

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF A 3D Ag(I) COORDINATION POLYMER BASED ON FLEXIBLE BIS(BENZIMIDAZOLE) AND 5-NITROISOPHTHALIC ACID CO-LIGANDS

X. Zhang, L. Liu, L. Qin, G.H. Cui

College of Chemical Engineering, Hebei United University, Tangshan, Hebei Province, P. R. China
E-mail: tscghua@126.com

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A new coordination polymer $\{[Ag_4(L)_3(nip)_2](H_2O)\}_n$ (L = 1,4-bis(5,6-dimethylbenzimidazol-1-yl)butane, H_2nip = 5-nitroisophthalic acid) is hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. The complex features a 3D **sqc117** supramolecular framework based on unique tetranuclear Ag(I) clusters which involve the ligand-supported Ag—Ag interactions.

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The rational and controllable synthesis of promising coordination networks and supramolecular architectures are still a difficult challenge in most cases [1—3]. As we know, apart from adopting multidentate and symmetric ligands as building blocks to construct these high-dimensional networks *via* the coordination-covalent bonding, the hydrogen bonds π — π stacking interaction [4, 5], and other weak interactions are also employed to increase their dimensionality. The weak Ag \cdots Ag interaction [6, 7] can be either ligand-supported [8, 9] or ligand-unsupported [10, 11] by the assistant ligands, and its length is comparable to a weak hydrogen bond [12]. The assembly of silver-organic coordination polymers have been a rapidly considerable research field [13, 14]. This stems not only from their potential applications as functional materials, but also from their intriguing variety of molecular architectures and topologies [15].

The 1,4-bis(5,6-dimethylbenzimidazol-1-yl)butane (L) ligand with the aliphatic core and the benzimidazole motif has remarkable features: (i) the nitrogen atoms of bis(benzimidazole) ligands have strong coordination ability and the $-(CH_2)_n$ -group is flexible [16—18]; (ii) the ligand contains both imidazole ring and larger conjugated π -system, capable of acting as hydrogen bond donors and for π — π stacking interaction. In continuation of our previous works [19], we report the synthesis and crystal structure of a new 3D supramolecular framework $\{[Ag_4(L)_3(nip)_2](H_2O)\}_n$ (H_2nip = 5-nitroisophthalic acid) which is governed by Ag—Ag interactions.

Experimental. Materials and physical measurements. All reagents and solvents for syntheses were purchased from commercial sources and used as received without further purification. The L ligand was prepared according to the literature [20]. The FT-IR spectrum (KBr pellets) was taken on a Nicolet FT-IR 360 spectrometer in the range 4000—400 cm^{-1} . The elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C elemental analyzer.

X-Ray crystallography. The crystallographic data for a suitable single crystal of the title complex were collected on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated MoK_{α}

Table 1

Selected bond lengths (Å) and angles (deg.) for the complex

Ag1—N3	2.221(4)	Ag2—N9	2.174(4)	Ag4—N7	2.297(4)
Ag1—N1	2.247(4)	Ag2—O10	2.231(3)	Ag4—O5	2.324(3)
Ag1—O7	2.457(3)	Ag3—O2	2.175(4)	Ag4—O6 ^E	2.239(3)
Ag2—N11	2.497(4)	Ag3—N5	2.133(4)		
N3—Ag1—N1	153.10(14)	N9—Ag2—O10	148.17(15)	O6 ^E —Ag4—N7	114.83(13)
N1—Ag1—O7	103.77(13)	N9—Ag2—N11	117.93(12)	O6 ^E —Ag4—O5	154.68(13)
N3—Ag1—O7	97.3(1)	N5—Ag3—O2	165.00(17)	N7—Ag4—O5	85.87(12)
O10—Ag2—N11	85.10(13)				

Symmetry codes: ^E = $-x, -y+1, -z+2$.

radiation ($\lambda = 0.71073 \text{ \AA}$) and the ω -2 θ scan mode at 293 K. The absorption correction was applied using the SADABS program [21]. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXTL program package [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of water molecule were located on a difference Fourier map, while other hydrogen atoms were included in the calculated positions and refined with anisotropic thermal parameters riding on the corresponding parent atoms. The selected bond lengths and bond angles are listed in Table 1. CCDC 956017 contains the supplementary crystallographic data for the complex. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

