

One Novel Ag(I) Compound Generated from Double Schiff-base Ligand with Quinoxaline-*N*-oxide as Terminal Binding Sites^①

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ABSTRACT One novel discrete coordination molecule with Ag^I centers, namely [Ag₃(L)₃(ClO₄)₃]·3CH₂Cl₂·6CH₃OH·1.5H₂O (**1**), has been synthesized based on the double Schiff-base ligand, 3,6-bis[2-(4-oxide-quinoxaline)-yl]-4,5-diaza-3,5-octadiene (L) and AgClO₄. The obtained Ag(I) compound was fully characterized by infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. **1** is of trigonal system space group *P*-31*c* with *a* = 16.320(2), *b* = 16.320(2), *c* = 20.108(6) Å, *T* = 173(2) K, *V* = 4638.2(16) Å³, *D_c* = 1.645 g/cm³, *M_r* = 2297.33, *Z* = 2, *F*(000) = 2334, *μ* = 0.970 mm⁻¹, Goodness-of-fit = 1.109, the final *R* = 0.0776, *wR* = 0.1813, *R* indices (all data) = 0.1196, *wR* = 0.2011. The compound exhibits a triple-helical [Ag₃L₃]³⁺ crown-like trimer, in which three Ag(I) atoms form an equilateral triangle with the Ag···Ag distance of 4.7 Å. Uncoordinated counterions ClO₄⁻ and solvent molecules methanol generate the hydrogen-bonded frameworks based on discrete molecular complex building blocks.

Keywords: crystal structure, double Schiff-base ligand, discrete coordination compound, hydrogen bond;

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1 INTRODUCTION

In the past few decades, discrete coordination compounds and coordination polymers based on polydentate organic ligands have attracted wide attention due to their novel structural topologies and properties^[1-4]. To date, the length, shape, conformation and coordinating orientation of organic ligands are dominant in affecting the structures of coordination molecular aggregates^[5]. Besides the ligand, the characteristics of counterions for instance charge, size, geometry and solvent templating effects imply that the polyatomic counterions and solvent intermedia play important roles in the self-assembly of functional coordination compounds^[6-9]. In the previous work of our task force, we have been exploring the metal-organic coordinated compounds based on the double Schiff-base ligands^[10-13]. The results show that such types of ligands are very useful to construct

novel polymeric and discrete compounds due to their chelated coordination model between the spacer moiety (-RC=N-N=CR-) and the terminal coordination groups. The heteroatom on the ligand ending groups (pyridine, pyrazine, and *N,N'*-dioxide quinoxaline) can be used not only as coordination atoms, but also as potential hydrogen bond acceptor to form hydrogen bonds with solvent molecules or counterions. These hydrogen bonds can further link the secondary building blocks (Ag₂L₂ or Ag₃L₃) into two- or three-dimensional novel topological structures. Pursuing our research in this area, we describe here the coordination chemistry of the double Schiff-base ligand 3,6-bis[2-(4-oxide-quinoxaline)-yl]-4,5-diaza-3,5-octadiene (L) with AgClO₄. In our previous work, the ligand reacted with AgSbF₆, AgPF₆ and AgBF₄ to obtain a polymer with a three-dimensional network structure and two discrete macromolecules^[14, 15]. The results showed that the template effect of anions may be

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responsible for the formation of compounds with different dimensions. Based on the above reasons, we replaced the silver salt with AgClO_4 and obtained a special $[\text{Ag}_3\text{L}_3]^{3+}$ crown-like trimer different from the previous compounds. There are complex hydrogen bond systems^[16, 17] in this compound based on ClO_4^- anions, solvent molecules and discrete molecular building blocks. These hydrogen bonds further linked these discrete molecules to form a three-dimensional network structure with hexagonal tunnels.

