

A one-dimensional coordination polymer based on a di-Schiff base supported trinuclear Cu^{II} subunit

Liangliang Zhang, Fuling Liu, Shuai Yuan, Xiaoyang Wang and Di Sun*

Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, People's Republic of China

Correspondence e-mail: dsun@sdu.edu.cn

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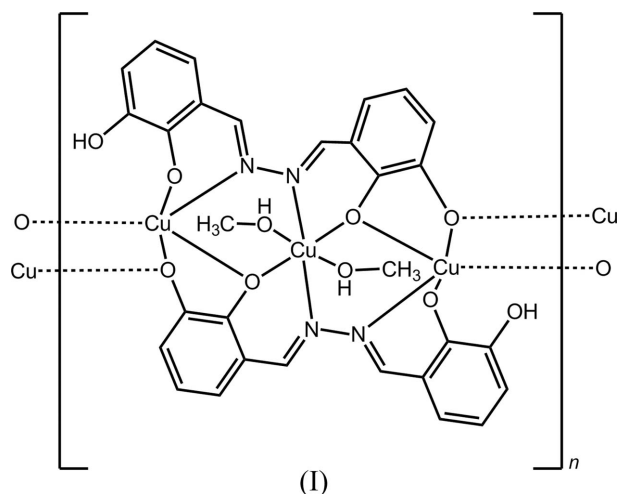
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A novel one-dimensional Cu^{II} coordination polymer, *catenapoly*[bis(μ_4 -3-[[2-(3-hydroxy-2-oxidobenzylidene)hydrazinylidene]methyl]benzene-1,2-diolato)dimethanoltricopper(II)], [Cu₃(C₁₄H₁₀N₂O₄)₂(CH₃OH)₂]_n, (I), was constructed with a di-Schiff base supported centrosymmetric trinuclear Cu^{II} subunit. In the subunit, two peripheral symmetry-related Cu^{II} cations have square-pyramidal CuNO₄ geometry and the central third Cu^{II} cation lies on an inversion centre with octahedral CuN₂O₄ geometry. In (I), each partially deprotonated di-Schiff base 3-[[2-(3-hydroxy-2-oxidobenzylidene)hydrazinylidene]methyl]benzene-1,2-diolate ligand (Hbcz³⁻) acts as a heptadentate ligand to bind the Cu^{II} centres into chains along the *a* axis. A centrosymmetric Cu₂O₂ unit containing an asymmetrically bridging O atom, being axial at one Cu atom and equatorial at the other Cu atom, links the trinuclear Cu^{II} subunit into a one-dimensional chain, which is reinforced by intramolecular phenol–methanol O–H...O and methanol–phenolate O–H...O hydrogen bonds. Inter-chain π – π stacking interactions between pyrocatechol units, with a distance of 3.5251 (18) Å, contribute to the stability of the crystal packing.

Comment

Significant interest in the coordination chemistry of polydentate Schiff bases arises not only from their ability to construct metal–organic molecular architectures using their N- and O-atom donors (Li *et al.*, 2003; Winpenny, 1998; Dong *et al.*, 2000), but also from their potential applications in enantioselective processes (Sreerama *et al.*, 2007), as magnetic materials (Andruh 2011), using their DNA binding and cleavage activities (Kou *et al.*, 2009), antimicrobial and antitumour activities (Poulter *et al.*, 2011), and antiradical activity (Puterova *et al.*, 2011), and as organic catalysts (Mukherjee *et al.*, 2011). The design of these polydentate ligands remains an important element for assembling coordination polymers with

fascinating topologies (Yang *et al.*, 2009). Compared with the widely used mono-Schiff bases (Jeewoth *et al.*, 1999), di-Schiff bases have two or more phenol –OH groups at the terminal positions and one aliphatic imine group between the aromatic rings, and therefore can exhibit diverse coordination modes of the metal ions and a concomitant tendency to form homo- and heteropolynuclear coordination complexes. In addition, they have flexible skeletons, which can rotate freely around the C–N and N–N single bonds to meet the requirements of the coordination geometries of the metal ions in the assembly process.



