

## Aqua(2,2'-bi-1*H*-imidazole)chloro-copper(II) chloro(iminodiacetato)-copper(II) monohydrate

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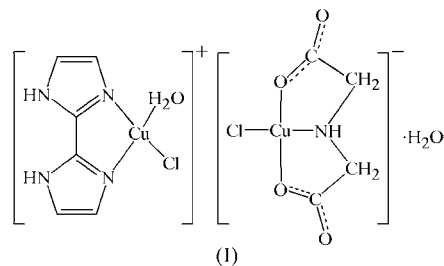
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In the title compound,  $[\text{CuCl}(\text{C}_6\text{H}_6\text{N}_4)(\text{H}_2\text{O})][\text{Cu}(\text{C}_4\text{H}_5\text{NO}_4)\text{Cl}]\cdot\text{H}_2\text{O}$ , the  $\text{Cu}^{\text{II}}$  atom in the cation is coordinated by one  $\text{Cl}^-$  ion, two N atoms of the 2,2'-biimidazole ligand and one aqua ligand. Within the anion, the  $\text{Cu}^{\text{II}}$  atom is bonded to one  $\text{Cl}^-$  ion, and one N and two O atoms of the iminodiacetate ligand. Neighbouring cations and anions are connected to each other by  $\text{Cu}\cdots\text{Cl}$  semi-coordination bonds of 2.830 (12) and 3.071 (12) Å, forming a  $\text{Cu}_2\text{Cl}_2$  rectangular unit. The dinuclear units further link into a polymeric chain along the *a* axis through  $\text{Cu}\cdots\text{O}_{\text{aqua}}$  interactions of 2.725 (3) Å. Including the long coordination bonds, the geometries around the Cu atoms in the cation and anion are square-pyramidal and distorted octahedral, respectively.

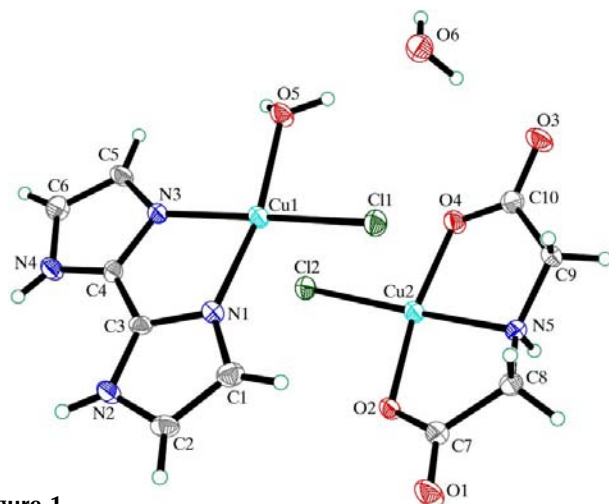
### Comment

The syntheses of some 3*d* metal complexes with either neutral or deprotonated 2,2'-biimidazole were reported for the first time by Holmes *et al.* (1961). Since then, the coordination chemistry and biochemical properties of 2,2'-biimidazole have been investigated by several workers (Usón & Gimeno, 1981; Liu & Su, 1996; Tadokoro & Nakasuji, 2000; Casas *et al.*, 2003; Zhang *et al.*, 2003; Mano *et al.*, 2005). This is not only because 2,2'-biimidazole ( $\text{H}_2\text{biim}$ ) is a ligand that can coordinate to transition metals in non-deprotonated ( $\text{H}_2\text{biim}$ ), mono-deprotonated ( $\text{Hbiim}^-$ ) and bis-diprotonated ( $\text{biim}^{2-}$ ) forms, but also because it is important as a biomimetic ligand, the imidazole ring of histidine having been frequently found in a variety of proteins and metalloenzymes (Cancela *et al.*, 2001; Sang *et al.*, 2002). In order to model the physical and chemical behaviour of natural systems, either unsubstituted or substituted 2,2'-biimidazole has been used as a ligand to design synthetic analogues of metalloenzymes. Thus, a variety of geometries and ligating modes of  $\text{H}_2\text{biim}$  to  $\text{Cu}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{V}^{\text{II}}$ ,  $\text{Ag}^{\text{I}}$  and  $\text{Cd}^{\text{II}}$  have been investigated (Bencini & Mani, 1988; Sigel *et al.*, 2000; Cancela *et al.*, 2001; Mori & Miyoshi, 2004; Atencio *et al.*, 2004). In addition, on account of the