2 EXPERIMENTAL

2.1 Reagents and instruments

AgClO_4 (Acros) was used as obtained without further purification. The ligand **L** was synthesized according to the literature^[14]. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the $400\sim 4000\text{ cm}^{-1}$ range using a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer.

Caution! The crystallization procedures involve AgClO_4 , which is a strong oxidizer and should be carefully operated.

2.2 Synthesis of complex 1

A CH_3OH solution (8 mL) of AgClO_4 (18.7 mg, 0.09 mmol) was slowly diffused into a CH_2Cl_2 solution (8 mL) of **L** (12.0 mg, 0.03 mmol). Yellow crystals formed in about 7 days in 54.6% yield (based on AgClO_4). Anal. Calcd. for $\text{Ag}_3\text{C}_{75}\text{H}_{93}\text{Cl}_9\text{N}_{18}\text{O}_{25.50}$: C, 39.21; H, 4.08; N, 10.97. Found: C, 39.23; H, 4.01; N, 10.99. IR (KBr pellet, cm^{-1}): 3417(s), 3123(s), 1638(w), 1578(w), 1492(w), 1401(s), 1249(w), 1216(w), 1089(s), 938(w), 910(w), 857(w), 771(w), 622(w).

2.3 X-ray crystallography

Suitable single crystals of **1** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 173(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$). The raw frame data for **1** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT^[18, 19]. Corrections for incident and diffracted beam adsorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. The structure was solved by a combination of direct methods and difference Fourier syntheses and structural analysis refined against F^2 by the full-matrix least-squares technique. Relevant interatomic bond distances and bond angles for **1** are given in Tables 1 and 2.

Table 1. Selected Bond Lengths (\AA) and Bond Angles ($^\circ$)

Bond	Dist.	Bond	Dist.
Ag(1)–N(1)	2.315(6)	Ag(1)–N(3)	2.365(6)
Ag(1)–N(3) ⁱ	2.365(6)	Ag(1)–N(1) ⁱ	2.315(6)
Angle	($^\circ$)	Angle	($^\circ$)
N(1)–Ag(1)–N(1) ⁱ	123.3(3)	N(1)–Ag(1)–N(3)	69.9(2)
N(1) ⁱ –Ag(1)–N(3)	130.2(2)	N(1)–Ag(1)–N(3) ⁱ	130.2(2)
N(1) ⁱ –Ag(1)–N(3) ⁱ	69.9(2)	N(3)–Ag(1)–N(3) ⁱ	143.0(3)

Symmetry code: ⁱ $-x + 1, -y + 1, -z + 3/2$

Table 2. Hydrogen Bond Lengths (\AA) and Bond Angles ($^\circ$)

D–H...A	d(D–H)	d(H...A)	d(D...A)	$\angle\text{DHA}$
C(12)–H(12c) ... O(1) ^{vi}	0.96	2.34	3.19(3)	146
O(4)–H(4) ... O(4) ^{vii}	0.85	2.01	2.74(2)	143
C(7)–H(7) ... O(2) ^{vi}	0.95	2.41	3.27(1)	121

Symmetry codes: ^{vi} $y, -x + y, -z + 1$; ^{vii} $-x + 1, -y + 1, -z + 1$

3 RESULTS AND DISCUSSION

3.1 Crystal structure of compound 1

Compound **1** was found to crystallize in the space group trigonal, $P\bar{3}1c$. Selected bond lengths and bond angles are shown in Table 1. X-ray single-crystal analysis revealed that there is only one type of crystallographic independent Ag(I)

ion in **1** (Fig. 1). Each Ag(I) ion lies in a distorted tetrahedral coordination environment $\{\text{AgN}_4\}$ which consists of two quinoxaline N-donors and two Schiff-base N-donors from three four-coordinated ligands, respectively. The dihedral angle between two terminal benzene rings is 73.17° . Different from the dimer formed by the ligand and other silver salts (AgBF_4 and AgPF_6), the compound exhibits a triple-helical

