

Controllable assembly of silver(I) complexes by variations of the carboxyl configuration: From a 2-D $(4^5 \cdot 6)_2(4^{18} \cdot 6^{10})$ layer to an unusual 3-D 5-connected self-penetrating $(4^4 \cdot 6^6)_2$ network

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ARTICLE INFO

Article history:

Received 17 June 2011

Accepted 7 September 2011

Available online 16 September 2011

Keywords:

Silver(I) complexes^a

trans-/*cis*-Epoxy succinate ligand

Carboxyl configuration

Crystal structure

Topology

ABSTRACT

The reaction of $\text{AgClO}_4 \cdot 6\text{H}_2\text{O}$ with $(+/-)$ -*trans*-epoxysuccinic acid (H_2tes) in the presence of 2,6-dimethylpyridine afforded a three-dimensional (3-D) Ag^I coordination polymer $[\text{Ag}_2(\text{tes})]_\infty$ (**1**), which exhibits an unusual 5-connected self-penetrating $(4^4 \cdot 6^6)_2$ topological net ($\text{tes} = (+/-)$ -*trans*-epoxysuccinate). Comparison of the structural differences with our relevant finding, a two-dimensional (2-D) (4,8)-connected $(4^5 \cdot 6)_2(4^{18} \cdot 6^{10})$ coordination polymer $[\text{Ag}_4(\text{ces})_2]_\infty$ (**S1**) ($\text{ces} = \text{cis}$ -epoxysuccinate), suggests that the carboxyl configuration on the ternary ring backbone of H_2tes or H_2ces ligand plays an important role in the construction of coordination networks.

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In recent years, the rational design and synthesis of silver(I) coordination polymers have attracted great interest due to not only their diversified structures and fascinating topologies but also their potential physical and chemical applications as functional materials [1–3]. In this field, utilizing suitable organic tectons with various functional groups which exhibit versatile coordination modes coordinating with metal atoms has been proven to be one of the most effective ways to construct novel crystalline materials [1a]. In addition, the flexibility of Ag^I coordination sphere, varying from linear to trigonal, tetragonal, square pyramidal, and octahedral, related to coordination numbers from 2 to 6, affords a good opportunity to study the mechanism of the self-assembly process. Furthermore, the topological structures of Ag^I coordination are subtle to the Ag –ligand interactions and the reaction conditions [1a].

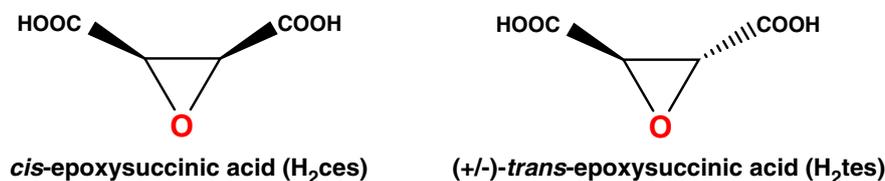
Amongst the organic ligands, especially rigid aromatic multicarboxylates such as benzene- [4], naphthalene- [5], anthracene- [6], pyrene- [7], and perylene-based derivatives [8] have been widely used to construct various coordination polymers. However, only a few coordination polymers based on the ligands with flexible ring skeletons, such as tetrahydrofuran-2,3,4,5-tetracarboxylic [9], 1,2,3,4-cyclobutanetetracarboxylic [10], 1,2,3,4,5,6-cyclohexanhexacarboxylic [11], and 1,2-cyclohexanedicarboxylic [12] acids, have been reported to date. This is probably due to the flexibility of the ligand skeletons, which makes it more difficult to predict and control their structures in the final coordination networks. In this context, *cis*-epoxysuccinic acid (also known as

(2*S*,3*R*)-oxirane-2,3-dicarboxylic acid, H_2ces , see Chart 1), has two chiral centers in the ternary ring backbone as well as a pair of carboxyl groups, which can be regarded as an interesting building tecton in coordination assemblies on the basis of following considerations: (1) it has two carboxyl groups that do not lie in one plane, which provide rich coordination modes and allow it to connect the metal ions in different directions. (2) The oxirane oxygen atom provides additional binding sites, and it can coordinate to the metal ions associated with two near carboxyl oxygen atoms. (3) Another structural feature of such coordination frameworks constructed from above-mentioned ligands with flexible ring skeletons is the close proximity and clustering of metal centers by virtue of skeletal flexibility. In our previous work, H_2ces has been successfully used to construct a series of Cu^{II} coordination complexes having dinuclear, 1-D, 2-D, and isolated Cu_{15} nanocluster structures under different pH conditions, which also exhibits interesting magnetic properties [13].

