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

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In the title compound, \([\text{CuCl}(\text{C}_2\text{H}_5\text{N}_2)(\text{H}_2\text{O})][\text{Cu}(\text{C}_4\text{H}_4\text{NO}_4)\cdot\text{Cl}]:\text{H}_2\text{O}\), the Cu\(^\text{II}\) atom in the cation is coordinated by one Cl\(^-\) ion, two N atoms of the 2,2\(^-\)-biimidazole ligand and one aqua ligand. Within the anion, the Cu\(^\text{II}\) atom is bonded to one Cl\(^-\) ion, and one N and two O atoms of the iminodiacetate ligand. Neighbouring cations and anions are connected to each other by Cu\(
abla\)···Cl semi-coordination bonds of 2.830 (12) and 3.071 (12) Å, forming a Cu\(_2\)Cl\(_2\) rectangular unit. The dinuclear units further link into a polymeric chain along the \(a\) axis through Cu\(
abla\)···O\(_\text{aq}\) 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 (H\(_2\)biim) is a ligand that can coordinate to transition metals in non-deprotonated (H\(_2\)biim), mono-deprotonated (H\(_2\)biim\(^+\)) and bis-diprotonated (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 H\(_2\)biim to Cu\(^\text{II}\), Co\(^{III}\), Ni\(^{III}\), V\(^{III}\), Ag\(^{I}\) and Cd\(^{II}\) 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 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).

![Figure 1](image)

The asymmetric unit of (I) contains one [CuCl(H\(_2\)biim)-(H\(_2\text{O}\))\(^+\)] cation, one [Cu(ida)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\(_\text{tridentate ida ligand (with two deprotonated carboxylate groups) and atom Cl}_2\). 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 Cu1···Cl2 and Cu2···Cl1 interactions of 2.830 (12) and 3.071 (12) Å, respectively, forming a neutral dinuclear unit through an irregular Cu1/Cl1/Cu2/Cl2 rectangle (Fig. 2). These neutral dinuclear units are further linked into a polymeric chain along the \(a\) axis by a Cu2···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...
there are two species, \([\text{CuCl}_2(\text{H}_2\text{biim})]\) and \([\text{Cu}(\text{H}_2\text{biim})_2]^{2+}\), biimidazole as a bridging ligand (Haddad et al., 1996). The compounds \([\text{Cu}(\text{H}_2\text{biim})(\text{dien})]\)ClO_4 (dien is diethylene-triamine) is a dinuclear complex with bisimidazole as a bridging ligand (Bencini & Mani, 1988). The compound \([\text{Cu}_2(\text{Me}_3\text{dien})(\text{biim})](\text{BPh}_4)_2\) (Me_3dien is 1,1,4,7-tetramethyl-1,2,4-triazine) is a dinuclear complex with bisimidazole as a bridging ligand (Haddad et al., 1979). The compounds \([\text{Cu}(\text{H}_2\text{biim})(\text{dien})]\)ClO_4 (dien is diethylenetriamine) and \([\text{Cu}(\text{H}_2\text{biim})(\text{salenNMe}_2)]\)ClO_4 (salenNMe_2 is N-salicylidene-2,3-dimethyl-1,2,3-triazole) are mononuclear mixed-ligand complexes (Liu & Su, 1996; Tadokoro & Nakajima, 2000).

As illustrated in Fig. 2, three hydrogen bonds, \(\text{N2} \leftrightarrow \text{H2A} \cdots \text{O2B}\), \(\text{N4} \leftrightarrow \text{H4A} \cdots \text{O1B}\) and \(\text{O5} \leftrightarrow \text{H5B} \cdots \text{O3C}\) (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). \(\text{CuCl}_2\cdot6\text{H}_2\text{O}\) (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 imidodiacetic 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**