$[\text{Ag}_3\text{L}_3]^{3+}$ crown-like trimer, in which three Ag(I) atoms form an equilateral triangle with Ag...Ag distance of 4.7 Å. In $[\text{Ag}_3\text{L}_3]^{3+}$, the terminal quinoxaline moieties define the bowl-like cavities above and below the Ag_3 plane. The dihedral angle between two neighboring benzene planes on the same side is ca. 86.06°. The distance between the quinoxaline-*N*-oxide O-donors on the same side of the trisilver plane is 10.087 Å, and the shortest distance between Ag(I) and O-donor is 6.36 Å. As indicated in Fig. 2, two ClO_4^- anions locate in each trimer and attach to it through the weak

interaction between Ag and O(3) with the distance of 3.07 Å. The other three O(2) atoms of one ClO_4^- anion act as hydrogen-bond acceptor to form the C–H...O hydrogen-bonding system along the *c* axis. The template effect of ClO_4^- is the key to the formation of the $[\text{Ag}_3\text{L}_3]^{3+}$ trimer. In the compounds formed by the ligand and other silver salts (AgBF_4 and AgPF_6), the distances between anions and silver centers are far, and there are no weak interactions between them.

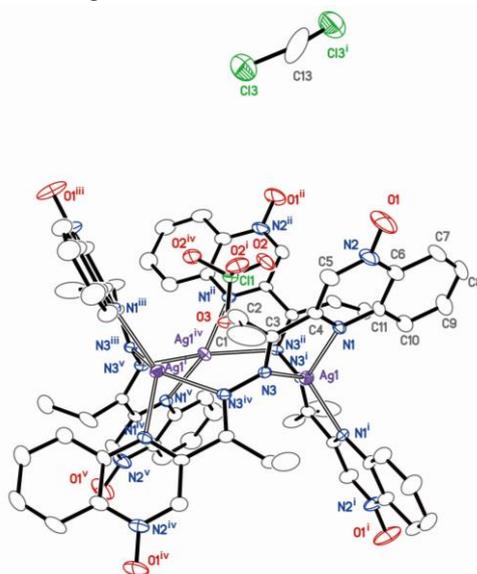


Fig. 1. ORTEP figure of 1.

Symmetry codes: ⁱ $-x + 1, -y + 1, -z + 3/2$; ⁱⁱ $-x + 1, -x + y + 1, z$; ⁱⁱⁱ $x - y, -y + 1, z$; ^{iv} $x, x - y, -z + 3/2$; ^v $-x + y + 1, y, -z + 3/2$

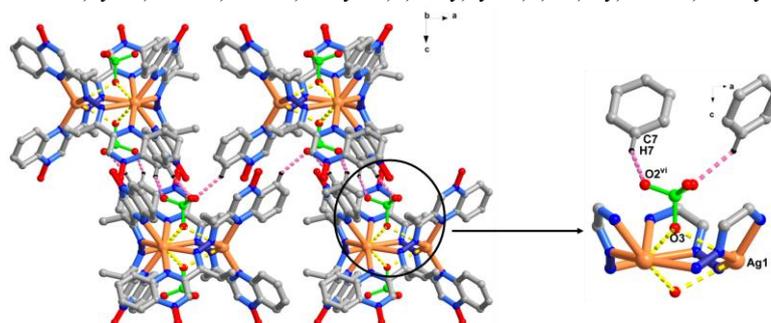


Fig. 2. Weak interactions between Ag and O(3) (yellow dotted lines) and hydrogen-bonding systems (pink dotted lines) ($d(\text{Ag}(1) \cdots \text{O}(3)) = 3.073$ Å, $d(\text{O}(2) \cdots \text{H}(7)) = 2.411$ Å, $\angle \text{C}(7) - \text{H}(7) \cdots \text{O}(2) = 121^\circ$). Symmetry code: ^{vi} $y, -x + y, -z + 1$

