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catena-Poly[[[pyridinecopper(II)]-bis[μ_3-4-(2-oxidobenzylideneamino)-benzoato]] dimethylformamide disolvate], a polymer composed of dimeric dicopper building units

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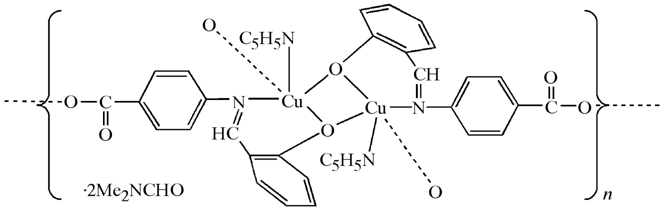
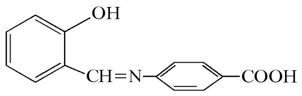
The title compound, $\{[Cu(C_{14}H_9NO_3)(C_5H_5N)]\cdot C_3H_7NO\}_n$ or $\{[Cu_2L_2(py)_2]\cdot 2DMF\}_n$ [py is pyridine, L is 4-(salicylideneamino)benzoate and DMF is dimethylformamide], is composed of dimeric dicopper $[CuL(py)]_2$ building units, which are interlinked into a one-dimensional chain through the formation of $Cu-O_{COO}$ bonds. The dimeric unit is centrosymmetric, containing two Cu^{II} atoms linked by bridging phenolate O atoms into a Cu_2O_2 plane with a chelating Cu—O bond length of 1.927 (2) Å and a bridging Cu—O bond length of 2.440 (2) Å. Interchain C—H⋯O and π–π stacking interactions are responsible for an extensive three-dimensional structure in which the resulting channels are filled by DMF solvent molecules.

Comment

The design and construction of metal–organic frameworks is of great interest owing to their potential as new functional materials, as well as their fascinating variety of topologies (Kitagawa *et al.*, 2004; Steel, 2005; Takaoka *et al.*, 2005). By rational choice of organic ligand and transition metal ion, one aims to modify the structure and the physical properties of complex architectures. Recently, use of a second building block has been demonstrated to be fruitful in constructing and analyzing structures of complex architecture (Kim *et al.*, 2001). Schiff bases are excellent as ligands and are employed for preparing complexes with special functions, such as biological activity, catalysis or magnetism. A salen-type Schiff base [H_2salen is bis(salicylidene)ethylenediamine] is one of the most appealing candidates for the formation of dimeric dinuclear complexes through the bridging phenolate O atoms (Bai *et al.*, 2006; Iskander *et al.*, 2000). Numerous dimeric copper complexes with these ligands exhibit antiferromagnetic exchange (Bai *et al.*, 2006; Shyu *et al.*, 1996). Considering that such dimers would exhibit unusual magnetic behavior when introduced into metal–organic frameworks as 'magnetic brick' building blocks, we focused our preparative efforts on exploiting these 'magnetic bricks' to create new architectures. In this work, the bridging ligand 4-(salicylideneamino)benzoic acid (H_2L), which was derived from the condensation of salicylaldehyde and 4-aminobenzoic acid, was exploited to bridge the 'bricks' of a dimeric dicopper complex into polymeric $\{[CuL(py)]_2\cdot 2DMF\}_n$ (py is pyridine and DMF is dimethylformamide), (I), through a self-assembly process.



(I)



H_2L

Single-crystal structural analysis reveals that the title compound, which crystallized in the triclinic $P\overline{1}$ group, is composed of dimeric $[CuL(py)]_2$ building units, which are interlinked through the formation of $Cu-O_{COO}$ bonds into a one-dimensional polymer along the crystallographic c axis. The asymmetric unit of (I) consists of half of the dimer along with one DMF solvent molecule (Fig. 1). The dimeric unit is

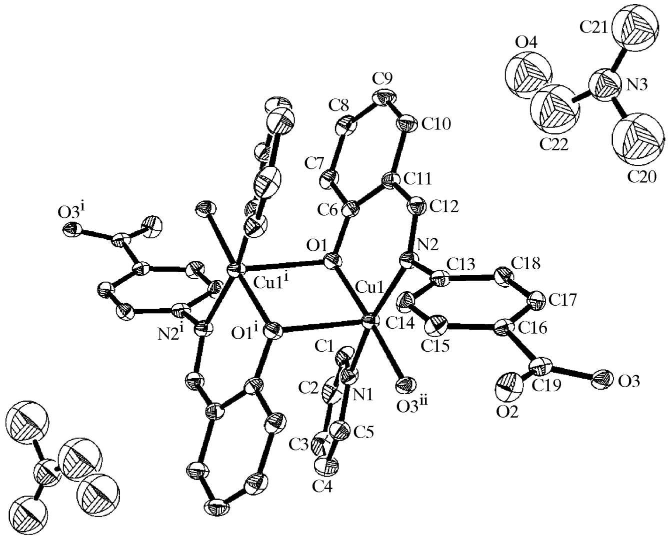


Figure 1
A displacement ellipsoid representation (at the 30% probability level) of the coordination environment of the Cu^{II} atom in the title compound. Unlabeled atoms are related by an inversion center to the labeled atoms. [Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 1, -y, -z$.]