The above considerations focused our attention on the polydentate di-Schiff base 3,3'-[[1*E*,2*E*]-hydrazinediylidene-bis(methanylylidene)]di(benzene-1,2-diol) (H₄bcz), which has been synthesized to assemble dinuclear triple-stranded helicates with Ti^{IV} and V^{IV} cations in the presence of alkali metal carbonate (Albrecht *et al.*, 2003; Siegers *et al.*, 2004). However, metal complexes of this versatile di-Schiff base ligand are rare. Polydentate Schiff base metal complexes

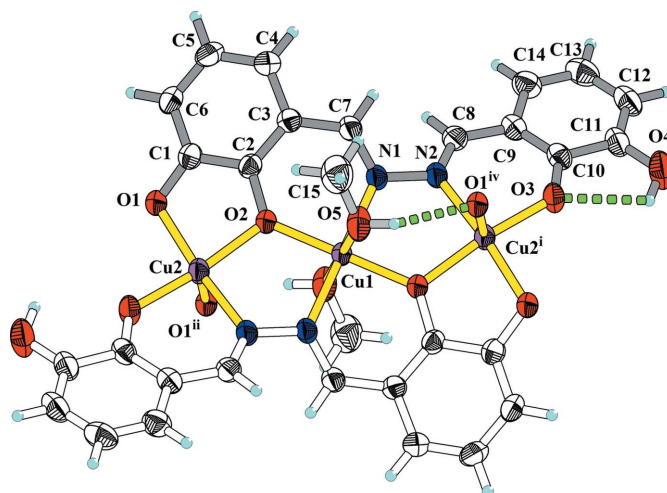
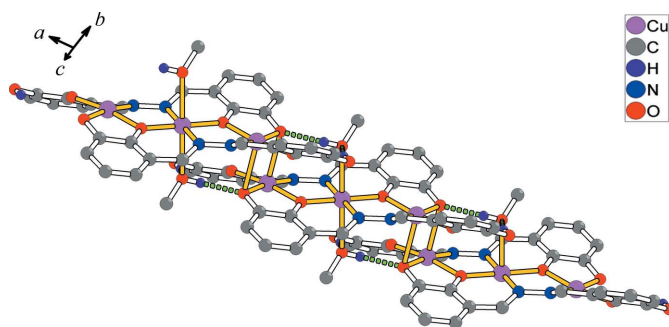


Figure 1
The structure of (I), showing the atom-numbering scheme and the coordination environment around the Cu^{II} centres. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular O–H...O hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iv) $x - 1, y, z$.]


Figure 2

A representation of the one-dimensional chains of (I). Hydrogen bonds are shown as dashed lines.

usually contain mono- or binuclear metal subunits (Mandal *et al.*, 1989; Ryan *et al.*, 1998), but Schiff base metal complexes with higher nuclearity are very difficult to achieve (Zou *et al.*, 2011). Remarkably, the H_4bcz ligand has four phenol –OH and two imine N-atom coordination sites, of which the four phenol –OH groups can be deprotonated, depending on the reaction conditions, so its coordination modes are difficult to control and predict when coordinating metal centres. Based on the above points and as part of our continuing investigations of coordination polymers (Sun *et al.*, 2009; Dai *et al.*, 2008), we have used H_4bcz to assemble a Cu^{II} one-dimensional coordination polymer, namely *catena*-poly[bis(μ_4 -3-[[2-(3-hydroxy-2-oxidobenzylidene)hydrazinylidene]methyl]benzene-1,2-diolato)dimethanoltricopper(II)], (I), in which a triply deprotonated form of H_4bcz binds three Cu^{II} cations to form a rare trinuclear Cu^{II} subunit.