{[Ag₄(L)₃(nip)₂](H₂O)}: C₈₂H₈₆Ag₄N₁₄O₁₃, $FW = 1907.13$, $T = 293 \text{ K}$, crystal size $0.16 \times 0.15 \times 0.15 \text{ mm}$, monoclinic, $P2_1/c$, $a = 18.3699(4) \text{ \AA}$, $b = 19.7595(4) \text{ \AA}$, $c = 22.6541(4) \text{ \AA}$, $\beta = 106.192(2)^\circ$, $V = 7896.8(3) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.604 \text{ g/cm}^3$, $\mu(\text{MoK}\alpha) = 1.050 \text{ mm}^{-1}$, a total of 30929 ($\theta_{\text{min}}/\theta_{\text{max}} = 2.67/25.02^\circ$), 13929 unique ($R_{\text{int}} = 0.0303$), 3695 ($F > 4\sigma_F$), 1030 parameters. GOOF = 0.999, $R1 = 0.0453$, $wR2 = 0.0911$ ($I > 2\sigma_I$), $R1 = 0.0770$, $wR2 = 0.1075$ (all data), max/min diff. peak $0.949 / -0.864 \text{ e/\AA}^3$.

Synthesis of {[Ag₄(L)₃(nip)₂](H₂O)}_n. In our team, almost perfect crystals were obtained by the hydrothermal synthesis [23, 24]. Contributing to the solvent extraction of a solid and crystal growth, the hydrothermal synthesis can offer a superior condition under autogenous pressure at 100–260 °C; as a result, the viscosity of water decreases and the diffusion process becomes more active.

The mixture of AgNO₃ (0.034 g, 0.2 mmol), the L ligand (0.069 g, 0.2 mmol), H₂nip (0.042 g, 0.2 mmol), and H₂O (14 ml) was sealed in a Teflon-lined stainless vessel, and then the pH value was adjusted to 6.5 by NaOH (0.5 M). The mixture was heated at 140 °C for 72 h under autogenous pressure and then the reaction system was cooled to room temperature at a rate of 5°/h. Colorless crystals were obtained by filtration, washed with H₂O—C₂H₅OH ($v/v = 1:4$) and dried in air. They are air-stable and do not dissolve in CH₃CN, C₂H₅OH, H₂O, and DMF. Yield: 59 % (based on Ag). Anal. Calcd. for C₈₂H₈₆Ag₄N₁₄O₁₃ (%): C 51.64, H 4.55, N 10.28. Found (%): C 51.40, H 4.62, N 10.42. IR (solid KBr pellet, cm⁻¹): 3429s, 3106w, 1580vs, 1507vs, 1472w, 1445w, 1380w, 1338vs, 1218m, 835m, 707w, 620m.

Results and discussion. Description of the crystal structure of {[Ag₄(L)₃(nip)₂](H₂O)}_n. A single crystal X-ray diffraction analysis has revealed that the complex crystallizes in the monoclinic system, space group $P2_1/c$, and displays a 3D supramolecular framework based on unique tetranuclear Ag(I) clusters. As shown in Fig. 1, the asymmetric unit contains four Ag(I) ions, two nip anions, three L ligands, and one free water molecule. The four crystallographically independent silver atoms have