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centrosymmetric, with the Cu_2O_2 plane bridged by two phenolate O atoms. The Cu$\cdots$Cu separation is 3.300 (5) Å and the Cu1—O1—Cu1^{i} angle is 97.50 (9)° in the Cu_2O_2 plane [symmetry code: (i) $-x + 1$, $-y$, $-z + 1$]. Such dimerization *via* the bridging phenolate O atoms has been noted previously in the generation of simple binuclear complexes.

In the dimeric unit, each copper(II) center is in a square-pyramidal geometric environment, with the basal plane consisting of a chelating phenolate O atom and an imine N atom from one ligand, a carboxylate O atom from a neighboring dimer, and a pyridyl N atom, and the apical site occupied by a bridging phenolate O atom from another ligand in the dimer. The coordination polyhedron around each copper center is best described as (4+1) distorted square pyramidal, with the value of the tetragonality parameter τ equal to 0.158 [$\tau = (\beta - \alpha)/60$, where α and β are the N1—Cu1—N2 and O1—Cu1—O3^{ii} angles, respectively (Addison *et al.*, 1984); symmetry code as in Table 1]. The Cu—O bond lengths (average 1.928 Å) are shorter than the Cu—N bonds (average 2.029 Å) in the basal plane. The chelating Cu—O length of 1.927 (2) Å is shorter than the bridging length of 2.440 (2) Å, as is the situation in $[Cu(LBPh_3)]_2$ [$LBPh_3$ is *N*-(salicylidene)-*N*′-(1-triphenylborylimidazol-2-ylmethylene)-1,3-propanediamine; Shyu *et al.*, 1996]. However, the Cu$\cdots$Cu separation in the Cu_2O_2 plane is longer than that in $[Cu(LBPh_3)]_2$ [3.085 (4) Å], possibly because of the steric hindrance of pyridyl rings and benzene rings around the Cu_2O_2 plane. The pyridyl ring is almost perpendicular to the Cu_2O_2 plane, with a dihedral angle of 91.6°. On further comparison with the most closely related phenolate-O-bridging dinuclear copper compounds, it was found that the bridging Cu—O bond lengths are similar to the chelating bonds if the chelating and bridged phenolate O atoms are in the same equatorial plane (Paschke *et al.*, 2003). The long bridging bond length and the long Cu$\cdots$Cu separation in the Cu_2O_2 plane reveal that the dimerization of the title compound is a little loose. In the polymer, there is one subunit of the binuclear Cu_2L_2 macrocycle, which is stabilized by π–π stacking interactions between the rings of the benzoate groups, with a centroid–centroid distance of 3.677 Å, an interplanar distance of 3.154 Å and a shift between the centroids of 1.890 Å. The Cu$\cdots$Cu distance in this macrocycle is 8.953 Å, a value intermediate between those observed for other Cu^{II}_2 complexes containing similar aromatic spacers (Paital *et al.*, 2007). Adjacent macrocycles are linked by two bridging phenolate O atoms. Therefore, this polymer can also be described as being composed of binuclear macrocycles interlinked through the formation of bridging Cu—O_{phenol} bonds (Fig. 2), based on the long bridging Cu—O_{phenol} distances.

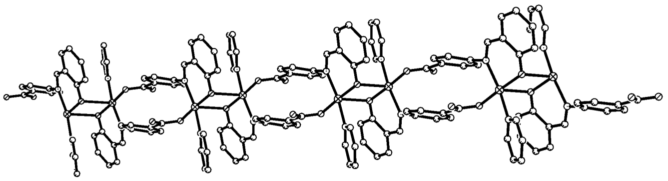

Figure 2
A view of the chain along the crystallographic *c* axis.

