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A binuclear iminodiacetato–copper(II) complex with the *N*,*N*′-bis(pyridin-4-ylmethylene)hydrazine ligand as spacer

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Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.004 Å
R factor = 0.047
wR factor = 0.116
Data-to-parameter ratio = 18.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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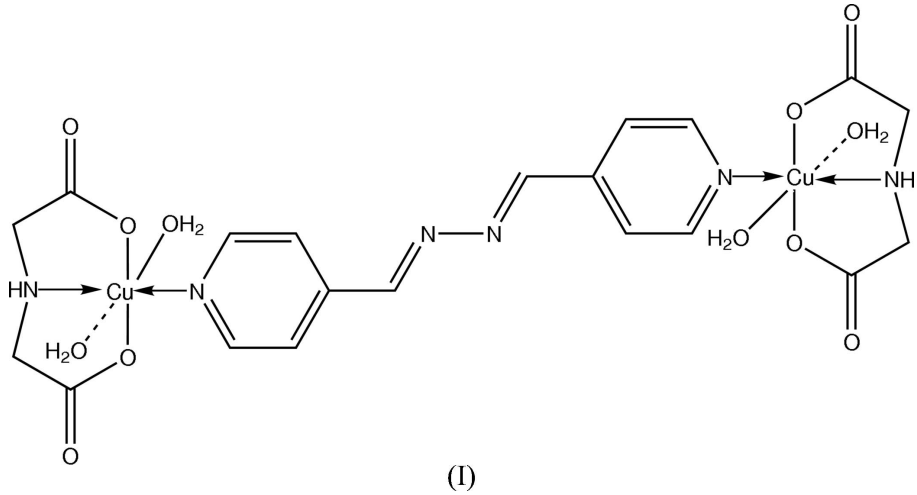
The centrosymmetric title compound, μ-*N*,*N*′-bis(pyridin-4-ylmethylene)hydrazine-bis[diaqua(iminodiacetato)copper(II)], $[Cu_2(C_4H_5NO_4)_2(C_{12}H_{10}N_4)(H_2O)_4]$, features a *trans*-$N_2O_4$ donor set that defines a heavily distorted octahedral geometry. Coordination is provided by a tridentate iminodiacetate (ida) dianion, one end of a bidentate bridging *N*,*N*′-bis(pyridin-4-ylmethylene)hydrazine ligand, which is disposed about a centre of inversion, and two water molecules. Extensive hydrogen bonding leads to a cohesive crystal structure.

Comment

Carboxylates have been used extensively in the synthesis of di- and polynuclear metal complexes (Rosi *et al.*, 2002; Zhang *et al.*, 2002). Iminodiacetic acid (H_2ida) is one such ligand, finding widespread synthetic applications. For example, using iminodiacetato–copper(II) as a building block and polypyridine-type molecules as common cross-linkers, several oligomeric complexes with aesthetically pleasing structural forms have been reported in recent times (Arena *et al.*, 1978; Murtha & Walton, 1974; Tribet *et al.*, 2003; Nardin *et al.*, 1980; Mukhopadhyay *et al.*, 2004). We report here the X-ray crystal structure analysis of a dinuclear iminodiacetato–copper(II) complex, $[(H_2O)_2$(ida)Cu-(μ-pmz)-Cu(ida)$(OH_2)_2]$, (I) (ida = iminodiacetate), involving the new ligand *N*,*N*′-bis(pyridin-4-ylmethylene)hydrazine (pmz) as a linear spacer.



(I)

The molecular structure of dinuclear (I) (Fig. 1 and Table 1) is centrosymmetric. Each Cu atom is coordinated by a tridentate ida dianion, two water molecules and one end of a

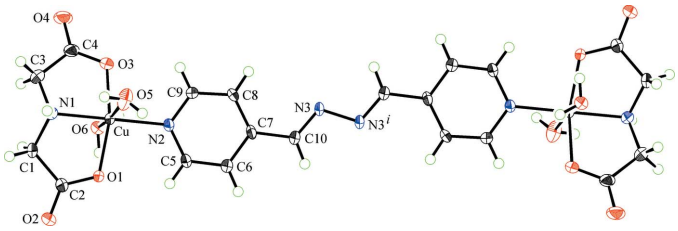


Figure 1
The molecular structure and crystallographic numbering scheme. Displacement ellipsoids are shown at the 35% probability level. [Symmetry code: (i) $2-x, -y, 2-z$.]

