

A mixed-valence chair-like tetranuclear copper(I,II) cluster with three linking modes of the 3,5-bis(2-pyridyl)-1,2,4-triazole ligand

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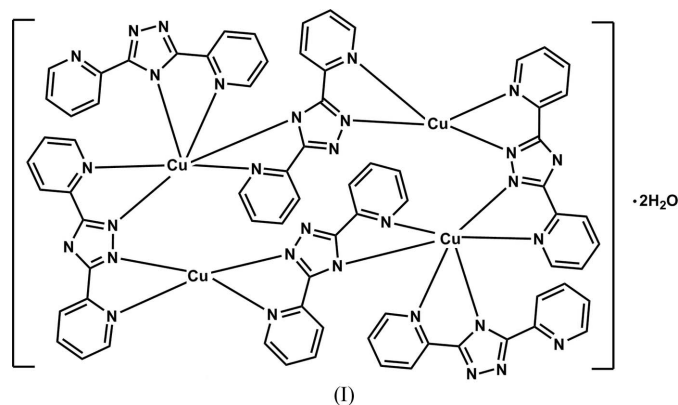
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In the tetranuclear copper complex tetrakis[μ -3,5-bis(2-pyridyl)-1,2,4-triazolido]bis[3,5-bis(2-pyridyl)-1,2,4-triazolido]dicopper(I)dicopper(II) dihydrate, $[\text{Cu}_2^{\text{I}}\text{Cu}_2^{\text{II}}(\text{C}_{12}\text{H}_8\text{N}_5)_6] \cdot 2\text{H}_2\text{O}$, the asymmetric unit is composed of one Cu^{I} center, one Cu^{II} center, three anionic 3,5-bis(2-pyridyl)-1,2,4-triazole (2-BPT) ligands and one solvent water molecule. The Cu^{I} and Cu^{II} centers exhibit $[\text{Cu}^{\text{I}}\text{N}_4]$ tetrahedral and $[\text{Cu}^{\text{II}}\text{N}_6]$ octahedral coordination environments, respectively. The three independent 2-BPT ligands adopt different chelating modes, which link the copper centers to generate a chair-like tetranuclear metallomacrocyclic with metal–metal distances of about $4.4 \times 6.2 \text{ \AA}$ disposed about a crystallographic inversion center. Furthermore, strong π – π stacking interactions and $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen-bonding systems link the tetracopper clusters into a two-dimensional supramolecular network.

Comment

In the past decade, pyridyl- and/or carboxylate-containing organic ligands have been mostly utilized in the synthesis of functional metal–organic coordination compounds (Kitagawa *et al.*, 2004; Ye *et al.*, 2005). Among these ligands, dipyridyl-type building blocks have been identified as excellent connectors to construct polynuclear clusters or one- to three-dimensional frameworks upon metalation. More recently, work on the modification of bipyridyl *via* the introduction of different spacers between two terminal pyridyl groups has produced several unexpected metal–organic architectures. In this regard, a series of angular dipyridyl derivatives, namely 2,5-bis(2/3/4-pyridyl)-1,3,4-oxadiazole or 4-*R*-3,5-bis(2/3/4-pyridyl)-1,2,4-triazole ($R = \text{H}, \text{NH}_2, \text{phenyl}, \text{pyridyl}, \text{etc.}$), have been intensively investigated (Dong *et al.*, 2005, and references therein; Du *et al.*, 2008, and references therein). Because of the specific geometry of such diazole- or triazole-containing

ligands and the coordination preferences of transition metals, many new types of coordination complexes with unprecedented topologies and potential applications have been prepared. As part of our ongoing research project dealing with the coordination chemistry of polyaza heteroaromatic ligands, we have synthesized a series of d^{10} transition metal ($\text{Cu}^{\text{I}}, \text{Ag}^{\text{I}}, \text{Zn}^{\text{II}}$ and Cd^{II}) triazolates utilizing dialkyl-substituted 1,2,4-triazole ligands (Zhai *et al.*, 2007, and references therein). This has encouraged us to continue this project and expand from dialkyl-substituted ligands to dipyridyl-substituted ligands. By controlling the reaction temperatures, the self-assembly of AgNO_3 and 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole under hydrothermal conditions has produced three novel high-dimensional coordination polymers (Zhai *et al.*, 2009). We report here the structure of the title complex, (I), in which a mixed-valence chair-like tetranuclear cluster is observed along with three independent 3,5-bis(2-pyridyl)-1,2,4-triazole (2-BPT) ligands; this is the first example that exhibits three different chelating modes of 2-BPT in the same structure.



