sub>(oxamido)-(NO<sub>3</sub>)<sub>2</sub>] (Wu *et al.*, 1992; Sletten, 1982; Youngme *et al.*, 1999). Furthermore, the square-based pyramidal distorted trigonal-bipyramidal stereochemistry has been observed previously in the bis(dpyam) complexes [Cu(dpyam)<sub>2</sub>Cl]Cl·4H<sub>2</sub>O, [Cu(dpyam)<sub>2</sub>Cl]Cl and [Cu(dpyam)<sub>2</sub>I]<sub>2</sub>I[ClO<sub>4</sub>] (Johnson & Jacobson, 1973; Jensen & Jacobson, 1981; Jacobson & Jensen, 1986).

## Experimental

The title complex was prepared by adding a hot solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.34 g, 1.0 mmol) in water (20 ml) to a boiling solution of dpyam (0.17 g, 1.0 mmol) in absolute ethanol (30 ml), after which CH<sub>3</sub>CH<sub>2</sub>COONa (0.29 g, 3.0 mmol) was added. After standing for a week, green crystals of (I) formed.

### Crystal data

[CuCl(C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> )(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> )]·H <sub>2</sub> O	Mo <i>K</i> α radiation
<i>M<sub>r</sub></i> = 361.28	λ = 0.71073 Å
Triclinic	Cell parameters from 5189 reflections
<i>P</i> 1̄	θ = 2.35–28.30°
<i>a</i> = 7.3993 (2) Å	μ = 1.666 mm <sup>-1</sup>
<i>b</i> = 8.9006 (2) Å	<i>T</i> = 293 (2) K
<i>c</i> = 11.7469 (3) Å	Block
α = 101.651 (1)°	0.48 × 0.36 × 0.18 mm
β = 100.540 (1)°	Green
γ = 93.448 (1)°	
<i>V</i> = 741.11 (3) Å <sup>3</sup>	
<i>Z</i> = 2	
<i>D<sub>x</sub></i> = 1.619 Mg m <sup>-3</sup>	
<i>D<sub>m</sub></i> not measured	

### Data collection

Siemens SMART CCD area-detector diffractometer  
ω scans  
Absorption correction: multi-scan, empirical (SADABS; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.502, *T*<sub>max</sub> = 0.754

6061 measured reflections  
3525 independent reflections  
3060 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.031  
θ<sub>max</sub> = 28.30°  
*h* = -9 → 9  
*k* = -11 → 11  
*l* = 0 → 15

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.031  
w*R* (*F*<sup>2</sup>) = 0.087  
*S* = 1.045  
3524 reflections  
200 parameters  
H atoms: see below  
w = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0466*P*)<sup>2</sup>]  
where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.42 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.50 e Å<sup>-3</sup>  
Extinction correction: SHELXTL (Sheldrick, 1997)  
Extinction coefficient: 0.004 (3)  
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—N2	1.970 (2)	Cu1—C11	2.489 (1)
Cu1—N1	1.972 (2)	O1—C11	1.258 (3)
Cu1—O1	2.012 (2)	O2—C11	1.262 (2)
Cu1—O2	2.049 (1)		
N2—Cu1—N1	93.95 (6)	N1—Cu1—C11	99.35 (5)
N2—Cu1—O1	156.84 (7)	O1—Cu1—C11	97.64 (5)
N1—Cu1—O1	97.65 (6)	O2—Cu1—C11	97.31 (5)
N2—Cu1—O2	98.81 (6)	O1—C11—O2	117.7 (2)
N1—Cu1—O2	156.84 (7)	O1—C11—C12	118.7 (2)
O1—Cu1—O2	64.14 (6)	O2—C11—C12	123.6 (2)
N2—Cu1—C11	100.19 (5)		

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3A···Cl1 <sup>i</sup>	0.86	2.34	3.170 (2)	164
O1W—H2W···O1	0.84 (4)	2.04 (4)	2.874 (3)	173 (4)
O1W—H1W···Cl1 <sup>ii</sup>	0.81 (4)	2.49 (4)	3.294 (2)	173 (4)
C1—H1···O1	0.93	2.39	2.997 (3)	122
C10—H10···O2	0.93	2.43	3.048 (3)	124

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

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 3 cm and the detector swing angle was -20°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections, and was found to be negligible. The reflection 010 was suppressed during refinement as it showed very poor agreement between *F*<sub>o</sub><sup>2</sup> and *F*<sub>c</sub><sup>2</sup>. After checking their presence in the difference map, all but water H atoms were fixed geometrically and allowed to ride on the attached atoms. The water H atoms were refined isotropically and rotating-group refinement was used for the methyl group.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graph-

ics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1404). Services for accessing these data are described at the back of the journal.

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## Diazidobis(1,10-phenanthroline-*N,N'*)-manganese(II)

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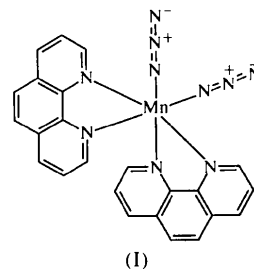
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## Abstract

The crystal structure of the title complex, [Mn(N<sub>3</sub>)<sub>2</sub>-(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>], shows the two 1,10-phenanthroline ligands and the two azido anions to be in a distorted octahedral arrangement around the Mn<sup>II</sup> atom, with the two azido ions in *cis* positions.

## Comment

In recent years, the azido ion has been shown to be a very versatile ligand in the field of coordination chemistry. The copper–azido system has been thoroughly studied from both the synthetic and magnetic points of view (Thompson *et al.*, 1995). At present, the chemistry of manganese–azido-bridged systems has been found to be characterized by the high dimensionality of the resulting complexes; in one case only, a dinuclear compound was obtained, while all the other derivatives are one-, two- or three-dimensional compounds (Escuer *et al.*, 1998). We report here the structure of a mononuclear manganese–azido complex, (I), with the two azido ions in *cis* positions.



The asymmetric unit of (I) consists of one-half of the title complex, with the other half generated by twofold symmetry; the Mn1 atom lies on the twofold axis. The two 1,10-phenanthroline (phen) ligands and

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