μ_2-bridging pmz ligand; the latter is situated about a centre of inversion. To a first approximation the *trans*-N_2O_4 donor set defines an octahedral coordination geometry about the Cu atom but significant distortions exist. The main deviation from ideal octahedral is found in the large separation between the Cu and O6 atoms. Hence, the Cu—O6 distance of 2.854 (3) Å is approximately 0.5 Å longer than the Cu—O5 distance of 2.338 (2) Å, which, in turn, is over 0.3 Å longer than the Cu—$O_{carboxylate}$ distances (see Table 1). This disparity is expected, considering that the Cu^{II} species is a Jahn–Teller ion. The Cu—N1/N2 bond distances are experimentally equivalent at 1.984 (2) and 1.993 (2) Å, respectively. At the other extreme, the coordination geometry might be described as square pyramidal with the water molecules associated along the tetragonal axis. In this description, the deviations of atoms O1, O3, N1 and N2 from their least-squares plane are −0.2050 (12), −0.2005 (11), 0.2232 (12) and 0.1823 (10) Å, respectively, with the Cu atom displaced 0.1423 (12) Å from this plane in the direction of more tightly held atom O5. The geometric parameters defining the ida dianion are as expected, and the five-membered chelate rings formed are close to planar, as revealed from the torsion angle data collected in Table 1. In the centrosymmetric pmz ligand, despite the observed planarity about the central portion, and the fact that the entire molecule is essentially planar, *e.g.* the C6/C7/C10/N3 torsion angle is −177.8 (3)°, there appears to be relatively little delocalization of π-electron density, as seen in the N3—N3^{i} and N3═C10 bond distances of 1.414 (4) and 1.267 (3) Å, respectively [symmetry code: (i) $2-x, -y, 2-z$].

The crystal structure is characterized by a number of hydrogen-bonding interactions, as summarized in Table 2. Each of the acidic O—H and N—H atoms participates in a hydrogen bond to an O- or N-atom acceptor. As both non-coordinating carboxylate O atoms, O2 and O4, as well as the azo N atom, N3, function as hydrogen-bond acceptors, each dinuclear unit has 16 points of contact with neighbouring molecules. The most obvious motif mediated by hydrogen bonding is a zigzag chain, as emphasized in the view down the crystallographic *a* axis shown in Fig. 2. The N-bound and one of the O5 H atoms at one end of one molecule each link a common carbonyl O4 atom derived from an effectively orthogonal molecule, and in this way the zigzag chain is propagated. The other contacts link translationally related chains to form a stable three-dimensional array with the zigzag

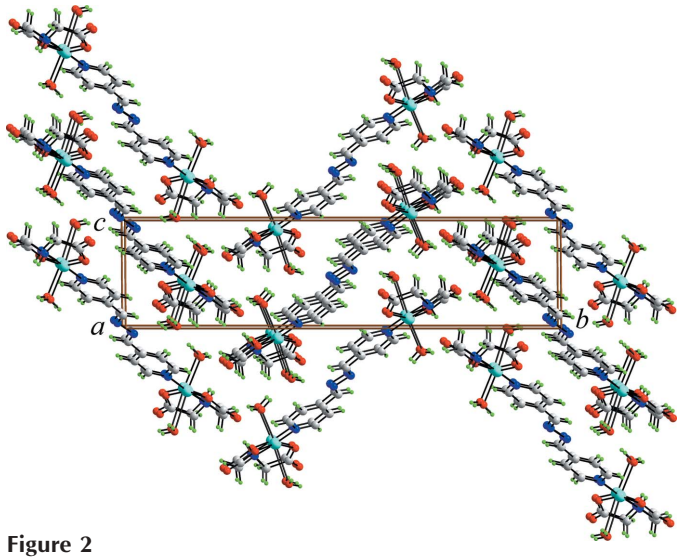


Figure 2
The crystal packing, viewed approximately down the *a* direction.

chains stacked along the *a* direction. The closest Cu···Cu separation in the structure occurs between atoms belonging to adjacent layers and therefore is greater than 6.6 Å. As can be seen from Fig. 2, the structure can also be described as being composed of layers along the *b* direction of alternating coordination polyhedra and spacer ligands.

Experimental

Synthesis and preparation of the crystal involved the preparation of the ligand and subsequent synthesis of the complex. Copper acetate dihydrate, pyridine 4-carboxaldehyde and hydrazine hydrate were purchased from Aldrich. All other chemicals were commercially available and used as received. Solvents were reagent grade. The sodium salt of iminodiacetic acid was prepared as described by Mukhopadhyay *et al.* (2004). For the synthesis of the ligand pmz, pyridine 4-carboxaldehyde (3.21 g, 30 mmol) and hydrazine hydrate (0.75 g, 15 mmol) were mixed in methanol (20 ml) and stirred for 2 h. The resulting solution was evaporated to approximately 5 ml, and a yellow solid precipitated. This was collected by filtration and recrystallized from hot methanol affording yellow needles, which were dried *in vacuo* over fused $CaCl_2$. Yield 2.86 g, 91%. Analysis calculated for $C_{12}H_{10}N_4$: C 68.57, H 4.76, N 26.67; found: C 67.95, H 4.56, N 26.12%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, p.p.m.): δ 8.76 (4H, *d*, 5.97 Hz), 8.57 (2H, *s*), 7.70 (4H, *d*, 5.97 Hz). For the synthesis of (I), to an aqueous solution of sodium iminodiacetate (0.09 g, 0.5 mmol) was added dropwise a solution of copper(II) acetate dihydrate (0.10 g, 0.5 mmol) in hot methanol (30 ml). The resultant solution was stirred for 30 min, during which time a blue solution was obtained. This was treated with pmz (0.053 g, 0.25 mmol) dissolved in methanol (10 ml), and a deep-blue solution was obtained. It was stirred for approximately 10 min, and a sky-blue compound was precipitated out and removed by filtration. The filtrate was diluted with water (10 ml). The resulting solution was left in air for slow evaporation. After about 3–4 weeks a blue–green crystalline compound was obtained along with X-ray diffraction quality crystals. This was filtered off, washed with acetone and dried *in vacuo*. Yield 0.043 g, 26%. Analysis calculated for $C_{20}H_{28}Cu_2N_6O_{12}$: C 35.76, H 4.17, N 12.51%; found: C 35.03, H 4.22, N 12.05%.