Compound (I) was separated from the hydrothermal reaction of CuCN and 2-BPT ligands as pure brown block-like crystals. The absence of characteristic bands at about 2100 cm^{-1} indicates that cyanide ions are not present in the structure of (I). The structural analysis shows that (I) possesses a centrosymmetric tetranuclear metallomacrocyclic structure. As shown in Fig. 1, one Cu^{I} center, one Cu^{II} center, three anionic 2-BPT ligands and one solvent water molecule occupy the asymmetric unit of (I). The Cu^{I} ion is in a distorted $[\text{Cu}^{\text{I}}\text{N}_4]$ tetrahedral environment (Table 1). The Cu^{II} center is six-coordinated by three pyridyl N atoms and three triazole N atoms to form an octahedral environment (see Table 1). The three 2-BPT ligands adopt distinct linking modes: *cisoid–cisoid* tetradentate, *cisoid–transoid* tetradentate and *transoid* bidentate. The *cisoid–cisoid* and *cisoid–transoid* 2-BPT ligands both act as μ_2 -bridges to connect two copper centers, and the *transoid* bidentate 2-BPT serves as a terminal ligand to complete the Cu^{II} octahedron. Because the two bidentate chelating sites are both fused to a five-membered ring, the central triazole ring and two 2-pyridyl groups are basically coplanar in the two tetradentate ligands [dihedral angles = $5.4 (4)$ and $6.5 (4)^\circ$]. However, the dihedral angle between the two pyridyl groups in the terminal bidentate 2-BPT ligand is

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49.5 (4)°, which is comparable to what is found in other structurally characterized complexes with similar chelating behavior (Dong *et al.*, 2005; Du *et al.*, 2008).

In contrast to the commonly expected grid-like tetranuclear architectures, this chair-like structure of (I) displays several unique features. The four metal centers in (I) define a quadrangle [Cu1···Cu2 = 4.4197 (11) Å, Cu1···Cu2ⁱ = 6.1869 (9) Å and Cu2···Cu1···Cu2ⁱ = 74.638 (13)°; symmetry code: (i) $-x + 1, -y + 1, -z + 1$; Fig. 2]. The two inversion-related *cisoid-transoid* ligands are engaged in a strong intramolecular face-to-face π - π interaction (*ca* 3.6 Å), which may effectively stabilize the chair-like metallomacrocyclic. The bi-chelating mode means that the two metal centers are basically coplanar with the organic ligand and so face-to-face separations should be close to the intermetallic distances in regular grid-like structures but can be shortened when the square distorts into a rhomb. Furthermore, intermolecular aromatic π - π stacking interactions between 2-pyridyl rings from terminal 2-BPT ligands are observed, with a centroid-centroid distance of 3.8406 (4) Å between the N1- and N1ⁱⁱⁱ-containing rings [symmetry code: (iii) $-x + 2, -y, -z + 1$], which link adjacent tetranuclear clusters into a one-dimensional chain. On the other hand, the chair-like clusters are also connected through pairwise O-H···N [O1···N3 = 2.945 (7) Å and O1···N10 = 3.089 (8) Å; Table 2] hydrogen bonds to give another one-dimensional chain. The two chains crosslink to form a two-dimensional supramolecular network as depicted in Fig. 3.

To the best of our knowledge, although the squares, grids and circular helicates have been extensively studied, such a chair-like metallomacrocyclic has been rarely described previously. Zhang and co-workers have created two similar chair-like tetranuclear compounds $\{[Cu_4(2-BPT)_4]\}$, (II)

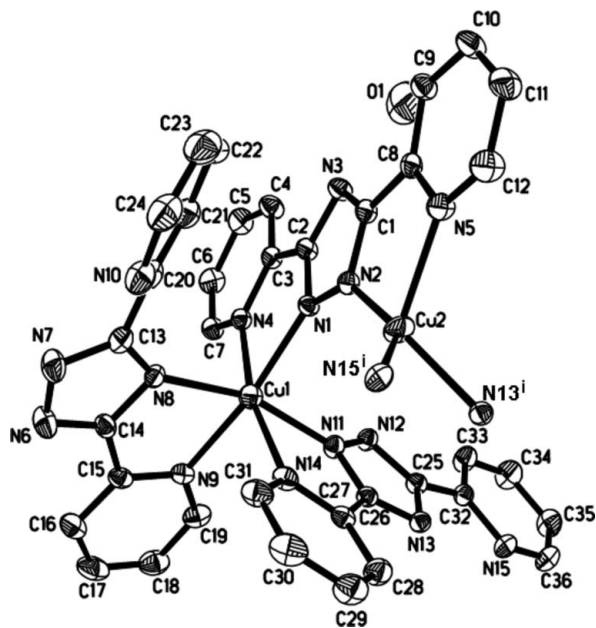


Figure 1
The asymmetric unit in (I), shown with 30% probability displacement ellipsoids. All H atoms have been omitted for clarity and atoms N13ⁱ and N15ⁱ have been added to complete the coordination sphere around Cu2. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

