

## [Cu(phen)<sub>2</sub>(μ-IDA)Cu(phen)](ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>OH: tridentate and monodentate binding to two copper(II) species by a bridging ligand

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Received 13 April 2004

Accepted 25 August 2004

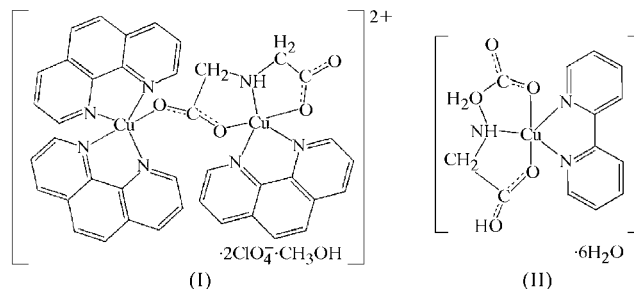
Online 25 September 2004

The stoichiometric reaction of 1,10-phenanthroline (phen), iminodiacetic acid (IDA-H<sub>2</sub>) and Cu(ClO<sub>4</sub>)<sub>2</sub> in a H<sub>2</sub>O-CH<sub>3</sub>OH (2:1) solution yields μ-iminodiacetato-2:1κ<sup>4</sup>O,N,O':O'-tris(1,10-phenanthroline)-1κ<sup>4</sup>N,N';2κ<sup>2</sup>N,N'-dicopper(II) diperchlorate methanol solvate, [Cu<sub>2</sub>(C<sub>4</sub>H<sub>5</sub>NO<sub>4</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>OH. The IDA ligand bridges the two Cu<sup>II</sup> ions *via* a carboxylate group and uses one further N and an O atom of the second carboxylate group to complete a *fac*-tridentate coordination at one Cu centre. A phen ligand completes a distorted square-pyramidal coordination at this metal atom, although there is weak coordination by a perchlorate O atom at a sixth position. The second Cu centre has a distorted trigonal-bipyramidal coordination to two phen moieties and a carboxylate O atom.

### Comment

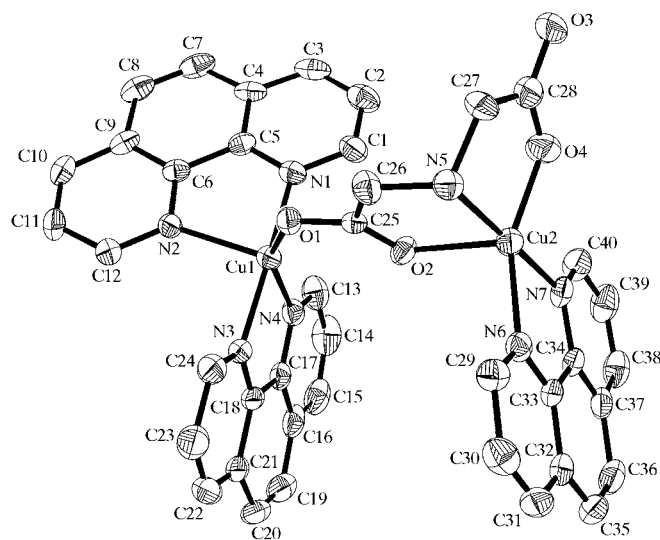
On account of the tridentate chelating property of the iminodiacetate (IDA) ligand and the flexibility of the Cu<sup>II</sup> coordination stereochemistry, extensive research has been devoted to the structures of a variety of {Cu(IDA)(H<sub>2</sub>O)<sub>2</sub>}<sub>n</sub> mixed-ligand complexes of Cu<sup>II</sup>, with IDA-like groups as primary ligands and N-heterocyclic donors as auxiliary ligands (Bugella-Altamirano, Choquesillo *et al.*, 2002; Bugella-Altamirano, González-Pérez *et al.*, 2002; Chatterjee & Stephen, 2001; de la Cueva *et al.*, 1998). Such ternary complexes are bioinorganic model compounds for mono- and dinuclear copper proteins. In this context, the Cu<sup>II</sup> complex serves as a metal centre, while the tridentate IDA ligand or IDA derivative acts as a protein-like moiety and the N-heterocyclic donors play the role of substrate or inhibitor. All mixed-ligand complexes having a Cu-IDA-like-N-heterocyclic donor ratio of 1:1:2 exhibit an IDA-like ligand in a *fac*-chelating conformation. In contrast, complexes with an equimolar Cu-IDA-like-N-heterocyclic donor ratio (1:1:1) have the Cu<sup>II</sup> ion in a distorted