Moreover, a 2-D (4,8)-connected $(4^5 \cdot 6)_2(4^{18} \cdot 6^{10})$ coordination polymer $[\text{Ag}_4(\text{ces})_2]_\infty$ (**S1**) ($\text{ces} = \text{cis}$ -epoxysuccinate) was obtained in this research. To further explore the influence of the carboxyl configuration on oxirane ring backbone on the structures and properties of their coordination polymers in this contribution, we subsequently chose $(+/-)$ -*trans*-epoxysuccinic acid (H_2tes), a configurational isomer of H_2ces , to construct a new 3-D Ag^I coordination network $[\text{Ag}_2(\text{tes})]_\infty$ (**1**) ($\text{tes} = (+/-)$ -*trans*-epoxysuccinate) by taking the advantage of the bridging coordination ability of its dicarboxylate groups together with the flexibility of its oxirane ring, which exhibits an unusual 5-connected self-penetrating $(4^4 \cdot 6^6)_2$ topology. Herein, we report the syntheses, crystal/topological structures, and properties of complexes **1** and **S1**.

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Complexes **1** and **S1** were obtained by the reaction of H_2tes or H_2ces , in the presence of excess 2,6-dimethylpyridine, with $AgClO_4 \cdot 6H_2O$ [14]. The compositions were confirmed by elementary analysis and IR spectra, and the phase purities of the bulk samples for luminescent/thermal measurement were identified by powder X-ray diffraction (PXRD, see Fig. S6 in the Supplementary material). Moreover, the luminescent/thermal properties of **1** and **S1** have been briefly investigated (see Figs. S4 and S5 in the Supplementary material).

Single crystal X-ray diffraction analysis reveals that complex **1** [15], $[Ag_2(tes)]_\infty$, has an interesting 3-D structure (see Figs. 1–4 and Figs. S1–S2 in the Supplementary material). The asymmetric unit contains two unique Ag^I ions ($Ag1$ and $Ag2$) and one fully deprotonated (+/–)-*trans*-epoxysuccinate (**tes**) ligand (see Fig. 1). If neglecting the $Ag1 \cdots Ag2$ bonding contact, $Ag1$ center is four-coordinated (also known as a distorted tetrahedral geometry) by four O atoms of four distinct **tes** ligands ($Ag1-O$: 2.219(3)–2.484(3) Å; $O-Ag1-O$: 77.29(13)–164.82(13)°; NOTE: we have ignored the longer $Ag \cdots O$ separations (>2.7 Å) in describing and drawing the metal coordination geometries, see Table S2 in the Supplementary material for detailed bond parameters). Also, if not considering the $Ag1 \cdots Ag2$ bonding contact, $Ag2$ center is three-coordinated (known as a Y-shaped coordination geometry) by three O atoms from three different **tes** ligands with the bond distances and angles of 2.195(4)–2.481(4) Å and 74.43(12)–126.04(13)° for $Ag2-O$ and $O-Ag2-O$, respectively (see also Table S2). Expect the longer $Ag-O$ lengths (>2.7 Å), all other $Ag-O$ bond distances and the bond angles around Ag^I ions are typical and comparable to those observed in the literature [16]. In addition, a very short $Ag \cdots Ag$ interaction (2.8388(6) Å) is observed between $Ag1$ and $Ag2$ bridged by carboxylate of **tes**, which is similar to those found in other complexes with $Ag \cdots Ag$ contacts (the Van der Waals $Ag \cdots Ag$ contact distance being 3.40 Å), and slightly shorter than that found in metallic silver (2.889 Å) [17]. Each **tes** ligand coordinates to seven Ag^I atoms (four $Ag1$ and three $Ag2$), where the carboxylate groups adopt the different $\mu_3-\eta^1:\eta^2$ -*syn*, *syn/syn,trans* mode for $O1-C1-O2$ and $\mu_4-\eta^2:\eta^2$ -*syn,trans* mode for $O3-C2-O4$