Crystal data

$[Cu_2(C_4H_5NO_4)_2(C_{12}H_{10}N_4)(H_2O)_4]$
M_r = 671.58
Monoclinic, $P2_1/n$
a = 6.5799 (6) Å
b = 27.775 (3) Å
c = 7.0321 (6) Å
β = 103.190 (4)°
V = 1251.2 (2) Å^3
Z = 2
D_x = 1.782 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1612 reflections
θ = 3.1–24.3°
μ = 1.78 mm^{-1}
T = 223 (2) K
Needle, blue
0.38 × 0.08 × 0.04 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.729, T_{max} = 0.931
10424 measured reflections
3624 independent reflections
2571 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 30.0°
$h = -8 \rightarrow 9$
$k = -39 \rightarrow 37$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.116
S = 1.01
3624 reflections
193 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9580 (19)	O2—C2	1.225 (3)
Cu—O3	1.965 (2)	O3—C4	1.265 (3)
Cu—O5	2.338 (2)	O4—C4	1.240 (4)
Cu—O6	2.854 (3)	N1—C1	1.467 (4)
Cu—N1	1.984 (2)	N1—C3	1.468 (4)
Cu—N2	1.993 (2)	N3—N3^{i}	1.414 (4)
O1—C2	1.272 (3)	N3—C10	1.267 (3)
O1—Cu—O3	156.67 (9)	Cu—O1—C2	114.40 (18)
O1—Cu—N1	84.36 (9)	Cu—O3—C4	114.48 (19)
O1—Cu—N2	95.21 (9)	Cu—N1—C1	107.69 (17)
O1—Cu—O5	107.63 (9)	Cu—N1—C3	108.87 (19)
O1—Cu—O6	83.23 (8)	Cu—N2—C5	121.39 (19)
O3—Cu—O5	93.53 (9)	Cu—N2—C9	120.33 (18)
O3—Cu—O6	76.29 (7)	C10—N3—N3^{i}	112.7 (3)
O3—Cu—N1	85.04 (9)	O1—C2—O2	124.8 (3)
O3—Cu—N2	96.63 (9)	O1—C2—C1	116.7 (2)
O5—Cu—O6	168.80 (8)	O2—C2—C1	118.4 (3)
O5—Cu—N1	92.47 (9)	O3—C4—O4	124.7 (3)
O5—Cu—N2	84.20 (9)	O3—C4—C3	117.8 (3)
O6—Cu—N1	91.29 (8)	O4—C4—C3	117.5 (3)
O6—Cu—N2	92.25 (8)	N3—C10—C7	123.3 (3)
N1—Cu—N2	176.36 (10)		
Cu—O1—C2—C1	−4.7 (3)	N1—C3—C4—O3	4.2 (4)
N1—C1—C2—O1	−14.1 (4)	C8—C7—C10—N3	1.9 (5)
Cu—O3—C4—C3	5.4 (3)	C6—C7—C10—N3	−177.8 (3)

Symmetry code: (i) $-x+2, -y, -z+2$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4^{ii}	0.92	2.17	3.073 (3)	165
O5—H5A···O4^{ii}	0.84 (1)	1.86 (1)	2.678 (4)	165
O5—H5B···O6^{iii}	0.84 (1)	1.94 (1)	2.770 (3)	174
O6—H6A···O2^{iv}	0.84 (1)	1.92 (1)	2.743 (3)	167
O6—H6B···N3^{v}	0.84 (1)	2.17 (1)	3.000 (3)	172

Symmetry codes: (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x, y, z+1$; (iv) $x+1, y, z$; (v) $x-1, y, z-1$.

The C- and N-bound H atoms were included in the riding-model approximation, with N—H = 0.92 Å, C(sp^2)—H = 0.94 Å and C—H(methylene) = 0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(N,C). The water H atoms were refined with a distance restraint of O—H = 0.84 (1) Å and U_{iso}(H) = 1.5U_{eq}(O). The maximum residual electron density peak was located 0.82 Å from the Cu atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *DIRDIF92 PATTY* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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