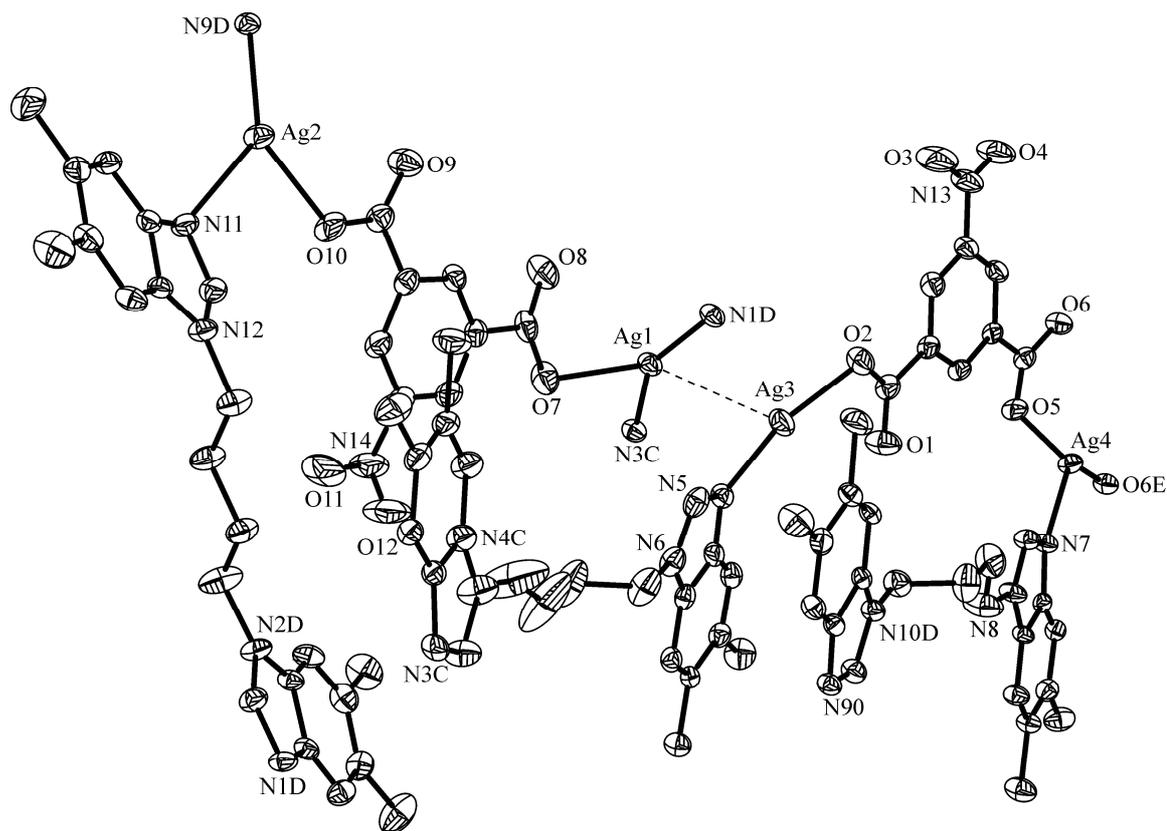
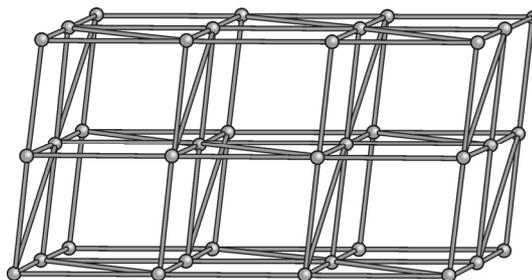


Fig. 1. The coordination environment around silver centers in the complex, dotted line indicates Ag—Ag interactions (symmetry code: C = $x, 1.5-y, -0.5+z$; D = $-x, y+0.5, 1.5-z$; E = $1-x, 1-y, 3-z$)

two different coordination numbers (two and three), which results in two different coordination geometries in the asymmetric unit. Ag1, Ag2, and Ag4 are all three-coordinated and exhibit a distorted *T*-shape geometry. Ag1 is ligated by one oxygen atom from the carboxylate group of the nip ligand and two nitrogen atoms from two individual bis(monodentate) **L** ligands. The coordination sites of Ag2 are similar to those of Ag1, and in this way Ag1 and Ag2 are connected together *via* two oxygen atoms of one bis(monodentate) nip ligand with the Ag1...Ag2 separation of 11.042(5) Å. The dihedral angle between the plane formed by Ag2, O10, C57 and the benzene ring of the nip ligand is 22.172(3)°. The Ag4 center is coordinated by two oxygen atoms (O5, O6^E, ^E = $1-x, 1-y, 3-z$) from two carboxylate groups of distinct nip anions and one nitrogen atom (N7) from the **L** ligand. Ag3 displays a linear geometry with two N/O coordination sites (N5 and O2 of the **L** and nip²⁻ ligands respectively). The Ag—O distances are in the range of 2.234(3)—2.457(3) Å; Ag—N lengths range from 2.133(4) Å to 2.497(4) Å (Table 1). The bond distances and angles (Table 1) are comparable to those in the similar coordination modes of Ag centers [25].