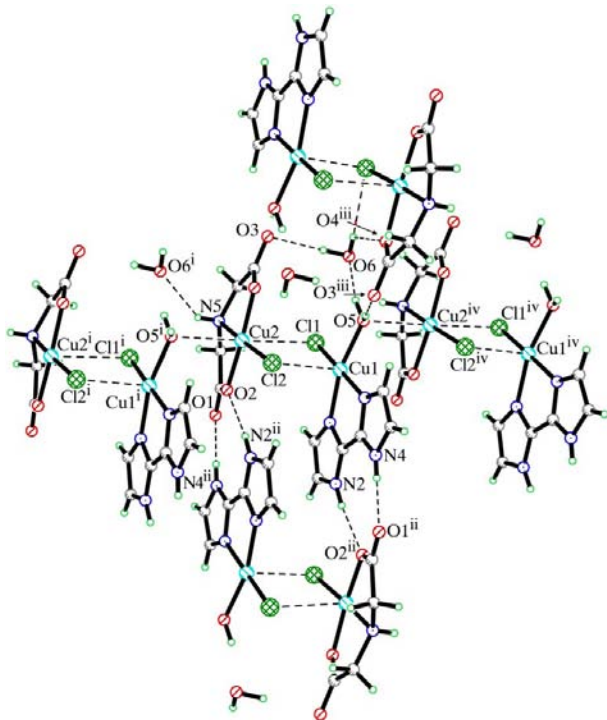
tridentate chelating property of the iminodiacetate (ida) ligand and the flexibility of the  $\text{Cu}^{\text{II}}$  coordination stereochemistry, we are interested in copper complexes with mixed ligands. We report here the synthesis and crystal structure of the title compound, (I).



The asymmetric unit of (I) contains one  $[\text{CuCl}(\text{H}_2\text{biim})(\text{H}_2\text{O})]^+$  cation, one  $[\text{Cu}(\text{ida})\text{Cl}]^-$  anion and one solvent water molecule (Fig. 1). Within the cation, atom Cu1 is bonded to atoms N1 and N3 of the 2,2'-biimidazole ligand, atom O5 of the aqua ligand and atom Cl1. The Cu—N and Cu—Cl bond lengths are 1.996 (3)–2.003 (3) and 2.2503 (12) Å, respectively (Table 1), comparable with those reported previously [1.98 (1)–2.17 (4) and 2.254 (4) Å; Bencini & Mani, 1988; Liu & Su, 1996]. The coordinated atoms around Cu1 are coplanar, with an r.m.s. deviation of 0.09 Å. In the anion, atom Cu2 is coordinated by an *O,N,O'*-tridentate ida ligand (with two deprotonated carboxylate groups) and atom Cl2. The coordinated atoms and Cu2 are coplanar, with an r.m.s. deviation of 0.02 Å. The cations and anions are arranged alternately and vertically along the *a* axis. Neighbouring cations and anions are connected to each other *via*  $\text{Cu1}\cdots\text{Cl2}$  and  $\text{Cu2}\cdots\text{Cl1}$  interactions of 2.830 (12) and 3.071 (12) Å, respectively, forming a neutral dinuclear unit through an irregular  $\text{Cu1}/\text{Cl1}/\text{Cu2}/\text{Cl2}$  rectangle (Fig. 2). These neutral dinuclear units are further linked into a polymeric chain along the *a* axis by a  $\text{Cu2}\cdots\text{O5}$  interaction of 2.725 (3) Å. Including the semi-coordination bonds, the configuration around Cu1 in the cation is square pyramidal, while Cu2 in the anion has a



**Figure 1**  
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
The hydrogen-bond network and weak coordination (dashed lines) in (I). [Symmetry codes: (i)  $1 + x, y, z$ ; (ii)  $1 - x, 2 - y, -z$ ; (iii)  $1 - x, 2 - y, 1 - z$ ; (iv)  $x - 1, y, z$ .]

distorted octahedral coordination, with atoms O5 and Cl1 at the apical positions.

The title compound is different from previously reported biimidazole copper complexes, not only in its constituent species and their structures but also in the interactions between the species. For example, in  $[\text{Cu}_{1.5}\text{Cl}_3(\text{H}_2\text{biim})_2]^{2+}$ , there are two species,  $[\text{CuCl}_2(\text{H}_2\text{biim})]$  and  $[\text{Cu}(\text{H}_2\text{biim})_2]^{2+}$ , with a  $\text{Cl}^-$  counter-ion. The  $[\text{CuCl}_2(\text{H}_2\text{biim})]$  molecules are linked into a polymeric structure by one of the coordinated Cl atoms acting as a bridge, and the  $[\text{Cu}(\text{H}_2\text{biim})_2]^{2+}$  cations exist as mononuclear complexes (Bencini & Mani, 1988). The compound  $[\text{Cu}_2(\text{Me}_5\text{dien})_2(\text{biim})](\text{BPh}_4)_2$  ( $\text{Me}_5\text{dien}$  is 1,1,4,7,7-pentamethyldiethylenetriamine) is a dinuclear complex with biimidazole as a bridging ligand (Haddad *et al.*, 1979). The compounds  $[\text{Cu}(\text{H}_2\text{biim})(\text{dien})]\text{ClO}_4$  ( $\text{dien}$  is diethylenetriamine) and  $[\text{Cu}(\text{H}_2\text{biim})(\text{salenNMe}_2)]\text{ClO}_4$  ( $\text{salenNMe}_2$  is *N*-salicylidene-*N,N'*-dimethylethylenediamine) are mononuclear mixed-ligand complexes (Liu & Su, 1996; Tadokoro & Nakasuji, 2000).