square-pyramidal coordination (4+1 type), or more rarely in an elongated octahedral coordination (4+2 or 4+1+1 type), and the IDA-like ligand adopts a *mer*-tridentate chelating role (Brandi-Blanco *et al.*, 2003; Román-Alpiste *et al.*, 1999). It was demonstrated that the stoichiometry and coordination character of the auxiliary ligand influence the coordination geometry of IDA. Compared with 2,2'-bipyridyl (Abarca *et al.*, 1993), 1,10-phenanthroline (phen) possesses a stronger coordination ability. On this basis, we selected phen as the secondary ligand and synthesized the title dinuclear Cu<sup>II</sup> complex, (I).

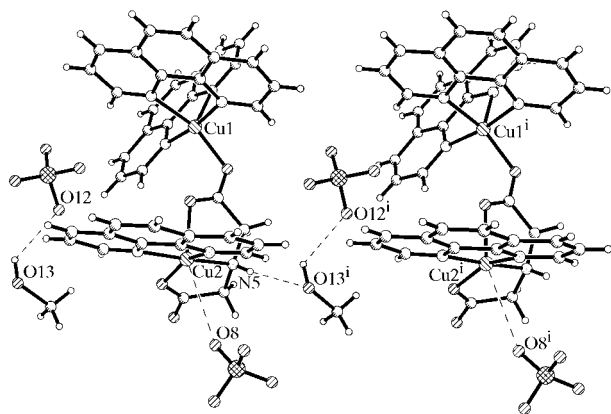


The molecular structure and crystal packing of (I) are illustrated in Figs. 1–3. Selected geometric parameters are listed in Table 1. In this new mixed-ligand dinuclear complex, IDA serves as a bridging ligand linking two different moieties, *viz.* [Cu(phen)<sub>2</sub>]<sup>2+</sup> and [Cu(phen)]<sup>2+</sup>, *via* a carboxylate group. Unexpectedly, the two Cu<sup>II</sup> ions exhibit totally different coordination geometries. The coordination polyhedron around atom Cu1 can be described as a distorted trigonal bipyramid, similar to those reported previously (Boys & Escobar, 1981; Anderson, 1975; Wei & Yang, 2004).

We are primarily interested in the coordination around atom Cu2, which is a distorted square pyramid to a bidentate



**Figure 1**  
The molecular structure of (I), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms, solvent molecules and counter-ions have been omitted for clarity.



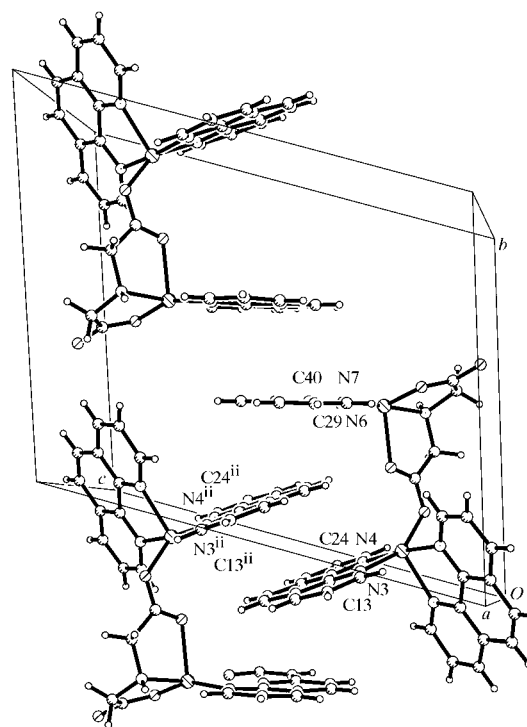
**Figure 2**  
The hydrogen-bonding network and octahedral coordination geometry around atom Cu2. [Symmetry code: (i)  $x - 1, y, z$ .]

phen ligand and an  $O,N,O'$ -tridentate chelating IDA ligand. Atom O2 of IDA occupies the apical position. The atoms in the basal plane, *viz.* N6 and N7 from phen, and N5 and O4 from IDA, are displaced from the least-squares plane by distances ranging from  $-0.24$  (2) to  $0.23$  (3) Å, with a tetrahedral distortion. Atom Cu2 is displaced by  $0.13$  (4) Å from the mean plane towards atom O2, a distance almost twice as far as the value reported for (2,2'-bipyridyl)(iminodiacetato)copper(II) hexahydrate, (II) (Abarca *et al.*, 1993).

