

A three-dimensional supramolecular network built with the zigzag chain complex bis(5-carboxy-1*H*-imidazole-4-carboxylato)copper(II)

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Received 17 December 2004

Accepted 22 December 2004

Online 22 January 2005

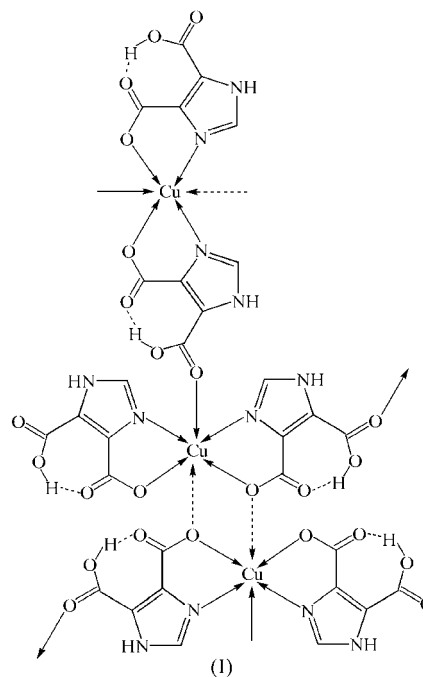
In the title complex, poly[copper(II)-di- μ -5-carboxy-1*H*-imidazole-4-carboxylato], $[\text{Cu}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2]_n$ or $[\text{Cu}(\text{H}_2\text{-Imda})_2]_n$, each imidazole moiety is bonded to the Cu atom *via* O and N atoms to give a square-planar coordination [Cu—O = 2.014 (2) and 2.016 (2) Å, and Cu—N = 1.982 (3) and 1.992 (2) Å]. The distorted square-pyramidal geometry at the Cu atom results from coordination to an adjacent O atom [Cu—O = 2.305 (2) Å], which generates zigzag chains. There is a sixth, weaker, octahedral coordination to the Cu atom from an inversion-related O atom [Cu—O = 3.090 (2) Å], which links the chains into sheets in the (100) plane. Imidazole moieties in the sheets are linked in the [100] direction by pairs of N—H...O and C—H...O hydrogen bonds, thus generating a three-dimensional network.

Comment

Imidazole-4,5-dicarboxylic acid (H_3Imda) can form three types of anions, namely Imda^{3-} , HImda^{2-} and H_2Imda^- , while interacting with metal ions. In the crystal structure of a mixed-valence $\text{Co}^{\text{II,III}}$ complex, $\text{Na}_2[\text{Co}_4(\text{Imda})_4(2,2'\text{-bipy})_4] \cdot 12\text{H}_2\text{O}$ (2,2'-bipy is 2,2'-bipyridine; Wang *et al.*, 2004), the Imda^{3-} trianion links adjacent Co atoms through both bidentate CO_2 groups and an imidazole entity into a square plane, which is capped at each corner by 2,2'-bipy ligands; adjacent square planes are linked by water- and CO_2 -bound Na^+ cations into a one-dimensional motif. The dinuclear mixed-valence $\text{Mn}^{\text{III,IV}}$ complex $\text{Mn}_2(\text{dtbsalpn})_2(\text{Imda})$ [$\text{H}_2\text{dtbsalpn}$ is 1,3-bis[(3,5-di-*tert*-butylsalicylidene)amino]propane] adopts a similar coordination pattern (Rajendiran *et al.*, 2003). Recently, the crystal structures of $M(\text{H}_2\text{Imda})_2(\text{H}_2\text{O})_2$ ($M = \text{Co}, \text{Cu}$ and Zn), in which the H_2Imda^- monoanion coordinates to the metal ion *via* only one N atom and one O atom of the monodentate CO_2 group, have been reported (Shimizu *et al.*, 2004).

We have obtained metal-cluster complexes by using mixed N- and O-atom ligands under hydrothermal conditions (Yin *et*

al., 2004). We employed the H_3Imda ligand to react with Cu^{II} in the presence of NaOH in the hope of synthesizing a new metal-cluster complex, but this reaction resulted in the title complex, $[\text{Cu}(\text{H}_2\text{Imda})_2]_n$ (I), being obtained serendipitously.