As shown in Fig. 1, the asymmetric unit of (I) contains two crystallographically independent Cu^{II} centres, one of which lies on a site of $\bar{1}$ symmetry, one $Hbcz^{3-}$ ligand and one coordinated methanol molecule. The central Cu1 atom is six-coordinated in an octahedral environment, in which the four in-plane donors are two phenolate O atoms and two imine N atoms belonging to two inversion-related $Hbcz^{3-}$ ligands, and the axial positions are occupied by O atoms from two methanol molecules. The outer Cu^{II} centres obviously have identical $CuNO_4$ ligand environments, owing to inversion symmetry. This geometry of the outer Cu^{II} centres could be described as slightly distorted square-pyramidal comprising four phenolate O and one imine N atom. The apical position is occupied by a phenolate O atom from the $Hbcz^{3-}$ ligand of a neighbouring subunit. The distortion of the $CuNO_4$ square pyramid is indicated by the calculated value of the τ_5 parameter (Addison *et al.*, 1984), which is 0.014 for atom Cu2 (for ideal square-pyramidal geometry, $\tau_5 = 0$).

The $Cu \cdots Cu$ separation between nearest neighbours within the trinuclear subunit is 3.3396 (3) Å, which is longer than that in a similar trinuclear Cu^{II} subunit with acetate bridging at the axial positions (Chiari *et al.*, 1985). The equatorial $Cu-O$ bond lengths in the Cu^{II} coordination environment range from 1.8795 (17) to 1.9459 (16) Å and the axial $Cu-O$ bond lengths, with an average value of 2.498 (9) Å, are longer than those in the equatorial plane, indicating the Jahn–Teller effect for both Cu^{II} centres (Murphy & Hathaway, 2003). The $Cu-N$

bond length has an average value of 1.99 (4) Å (Table 1). The ligand adopts a twisted conformation, with a $C8-N2-N1-C7$ torsion angle of -42.6 (3)° around the $N2-N1$ bond.

It is clear from the structure of (I) that each H_4bcz molecule is partially deprotonated to form the $Hbcz^{3-}$ trianion, which acts as a heptadentate ligand (three phenolate O-atom donors and two imine N-atom donors) to chelate four Cu^{II} centres, three from one trinuclear subunit and the fourth from a neighboring subunit. A centrosymmetric Cu_2O_2 unit containing asymmetrically bridging O atom, O1, being axial at one Cu atom and equatorial at the other Cu atom, plays a crucial role in extending the trinuclear Cu^{II} subunits into a one-dimensional chain along the *a* axis (Fig. 2). Notably, there is a $Cu \cdots Cu$ separation of 3.0936 (5) Å in the Cu_2O_2 unit, which is much shorter than that within the trinuclear subunit. In addition, two types of intrachain $O-H \cdots O$ hydrogen bonds are observed within the one-dimensional chain, *viz.* phenol–methanol $O-H \cdots O$ and methanol–phenolate $O-H \cdots O$ (first and second entries, respectively, in Table 2), and these also play an important role in stabilizing the one-dimensional chain. According to graph-set notation (Bernstein *et al.*, 1995), the two types of intrachain $O-H \cdots O$ hydrogen bond form a cyclic $R_2^2(9)$ motif. Interchain $\pi-\pi$ stacking interactions between pyrocatechol units [$Cg1 \cdots Cg1^v = 3.5251$ (18) Å, where $Cg1$ is the centroid of the $C9-C14$ ring; symmetry code: (v) $-x, -y + 1, -z$] contribute to the stability of the crystal packing.

The linear trinuclear Cu^{II} subunit of (I) is very different from that of the previously reported discrete complex [$Cu_3(H_2L)(L) \cdot 2H_2O$, (II) [H_4L is *N,N'*-bis(3-hydroxysalicylidene)butane-1,4-diamine; Sanmart *et al.*, 1999], where the three Cu^{II} centres are held together by two phenolate bridges to form an isosceles triangle with a $Cu \cdots Cu$ separation of 3.413 (3) Å, which is longer than the shortest $Cu \cdots Cu$ separation in (I). The formation of different trinuclear Cu^{II} subunits could be attributed to the existence of the long $-(CH_2)_4-$ spacer between two imine groups in H_4L , which allows H_4L to twist and so achieves in (II) an isosceles triangle arrangement of three Cu^{II} centres, instead of the linear arrangement found in (I).