\[
\begin{align*}
\text{Z} &= 2 \\
\text{D}_m &= 2.020 \text{ Mg m}^{-3} \\
\text{Mo K} \alpha \text{ radiation} \\
\text{Triclinic, \(P\bar{T}\)} \quad b &= 6.7053 (18) \text{ Å} \\
\theta &= 2.4-27^\circ \\
\mu &= 2.96 \text{ mm}^{-1} \\
\alpha &= 90.272 (3)^\circ \\
\beta &= 101.316 (3)^\circ \\
\gamma &= 103.116 (4)^\circ \\
\text{\(V\)} &= 820.8 (4) \text{ Å}^3 \\
\text{Data collection} \\
\text{Bruker SMART 1K CCD area-detector diffractometer} \\
\varphi \text{ and } \omega \text{ scans} \\
\text{Absorption correction: multi-scan, } (\text{SADABS}; \text{Stehlik, 1996}) \\
\text{\(T\text{max} = 0.384, \text{T\text{min} = 0.0756} \) \\
\text{1438 measurements} \\
\text{H-atom parameters constrained} \\
\text{\(R_{	ext{free}} = 0.018 \) } \\
\text{2826 reflections} \\
\text{226 parameters} \\
\text{H-atom parameters constrained} \\
\text{\(w = 1/\sigma^2(F^2) + (0.0483P)^2 \)} \\
\text{where } P = (\sigma^2(F^2) + 2F^2)/3 \\
\text{\(\Delta\sigma_{\text{max}} = 0.54 \text{ e Å}^{-3}\) } \\
\text{\(\Delta\sigma_{\text{min}} = -0.54 \text{ e Å}^{-3}\) } \\
\text{Table 1} \\
\text{Selected geometric parameters (Å, \(^\circ\).} \\
\text{Cu1-\text{O3} \quad 1.974 (3)} \\
\text{Cu1-\text{N1} \quad 2.003 (3)} \\
\text{Cu1-\text{C11} \quad 2.250 (2)} \\
\text{Cu2-\text{O4} \quad 2.040 (3)} \\
\text{Cu2-\text{C2} \quad 2.289 (3)} \\
\text{O5-\text{Cu1-\text{N3} \quad 1.280 (2)} \text{Cu1-\text{C11} \quad 2.250 (2)} \text{Cu1-\text{C2} \quad 2.289 (3)} \text{Cu2-\text{O4} \quad 2.040 (3)} \text{Cu2-\text{C2} \quad 2.289 (3)} \\
\text{Table 2} \\
\text{Hydrogen-bond geometry (Å, \(^\circ\).} \\
\text{D-H \cdots A} \\
\text{N5-\text{H5A} \cdots \text{O6B} \quad 0.79 \quad 2.44 \quad 3.087 (4)} \\
\text{N4-\text{H4B} \cdots \text{O1A} \quad 0.79 \quad 2.19 \quad 3.257 (4)} \\
\text{N2-\text{H2A} \cdots \text{O2A} \quad 0.64 \quad 2.37 \quad 3.267 (4)} \\
\text{N6-\text{H6A} \cdots \text{O3A} \quad 0.84 \quad 2.50 \quad 3.277 (4)} \\
\text{N6-\text{H6B} \cdots \text{O4A} \quad 0.84 \quad 2.50 \quad 3.077 (4)} \\
\text{N5-\text{H5B} \cdots \text{O3B} \quad 0.77 \quad 1.95 \quad 2.716 (4)} \\
\text{N5-\text{H5A} \cdots \text{O6B} \quad 0.86 \quad 1.87 \quad 2.716 (4)} \\
\text{Symmetry codes: (i) x+1, y, z; (ii) -x+1, -y+2, -z; (iii) -x+1, -y+2, -z+1.} \\
\text{Acta Cryst. (2005). C61, m10–m12} \\
\text{Gao, Wei, Li and Yang \cdot [CuCl(C6H5N4)(H2O)]Cu[C6H4NO2Cl]-H2O} \text{ m11}
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 $U_{iso}(H) = 1.2U_{eq}(C)$. 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 $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$.

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.

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References