

Dinuclear Ag(I) Complex with Cyanuric Acid Ligand: Synthesis, Crystal Structure and Luminescent Properties

BAOYONG ZHU

Department of Chemistry, Dezhou University, Shandong, 253023, P.R. China
Fax: (86)(534)8985835; Tel: (86)(534)8985835; E-mail: zhubaoyong@yhaoo.cn

The dinuclear Ag(I) complex $\text{Ag}_2(\text{CA})_4 \cdot \text{H}_2\text{O}$ (CA = cyanuric acid), has been synthesized hydrothermally. The crystal structure is of monoclinic, space group C2/c with $a = 9.627(5)$, $b = 12.500(5)$, $c = 19.161(5)$ Å, $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3\text{Ag}_2)_4 \cdot \text{H}_2\text{O}$, $M_r = 764.08$, $V = 2232.1(1)$ Å³, $D_c = 2.274$ g/cm³, $F(000) = 1496$, $\mu = 1.856$ cm⁻¹ and $Z = 4$, the final $R = 0.0252$, $WR = 0.0611$ and $S = 1.015$ for 2165 observed reflections with $I > 2\sigma(I)$. The cyanuric acid ligand came from the *in situ* hydrolysis of melamine and cyanuric chloride under the hydrothermal conditions. The X-ray crystal structure analysis indicates that the complex is a 3D coordinated framework, which is constructed by the combination of coordination bonds, hydrogen bonds, π - π stacking interaction and Ag...Ag interactions. Fluorescent analyses of the dinuclear Ag(I) complex show intense photoluminescence at 440 nm in the solid state, which means the complex may be potential candidate for photoactive material.

Key Words: Hydrothermal synthesis, Coordination polymer, Crystal structure, Luminescence.

INTRODUCTION

The cyanuric acid (CA) $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$, is a sturdy, robust small molecule and possesses six functional groups. It is widely used in organic supramolecular chemistry^{1,2} and industrial areas³. As a mildly acidic compound, its pK_a values are 6.85, 10.91 and > 12 for the generation of the mono- (CA^-) , di- (CA^{2-}) and trianionic (CA^{3-}) forms, respectively⁴. The CA^- anion is easily achieved and the CA^{2-} can be made by careful control of the reaction equilibrium, but the CA^{3-} form is much more difficult to be achieved. Despite the monoanionic form is easier to be achieved than the di- and trianionic forms, there has so far been a few reports^{5,6} about its use as an anionic ligand in coordination complexes with transition metals.

In construction of coordination polymers, the coordinatively flexible metal ions, such as silver(I), whose complexes always aggregate with a metal-metal interaction that is shorter than the van der Waals distance (3.40 Å for Ag), are frequently used because of their high affinities to N and O donors. Interesting polynuclear silver(I) complexes with different frameworks and topologies have been synthesized so far⁷⁻⁹; some of these complexes show good conductivity and luminescent properties^{10,11}. During the course of investigations of the properties of triazine derivatives in solutions, we have isolated a novel silver(I) compound with monodentate CA possessing three

dimensional supramolecular structure constructed by the combination of coordination bonds, hydrogen bonds, π - π stacking interactions and Ag...Ag interactions. Here, we report the synthesis, crystal structure and luminescent properties of the dinuclear Ag(I) complex with cyanuric acid *i.e.*, $\text{Ag}_2(\text{CA})_4\cdot\text{H}_2\text{O}$.

EXPERIMENTAL

All analytical grade reagents were purchased commercially and used without further purification. Elemental analyses were carried out on an EA1112 CHNS elemental analyzer. Fluorescence spectrum was measured on a RF-540 fluorescence spectrometer.

Synthesis of $\text{Ag}_2(\text{CA})_4\cdot\text{H}_2\text{O}$: A mixture of melamine (2.5 mmol), cyanuric chloride (2.5 mmol) and silver nitrate (8.75 mmol) was placed into a 30 mL Teflon-lined autoclave containing water (20 mL) as solvent. The autoclave was heated at a heating rate of 1 °C/min to 220 °C and kept at this temperature for 3 h, then cooled at a cooling rate of 1 °C/min to room temperature. The products with about 45 % yield based on cyanuric chloride were isolated after washing with 25 % ammonia solution. Elemental analysis (%): calcd. (%) for $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3\text{Ag}_2)_4\cdot\text{H}_2\text{O}$: C 19.30, H 1.34, N 22.5; found. (%): C 19.33, H 1.30, N 22.47.