(see Fig. 2). Interestingly, if only considering the connections between **tes** ligands and $Ag2$ ions, the $Ag2$ ions are linked together by **tes** ligands to form a 2-D layer (see Fig. S1 in the Supplementary material) and the alternately arrangement of left- and right-handed helices with a pitch of 7.6978(8) Å are found. Furthermore, the $Ag1$ ions are connected by **tes** ligands to give rise to the final 3D framework (see Fig. 3).

As we all know, the analysis of chemical topology provides a convenient method to understand the connectivity between the components of the crystal structures [18]. From the topological view, if the $Ag1 \cdots Ag2$ bimetallic unit and **tes** ligand in **1** were regarded as isolated nodes, they both act as non-planar 5-connected nodes (see Fig. 4). Such a 3-D network exhibits a rare example of 5-connected topology with the Schläfli symbol of $(4^4 \cdot 6^6)_2$. In general, networks with 5-connectivity are quite limited, owing to the difficulty in generating 5-connecting metal centers/clusters and organic tectons [19f]. Thus far, only several examples for 5-connected coordination polymers have been reported [19, 20], such as **bnn** net (or boron nitride) ($4^6 \cdot 6^4$) [19a], **sqp** net ($4^4c \cdot 6^6$)

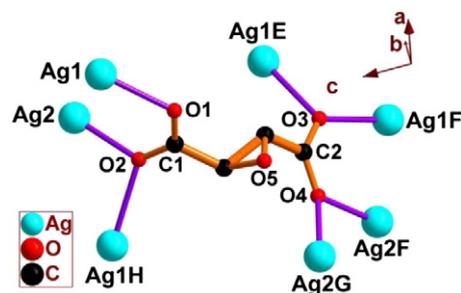


Fig. 2. A portion view of **1** showing the coordination modes of **tes** ($\mu_3-\eta^1:\eta^2$ mode for $O1-C1-O2$ carboxylate group and $\mu_4-\eta^2:\eta^2$ mode for $O3-C2-O4$ carboxylate group; $E = -x + 2, y + 1/2, -z - 1/2$; $F = x - 1, -y - 1/2, z - 1/2$; $G = -x + 1, y - 1/2, -z - 1/2$; $H = x - 1, y, z$).

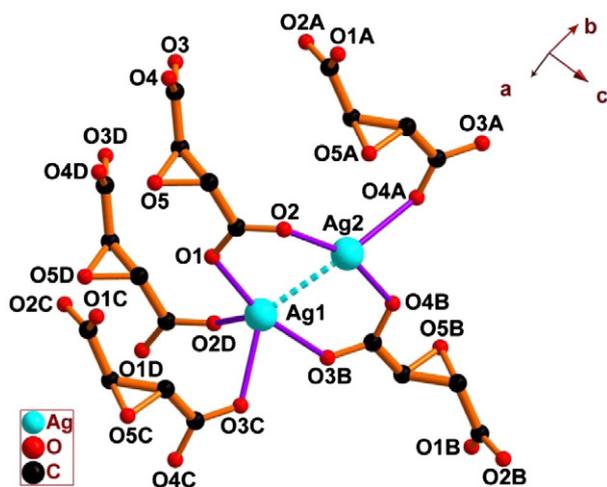


Fig. 1. View of the local coordination environment of Ag^I in **1**, showing the $Ag1 \cdots Ag2$ interactions (cyan dashed lines) ($A = -x + 1, y + 1/2, -z - 1/2$; $B = x + 1, -y - 1/2, z + 1/2$; $C = -x + 2, y - 1/2, -z - 1/2$; $D = x + 1, y, z$).

