

## Poly[[ $\mu_3$ -2-(carboxylatomethyl)-benzoato- $\kappa^3$ O<sup>1</sup>:O<sup>2</sup>:O<sup>2</sup>]]bis(1*H*-imidazole- $\kappa$ N<sup>3</sup>)copper(II)]

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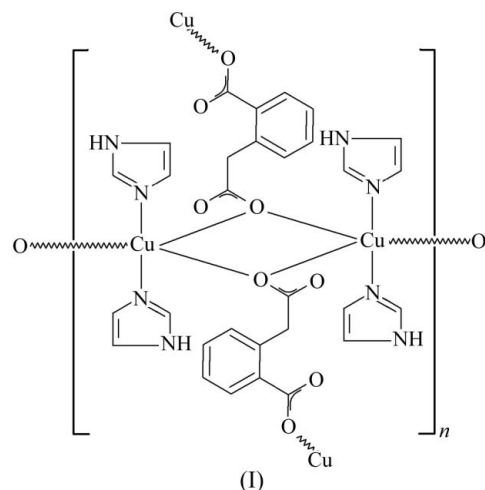
In the title polymeric compound,  $[\text{Cu}(\text{C}_9\text{H}_6\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2]_n$ , the copper(II) cation occupies an  $\text{N}_2\text{O}_3$  coordination sphere defined by two 1*H*-imidazole (imid) ligands in *trans* positions and three carboxylate O atoms from three different 2-(carboxylatomethyl)benzoate ( $\text{hpt}^{2-}$ ) dianions. The geometry is that of a square pyramid with one of the O atoms at the apex, bridging neighbouring metal centres into an  $[-\text{ON}_2\text{CuO}_2-\text{CuN}_2\text{O}-]$  dinuclear unit. These units are in turn connected by hpt anions into a reticular mesh topologically characterized by two types of loops, *viz.* a four-membered  $\text{Cu}_2\text{O}_2$  diamond motif and a 32-membered  $\text{Cu}_4\text{O}_8\text{C}_{20}$  ring. The imid groups do not take part in the formation of the two-dimensional structure, but take part in the  $\text{N}-\text{H}\cdots\text{O}$  interactions. These arise only within individual planes, interplanar interactions being only of the van der Waals type.

### Comment

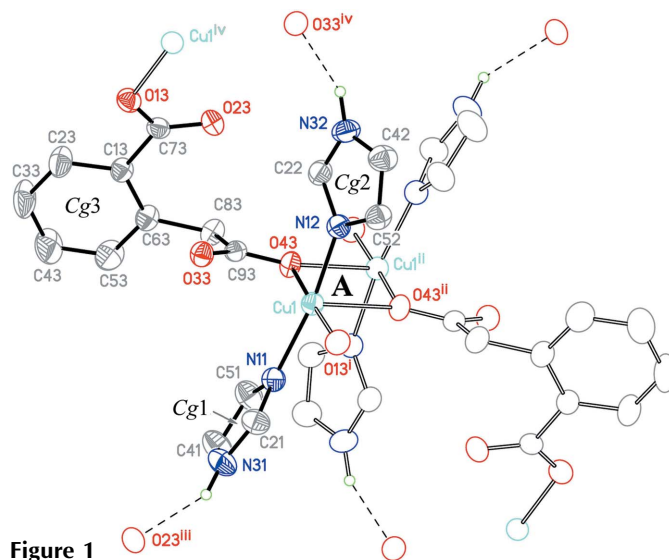
The study of organic–inorganic hybrid coordination frameworks is a key part of modern structural chemistry, mainly due to the potential properties of these materials. In these ‘prediction, design, synthesis and structural analysis’ exercises, the ligands usually preferred are those characterized by versatility, coordination capabilities and, ultimately, a large number of possible coordination modes (Archer, 2001). Benzenecarboxylic acids of flexible structure, such as homophthalic acid ( $\text{H}_2\text{hpt}$ ), the ligand of interest to us, comply with many of these requisites and have largely proven to be useful in constructing complex frameworks with varied topology (He *et al.*, 2006; Cavellec *et al.*, 2003; Pan *et al.*, 2003; Wan *et al.*, 2003).