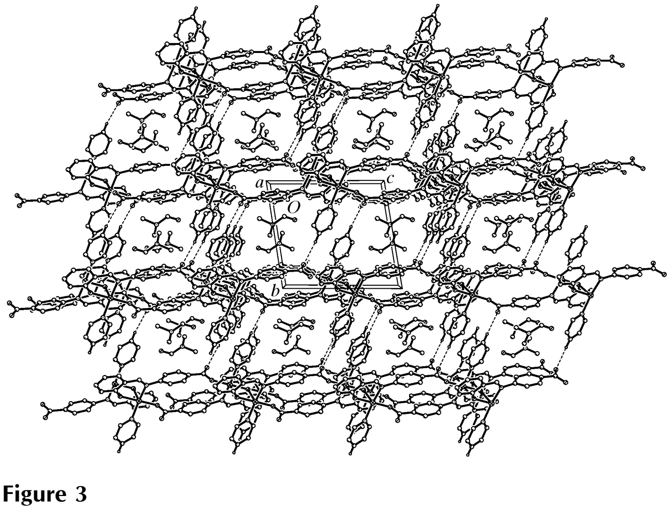

Figure 3
The packing of the title compound, projected along the *a* axis. The three-dimensional network with channels is obtained by interchain C—H$\cdots$O interactions and π–π stacking. DMF solvent molecules are encapsulated in the channels.

It is worth noting that unusual supramolecular interactions in the solid state, including C—H$\cdots$O hydrogen bonds and π–π stacking, generate a unique supramolecular architecture. Interchain C3—H3$\cdots$O2^{iii} contacts [C3$\cdots$O2^{iii} = 3.300 (5) Å, H3$\cdots$O2^{iii} = 2.45 Å and C3—H3$\cdots$O2^{iii} = 152°; symmetry code: (iii) x, $y - 1$, $z + 1$], together with π–π stacking interactions between pyridyl rings (the centroid–centroid distance is 3.718 Å, the interplanar distance is 2.738 Å and the shift between the centroids is 2.517 Å), drive polymers to arrange along the crystallographic *b* axis, while the polymers also extend along the *a* axis through interchain π–π stacking interactions between aromatic rings of salicylaldimine groups (the centroid–centroid distance is 3.638 Å, the interplanar distance is 2.742 Å and the shift between the centroids is 2.391 Å) (Müller-Dethlefs & Hobza, 2000). These weak interactions are responsible for an extensive three-dimensional structure in which the resulting channels are filled by DMF solvent molecules (Fig. 3).

Experimental

For the synthesis of H_2L, a solution of salicylaldehyde (0.9780 g, 8 mmol) in CH_3OH (10 ml) was added to a solution of 4-aminobenzoic acid (1.096 g, 8 mmol) in CH_3OH (50 ml) with stirring. A large amount of yellow precipitate was formed immediately. The slurry mixture was stirred vigorously for a further 4 h and filtered. The yellow powder product was recrystallized from CH_3CH_2OH (80 ml) for purification. For the synthesis of the title complex, a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.0373 g, 0.1 mmol) in DMF (5 ml) was added to a solution of H_2L (0.0482 g, 0.2 mmol) and Et_3N (0.0552 ml, 0.4 mmol) in DMF (5 ml) with stirring. The resulting precipitate was filtered off and dissolved in pyridine (2 ml). Ethyl ether was diffused into the pyridine solution. Two weeks later, crystals were selected for X-ray diffraction.

Crystal data

[Cu($C_{14}H_9NO_3$)(C_5H_5N)]·C_3H_7NO
M_r = 454.96
Triclinic, $P\overline{1}$
a = 8.9547 (13) Å
b = 10.6215 (15) Å
c = 11.3899 (16) Å
α = 80.393 (5)°
β = 86.408 (3)°
γ = 80.138 (2)°
V = 1051.7 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 298 (2) K
0.23 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min}$ = 0.752, $T_{\max}$ = 0.842
7282 measured reflections
4757 independent reflections
3900 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.093

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.184
S = 1.09
4757 reflections
246 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.07 e Å^{-3}
$\Delta\rho_{\min}$ = −0.64 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.927 (2)	Cu1—N2	2.020 (3)
Cu1—O1$^{\rm i}$	2.440 (2)	Cu1—N1	2.038 (3)
Cu1—O3$^{\rm ii}$	1.930 (2)		
O1—Cu1—O3$^{\rm ii}$	176.68 (9)	O1—Cu1—O1$^{\rm i}$	82.50 (9)
O1—Cu1—N2	90.46 (10)	O3$^{\rm ii}$—Cu1—O1$^{\rm i}$	94.38 (10)
O3$^{\rm ii}$—Cu1—N2	91.26 (10)	N2—Cu1—O1$^{\rm i}$	100.60 (10)
O1—Cu1—N1	89.10 (11)	N1—Cu1—O1$^{\rm i}$	92.06 (10)
O3$^{\rm ii}$—Cu1—N1	89.86 (11)	Cu1—O1—Cu1$^{\rm i}$	97.50 (9)
N2—Cu1—N1	167.16 (12)		

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

All H atoms were positioned geometrically, with C—H distances of 0.93 or 0.96 Å, and refined using a riding model.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3097). Services for accessing these data are described at the back of the journal.

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