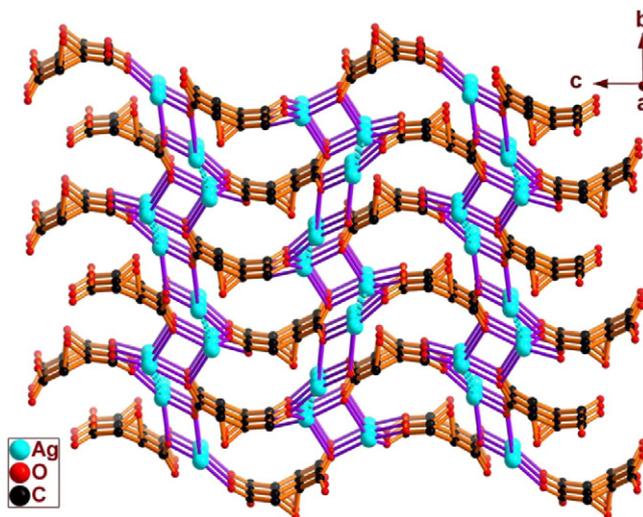


Fig. 3. Part of crystal packing of 3-D network in **1** viewed along the *a* axis.

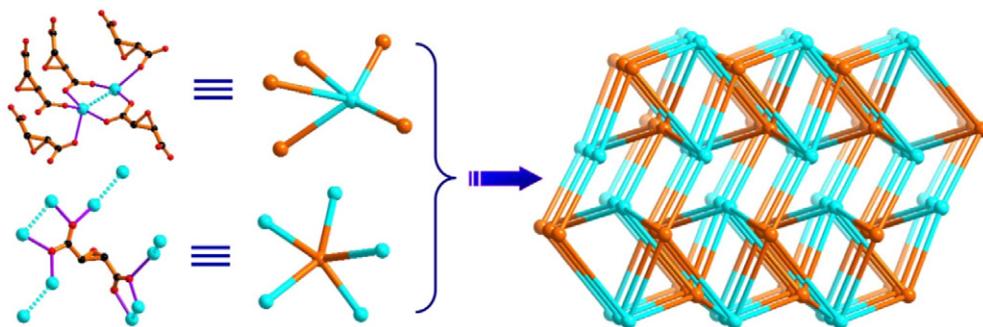


Fig. 4. A schematic representation of the 3-D 5-connected network with the Schläfli symbol of $(4^4 \cdot 6^6)_2$, illustrating the connectivity of $\text{Ag}1 \cdots \text{Ag}2$ units (cyan spheres) and **tes** ligands (orange spheres).

[19b], **nov** net ($4^4 \cdot 6^6$) [19c,d], and 6^{10} -nets (**1oh** [19e], **ghw** [19f], **rld-z** [19g], and **fnu** [19h]), which all contains 5-connecting topological patterns with trigonal-bipyramidal or square-pyramidal nodes. Compared with the simplest 5-connected nets (**bnn**, **sqp**, **nov**, **loh**, and **ghw**), nets **rld-z** and **fnu** are rare examples of self-interpenetrated 5-connected network. Furthermore, our structure of **1** contains two types of distorted non-planar 5-connected nodes (see Fig. 4). Interestingly, the catenated 4- and 8-rings are the shortest topological rings and they interlocked with each other. Such linkage results in the formation of final 3-D 5-connected self-penetrating $(4^4 \cdot 6^6)_2$ topology (see Fig. S2 in the Supplementary material) [21].

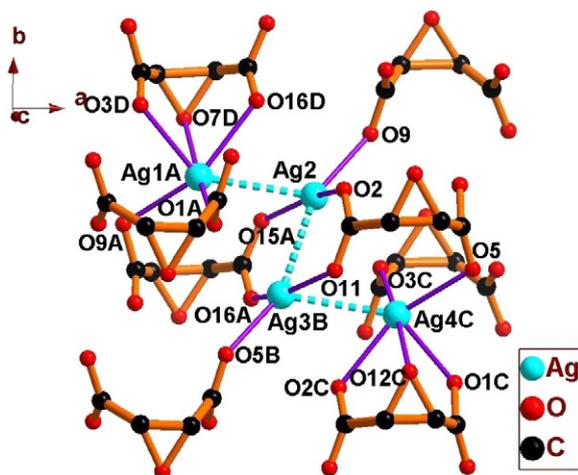


Fig. 5. View of the local coordination environment of Ag^{I} in **S1**.