All three phen ligands in (I) have a nearly planar conformation [maximum deviation =  $0.048$  (6) Å]. Atom N7 of phen is in a *trans* position to atom N5 of IDA. The entry of atom N6 forces the IDA–Cu2 chelate ring to bend along the Cu2–N5 bond. Thus, the IDA ligand forms two five-membered chelate rings sharing the Cu2–N5 bond, with a dihedral angle of  $71.34$  (19)°, adopting a *fac*-tridentate chelating role in accordance with the 1:1:2 coordination rule. In addition, atom Cu2 is weakly coordinated by a sixth atom, O8 of the  $\text{ClO}_4^-$  anion, with a Cu2···O8 distance of  $3.232$  (11) Å (Fig. 2). Therefore, the overall coordination configuration around Cu2 is actually a distorted octahedron. Thus, IDA plays dual roles, as a tridentate chelate to Cu2 and as a bridge between Cu1 and Cu2.

In the title dinuclear complex, it is noticeable that the source of the tridentate chelate atoms of IDA is different from those of the earlier reported complexes. In these, no matter which conformation IDA assumes, *mer* or *fac*, the carboxylate group is distorted by coordination so that the longer C–O bond is bound to the metal. However, in (I), one carboxylate group binds to two Cu atoms and it is notable that the longer C–O bond is to Cu1 and the shorter to Cu2, where it is part of the tridentate coordination. This is in accord with the corresponding Cu–O bonds, that to Cu2 being longer than that to Cu1. Furthermore, while the binding to Cu1 takes place in the equatorial plane of the trigonal bipyramid, that to Cu2 lies on the Jahn–Teller axis (along with the perchlorate) and would be expected to lengthened.

Details of the hydrogen-bonding geometry of (I) are listed in Table 2. As illustrated in Fig. 2, the packing has a network of



**Figure 3**  
The  $\pi$ – $\pi$  stacking interactions in (I). Solvent molecules and counter-ions have been omitted for clarity. [Symmetry code: (ii)  $1 - x, -y, 1 - z$ .]

hydrogen bonds. These are mainly formed between methanol molecules, atom N5 of IDA and the O atoms of the  $\text{ClO}_4^-$  anion.

Furthermore, a more interesting phenomenon observed is shown in Fig. 3. Pairs of phen ligands from neighbouring complexes are interleaved to form a stack along the *b* axis. Phen planes 1 (C13A–C24A/N3A/N4A) and 2 (C13–C24/N3/N4) are symmetry related and oriented in a parallel fashion, the shortest interatomic distance, *viz.* C18···C20( $1 - x, -y, 1 - z$ ), being  $3.294$  (11) Å, which is shorter than the distance (3.4 Å) between neighbouring base pairs in DNA (Neidle, 1999), indicating significant  $\pi$ – $\pi$  packing interactions. Phen plane 3 (C29–C40/N6/N7) is non-parallel to plane 1, the angle between them being  $20.0$  (5)°. The shortest interatomic distance, *viz.* C19···C33( $1 - x, -y, 1 - z$ ), is  $3.126$  (11) Å, showing an even stronger  $\pi$ – $\pi$  stacking interaction. Therefore,  $\pi$ – $\pi$  stacking interactions dominate throughout the crystal structure of (I), stabilizing the crystal packing together with the hydrogen-bonding interactions.

## Experimental

For the preparation of the title compound, 1,10-phenanthroline (0.0793 g, 0.4 mmol), iminodiacetic acid (0.0266 g, 0.2 mmol) and  $\text{Cu}(\text{ClO}_4)_2$  (0.0766 g, 0.4 mmol) were dissolved in a  $\text{H}_2\text{O}$ – $\text{CH}_3\text{OH}$  (2:1) solution. The mixture was refluxed for 30 min with stirring and then cooled slowly, before being filtered and kept at room temperature. Blue block-shaped crystals of (I) grew after two weeks.

