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catena-Poly[bis[(2,2-bipyridine-κ^2N,N')copper(II)]-μ_4-1,2,4,5-benzenetetracarboxylato-κ^4O^1:O^2:O^3:O^4]

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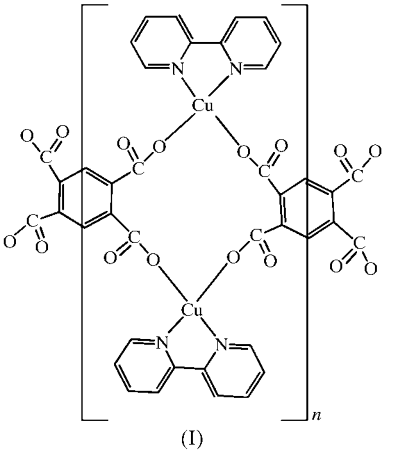
In the title complex, $[\mathrm{Cu_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2}]_n$, the Cu$^{\mathrm{II}}$ cation has a four-coordinated environment, completed by two carboxyl O atoms belonging to two 1,2,4,5-benzenetetracarboxylate anions (TCB^{4-}) and two N atoms from one 2,2′-bipyridine (2,2′-bipy) ligand, forming a distorted square-planar geometry. The [Cu(2,2′-bipy)]$^{2+}$ moieties are bridged by TCB^{4-} anions, which lie about inversion centres, forming an infinite one-dimensional coordination polymer with a double-chain structure along the *a* axis. A two-dimensional network structure is formed *via* a face-to-face π–π interaction between the 2,2′-bipy rings belonging to two adjacent double chains, at a distance of approximately 3.56 Å.

Comment

In recent years, the design and construction of metal–organic coordination polymers have been extensively studied, due to the crystallographic diversity of these compounds and their potential applications in catalysis, non-linear optics and gas adsorption (Chen *et al.*, 2003; Eddaoudi *et al.*, 2001; Shi *et al.*, 2003; Stein *et al.*, 1993). In this field, 1,2,4,5-benzenetetracarboxylic acid (H$_4$TCB) is a good bridging ligand, and numerous complexes with TCB^{4-} anions have been prepared. The TCB^{4-} anions usually coordinate to metal ions in a μ_2-bridging mode (Hu *et al.*, 2003) and occasionally in a μ_4-bridging mode (Shi *et al.*, 2001), while in the title complex, $[\mathrm{Cu(TCB)_{0.5}(2,2'\text{-}bpy)}]_n$, (I), each TCB^{4-} anion binds four Cu$^{\mathrm{II}}$ ions in a tetra-monodentate mode. Moreover, it should be pointed out that new complexes are constantly being obtained *via* different reaction conditions, such as the use of different solvents, synthesis conditions or H-atom acceptors.



(I)

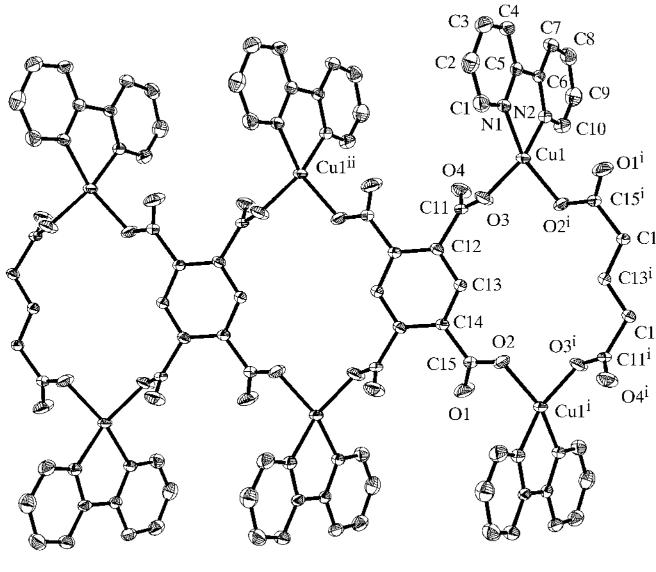


Figure 1
The coordination environment of the Cu$^{\mathrm{II}}$ cation in (I), with the atom-numbering scheme, showing the double-chain structure with cavities of approximately 4.5 × 6.1 Å, viewed along the *b* axis [symmetry codes: (i) $-x$, $1-y$, $-z$; (ii) $x-1$, y, z]. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