In the crystal structure of the complex, there are two coordination modes of nip ligands: in the first one, the two carboxylate groups adopt the monodentate coordination mode to bridge Ag1 and Ag2 atoms; in the second one, a carboxylate group adopts the bidentate coordination mode to connect two symmetrical Ag4, and the remaining carboxylate group affords only one O atom to coordinate to Ag3, whereas the nitro group is not involved in the coordination. The flexible **L** ligand acts as a bis(monodentate) coordination mode with *trans*-conformation and exhibits three different types of flexibility here. The dihedral angles between the two benzimidazole rings of three distinct flexible **L** ligands are 14.4°, 4.13°, and 8.54° respectively. The Ag...Ag distances bridged by the three kinds of **L** ligands are 13.7953(6) Å, 13.7499(6) Å, and 13.4989(5) Å respectively. The most interesting feature of the complex is that there are two kinds of Ag(I) tetranuclear clusters connected by ligand-supported

Fig. 2. The 8-connected uninodal 3D sqc117 net of the complex



Ag—Ag interactions, which are Ag3—Ag1—Ag1A—Ag3A and Ag2—Ag4A—Ag4B—Ag2F ($A = -x, -y+1, -z+2$; $B = -1+x, y, -1+z$; $F = -1-x, 1-y, 1-z$) with different Ag—Ag lengths of 2.9881(8)—3.0272(6) Å and 2.8937(7)—3.0964(6) Å respectively. The Ag—Ag distances are comparable to the value of 2.89 Å in metallic silver and to 3.0356(14) Å in the $\{[\text{Ag}(\text{bpy})][\text{Ag}(\text{Hsip})(\text{bpy})] \cdot (\text{H}_2\text{O})_2\}_n$ complex [26]. The two kinds of the tetranuclear Ag(I) clusters are then connected by **L** and nip ligands to form a 3D complicated framework. In addition, strong intermolecular hydrogen bonding interactions between lattice water and uncoordinated oxygen atoms from carboxylate groups ($\text{O1W} \cdots \text{O9} = 2.795(8)$ Å, $\text{O1W}—\text{O1G} = 2.773(8)$ Å, $\text{O1W}—\text{H1WA} \cdots \text{O9} = 171$, $\text{O1W}—\text{H1WB} \cdots \text{O1G} = 178$, symmetry code: $G: 2-x, 1-y, 2-z$) are also contained in this structure, presumably helping to further reinforce the 3D network. In order to understand better the architecture of the complex, the intricate framework was simplified and analyzed by TOPOS 4.0 [27]. Each tetranuclear Ag(I) cluster connecting eight adjacent tetranuclear clusters can be regarded as an 8-connected node; each **L** and nip ligand bridging two tetranuclear clusters should be considered as linkers. Therefore, this framework becomes a uninodal 8-connected 3D sqc117 topology with the point symbol of $(3^6.4^{12}.5^8.6^2)$, and the extended point symbol is $(3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.5.5.5.5.5_2.5_2.5_4.5_4.6_2.6_8)$ (Fig. 2). To the best of our knowledge, the complex prepared in this work represents the first example of a 3D sqc117 net based on such unique Ag(I) tetranuclear clusters. The π — π stacking interactions between the adjacent **L** ligands also increase the stability of the framework.

IR spectrum. The main features of the IR spectrum of the title complex are assigned to the carboxylate groups, water molecules, and N-containing ligands. There is no absorption peak between 1730 cm^{-1} and 1690 cm^{-1} , indicating that all carboxyl groups of the organic moieties are deprotonated [28]. The bands at 707 cm^{-1} can be attributed to the $\nu_{\text{C-N}}$ stretching of the N-heterocyclic rings of the **L** ligand. The characteristic bands at 1580 cm^{-1} and 1338 cm^{-1} are due to the vibrations of the carboxylate groups. The strong broad bands centered at around 3429 cm^{-1} are related to the O—H stretching vibration modes of water molecules [29]. The absorption bands at about 1507 cm^{-1} and 1218 cm^{-1} arise from the nitro groups of the nip ligand.

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