(Zhang *et al.*, 2005a), and $[Cu_2Cu_2(2-BPT)_4(2-pa)_2] \cdot 2H_2O$, (III) (2-Hpa is pyridine-2-carboxylic acid; Zhang *et al.*, 2005b) with the same ligands generated *via in situ* oxidative cycloaddition of 2-cyanopyridine and ammonia under solvothermal conditions. Like the title compound, (II) crystallizes in the space group $P2_1/c$, but four tetrahedral copper(I) centers form a quasi-rectangle with a Cu2···Cu1···Cu2ⁱ angle of 90.7°. Replacement of the two terminal 2-BPT ligands in (I) by pyridine-2-carboxylate generates compound (III) which crystallizes in the space group $P\bar{1}$. As pointed out by Zhang *et al.* (2005a), the unique structure of 2-BPT usually gives a five-membered ring upon complexation, but a six-membered ring is commonly observed for a grid and a long and flexible ring is required for a helicate. Thus, no grid or other hypothetical circular helicate compounds have been synthesized with 2-BPT ligands to date.

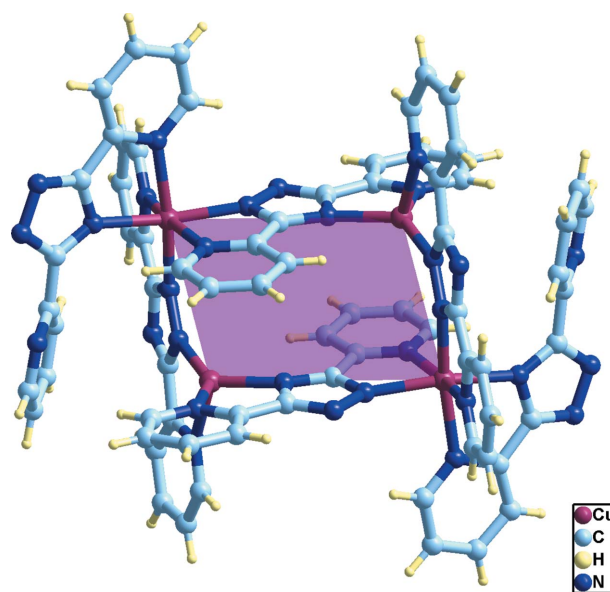


Figure 2
The chair-like tetranuclear metallomacrocyclic structure of (I).

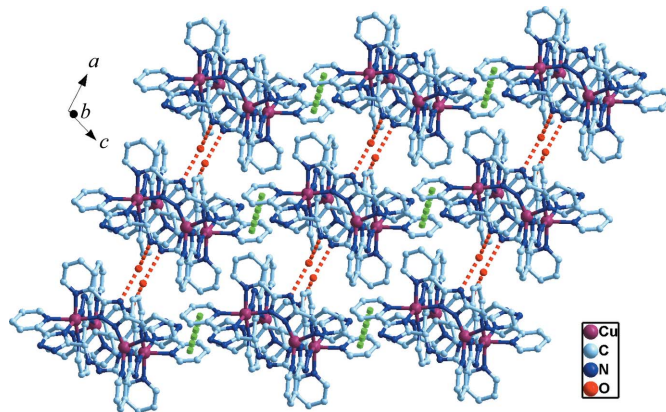


Figure 3
The two-dimensional supramolecular network of (I) generated by π - π interactions (green broken lines in the electronic version of the paper) and O-H···N hydrogen bonds (red broken lines). All H atoms have been omitted for clarity.

Upon excitation of solid samples of (I) at $\lambda = 278$ nm, intense bands in the emission spectra are observed at 380 nm. To understand more thoroughly the nature of the emission band, we also investigated the luminescence of the organic ligand. The rigid 2-BPT exhibits an emission with a maximum at $\lambda = 420$ nm upon excitation at $\lambda = 357$ nm. In our opinion, the emission of complex (I) is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer in nature, and may be assigned to intraligand fluorescence emission because of the similarity of the emission bands of the title compound and the organic ligand. Compared with the organic ligands, the enhancement and marked blueshifts are due to the unique coordination of the organic ligands to the copper center, increasing the ligand conformational rigidity, thereby reducing the nonradiative decay of the intraligand ($\pi-\pi^*$) excited state (Ding *et al.*, 2006).