The title complex is shown in Fig. 1, with selected geometric parameters listed in Table 1. Both H_2Imda^- monoanions chelate the Cu atom in a *syn* mode, which does not resemble that found in the $M(\text{H}_2\text{Imda})_2(\text{H}_2\text{O})_2$ ($M = \text{Co}, \text{Cu}$ and Zn) complexes (Shimizu *et al.*, 2004). In the asymmetric unit in (I), the coordination geometry of the Cu atom may be described as slightly distorted square pyramidal, with two O atoms (O1 and O11) of monodentate CO_2 groups and two N atoms (N3 and N13) of two H_2Imda^- imidazole moieties in the basal plane, and an O atom [$\text{O}4(x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2})$] of a monodentate CO_2 group of an adjacent H_2Imda^- species occupying

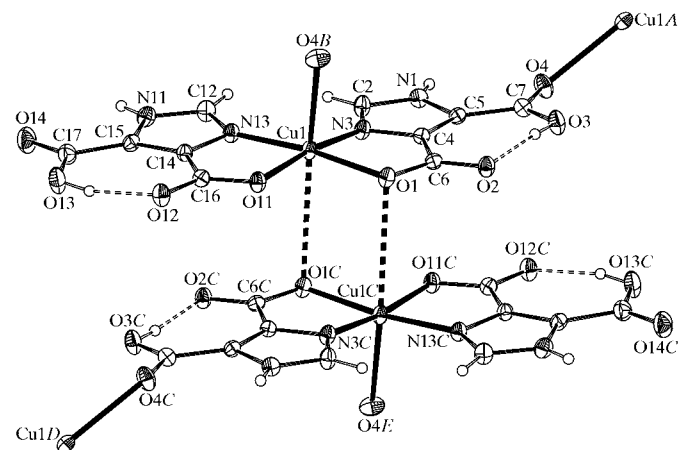


Figure 1
A segment of the structure of the title complex, with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (A) $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (B) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (C) $1 - x, 1 - y, 1 - z$; (D) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (E) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

the apical position. There is a sixth, weaker, $\text{Cu} \cdots \text{O}$ coordination to atom O1^{h} in the inversion-related complex at $(-x+1, -y+1, -z+1)$. Such $[4+1+1]$ -coordination is not uncommon; a search of the Cambridge Structural Database

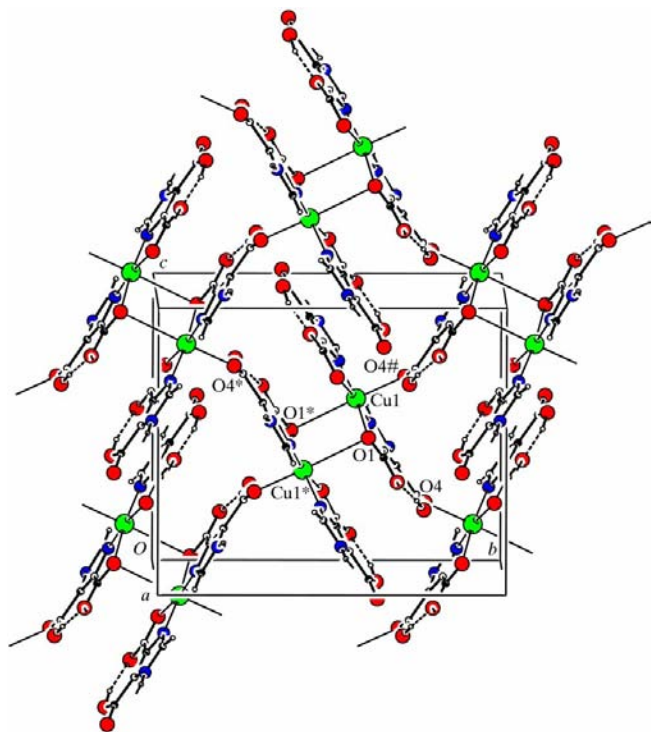


Figure 2
A view of the two-dimensional network in the (100) plane. Atoms labeled with an asterisk (*) or a hash (#) are at the symmetry positions $(1-x, 1-y, 1-z)$ and $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, respectively.

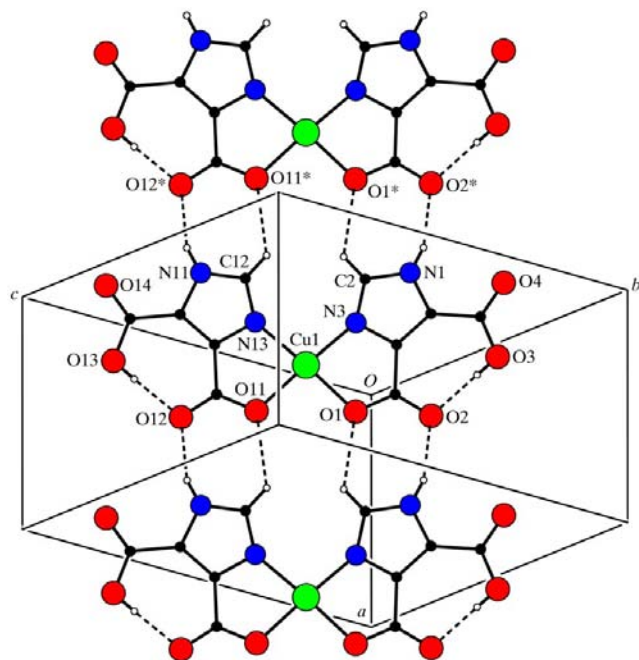


Figure 3
A view showing the chain of $\text{Cu}(\text{H}_2\text{Imda})_2$ moieties along $[100]$ linked by pairs of $\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds. Atoms labeled with an asterisk (*) are at the symmetry position $(-1+x, y, z)$.