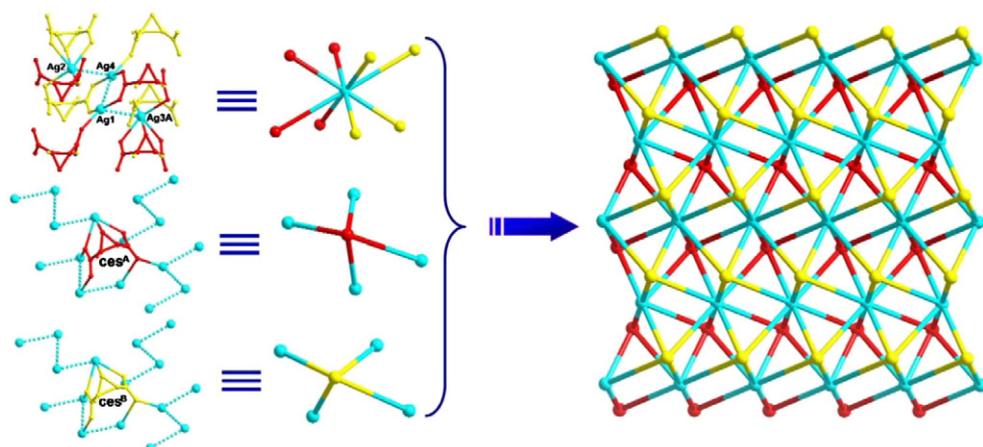


Fig. 6. A schematic representation of the (4,8)-connected $(4^5 \cdot 6^6)_2(4^{18} \cdot 6^{10})$ topological net of **S1** (cyan spheres: $\text{Ag}1 \cdots \text{Ag}2 \cdots \text{Ag}3\text{A} \cdots \text{Ag}4$ tetrametallic units; $\text{A} = x + 1/2, -y, z$; red spheres: **ces**^A; yellow spheres: **ces**^B).

In comparison with **1**, when we used *cis*-epoxysuccinic acid (H_2ces) instead of $(+/-)$ -*trans*-epoxysuccinic acid (H_2tes) in this research, a 2-D (4,8)-connected $(4^5 \cdot 6^6)_2(4^{18} \cdot 6^{10})$ topological net (complex **S1**) was obtained under the same conditions (see Figs. 5, 6 and Fig. S3; brief description and discussion of **S1** is in the Supplementary material). Our results, therefore, indicate that the configurational difference of carboxyl groups on the ternary ring backbone of H_2tes and H_2ces plays an important role in the formation of **1** and **S1**, which, from the viewpoint of ligand design, may offer effective means for constructing unique coordination architectures with interesting topology just by variations of the carboxyl configuration on flexible ring backbones.

Also, the solid-state photoluminescent properties of complexes **1** and **S1** were investigated at room temperature, as shown in Fig. S4 in the Supplementary material. The blue luminescence emission bands with the peak maxima (λ_{max}) were observed at 530 nm ($\lambda_{\text{ex}} = 327$ nm) for **1** and 416 nm ($\lambda_{\text{ex}} = 341$ nm) for **S1**, respectively. To further analyze the nature of these emission bands, the photoluminescent properties of free H_2tes or H_2ces have also been investigated under the same experimental conditions. It should be pointed out that the free H_2tes and H_2ces ligands display very weak luminescence. According to the literature [22], we can presume that the enhancement of luminescence in **1** and **S1** may be mainly derived from Ag–Ag interactions and the nature of its emitting states strongly depends on the number of metal centers and the interactions between them. Our structures of **1** and **S1** represent two new examples of the room-temperature luminescent Ag^{I} -containing coordination polymers with novel topological networks.