Interestingly, there are two sets of crown complexes that are oriented in different directions in the solid state. Three neighboring $[\text{Ag}_3\text{L}_3]^{3+}$ units with the same orientation surround disordered ClO_4^- anion to generate a cavity (Fig. 3). The remarkable feature of **1** is its hydrogen-bonding system. As shown in Fig. 3, there are two independent sets of O(4)–H(4)··O(4) and C(12)–H(12c)··O(1) interactions generated from methanol molecules or methanol and trimers. The hydroxyl groups on methanol molecules are linked to

each other by O–H··O interactions which connect six methanol molecules into a hexamer methanol cluster. Six oxygen atoms are in the same plane with the O··O distance to be 2.74 Å. Methyl groups are located alternately above and below the plane and connected with the quinoxaline-*N*-oxide groups of the ligands through C–H··O interactions. Each solvent molecular cluster serves as the node to connect three $[\text{Ag}_3\text{L}_3]^{3+}$ units in the upper and lower layer by hydrogen bonds. Furthermore, the crown subunits 2D layers are stacked

ABAB along the *c* axis and joined together through interlayer O–H··O and C–H··O interactions to generate a 3D H-bonded framework. This compound is similar to the cascade structure we reported before^[12]. Along the *c* axis, the compound is comparable to Russian Matroshka (nesting) dolls. Three [Ag₃L₃]³⁺ units host cage traps a methanol cluster guest, which further encapsulates disordered ClO₄⁻ counterions. Taken all together, the synergistic effect of the solvent-

hydrogen-bonding interactions^[20] results in the formation of a 3D framework (Fig. 4). However, in the compounds we have reported before, there are hydrogen bonds between anions and [Ag₂L₂]²⁺ units but the H-bonding interactions between [Ag₂L₂]²⁺ units are the driving force that makes the compounds extend into 1D or 2D structures in the space. In the solid state, the 3D H-bonded network exhibits a beautiful hexagon tunnel-type architecture (Fig. 4).

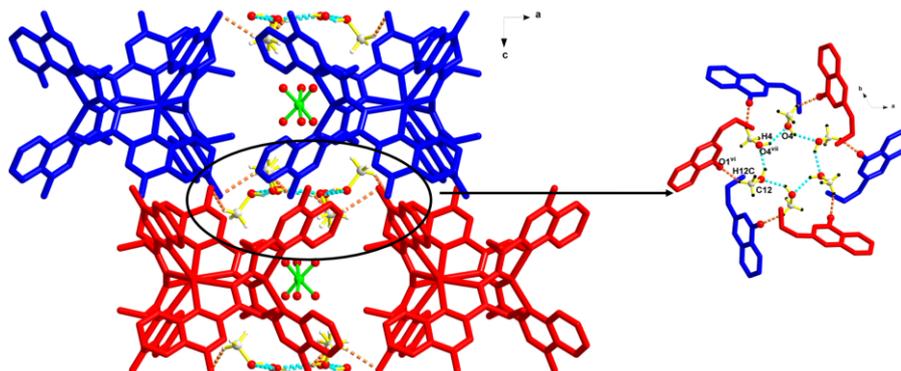


Fig. 3. 2D hydrogen-bonded nets viewed down the *b* (a) and *c* (b) axes. The hydrogen bonds are shown as orange and blue dotted lines. ($dO(1) \cdots H(12c) = 2.341 \text{ \AA}$, $dO(4) \cdots H(4) = 2.014 \text{ \AA}$, $\angle C(12)-H(12c) \cdots O(1) = 146^\circ$, $\angle O(4)-H(4) \cdots O(4) = 143^\circ$).