Interest in these types of materials, and in hpt-based materials as representatives, has been growing over the last

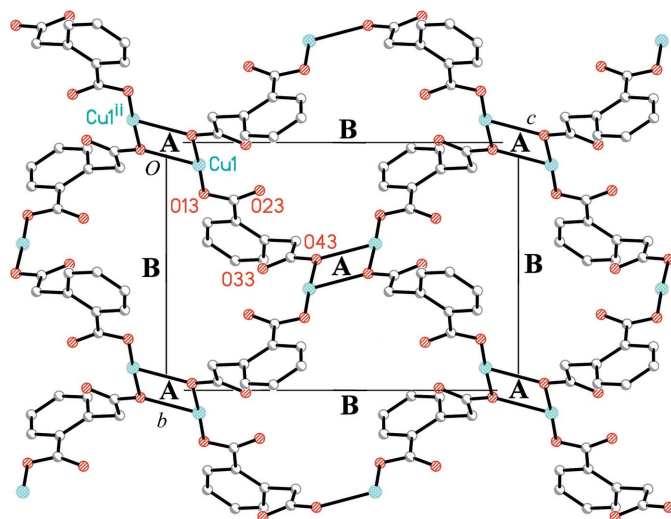
decade, as indicated by the number of hpt complexes reported. The first study by Cotton *et al.* (2001) was followed by only two more examples (Burrows *et al.*, 2003, 2004) within five years, but in the next five years (*i.e.* 2006–2011), a total of 18 new hpt complexes were recorded [Cambridge Structural Database (CSD), Version 5.32; Allen, 2002], indicating a strong upward trend.



In these reported structures, the hpt ligand showed varied binding capabilities by displaying nine different coordination modes. We refer the interested reader to Atria *et al.* (2011) for a comprehensive review of the ways in which the ligand has been shown to bind to metal centres. In this same report, two new isomorphous hpt structures were presented, namely  $M[(\text{Hdap})(\text{hpt})(\text{H}_2\text{O})]_2 \cdot 4\text{H}_2\text{O}$  (where dap is 2,6-diamino-



**Figure 1** The molecular structure of (I). Displacement ellipsoids are drawn at the 40% probability level. Independent atoms are shown with solid bonds and shaded ellipsoids, while symmetry-related atoms have hollow bonds and boundary ellipsoids. Hydrogen bonds are shown as dashed lines. For clarity, only those H atoms involved in hydrogen bonding are shown. Cg1, Cg2 and Cg3 are the centroids of the N11/C21/N31/C41/C51, N12/C22/N32/C42/C52 and N13/C23/N33/C43/C53, rings, respectively. Label ‘A’ denotes the centrosymmetric  $\text{Cu}_2\text{O}_2$  diamond-like motif. [Symmetry codes: (i)  $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 2, -y + 1, -z + 1$ ; (iii)  $x, y + 1, z$ ; (iv)  $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$ .]

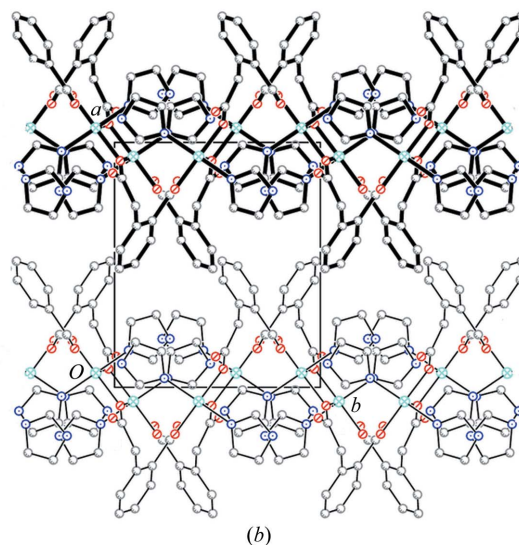
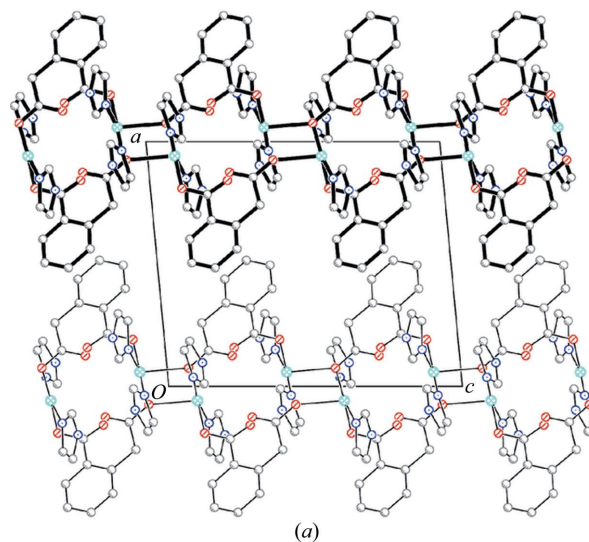
**Figure 2**

A packing view of (I), along the [100] direction, showing the (100) two-dimensional mesh and the elementary loops (**A** and **B**) from which it is constructed. Imidazole rings and H atoms have been omitted for clarity. [Symmetry code: (ii)  $-x + 2, -y + 1, -z + 1$ .]

purine and  $M$  is  $\text{Ni}^{\text{II}}$  or  $\text{Co}^{\text{II}}$ ); in these structures, the hpt anion displayed an unusual (and at the time unreported)  $\mu\text{-}\kappa^1\text{O}$  coordination mode.

