# The Syntheses and Structures of Two Silver Compounds Based on Phdat<sup>1</sup>

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**Abstract**—Based on the organic ligand 2,4-diamine-6-phenyl-1,3,5-triazine (Phdat), two Ag(I) compounds, Ag(Phdat)<sub>2</sub>(NO<sub>3</sub>) (I) and Ag(Phdat)<sub>2</sub>(OAc) (II), have been synthesized and characterized by single crystal X-ray diffractions, elemental analyses, and IR spectra. Compounds I and II are mononuclear and binuclear structures, respectively, and with the help of N–H…O and N–H…N hydrogen bonds and  $\pi$ … $\pi$  packing interactions, the 3D supramolecular networks are built up.

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## **INTRODUCTION**

In past few decades some coordination compounds have been synthesized, exhibit diverse structural motifs, as well as showing potential applications in gas storage [1], as magnetic [2] and optoelectronic materials [3]. The key factor that influences the structures and properties is the choice of the organic ligands. Good ligands not only provide the donor atoms at specific positions to coordinate the metal ion, but also provide potential interaction sites to generate noncovalent interactions, such as hydrogen-bonding and  $\pi-\pi$  stacking interactions. 2,4-Diamine-6-R-1,3,5triazine ( $R = NH_2$ , Phenyl,  $CH_3$ ) are the desired ligands [4-8], which contain five nitrogen atoms, two amino nitrogen atoms considered as perfect H-bond donors, three triazine-nitrogen atoms being apt to coordinate to transition metals especially silver(I) or as H-bond acceptors. Besides, aromatic rings can provide potential  $\pi - \pi$  stacking interactions.

So herein, we used 2,4-diamine-6-phenyl-1,3,5triazine (Phdat) and  $Ag^+$  ion as the starting materials, and synthesized two compounds,  $Ag(Phdat)_2(NO_3)$ (I) and  $Ag(Phdat)_2(OAc)$  (II). As far as we know, the related compounds with Phdat are seldom reported [9].

### EXPERIMENTAL

Materials and physical measurements. AgNO<sub>3</sub>, AgOAc are of A.R. grade and used as purchased. Phdat (99+%) is purchased from ACROS. Infrared spectra were recorded on a Nicolet 170 FT-IR spectropho-

tometer using KBr pellets in the range of 400– $4000 \text{ cm}^{-1}$ . Elemental analyses were performed via Vario EL III Etro Elemental Analyzer. Thermogravimetric analysis (TGA) was performed under atmosphere with a heating rate of 10°C min<sup>-1</sup> using TGA/SDTA851e.

X-ray crystallography. The colorless block crystals of compounds I and II were selected for X-ray diffraction analyses, with dimensions of 0.44 × 0.37 × 0.23 mm and 0.20 × 0.14 × 0.11 mm. X-ray singlecrystal data were collected at 296(2) K on a Bruker Apex-II CCD areadetector diffractometer with a Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). Data reduction and absorption correction were made with empirical methods. The structure was solved by direct methods and refined by full-matrix least-squares techniques using SHELXL-97 [10]. Anisotropic displacement parameters were refined for all non-hydrogen atoms, and all hydrogen atoms were added in the riding model without refinement. Crystal data and refinement details are presented in Table 1.

Supplementary material for structures of I and II has been deposited with the Cambridge Crystallographic Data Centre (nos. 836177 and 836178; deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

Synthesis of I.  $AgNO_3$  (2 mmol), Phdat (1 mmol) and  $H_2O$  (10 mL) were added to a Teflon-lined vessel, with stirring about 20 min. Then the mixture was sealed in stainless-steel autoclave and heated to 120°C for 72 h, then cooled to room temperature. Colorless