Symmetry codes: ^{vi} $y, -x + y, -z + 1$; ^{vii} $-x + 1, -y + 1, -z + 1$

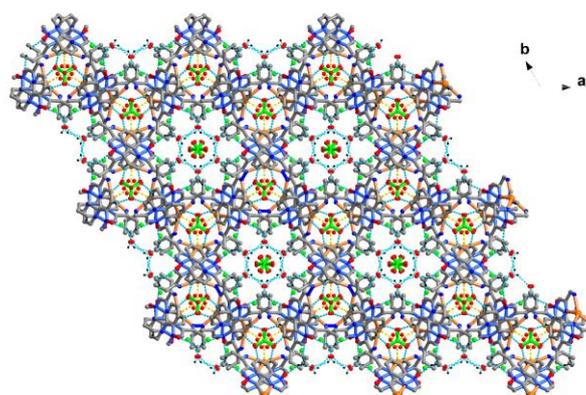
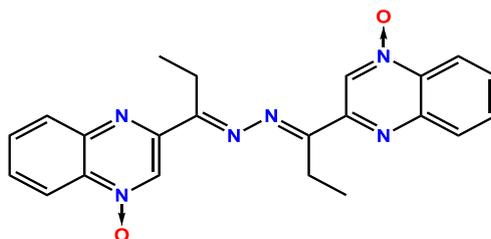


Fig. 4. 3D framework of 1. The hydrogen bonds are shown as blue dotted lines

4 CONCLUSION

In summary, the double Schiff-base ligand L with *N,N*-dioxide quinoxaline as the terminal coordination group can be used as a polydentate or chelating ligand to coordinate transition metal ions. One novel discrete coordination compound with Ag^I centers has been obtained based on such ligand and further connected to a three-dimensional network

under the action of hydrogen bonds. Compared with other Ag₂L₂ discrete compounds formed by the ligand and silver ions (AgPF₆, AgBF₄), the structure of anions, weak interaction between anions and metal centers play important roles in forming the triple-helical [Ag₃L₃]³⁺ crown-like trimer. The methanol solvent rings connected by hydrogen bonds further link these discrete molecules into a three-dimensional network structure.