As illustrated in Fig. 2, three hydrogen bonds, *viz.*  $\text{N}2-\text{H}2\text{A}\cdots\text{O}2\text{B}$ ,  $\text{N}4-\text{H}4\text{A}\cdots\text{O}1\text{B}$  and  $\text{O}5-\text{H}5\text{B}\cdots\text{O}3\text{C}$  (Table 2), link neighbouring cations and anions alternately into a chain along the *b* axis. The water molecule of crystallization (O6) is involved in five hydrogen bonds, joining four neighbouring ions, one cation and three anions together.

## Experimental

The 2,2'-biimidazole ligand was synthesized by a modification of the published procedure of Melloni *et al.* (1972).  $\text{CuCl}_2\cdot 6\text{H}_2\text{O}$  (0.17 g, 1 mmol) and 2,2'-biimidazole (0.134 g, 1 mmol) were suspended in

water. To the resulting mixture, concentrated aqueous HCl was added until the suspension became clear. An aqueous solution (5 ml) containing iminodiacetic acid (0.133 g, 1 mmol) was then added dropwise. The resulting solution was stirred for 1 h, filtered, and the filtrate allowed to stand at room temperature. Blue crystals of (I) appeared after two months by slow evaporation of the aqueous solution.

## Crystal data

$[\text{CuCl}(\text{C}_6\text{H}_6\text{N}_4)(\text{H}_2\text{O})]\cdot$   
 $[\text{Cu}(\text{C}_4\text{H}_5\text{NO}_4)\text{Cl}]\cdot\text{H}_2\text{O}$   
 $M_r = 499.25$   
Triclinic,  $P\bar{1}$   
 $a = 6.7053$  (18) Å  
 $b = 8.823$  (2) Å  
 $c = 14.547$  (4) Å  
 $\alpha = 90.272$  (3)°  
 $\beta = 101.316$  (3)°  
 $\gamma = 103.116$  (4)°  
 $V = 820.8$  (4) Å<sup>3</sup>

$Z = 2$   
 $D_x = 2.020$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 1069 reflections  
 $\theta = 2.4\text{--}27^\circ$   
 $\mu = 2.96$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
Block, blue  
 $0.40 \times 0.10 \times 0.10$  mm

## Data collection

Bruker SMART 1K CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan, (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.384$ ,  $T_{\text{max}} = 0.756$   
3388 measured reflections

2826 independent reflections  
2279 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -9 \rightarrow 10$   
 $l = -16 \rightarrow 17$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.100$   
 $S = 1.00$   
2826 reflections  
226 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0483P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.54$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.54$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O5	1.974 (3)	Cu2—N5	1.991 (3)
Cu1—N3	1.996 (3)	Cu2—Cl2	2.2354 (12)
Cu1—N1	2.003 (3)	Cu1···Cl2	2.8311 (15)
Cu1—Cl1	2.2503 (12)	Cu1···O2 <sup>iv</sup>	3.030 (3)
Cu2—O4	1.935 (3)	Cu2···Cl1	3.0713 (15)
Cu2—O2	1.965 (3)	Cu2···O5 <sup>i</sup>	2.721 (3)
O5—Cu1—N3	91.79 (12)	O4—Cu2—O2	167.62 (12)
O5—Cu1—N1	165.83 (13)	O4—Cu2—N5	84.04 (13)
N3—Cu1—N1	82.01 (13)	O2—Cu2—N5	84.02 (12)
O5—Cu1—Cl1	90.58 (9)	O4—Cu2—Cl2	95.02 (9)
N3—Cu1—Cl1	175.67 (10)	O2—Cu2—Cl2	96.72 (9)
N1—Cu1—Cl1	94.87 (10)	N5—Cu2—Cl2	176.69 (10)

Symmetry codes: (i)  $x + 1, y, z$ ; (iv)  $x - 1, y, z$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

	D—H	H···A	D···A	D—H···A
N5—H5C···O6 <sup>i</sup>	0.79	2.44	3.087 (4)	140
N4—H4···O1 <sup>ii</sup>	0.79	1.91	2.689 (4)	170
N2—H2A···O2 <sup>iii</sup>	0.86	2.19	3.035 (4)	168
O6—H6A···O3	0.94	2.05	2.989 (4)	174
O6—H6B···Cl2 <sup>iii</sup>	0.88	2.50	3.327 (3)	156
O6—H6B···O4 <sup>iii</sup>	0.88	2.48	3.077 (5)	125
O5—H5B···O3 <sup>iii</sup>	0.77	1.95	2.716 (4)	170
O5—H5A···O6	0.86	1.87	2.716 (4)	168

Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x + 1, -y + 2, -z$ ; (iii)  $-x + 1, -y + 2, -z + 1$ .

H atoms attached to C atoms were placed in geometrically idealized positions, with C–H distances in the range 0.93–0.97 Å, and were constrained to ride on their carrier atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . H atoms attached to N and O (water) atoms were located in difference Fourier maps and constrained to ride on their carrier atoms, with N–H distances in the range 0.79–0.86 Å and O–H distances in the range 0.86–0.94 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  or  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1205). Services for accessing these data are described at the back of the journal.

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