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Doromotor	Value				
Farameter	Ι	II			
М	544.30	541.34			
Crystal system	Monoclinic	Orthorhombic			
Space group	$P2_{1}/n$	Pnnm			
<i>a</i> , Å	12.2311(7)	12.9113(9)			
<i>b</i> , Å	13.1227(8)	14.8538(11)			
<i>c</i> , Å	13.4304(7)	12.0376(9)			
β, deg	93.2730(10)	90			
$V, Å^3$	2152.1(2)	2308.6(3)			
Ζ	4	4			
$\rho$ , mg/m <sup>-3</sup>	1.680	1.558			
<i>F</i> (000)	1096	1096			
$\mu$ , mm <sup>-1</sup>	0.983	0.912			
Reflections measured	9215	12834			
Independent reflections	3777	2983			
<i>R</i> <sub>int</sub>	0.0219	0.0641			
GOOF	1.085	1.016			
R <sup>a</sup>	0.0392	0.0509			
<i>Rw</i> <sup>b</sup>	0.1008	0.1205			
Largest and mean delta/sigma	0.000/0.000	0.000/0.000			
Largest difference peak, $e/Å^3$	0.708/-0.629	0.790/-0.840			
Note: <sup>a</sup> $R = \Sigma(  F_0  -  F_c  )/\Sigma F_0 $ , <sup>b</sup> $Rw =$					
$\{\Sigma w[(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma w[(F_{o}^{2})^{2}]\}, \ w = 1 / [\sigma^{2}(F_{o}^{2}) + (aP)^{2} +$					
$bP$ ], $P = (F_0^2 + 2F_c^2)/3$ ]. I: $a = 0.0502, b = 1.6661$ ; II: $a =$					

Table 1. Crystallographic data and details of the experiment and refinement of complexes I and II

block crystals I were obtained (0.15 g, yield 27.6% based on Phdat).

For  $C_{18}H_{18}N_{11}O_3Ag$ anal. calcd., %: C, 39.72; H, 3.33;

0.0601, b = 0.5153.

Found, %: C. 39.33: H. 3.07: N. 28.01	-			
	Found, %:	C, 39.33;	Н, 3.07;	N, 28.01.

N, 28.31.

Synthesis of II. Replacement of  $AgNO_3$  (2 mmol) by AgOAc (2 mmol), a small amount of colorless block crystals II were obtained.

For $C_{20}H_{21}N_{10}O_2Ag$							
anal. calcd., %:	C, 44.38;	Н, 3.91;	N, 25.88.				
Found, %:	C, 44.08;	Н, 4.22;	N, 25.52.				

#### **RESULTS AND DISCUSSION**

The Ag(I) atom of I is coordinated by two triazine ring N atoms of two monodentate Phdat ligands, forming a broken line with NAgN angle of  $145.39(12)^{\circ}$ (Fig. 1a), smaller than that of the similar mononuclear compound Ag(melamine)<sub>2</sub>NO<sub>3</sub> [11] as well as that of the compound [Ag(Phdat)](BF<sub>4</sub>) [9]. The Ag–N lengths are about 2.197(3)–2.210(3) Å. Two neighbouring Ag<sup>+</sup> ions are linked by Ag–O weak interactions with Ag–O bond distances of 2.807 and 2.860 Å, where Ag<sup>+</sup> ion formed in distorted tetrahedron. Similar interactions are also found in Ag(melamine)<sub>2</sub>NO<sub>3</sub>, [Ag(NO<sub>3</sub>)(melamine)]<sub>n</sub> and [Ag(melamine)<sub>2</sub>]ClO<sub>4</sub> [12, 13], where Ag–O distances are 2.7924 and 2.569 Å, respectively, shorter than that of I.

In the Phdat ligand, the triazine rings are practically perfectly flat (aplanarities 0.0070 and 0.0074 Å), but the phenyl rings show more aplanar with the root mean square aplanarities of 0.0108 and 0.0123 Å. The interplanar angles of two rings in the ligands are  $6.2^{\circ}$ and 31°. As shown in Fig. 2a, in the structure of the compound **I**, there are two noticeable motives for assembly between the elemental building blocksnamely, triazine-phenyl and triazine-triazine  $\pi{-}\pi$ stacking. Obviously the triazine-phenyl  $\pi - \pi$  stacking interaction is stronger than that of triazine-triazine, which can be seen by the vertical plane-plane distances between two rings, 3.45 and 3.95 Å, respectively, compared with the reported [14-16]. The centroid-centroid distances are 3.54 and 4.23 Å, with the angles between planes of  $6.2^{\circ}$  and  $0^{\circ}$ , respectively. The stacking extends along x axis direction and leads to the formation of 2D layer structure.

