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A mixed-valence copper coordination polymer generated by a hydrothermal metal/ligand redox reaction process

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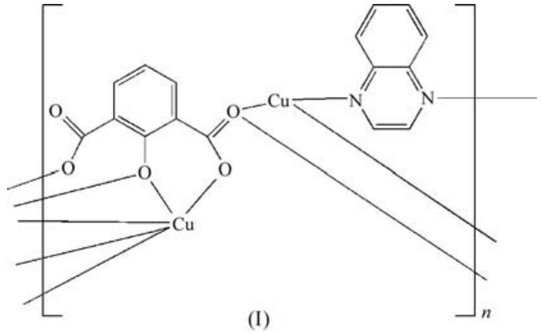
The title coordination polymer, poly[(μ_4-2-oxidoisophthalato-$\kappa^6O^1,O^2:O^2,O^3:O^{3'}:O^{3'}$)($\mu_2$-quinoxaline-$\kappa^2N:N'$)copper(I)copper(II)], $[Cu_2(C_8H_3O_5)(C_8H_6N_2)]_n$, contains two crystallographically distinct Cu ions, one quinoxaline (QA) unit and one 2-oxidoisophthalate trianion (*L*) derived from 2-hydroxyisophthalic acid (H_3L). The Cu^{II} ion is strongly coordinated by four O atoms in a distorted square geometry, of which two belong to two phenoxide groups and the other two to carboxylate groups of two *L* ligands. In addition, the Cu^{II} cation interacts weakly with a symmetry-related carboxylate O atom which belongs to the *L* ligand in an adjacent layer, giving a square-pyramidal coordination geometry. The Cu^I ion is trigonally coordinated by two N atoms from two QA molecules and one O atom from an *L* carboxylate group. The Cu^I centres are bridged by QA ligands to give a chain along the *c* axis. Two Cu^{II} ions and two *L* ligands form a $[Cu_2L_2]^{2-}$ 'metallo-ligand', which coordinates two Cu^I ions. Thus, the chains of Cu^I and QA are linked by the $[Cu_2L_2]^{2-}$ metallo-ligand to yield a two-dimensional (6,3) sheet. These sheets are further linked by symmetry-related carboxylate O atoms of neighbouring layers into a three-dimensional framework. The *in situ* reaction from benzene-1,2,3-tricarboxylic acid (H_3L1) to *L* in the present system has rarely been observed before, although a few novel *in situ* reactions, such as ligand oxidative coupling, hydrolysis and substitution, have been observed during the hydrothermal process.

Comment

Extended frameworks of coordination polymers, based on complexes of transition metals and multifunctional bridging ligands, are of great research interest (Eddaoudi *et al.*, 2001; Hagrman *et al.*, 1999; Noveron *et al.*, 2002; Batten & Robson, 1998). The hydro(solvo)thermal method is a useful technique for the construction of highly stable robust metal–organic frameworks (Chen & Liu, 2002; Yang *et al.*, 2007; Tong *et al.*, 2000). It has been found that *in situ* reactions, such as ligand oxidative coupling, hydrolysis, substitution and the redox process of copper can occur under hydro(solvo)thermal conditions (Maji *et al.*, 2004). These reactions represent promising new routes for constructing novel coordination polymers.



(I)

The chemistry of mixed-valence $Cu^{I,II}$ complexes is of great importance. We are interested in developing mixed-valence $Cu^{I,II}$ complexes under hydrothermal conditions because of their superior electronic, optical and magnetic properties (Maji *et al.*, 2004). In consideration of the fact that several $Cu^{I,II}$ complexes contain N-heterocyclic and carboxylate ligands, we deduce that benzene-1,2,3-tricarboxylic acid (H_3L1) and quinoxaline (QA) are possibly good ligands for the construction of mixed-valence $Cu^{I,II}$ complexes (Zhang & Fang, 2005). In this work, the hydrothermal reaction of H_3L1, QA and divalent copper(II) salts resulted in a new mixed-valence $Cu^{I,II}$ coordination polymer, the title compound, $[Cu^ICu^{II}L(QA)]_n$, (I), where *L*1 was transformed into 2-oxdoisophthalate (*L*).

Compound (I) was obtained under hydrothermal conditions at 453 K. Once formed, the compound is insoluble in most solvents, including water. As shown in Fig. 1, the asymmetric unit contains two crystallographically unique Cu atoms, one unique QA ligand and one unique trianionic *L* ligand. Atom Cu1 is primarily coordinated to four O atoms [O2, O3, O3^i and

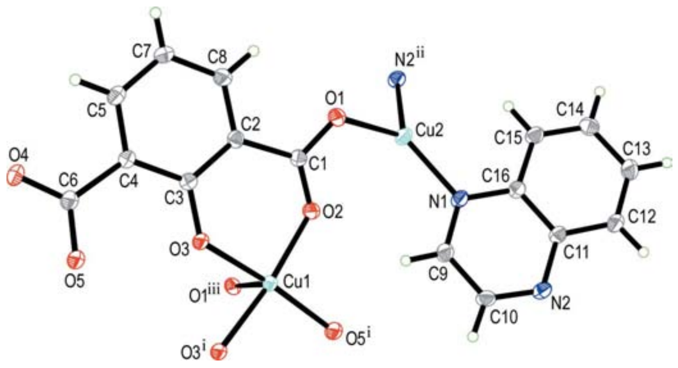


Figure 1
A view of the local coordination of the Cu^I and Cu^{II} atoms in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $1 + x, y, z$.]