Experimental

A mixture of CuCN (0.09 g, 1.0 mmol), $K_4Fe(CN)_6 \cdot 3H_2O$ (0.42 g, 1.0 mmol) and 3,5-bis(2-pyridyl)-1,2,4-triazole (2-BPT; 0.33 g, 1.5 mmol) in water (10 ml) was introduced into a Parr Teflon-lined stainless steel vessel (25 ml). The vessel was sealed and heated at 453 K for 5 d under autogenous pressure. After the reaction mixture had been cooled to room temperature over a period of 72 h, brown block-like crystals of (I) were produced (yield 68%, based on Cu). Analysis calculated for $C_{72}H_{52}Cu_4N_{30}O_2$: C 53.26, H 3.23, N 25.88%; found: C 53.35, H 3.18, N 25.63%. IR (KBr, cm^{-1}): 3418 (*m*), 3062 (*w*), 1600 (*s*), 1566 (*m*), 1516 (*w*), 1493 (*s*), 1461 (*s*), 1436 (*m*), 1412 (*s*), 1276 (*w*), 1255 (*w*), 1188 (*w*), 1168 (*w*), 1091 (*w*), 1047 (*w*), 1011 (*w*), 797 (*s*), 748 (*s*), 724 (*m*), 634 (*w*), 563 (*w*), 464 (*w*).

Crystal data

$[Cu_4(C_{12}H_8N_5)_6] \cdot 2H_2O$	$V = 3475.7$ (6) \AA^3
$M_r = 1623.60$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.5696$ (10) \AA	$\mu = 1.28$ mm^{-1}
$b = 27.589$ (2) \AA	$T = 298$ K
$c = 12.6090$ (14) \AA	$0.23 \times 0.20 \times 0.04$ mm
$\beta = 109.039$ (2)°	

Data collection

Bruker SMART CCD diffractometer	17303 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	6122 independent reflections
$T_{min} = 0.757$, $T_{max} = 0.948$	4601 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	487 parameters
$wR(F^2) = 0.170$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 0.65$ e \AA^{-3}
6122 reflections	$\Delta\rho_{min} = -1.16$ e \AA^{-3}

H atoms were positioned geometrically and included in the refinement using a riding model [$C-H = 0.93$ \AA , $O-H = 0.85$ \AA and $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$]. The directions of the O—H vectors were aligned with peaks initially located from difference maps. The maximum residual electron density is located 0.70 \AA from atom Cu2 and the minimum density lies 0.42 \AA from atom Cu1.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	2.103 (4)	Cu1—N14	2.225 (4)
Cu1—N11	2.119 (4)	Cu2—N2	1.957 (4)
Cu1—N8	2.149 (4)	Cu2—N13 ⁱ	2.040 (4)
Cu1—N4	2.209 (4)	Cu2—N15 ⁱ	2.051 (4)
Cu1—N9	2.215 (4)	Cu2—N5	2.179 (4)
N1—Cu1—N4	76.41 (14)	N11—Cu1—N4	94.10 (14)
N1—Cu1—N8	100.13 (15)	N11—Cu1—N9	92.04 (15)
N1—Cu1—N9	169.46 (15)	N11—Cu1—N8	163.13 (14)
N1—Cu1—N11	92.56 (15)	N11—Cu1—N14	75.99 (14)
N1—Cu1—N14	96.53 (14)	N2—Cu2—N5	80.14 (15)
N4—Cu1—N9	93.81 (14)	N2—Cu2—N13 ⁱ	130.59 (16)
N4—Cu1—N14	167.72 (14)	N2—Cu2—N15 ⁱ	140.54 (17)
N8—Cu1—N4	99.63 (14)	N13 ⁱ —Cu2—N5	113.08 (16)
N8—Cu1—N9	77.39 (15)	N13 ⁱ —Cu2—N15 ⁱ	81.75 (15)
N8—Cu1—N14	91.44 (14)	N15 ⁱ —Cu2—N5	110.23 (17)
N9—Cu1—N14	93.78 (14)		

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A \cdots N3	0.85	2.14	2.945 (7)	159
O1—H1B \cdots N10 ⁱⁱ	0.85	2.28	3.089 (8)	159

Symmetry code: (ii) $x + 1, y, z$.

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 publCIF (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3127). Services for accessing these data are described at the back of the journal.

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