In pursuit of our interest in the different architectures to which the hpt ligand can give rise, we present herein a new copper(II) complex poly[[ $\mu_3$ -2-(carboxylatomethyl)benzoato]bis(1*H*-imidazole)copper(II)], (I), incorporating a fully deprotonated 2-(carboxylatomethyl)benzoate dianion ( $\text{hpt}^{2-}$ ) and 1*H*-imidazole (imid) as an ancillary ligand. This structure exhibits yet another new bridging coordination mode for the  $\text{hpt}^{2-}$  anion.

Fig. 1 presents an ellipsoid plot of the (extended) asymmetric unit of (I), showing the complete coordination environment of the copper(II) cation and the dinuclear unit it gives rise to: two independent imid groups are in mutually *trans* positions [ $\text{N}-\text{Cu}-\text{N} = 169.82(9)^\circ$ ] and three symmetry-related  $\text{hpt}^{2-}$  anions complete a  $\text{CuN}_2\text{O}_2+\text{O}$  square-pyramidal arrangement, with a rather regular base [ $\text{Cu}-L$  distance range =  $1.9643(18)$ – $2.0060(18)$  Å and  $L-\text{Cu}-L$  *cis*-angle range =  $88.60(8)$ – $91.39(8)^\circ$ ;  $L$  = basal N or O], and a Jahn–Teller elongated apical bond [ $\text{CuI}-\text{O43}^{\text{ii}} = 2.4269(17)$  Å; symmetry code: (ii)  $-x + 2, -y + 1, -z + 1$ ] tilted by  $16.2(2)^\circ$  from the normal to the mean basal plane. The  $\mu_3, \kappa^2\text{-O}:\text{O}':\text{O}'$  mode displayed by  $\text{hpt}^{2-}$  is novel and should be added to those listed in Atria *et al.* (2011). The imidazole ligands only interact with the rest of the structure *via* hydrogen-bonding interactions (see below). The  $\text{hpt}^{2-}$  anions, instead, play a leading role in the spatial arrangement, defining a dinuclear substructure *via* the sharing of atom O43 with two different coordination polyhedra ('**A**' in Figs. 1 and 2), with a  $\text{CuI}\cdots\text{CuII}$  distance of  $3.5710(8)$  Å [symmetry code: (ii)  $-x + 2, -y + 1, -z + 1$ ]. The resulting  $\text{Cu}_2\text{O}_2$  diamond-like motif, in turn, appear as the nodes of much larger macrocycles determined by the stretched out  $\text{hpt}^{2-}$  carboxylate and methylcarboxylate arms, forming large  $\text{Cu}_4\text{O}_8\text{C}_{20}$  loops [or

**Figure 3**

Two different side views of the (100) planes, *viz.* (a) projected down [010] and (b) projected down [001], drawn in different line densities for clarity. H atoms have been omitted for clarity.

( $\text{CuO}_2\text{C}_5$ )<sub>4</sub>, '**B**' in Fig. 2]. The final structure can be envisaged as the concatenation into a two-dimensional mesh of these two kinds of small and large loops. Even if imid ligands point outwards, with no direct intervention in the mesh formation, they contribute to the mesh stability through two strong  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds described in Table 2 and shown in Fig. 1. In these contacts, the donor atoms are the protonated imid N atoms, while the acceptors are the two carboxylate O atoms not involved in coordination. These contacts, as well as the remaining (though weaker) interactions of the  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\pi$  types shown in Table 2, are internal to the two-dimensional structures and do not link adjacent planes; interplanar stability appears to be achieved through van der Waals forces only.

Fig. 3 shows two lateral views of these planes, depicting this lack of close contacts. The views in Fig. 3 might be deceptive in suggesting some kind of  $\pi-\pi$  interaction between benzene  $\text{hpt}^{2-}$  groups; this is just a perspective artifact since the

centroids of neighbouring  $\text{hpt}^{2-}$  groups in adjacent planes lie more than 5.5 Å apart and the rings they belong to are far from parallel (dihedral angle  $> 75^\circ$ ).