Experimental

H_4bcz was synthesized by a modification of the procedure of Albrecht *et al.* (2003). 2,3-Dihydroxybenzaldehyde (2.76 g, 20.0 mmol), *p*-toluenesulfonic acid (20 mg) and hydrazine hydrate (600 mg, 12.00 mmol) were dissolved in toluene (68 ml). After heating overnight with continuous removal of water by distillation, followed by cooling to room temperature, the precipitated product was filtered off, giving 2.58 g (95% yield) of an orange solid, *i.e.* H_4bcz . 1H NMR (300 MHz $CDCl_3$): δ 10.85 (*s, br*, 2H), 9.39 (*s, br*, 2H), 8.95 (*s*, 2H), 7.11 (*dd*, 2H), 6.94 (*dd*, 2H), 6.77 (*t*, 2H). A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (30 mg 0.12 mmol) and H_4bcz (20 mg, 0.07 mmol) was dissolved in methanol (20 ml) and the solution stirred until complete dissolution was achieved. The solution was then filtered, and the filtrate was capped and allowed to stand at room temperature. Black crystals of (I) were collected after about one week (yield 47%, based on H_4bcz).

Table 1

Selected geometric parameters (Å, °).

Cu1—O2	1.9103 (16)	Cu2—O1	1.9332 (17)
Cu1—N1	2.033 (2)	Cu2—O2	1.9459 (16)
Cu1—O5	2.507 (2)	Cu2—N2 ⁱ	1.946 (2)
Cu2—O3 ⁱ	1.8795 (17)	Cu2—O1 ⁱⁱ	2.4894 (18)
O2 ⁱ —Cu1—N1	89.20 (7)	O1—Cu2—O2	84.41 (7)
O2—Cu1—N1	90.80 (7)	O3 ⁱ —Cu2—N2 ⁱ	93.42 (8)
O2 ⁱ —Cu1—O5	85.99 (7)	O1—Cu2—N2 ⁱ	171.60 (8)
O2—Cu1—O5	94.01 (7)	O2—Cu2—N2 ⁱ	90.51 (7)
N1—Cu1—O5	86.87 (8)	O3 ⁱ —Cu2—O1 ⁱⁱ	95.81 (7)
N1 ⁱ —Cu1—O5	93.13 (8)	O1—Cu2—O1 ⁱⁱ	92.16 (7)
O3 ⁱ —Cu2—O1	90.67 (8)	O2—Cu2—O1 ⁱⁱ	92.15 (7)
O3 ⁱ —Cu2—O2	170.80 (8)	N2 ⁱ —Cu2—O1 ⁱⁱ	94.71 (7)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$.**Crystal data**[Cu₃(C₁₄H₁₀N₂O₄)₂(CH₄O)₂] $M_r = 793.17$ Triclinic, $P\bar{1}$ $a = 7.9019$ (5) Å $b = 10.2333$ (7) Å $c = 10.4441$ (7) Å $\alpha = 112.281$ (3)° $\beta = 95.373$ (4)° $\gamma = 104.862$ (3)° $V = 737.93$ (8) Å³ $Z = 1$ Mo $K\alpha$ radiation $\mu = 2.21$ mm⁻¹ $T = 298$ K

0.12 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEXII CCD

area-detector diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.777, T_{\max} = 0.809$

9076 measured reflections

3323 independent reflections

2686 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.022$ **Refinement** $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.093$ $S = 1.05$

3323 reflections

221 parameters

2 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.47$ e Å⁻³ $\Delta\rho_{\min} = -0.25$ e Å⁻³

C-bound H atoms were placed geometrically and treated as riding, with C—H = 0.96 (methyl) or 0.93 Å (aromatic and methylene), and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the methanol ligand and the hydroxy group were found in a difference Fourier map and refined with an O—H distance restraint of 0.82 (2) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: SAINT (Bruker, 2005); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2008); software used to prepare material for publication: publCIF (Westrip, 2010).

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Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4A \cdots O3	0.859 (18)	2.14 (3)	2.638 (3)	117 (3)
O4—H4A \cdots O5 ⁱⁱⁱ	0.859 (18)	2.23 (2)	3.029 (3)	154 (3)
O5—H5B \cdots O1 ^{iv}	0.799 (17)	1.985 (18)	2.779 (3)	173 (4)

Symmetry codes: (iii) $-x, -y + 1, -z + 1$; (iv) $x - 1, y, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3148). Services for accessing these data are described at the back of the journal.

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