Scheme 1. Schiff-base ligand used in the construction of coordination compounds

REFERENCES

- (1) Su, C. Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; Loye zur, H. C. Exceptionally stable, hollow tubular metal-organic architectures: synthesis, characterization, and solid-state transformation study. *J. Am. Chem. Soc.* **2004**, 126, 3576–3586.
- (2) Dong, Y. B.; Wang, P.; Ma, J. P.; Zhao, X. X.; Tang, B.; Huang, R. Q. Coordination-driven nanosized lanthanide “molecular lantern” with tunable luminescent properties. *J. Am. Chem. Soc.* **2007**, 129, 4872–4873.
- (3) Kitagawa, S.; Kitaura, R.; Noro, S. I. Functional porous coordination polymers. *Angew. Chem., Int. Ed.* **2004**, 43, 2334–2375.
- (4) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; Keeffe, M. O.; Yaghi, O. M. Modular chemistry: secondary building units as a basis for the design of highly porous and robust metal-organic carboxylate frameworks. *Acc. Chem. Res.* **2001**, 34, 319–330.
- (5) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Supramolecular coordination: self-assembly of finite two- and three-dimensional ensembles. *Chem. Rev.* **2011**, 111, 6810–6918.
- (6) Wisner, J. A.; Beer, P. D.; Drew, M. G. B.; Sambrook, M. R. Anion-templated rotaxane formation. *J. Am. Chem. Soc.* **2002**, 124, 12469–12476.
- (7) Dong, Y. B.; Xu, H. X.; Ma, J. P.; Huang, R. Q. Silver(I) coordination polymers based on a nano-sized bent bis(3-acetylenylphenyl-(4-cyanophenyl)oxadiazole) ligand: the role of ligand isomerism and the templating effect of polyatomic anions and solvent intermediates. *Inorg. Chem.* **2006**, 45, 3325–3343.
- (8) Zapata, F.; Gonzalez, L.; Caballero, A.; Bastida, A.; Bautista, D.; Molina, P. Interlocked supramolecular polymers created by combination of halogen- and hydrogen-bonding interactions through anion template self-assembly. *J. Am. Chem. Soc.* **2018**, 140, 2041–2045.
- (9) Wang, C. J.; Ma, H. R.; Wang, Y. Y.; Liu, P.; Zhou, L. J.; Shi, Q. Z.; Peng, S. M. Subtle structural changes in coordination chains: influence of the flexibility of the precursor ligands and of the solvent. *Cryst. Growth Des.* **2007**, 7, 1811–1817.
- (10) Dong, Y. B.; Zhao, X.; Tang, B.; Huang, R. Q.; Wang, H. Y.; Mark, D. S.; Loye zur, H. C. Novel organic-inorganic composite coordination polymers generated from new multidentate Schiff-base ligand and Ag(I) salts. *Chem. Commun.* **2004**, 2, 220–221.
- (11) Dong, Y. B.; Wang, L.; Ma, J. P. Ag(I) complexes generated from double Schiff-base ligand with thiazole as the terminal binding sites. *Cryst. Growth Des.* **2006**, 6, 2475–2485.
- (12) Dong, Y. B.; Wang, L.; Ma, J. P.; Huang, R. Q. A novel cascade supramolecular complex with a reversible nanosized 18-component H-bonded $\{(C_6H_6)_6(SbF_6)_{12}\}_{12}$ -cage unit templated by achiral metal-organic complex. *Inorg. Chem.* **2006**, 45, 9157–9159.
- (13) Dong, Y. B.; Zhang, H. Q.; Ma, J. P.; Huang, R. Q. Novel one- and two-dimensional Ag(I) networks generated from double base ligands with disubstituted quinoxaline diazenes as the terminal binding sites. *Cryst. Growth Des.* **2005**, 5, 1857–1866.
- (14) Cheng, J. Y.; Wang, P.; Ma, J. P.; Liu, Q. K.; Dong, Y. B. Nanoporous Ag(I)-MOF showing unique selective adsorption of benzene among its organic analogues. *Chem. Commun.* **2014**, 50, 13672–13675.
- (15) Ren, X. H.; Wang, P.; Su, J.; Cheng, J. Y. Syntheses and crystal structures of two discrete complexes generated from 3,6-bis(2-(4-oxide-quinoxaline-yl)-4,5-diaza-3,5-octadiene) and Ag(I) salt. *Chin. J. Inorg. Chem.* **2019**, 35, 1436–1444.
- (16) Wang, Z. Q.; Zhou, L. J.; Wang, Y. L. A Dy(III)-K(I)-biphenyl-3,3'-disulfonyl-4,4'-dicarboxylate compound: structure and luminescence. *Chin. J. Struct. Chem.* **2019**, 38, 1194–1199.
- (17) Wang, Y. L.; Wei, Z.; Mao, W. X.; Zhou, S. J.; Geng, K. S.; Dou, Y. P.; Kang, Y. F.; Liao, B. Syntheses, crystal structures, and properties of two new lanthanide coordination polymers constructed from benzimidazole-5,6-dicarboxylic acid. *Chin. J. Struct. Chem.* **2019**, 38, 1029–1037.
- (18) (a) Sheldrick, G. M. *SHELXTL Ver. 5.1*, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA **1997**.
(b) *SMART Ver. 5.625* and *SAINT+ Ver. 6.02a*, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA **1998**.
- (19) Sheldrick G. M. *SADABS*, University of Göttingen, Germany **1996**.
- (20) Han, L. L.; Zhang, X. Y.; Chen, J. S.; Li, Z. H.; Sun, D. F.; Wang, X. P.; Sun, D. Silver(I)/bipyrazole/dicarboxylate interpenetrated coordination networks: spontaneous chiral resolution, modulation of topologies, water clusters, and photoluminescences. *Cryst. Growth Des.* **2014**, 14, 2230–2239.