Structure determination: A colourless single crystal with dimensions of 0.47 mm \times 0.22 mm \times 0.05 mm was mounted on a glass fiber and the data were collected on a Bruker SMART-APEX CCD diffractometer (graphite monochromatized Mo K_α radiation, $\lambda = 0.71073 \text{ \AA}$) using an ω and ϕ scan mode. For the present dinuclear Ag(I) complex, a total of 6807 reflections were collected at 298(2) K in the range of $2.20^\circ \leq \theta \leq 27.54^\circ$, of which 2556 were unique with $R_{\text{int}} = 0.0178$ and 2165 were observed with $I > 2\sigma(I)$. Lorentz-polarization corrections and empirical absorption were applied to the data. The crystal structure of the dinuclear Ag(I) complex was solved by direct method using SIR97¹² program and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on all F^2 data using SHELXL97¹³, H atoms bonded to N atoms were added according to theoretical models, assigned isotropic displacement parameters and allowed to ride on their respective parent atoms, the $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{N})$. The positions of the H atoms of the water molecule were obtained from Fourier map and refined using a riding model; the $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{O})$. Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0252$ and $wR_2 = 0.0611$, $w = 1/[\sigma^2(F_o^2) + (0.1286P)^2 + 14.3307P]$, where $P = (F_o^2 + 2F_c^2)/3$. The highest and lowest residual peaks in the final difference Fourier map are 0.546 and -0.557 e/\AA^3 , respectively, $(\Delta/\sigma)_{\text{max}} = 0.000$. The single suite WINGX was used as an integrated system for all the crystallographic programs¹⁴.

RESULTS AND DISCUSSION

Description of the crystal structure: The asymmetry unit of the dinuclear Ag(I) complex is shown in Fig. 1. In each asymmetry unit there are two Ag(I) ions, two cyanuric acid ligands and one water molecule. The Ag atoms are located in the

inversion center positions and other atoms are in the general positions. Each Ag(I) center (Ag1, Ag2) coordinates to one N atom (N1 and N4) from two different cyanuric acid ligands in monodentate mode. The Ag-N bond lengths are both 2.082(2) Å (Table-1), which is similar to those observed previously¹⁰. The two cyanuric acid moieties are parallel to each other indicated by the N-Ag-N angle (Table-1). The Ag-Ag distance is 3.038 Å and it is shorter than the sum of van Der Waals radii of two Ag ions (3.40 Å), which indicates a weak Ag...Ag interactions between them.

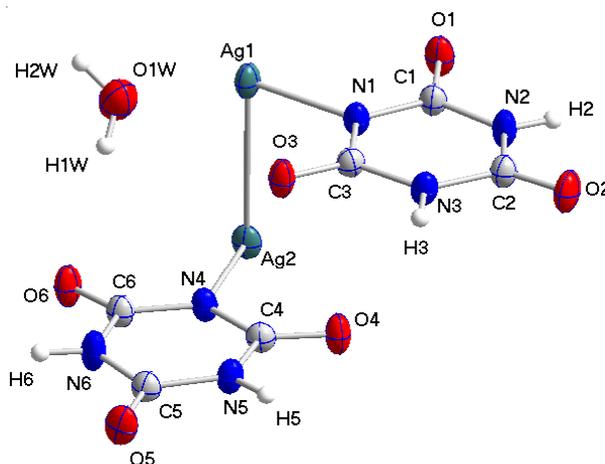


Fig. 1. Asymmetry unit of the title complex with 50 % thermal ellipsoid probability

TABLE-1
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Dist.	Bond	Dist.
Ag(1)-N(1)	2.083(2)	Ag(1)-Ag(1A)	3.038(1)
Ag(2)-N(4)	2.082(2)	-	-
Angle	(°)	Angle	(°)
N(1)-Ag(1)-Ag(2)	90.20(6)	N(4)-Ag(2)-Ag(1)	90.23(6)

Fig. 2 gives the interlayer hydrogen bonds of the dinuclear Ag(I) complex. Crystal analysis reveals that the structure is staggered. Because of such a staggered structure and the water molecules, extensive hydrogen bonds are formed. Besides the intralayer N-H...O hydrogen bonds, there are interlayer hydrogen bonds between H₂O and the O from the cyanuric acid ligands above and below the H₂O molecule (Table-2). Thus, a supramolecular ladder with eight-membered rings is made up. If the oxygen atoms of H₂O molecules are omitted, the ladder just makes up stable six-membered rings with chair conformation. The existence of this conformation makes the structure stable¹⁵. Additionally, the distance between the centroids of the intermolecular cyanuric acid rings (3.334 Å) is much shorter than the maximum contact for the π - π stacking interaction (3.8 Å for centroid-centroid distance), indicating there are obvious π - π stacking interactions (Fig. 3).