Large loops like the  $(\text{CuO}_2\text{C}_5)_4$  one herein, or, more generally,  $(M-L)_4$ , with  $M$  being any transition metal and  $L$  being the 'looping' ligand, are not uncommon in three-dimensional structures. Sometimes they appear to be embracing smaller embedded loops and in this context the larger loops are not so relevant from a structural point of view. However, the CSD (Allen, 2002) contains several examples of rings of a similar size to those in (I) which also constitute primary building units in the crystal architecture. Surprisingly, in most of them, the ligand  $L$  was a close relative of some of the members of the benzylcarboxylate family. Some examples, given in the sequence [CSD refcode:  $M-L$  (reference)] are: ATORIK: Zn-isophthalohydrazide (He *et al.*, 2004); FUDHOC, FUDHUI, FUHYAJ, FUHYAJ01, FUHYEN01, FUHYIR: Cu-trimesic acid (Ene *et al.*, 2009); SOMLUC: Ni-pyrazole-3,5-dicarboxylate (Bai *et al.*, 2008); TIGLAW: Co-pyrazole-3,5-dicarboxylate (Pan *et al.*, 2001); TUHFIM: Co-*tert*-butylisophthalate (Du *et al.*, 2009).

Many of these examples display free open loops where solvents of different kinds and shapes (water or pyridyl-methanol) reside. In the present case of (I), in contrast, the bulky  $\text{hpt}^{2-}$  and imid groups are directed towards the loop centre, thus limiting the hosting capability of the compound.

## Experimental

Complex (I) was synthesized by adding an aqueous solution (80 ml) of copper acetate monohydrate (1 mmol) to an aqueous solution containing homophthalic acid (0.5 mmol) and NaOH (1 mmol). The mixture was heated under reflux for 20 min. An ethanolic solution (30 ml) of imidazole (0.5 mmol) was added slowly and the final solution was maintained under reflux for 4 h. Single crystals suitable for X-ray diffraction studies were obtained by slow concentration of the solution.

### Crystal data

|   |   |
|---|---|
| $[\text{Cu}(\text{C}_5\text{H}_6\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2]$ | $V = 1638.2 (6) \text{ \AA}^3$            |
| $M_r = 377.84$  | $Z = 4$                                   |
| Monoclinic, $P2_1/c$  | Mo $K\alpha$ radiation                    |
| $a = 11.817 (3) \text{ \AA}$  | $\mu = 1.36 \text{ mm}^{-1}$              |
| $b = 9.871 (2) \text{ \AA}$   | $T = 298 \text{ K}$                       |
| $c = 14.106 (3) \text{ \AA}$  | $0.37 \times 0.16 \times 0.12 \text{ mm}$ |
| $\beta = 95.305 (4)^\circ$  |   |

### Data collection

|   |  |
|---|--|
| Bruker SMART CCD area-detector diffractometer                     | 13360 measured reflections             |
| Absorption correction: multi-scan (SADABS in SAINT; Bruker, 2002) | 3654 independent reflections           |
| $T_{\min} = 0.79, T_{\max} = 0.89$                                | 2886 reflections with $I > 2\sigma(I)$ |
|   | $R_{\text{int}} = 0.029$               |

### Refinement

|                                 |  |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.109$               | $\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$                    |
| $S = 1.06$                      | $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$                   |
| 3654 reflections                |  |
| 225 parameters                  |  |

**Table 1**  
Selected bond lengths (Å).

|                      |             |                       |             |
|----------------------|-------------|-----------------------|-------------|
| Cu1—O13 <sup>i</sup> | 1.9643 (18) | Cu1—O43               | 2.0060 (18) |
| Cu1—N12              | 1.987 (2)   | Cu1—O43 <sup>ii</sup> | 2.4269 (17) |
| Cu1—N11              | 2.003 (2)   |                       |             |

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

**Table 2**  
Hydrogen-bond geometry (Å, °).

Cg2 is the centroid of the N12/C22/N32/C42/C52 ring.

| $D-H \cdots A$                      | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------------------------|----------|--------------|--------------|----------------|
| N31—H31 $\cdots$ O23 <sup>iii</sup> | 0.84 (4) | 2.01 (4)     | 2.824 (3)    | 163 (4)        |
| N32—H32 $\cdots$ O33 <sup>iv</sup>  | 0.87 (4) | 1.85 (4)     | 2.699 (3)    | 162 (4)        |
| C21—H21 $\cdots$ O33 <sup>i</sup>   | 0.93     | 2.35         | 3.096 (4)    | 137            |
| C22—H22 $\cdots$ O23                | 0.93     | 2.57         | 3.482 (3)    | 167            |
| C51—H51 $\cdots$ Cg2 <sup>ii</sup>  | 0.93     | 2.66         | 3.294 (3)    | 126            |

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

All the H atoms were clearly seen in a difference Fourier map, but while H atoms attached to N atoms were refined freely, those on C atoms were repositioned at their expected locations and allowed to ride both with respect to their coordinates ( $C-H = 0.93-0.97 \text{ \AA}$ ) and their isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3055). Services for accessing these data are described at the back of the journal.

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