In (I), each Cu$^{\mathrm{II}}$ cation has a four-coordinated environment, completed by two carboxyl O atoms belonging to two TCB^{4-} anions and two N atoms from one 2,2′-bipy ligand (Fig. 1). The bond lengths around the Cu$^{\mathrm{II}}$ centres are 1.956 (2) Å for Cu1—O3, 1.972 (2) Å for Cu1—O2$^{\mathrm{i}}$, 1.978 (2) Å for Cu1—N2 and 1.987 (2) Å for Cu1—N1 [symmetry code: (i) $-x$, $1-y$, $-z$]. The N2—Cu1—N1, O3—Cu1—O2$^{\mathrm{i}}$, O3—Cu1—N1 and O2$^{\mathrm{i}}$—Cu1—N2 bond angles are in the range 81.80 (10)–98.33 (10)°, significantly different from the ideal value.

From these bond lengths and angles, we can best describe the coordination of the Cu$^{\mathrm{II}}$ cation as a distorted square-planar geometry. Moreover, the coordination mode of the TCB^{4-} anion is similar to that in $[\mathrm{Cu_2(TCB)(phen)_2}]_n\cdot n\mathrm{H_2O}$ (Shi *et al.*, 2001); the four carboxylate groups are all deprotonated and coordinate to four Cu$^{\mathrm{II}}$ cations in a monodentate fashion, forming an infinite one-dimensional ribbon-like double-chain structure with cavities of approximately 4.5 × 6.1 Å along the *a* axis (Fig. 1). The Cu1$\cdots$Cu1$^{\mathrm{i}}$ and Cu1$^{\mathrm{i}}\cdots$Cu1$^{\mathrm{ii}}$ separation distances are 7.931 and 7.279 Å, respectively [symmetry code: (ii) $x-1$, y, z]. Furthermore, there are π–π interactions between the aromatic rings of 2,2′-bipy ligands belonging to two adjacent double chains, at a distance of approximately 3.56 Å, resulting in a two-dimensional network structure (Fig. 2).

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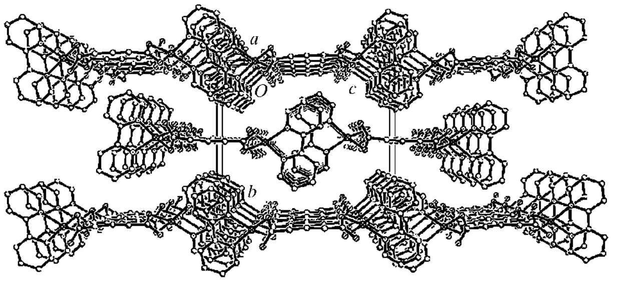

Figure 2
A view of the two-dimensional network structure in (I), formed by π–π interactions.

Experimental

A solution (10 ml) of dimethylformamide containing $CuCl_2\cdot 2H_2O$ (0.5 mmol, 0.085 g) and H_4TCB (0.5 mmol, 0.127 g) was added slowly to a solution (10 ml) of dimethylformamide containing 2,2′-bipy (0.5 mmol, 0.078 g). The mixture was stirred for 30 min and then left to stand at room temperature for about a month. Light-blue prism-shaped crystals of (I) were obtained.

Crystal data

$[Cu_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2]$
$M_r = 689.56$
Monoclinic, $P2_1/n$
$a = 7.2794$ (7) Å
$b = 12.5009$ (12) Å
$c = 14.4436$ (14) Å
$\beta = 104.021$ (2)°
$V = 1275.2$ (2) Å^3
$Z = 2$

$D_x = 1.796$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 532 reflections
$\theta = 2.4$–$22.0°$
$\mu = 1.73$ mm^{-1}
$T = 273$ (2) K
Prism, blue
0.32 × 0.29 × 0.24 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.582$, $T_{\max} = 0.663$
9055 measured reflections

2263 independent reflections
2179 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 25.1°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.087$
$S = 1.16$
2263 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.7086P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 Å, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: SQ1144). Services for accessing these data are described at the back of the journal.

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