In conclusion, we have successfully constructed one 3-D (**1**) and one 2-D (**S1**) Ag^{I} coordination polymers, which exhibits a binodal 5-connected self-penetrating $(4^4 \cdot 6^6)_2$ and a (4,8)-connected $(4^5 \cdot 6^6)_2(4^{18} \cdot 6^{10})$ topological nets, respectively, by employing flexible $(+/-)$ -

trans-epoxysuccinic acid (H₂tes) or *cis*-epoxysuccinic acid (H₂ces) ligands. The structural difference between **1** and **S1** is attributable to the intervention of different carboxyl configuration on oxirane ring backbone of H₂tes or H₂ces. Finally, such flexible heteroalicyclic dicarboxylate ligands with different carboxyl configuration might be generally applicable for different d¹⁰ transition metal ions, such as Zn^{II} and Cd^{II}, to construct more functional crystalline solids with desired structures and potentially useful properties.

Acknowledgments

This work was supported by the National Natural Science Fund of China (Grant Nos. 20801049 and 21071129), Henan Outstanding Youth Science Fund (114100510017), and Program for New Century Excellent Talents in University (NCET-10-0143).

Appendix A. Supplementary material

CCDC 828327 and 828328 contain the supplementary crystallographic data for [Ag₂(tes)₂] (**1**) and [Ag₄(ces)₂]_∞ (**S1**), respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from The Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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- Complexes **1** and **S1** were synthesized by layered method. A solution of 0.05 mmol acid (H₂tes for **1** and H₂ces for **S1**) in CH₃OH (10 mL) in the presence of excess 2,6-dimethylpyridine (for adjusting the pH value to basic condition) was carefully layered on top of a H₂O solution (15 mL) of AgClO₄·6H₂O (0.1 mmol) in a test tube. Colorless block single crystals of **1** and **S1** suitable for X-ray analysis appeared at the tube wall after ca. two or three weeks at room temperature. For **1**, yield: ~40% based on H₂tes. Anal. Calcd for C₄H₂Ag₂O₅: C, 13.89; H, 0.58%; Found: C, 13.75; H, 0.64%. IR (KBr, cm⁻¹): 3421m (br), 1611vs, 1392s, 1362m, 1275m, 1088w, 957w, 900m, 850w, 779w, 688m, 490w. For **S1**, yield: ~50% based on H₂ces. Anal. Calcd for C₈H₄Ag₄O₁₀: C, 13.89; H, 0.58%; Found: C, 13.78; H, 0.67%. IR (KBr, cm⁻¹): 3450m (br), 1627s, 1607vs, 1565s, 1438s, 1420s, 1397m, 1353m, 1307w, 1286m, 1223w, 1171w, 1063m, 937s, 876w, 850m, 791s, 739w, 677m, 653m, 536m, 517w, 494w.
- Crystal data for **1**: C₄H₂Ag₂O₅, M = 345.80, Monoclinic, space group P2₁/c, a = 5.1567(2), b = 7.6978(4), c = 16.1233(8) Å, β = 99.987(4), V = 630.32(5) Å³, Z = 4, D_c = 3.644 Mg m⁻³, μ(Mo-Kα) = 6.174 mm⁻¹, F(000) = 640, T = 294(2) K, 2194 reflections measured, 1100 unique (R_{int} = 0.0208), final R₁ = 0.0236, wR₂ = 0.0412 [for selected data with I > 2σ(I)], GOF = 0.952 for all data. Crystal data for **S1**: C₈H₄Ag₄O₁₀, M = 691.59, Orthorhombic, space group Pca2₁, a = 13.0325(4), b = 5.37760(10), c = 17.1501(4) Å, V = 1201.94(5) Å³, Z = 4, D_c = 3.822 Mg m⁻³, μ(Mo-Kα) = 6.476 mm⁻¹, F(000) = 1280, T = 294(2) K, 7122 reflections measured, 1754 unique (R_{int} = 0.0319), final R₁ = 0.0398, wR₂ = 0.0992 [for selected data with I > 2σ(I)], GOF = 1.040 for all data.
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