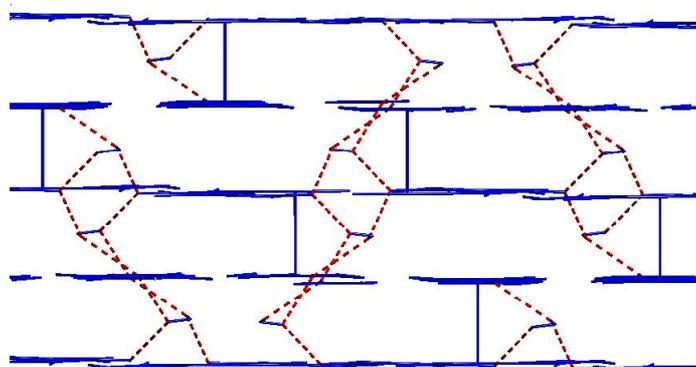
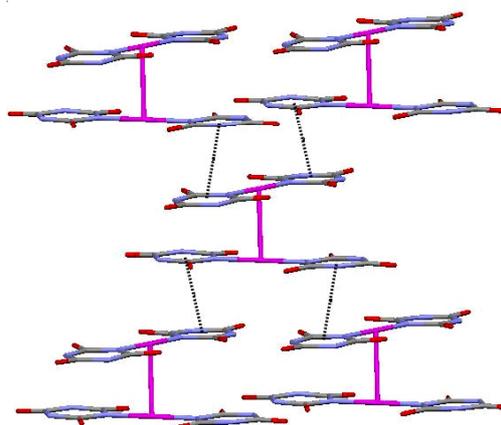


Fig. 2. Interlayer hydrogen bonds

TABLE-2
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠ DHA
O1W-H2W...O5 ⁱ	0.83	2.43	2.981(3)	124.3
O1W-H2W...O5 ⁱⁱ	0.83	2.21	2.986(3)	154.3
O1W-H1W...O2 ⁱⁱⁱ	0.83	2.47	2.985(3)	120.5
O1W-H1W...O2 ^{iv}	0.83	2.19	2.987(3)	158.9
N6-H6...O6 ^v	0.86	1.94	2.798(3)	172.2
N5-H5...O4 ^{iv}	0.86	1.94	2.793(3)	173.7
N3-H3...O3 ^{iv}	0.86	1.93	2.790(3)	174.3
N2-H2...O1 ^{vi}	0.86	1.95	2.801(3)	171.8

Symmetry codes: (i) $-x + 1/2, -y + 3/2, -z$; (ii) $x-1/2, y-1/2, z$; (iii) $x-1/2, -y + 3/2, z-1/2$; (iv) $-x + 1, y, -z + 1/2$; (v) $-x, -y + 2, -z$; (vi) $-x + 1/2, -y + 3/2, -z + 1$.

Fig. 3. Intermolecular π - π stacking interactions

In the present complex, the cyanuric acids are generated *in situ* hydrolysis of melamine and cyanuric chloride under hydrothermal condition. They are linked

into 2D sheets perpendicular to b axis by CA-Ag coordination bonds and strong intralayer N-H...O hydrogen bonds. These sheets are further linked to form infinite 3D coordination framework by Ag...Ag interactions, intermolecular offset π - π stacking interactions and relatively weak O4-H4...O hydrogen bonds. The average distance between neighboring sheets is 3.125 Å.

Fluorescence property: Silver(I) complexes are better known to emit photoluminescence at low temperature¹⁶. In present case at room temperature, the synthesized complex in the solid state shows virtually intense photoluminescence with emission max at 440 nm, compared with the free ligand with a broad emission band, upon excitation at 370 nm. Fig. 4 shows the emission spectrum of the present complex and the free ligand in the solid state at room temperature. Because the free ligand shows weak luminescence, the strong luminescence of compound **1** may contribute to the ligand-to-metal charge-transfer (LMCT) and metal centered (MC) $d \rightarrow s$ transitions¹⁷. The slight red shift may be related to the deprotonation of the free ligand as well as the coordination to the Ag atom¹⁸. The results here suggest that the present complex may be a good candidate for solvent-resistant blue fluorescent material because it is insoluble in the common solvents such as ethanol, chloroform, acetone, acetonitrile, benzene and water.