(July 2004 release; Allen, 2002) for compounds with octahedral coordination at the Cu atom in compounds with a CuN_2O_4 moiety and the sixth $\text{Cu}-\text{O}$ coordination distance in the ranges 2.6–2.8, 2.8–3.0, 3.0–3.2 and 3.2–3.4 Å yielded 51, 72, 62 and 61 hits, respectively. Atoms O1, O11, N3 and N13 form a plane with a mean deviation of 0.009 Å; atom Cu1 lies 0.1218 (13) Å from this plane, and the remaining two atoms, O4B and O1C (see Fig. 1 for symmetry codes), lie 2.419 (3) and -2.873 (4) Å, respectively, from the basal plane. The two carboxyl hydroxy groups form intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds to adjacent carboxyl O atoms (Table 2).

One H_2Imda^- monoanion (containing atoms N3, O1 and O4) uses both CO_2 groups and an imidazole N atom to link to adjacent Cu atoms to form a zigzag chain *via* an n -glide operation, both CO_2 groups being monodentate. Adjacent chains are then linked by inversion-related pairs of the weaker $\text{Cu} \cdots \text{O1C}$ and $\text{O1} \cdots \text{CuC}$ interactions [the suffix C corresponds to the symmetry code $(1-x, 1-y, 1-z)$] to generate a sheet in the (100) plane, as shown in Fig. 2. These sheets are linked by pairs of $\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2), which link the $\text{Cu}(\text{H}_2\text{Imda})_2$ moieties into chains extending along $[100]$ (Fig. 3). The combination of these hydrogen bonds and the $\text{Cu}-\text{O}$ bonds shown in Fig. 2 then develops a three-dimensional network.

Experimental

An aqueous solution (10 ml) of imidazole-4,5-dicarboxylic acid (0.078 g, 0.5 mmol) was adjusted to a pH of 5 with a 1 M NaOH solution at 333 K. The solution was then transferred to a 25 ml Teflon-lined stainless steel vessel that containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.182 g 0.75 mmol). The vessel was sealed and heated to 413 K for 12 d, and then cooled at a rate of 5 K h^{-1} to 373 K. The vessel was kept at 373 K for 10 h before being cooled to room temperature. Long blue parallelepiped crystals were separated by hand (yield 13%).

Crystal data

$[\text{Cu}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2]$
 $M_r = 373.73$
 Monoclinic, $P2_1/n$
 $a = 7.112$ (1) Å
 $b = 14.676$ (3) Å
 $c = 12.145$ (2) Å
 $\beta = 96.65$ (3)°
 $V = 1259.1$ (4) Å³
 $Z = 4$

$D_x = 1.972$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 2318 reflections
 $\theta = 3.2$ – 28°
 $\mu = 1.79$ mm^{-1}
 $T = 293$ (2) K
 Parallelepiped, blue
 $0.30 \times 0.10 \times 0.06$ mm

Data collection

Rigaku R-Axis RAPID imaging-plate diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.807$, $T_{\text{max}} = 0.898$
 4554 measured reflections

3038 independent reflections
 2318 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 28.0^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 19$
 $l = -16 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.101$
 $S = 1.03$
 3038 reflections
 210 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.1086P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.56$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N13	1.982 (3)	Cu1—O1	2.016 (2)
Cu1—N3	1.992 (2)	Cu1—O4 ⁱ	2.305 (2)
Cu1—O11	2.014 (2)	Cu1—O1 ⁱⁱ	3.090 (2)
N13—Cu1—N3	97.68 (10)	N3—Cu1—O1	83.93 (9)
N13—Cu1—O11	83.90 (9)	O11—Cu1—O1	93.64 (8)
N3—Cu1—O11	172.26 (10)	O1 ⁱⁱⁱ —Cu1—O4 ⁱ	161.07 (9)
N13—Cu1—O1	173.20 (10)		

 Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O2	0.82	1.82	2.642 (3)	175
O13—H13...O12	0.82	1.85	2.653 (3)	165
N1—H1...O2 ⁱⁱⁱ	0.86	2.02	2.837 (3)	158
N11—H11...O12 ⁱⁱⁱ	0.86	2.02	2.825 (3)	156
C2—H2...O1 ⁱⁱⁱ	0.93	2.48	3.133 (4)	128
C12—H12...O11 ⁱⁱⁱ	0.93	2.50	3.160 (4)	129

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

All H atoms were found in difference maps and subsequently allowed for in the refinements as riding atoms [C—H = 0.93 Å, N—H = 0.86 Å, O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$].

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Natural Science Foundation of China (grant No. 20301014) and the Innovation Foundation for Young Scientific Talents of Fujian Province of China (grant No. 2002 J004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1804). Services for accessing these data are described at the back of the journal.

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