Crystal data

[Cu<sub>2</sub>(C<sub>4</sub>H<sub>5</sub>NO<sub>4</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]-  
(ClO<sub>4</sub>)<sub>2</sub>·CH<sub>4</sub>O  
M<sub>r</sub> = 1029.74  
Triclinic, P $\bar{1}$   
a = 10.511 (3) Å  
b = 13.707 (4) Å  
c = 15.551 (5) Å  
α = 72.785 (4)°  
β = 82.336 (4)°  
γ = 78.048 (5)°  
V = 2087.6 (11) Å<sup>3</sup>

Data collection

Bruker SMART 1K CCD area-  
detector diffractometer  
φ and ω scans  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 2000)  
T<sub>min</sub> = 0.710, T<sub>max</sub> = 0.710  
8597 measured reflections

Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.077  
wR(F<sup>2</sup>) = 0.179  
S = 1.03  
7184 reflections  
587 parameters

Z = 2  
D<sub>x</sub> = 1.638 Mg m<sup>-3</sup>  
Mo Kα radiation  
Cell parameters from 2337  
reflections  
θ = 2.3–22.0°  
μ = 1.22 mm<sup>-1</sup>  
T = 297 (2) K  
Block, blue  
0.30 × 0.30 × 0.30 mm  
7184 independent reflections  
4501 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.032  
θ<sub>max</sub> = 25.0°  
h = -11 → 12  
k = -7 → 16  
l = -18 → 18

H-atom parameters constrained  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0826P)<sup>2</sup>]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δσ)<sub>max</sub> < 0.001  
Δρ<sub>max</sub> = 0.71 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.43 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.956 (4)	Cu2—N6	2.043 (5)
Cu1—N1	1.984 (5)	Cu2—O2	2.205 (4)
Cu1—N3	1.986 (5)	O1—C25	1.266 (7)
Cu1—N4	2.071 (5)	O2—C25	1.224 (7)
Cu1—N2	2.150 (5)	O3—C28	1.238 (8)
Cu2—O4	1.907 (5)	O4—C28	1.256 (9)
Cu2—N7	1.975 (5)	N5—C26	1.465 (8)
Cu2—N5	1.997 (5)	N5—C27	1.472 (7)
O1—Cu1—N1	94.56 (18)	O4—Cu2—N7	92.2 (2)
O1—Cu1—N3	93.7 (2)	O4—Cu2—N5	86.5 (2)
N1—Cu1—N3	171.7 (2)	N7—Cu2—N5	176.2 (2)
O1—Cu1—N4	152.25 (19)	O4—Cu2—N6	156.0 (2)
N1—Cu1—N4	91.9 (2)	N7—Cu2—N6	81.2 (2)
N3—Cu1—N4	81.1 (2)	N5—Cu2—N6	101.3 (2)
O1—Cu1—N2	109.21 (18)	O4—Cu2—O2	102.52 (19)
N1—Cu1—N2	80.3 (2)	N7—Cu2—O2	95.05 (18)
N3—Cu1—N2	96.21 (19)	N5—Cu2—O2	81.80 (18)
N4—Cu1—N2	98.48 (19)	N6—Cu2—O2	101.02 (17)
N1—Cu1—O1—C25	-85.2 (4)	N5—Cu2—O2—C25	-2.3 (4)
N3—Cu1—O1—C25	95.6 (4)	N6—Cu2—O2—C25	97.8 (4)
N4—Cu1—O1—C25	17.7 (6)	N7—Cu2—O4—C28	-172.1 (5)
N2—Cu1—O1—C25	-166.5 (4)	N5—Cu2—O4—C28	11.4 (5)
O4—Cu2—O2—C25	-86.8 (4)	N6—Cu2—O4—C28	-98.9 (7)
N7—Cu2—O2—C25	179.8 (4)		

All H atoms were treated as riding atoms, with C—H(CH) = 0.93, C—H(CH<sub>2</sub>) = 0.97, C—H(CH<sub>3</sub>) = 0.96, N—H = 0.80 and O—H =

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O13—H13A...O12	0.96	2.41	3.064 (17)	125
N5—H5...O13 <sup>i</sup>	0.80	2.26	3.027 (11)	163

Symmetry code: (i) x - 1, y, z.

0.96 Å, and with U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(CH, NH, CH<sub>2</sub>) or 1.5U<sub>eq</sub>(CH<sub>3</sub>, OH).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 1999); software used to prepare material for publication: SHELXTL/PC.

The work was supported financially by the National Natural Science Foundation of China (grant No. 20171031). The authors are indebted to Professor Miao-Li Zhu for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1091). Services for accessing these data are described at the back of the journal.

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