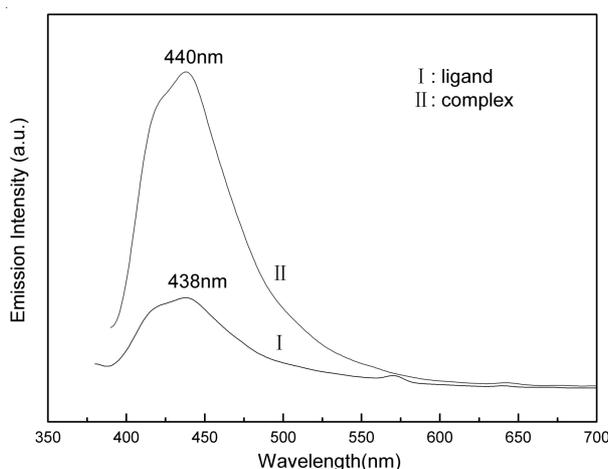


Fig. 4. Photo-induced emission spectrum of the title complex and ligand in the solid state at room temperature

Conclusion

In summary, the dinuclear Ag(I) complex has been successfully synthesized and the crystal structure was determined by single crystal X-ray diffraction. Photoluminescence spectrum shows the title complex is a good blue fluorescent material.

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REFERENCES

1. M. Arduini, M. Crego-Calama, P. Timmerman and D.N. Reinhoudt, *J. Org. Chem.*, **68**, 1097 (2003).
2. V. Berl, M. Schmutz, M.J. Krische, R.G. Khoury and J.M. Lehn, *Chem. Eur. J.*, **8**, 1227 (2002).
3. D.L. Siebers and J.A. Caton, *Combust. Flame*, **79**, 31 (1990).
4. S. Aoki, M. SHiro, T. Koike and E. Kimura, *J. Am. Chem. Soc.*, **122**, 576 (2000).
5. L.R. Fallvelo, I. Pascual, M. Tomas and E.P. Urrioldebeitia, *J. Am. Chem. Soc.*, **119**, 11894 (1997).
6. J. Server-Carrio, E. Escriva and J.V. Folgado, *Polyhedron*, **17**, 1495 (1998).
7. X. Liu, G.C. Guo, M.L. Fu, X.H. Liu, M.S. Wang and J.S. Huang, *Inorg. Chem.*, **45**, 3679 (2006).
8. S.L. Zheng, M.L. Tong and X.M. Chen, *Coord. Chem. Rev.*, **246**, 185 (2003).
9. R. Curran, J. Lenehan, M. McCann, K. Kavanagh, M.A. Devereux, D. Egan, G. Clifford, K. Keane, B.S. Creaven and V. McKee, *Inorg. Chem. Commun.*, **10**, 1149 (2007).
10. C.N.R. Rao, A. Ranganathan, V.R. Pedireddi and A.R. Raju, *Chem. Commun.*, 39 (2000).
11. Y.B. Dong, H.X. Xu, J.P. Ma and R.Q. Huang, *Inorg. Chem.*, **45**, 3325 (2006).
12. A. Altomare, M.C. Burla, M. Camalli, G.L. Casciarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, **32**, 115 (1999).
13. G.M. Sheldrick, *Acta Cryst.*, **A64**, 112 (2008).
14. L.J. Farrugia, *J. Appl. Crystallogr.*, **32**, 837 (1999).
15. H.B. Jia, J.H. Yu, J.Q. Xu, L. Ye, H. Ding, W.J. Jing, T.G. Wang, J.N. Xu and Z.C. Li, *J. Mol. Struct.*, **641**, 23 (2002).
16. D.H. Pierre and F. Daniel, *Coord. Chem. Rev.*, **171**, 351 (1998).
17. F. Sabin, C.K. Ryu, P.C. Ford and A. Vogler, *Inorg. Chem.*, **31**, 1941 (1992).
18. J.Y. Hu, J.A. Zhao, H.W. Hou and Y.T. Fan, *Inorg. Chem. Commun.*, **11**, 1110 (2008).

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