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

The centrosymmetric title compound, μ-N,N'-bis(pyridin-4-ylmethylene)hydrazine-bis[diaqua(iminodiacetato)copper(II)], [Cu₂(C₄H₅NO₄)₂(C₁₂H₁₀N₄)(H₂O)₄], features a trans-N₂O₄ 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 (H₂ida) is one such ligand, finding widespread synthetic applications. For example, using iminodiacetato–copper(II) as a building block and poly-pyridine-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, [(H₂O)₂(ida)Cu-(μ-p mz)-Cu(ida)(OH₂)]₂, (I) (ida = iminodiacetate), involving the new ligand N,N'-bis(pyridin-4-ylmethylene)hydrazine (pmz) as a linear spacer.

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
The C10 bond distances of 1.414 (4) and 1.267 (3) Å, respectively, with the Cu atom displaced 0.1423 (12) Å from the entire molecule is essentially planar, observed planarity about the central portion, and the fact that Table 1. In the centrosymmetric pmz ligand, despite the planar, as revealed from the torsion angle data collected in and the five-membered chelate rings formed are close to geometric parameters defining the ida dianion are as expected, this plane in the direction of more tightly held atom O5. The torsion angle is/C0

Crystallographic bonding is a zigzag chain, as emphasized in the view down the molecules. The most obvious motif mediated by hydrogen dinuclear unit has 16 points of contact with neighbouring azo N atom, N3, function as hydrogen-bond acceptors, each coordinating carboxylate O atoms, O2 and O4, as well as the hydrogen bond to an O- or N-atom acceptor. As both non-acidic O—H and N—H atoms participate in a 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 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) dissolved in 40 ml methanol were 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 CaCl₂. Yield 2.86 g, 91%. Analysis calculated for C₁₀H₁₂N₂O₄: C 35.76, H 4.76, N 12.67; found: C 35.76, H 4.76, N 12.51%.1H NMR (300 MHz, CDCl₃, 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 formed. 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 C₂₂H₂₅Cu₂N₆O₁₂: C 35.76, H 4.17, N 12.51%; found: C 35.03, H 4.22, N 12.05%.

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.]

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

[Cu₂(C₄H₅NO₄)₂(C₁₂H₁₀N₄)(H₂O)₄]

Mo Ka radiation

Cell parameters from 1612 reflections

\( a = 6.5799 (6) \, \text{Å} \)
\( b = 27.775 (3) \, \text{Å} \)
\( c = 7.0321 (6) \, \text{Å} \)
\( \beta = 103.190 (4) ^\circ \)
\( V = 1251.2 (2) \, \text{Å}³ \)
\( Z = 2 \)

Data collection

Bruker SMART CCD diffractometer

\( V = 1251.2 (2) \, \text{Å}³ \)
\( \theta = 7.0321 (6) \, \text{Å} \)
\( \mu = 1.78 \, \text{mm}^{-1} \)

Absorption correction: multi-scan

\( \mu = 1.78 \, \text{mm}^{-1} \)

\( T = 223 (2) \, \text{K} \)

Needle, blue

Data collection:

SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 1997); 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.

This work was supported by the Council of Scientific and Industrial Research (CSIR), New Delhi. Two of us (NK and PBC) also thank the CSIR for the award of research fellowships. The Queensland Government, for the award of a Smart Returns Fellowship to ERTT, is also thanked.

Table 2

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H—A</th>
<th>D—A</th>
<th>D—H—A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H1...O4i</td>
<td>0.92</td>
<td>2.17</td>
<td>3.073 (3)</td>
<td>165</td>
</tr>
<tr>
<td>O5—H5A...O4iv</td>
<td>0.84 (1)</td>
<td>1.86 (1)</td>
<td>2.678 (4)</td>
<td>165</td>
</tr>
<tr>
<td>O5—H5B...O6ivii</td>
<td>0.84 (1)</td>
<td>1.94 (1)</td>
<td>2.770 (3)</td>
<td>174</td>
</tr>
<tr>
<td>O6—H6A...O2vi</td>
<td>0.84 (1)</td>
<td>1.92 (1)</td>
<td>2.743 (3)</td>
<td>167</td>
</tr>
<tr>
<td>O6—H6B...N3v</td>
<td>0.84 (1)</td>
<td>2.17 (1)</td>
<td>3.000 (3)</td>
<td>172</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) \( x, -\frac{1}{2} - y, z + \frac{1}{2} \); (ii) \( x, y, z + 1 \); (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(sp²)—H = 0.94 Å and C—H(methylene) = 0.98 Å, and with \( U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(N,C) \). 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.

References


Bruker (2000). SMART, SAINT (Versions 5.6) and SADABS (Version 2.01). Bruker AXS Inc., Madison, Wisconsin, USA.