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O5^{i}; symmetry code: (i) $2 - x, -y, 2 - z$] in a distorted square geometry, of which two belong to two phenoxide groups and the other two to carboxylate groups of two *L* ligands. In addition, atom Cu1 interacts weakly with atom O1^{iii} [2.6852 (16) Å; symmetry code: (iii) $1 + x, y, z$], which belongs to an *L* ligand in an adjacent layer. Therefore, Cu1 has square-pyramidal coordination geometry. Atom Cu2 is trigonally coordinated by two N atoms [N1 and N2^{ii}; symmetry code: (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$] from two QA molecules and one O atom (O1) from an *L* carboxylate group.

Cu^{II} ions with d^9 configurations tend to have a square-pyramidal or axially elongated octahedral coordination geometry, while Cu^{I} ions with d^{10} configurations often adopt a trigonal or tetrahedral coordination geometry (Zhang & Fang, 2005). The coordination geometry of the copper centres, in combination with the charge balance, indicates that in compound (I) atom Cu1 is dipositive and atom Cu2 is monopositive. The Cu^{I} ions are bridged by QA ligands to give a chain along the *c* axis. Two Cu^{II} ions and two *L* ligands form a $[Cu_2L_2]^{2-}$ 'metallo-ligand', which coordinates two Cu^{I} ions. Thus, the chains of Cu^{I} and QA units are linked by the $[Cu_2L_2]^{2-}$ metallo-ligand to yield a (6,3) sheet in the $(10\overline{1})$ plane (Fig. 2). These sheets are further linked by the Cu1—O1 interaction into a three-dimensional framework.

It is worth noting that a new *in situ* reaction occurs in the $CuCl_2 \cdot 2H_2O/H_3L1/QA$ system under hydrothermal conditions. The *L*1 ligand was transformed into *L via* decarboxylation and hydroxylation steps. The *in situ* transformation from *L*1 to *L* in the present system has rarely been observed before, although a similar reaction process whereby mixed-valence Cu^{I,II} species and *in situ* synthesis of *L* are simultaneously generated under the hydrothermal reaction of isophthalate and 4,4′-bipyridine with $Cu(NO_3) \cdot 3H_2O$ has been reported (Tao *et al.*, 2002). So far, a few novel *in situ* reactions such as ligand oxidative coupling, hydrolysis and substitution have been observed during the hydrothermal process (Tao *et al.*, 2002), in which many factors, including the nature of the metal ion and the temperature, pressure and pH have been found to influence the reaction outcome significantly. As far as the present system is concerned, the pH value may play a key role in the transformation of *L*1 to *L*.

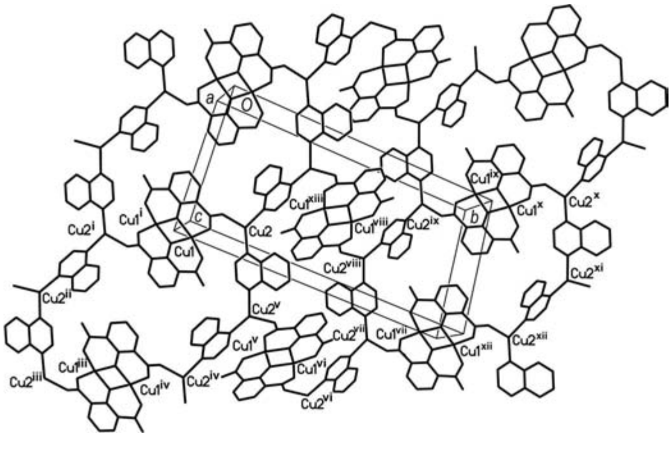

Figure 2
A view of the layer structure of (I) in the $(10\overline{1})$ plane. For the sake of clarity, all H atoms have been omitted. [Symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{5}{2} - z$; (iii) $3 - x, -y, 3 - z$; (iv) $1 + x, y, 1 + z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z$; (vii) $2 - x, 1 - y, 2 - z$; (viii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ix) $1 - x, 1 - y, 1 - z$; (*x*) $x - 1, 1 + y, z - 1$; (xi) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (xii) $x, 1 + y, z$; (xiii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.]

Experimental

A mixture of $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.5 mmol), H_3L1 (0.070 g, 0.33 mmol) and QA (0.065 g, 0.5 mmol) was dissolved in distilled water (10 ml); this was followed by the addition of triethylamine until the pH was in the range 5.5–6.3. The resulting solution was stirred for about 1 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 453 K for 5 d under autogenous pressure. Afterwards, the reaction system was cooled slowly to room temperature. Dark-red block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 29%, based on Cu).

Crystal data

$[Cu_2(C_8H_3O_5)(C_8H_6N_2)]$
$M_r = 436.33$
Monoclinic, $P2_1/n$
$a = 5.2011$ (2) Å
$b = 23.5553$ (11) Å
$c = 12.2402$ (6) Å
$\beta = 101.7190$ (10)°
$V = 1468.33$ (11) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.93$ mm^{-1}
$T = 293$ (2) K
0.31 × 0.27 × 0.19 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.391$, $T_{max} = 0.575$
8982 measured reflections
3402 independent reflections
2852 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.071$
$S = 0.96$
3402 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

The carbon-bound H atoms were generated geometrically (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. No H atoms were found in the vicinity of the carboxyl or hydroxyl O atoms, consistent with the relevant C—O distances. The small voids within the structure were found to contain no significant electron density.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3240). Services for accessing these data are described at the back of the journal.

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