Between the neighbouring layers, the hydrogen bonds help to construct 3D network, which are N-H···N hydrogen bonds between NH<sub>2</sub> and the uncoordinated triazine–N atoms, N–H···O hydrogen bonds between NH<sub>2</sub> and NO<sub>3</sub><sup>-</sup> (Table 2).

As we know,  $CH_3COO^-$  group is one excellent bridging ligand, in complex II, both Ag(I) atoms, besides coordinated by two triazine ring N atoms of two monodentate Phdat ligands, are bridged by two  $\mu_2:\eta^I:\eta^I-CH_3COO^-$  groups, forming distorted tetrahedron configurations with the bond angles in the range of 99.87(9)°-133.61(15)° (Fig. 1b). The Ag-N lengths are about 2.292(4)-2.347(5) Å, which are longer than those of I. The Ag-O length is 2.372(3) Å.

In Phdat, the triazine ring (C(1), C(2), C(3), C(4), C(1A), C(2A)) shows more aplanar (aplanarity of 0.0493 Å) than other phenyl and triazine rings (aplanarities 0.0140, 0.0105 and 0.0165 Å). The interplanar angles of two rings in the ligands are  $0.9^{\circ}$  and  $9.2^{\circ}$ , smaller than that (31°) of I, so more offset  $\pi \cdots \pi$  stacking interactions are found in II. From Fig. 2b, all of the aromatic rings of II containing benzene and triazine rings involves in  $\pi \cdots \pi$  stacking interactions, namely, benzene-triazine  $\pi \cdots \pi$  stacking interactions, which help the dinuclear units forming 2D network. The ver-



Fig. 1. The ellipsoid diagram at 30% of compounds I (a) and II (b).

tical plane-plane distances between triazine and phenyl are 3.49 and 3.77 Å and the centroid-plane distances are 3.61 and 3.84 Å, with angles between planes of  $9.2^{\circ}$  and  $0.9^{\circ}$ .

Between the neighbouring 2D layers, there are several hydrogen bonds containing  $N-H\cdots N$  hydrogen bonds between  $NH_2$  and the uncoordinated triazine-N atoms,  $N-H\cdots O$  hydrogen bonds between  $NH_2$  and  $CH_3COO^-$ , resulting in the formation of 3D hydrogen bonds network (Table 2).

IR spectra of I and II are similar for their structural similarity. The stretching vibrations of N–H and C–H are found ranging from 3500 to 3100 cm<sup>-1</sup>. The peaks at about 1650–1500 cm<sup>-1</sup> are attributed to the aromatic rings stretching, 820-700 cm<sup>-1</sup> for the rings C–H in-plane vibration and out-of-plane vibration.

TGA was performed for I from Fig. 3, at approximately 200°C, the compound I started a first sharp mass loss of 40%, which suggested the compound I doesn't contain small solvent molecules, corresponding to the structure. In succession, from 300 to 550°C, two mass reductions were observed and finally 20.1% of the remnants were left, which should be Ag (19.8% calculated).



(a)

**Fig. 2.**  $\pi - \pi$  diagram in compound I (a) and II (b).



Fig. 3. TGA diagram for the compound I.

Contect D-H…A	Distance, Å		Angle		
	Н…А	D…A	D−H…A, deg		
I					
$N(4) - H(4B) \cdots N(8)^{\#1}$	2.18	3.030(4)	173		
$N(5)-H(5A)\cdots N(7)^{#2}$	2.37	3.200(4)	162		
$N(5)-H(5B)\cdots O(2)$	2.16	2.975(5)	158		
$N(9) - H(9A) \cdots N(1)^{#3}$	2.15	3.005(4)	178		
$N(9)-H(9B)\cdots O(2)$	2.41	3.137(6)	143		
$N(10)-H(10A)\cdots N(2)^{#4}$	2.23	3.080(4)	172		
' II					
$N(4) - H(4B) \cdots N(6)^{\#1}$	2.27	3.126(5)	173		
$N(4)-H(4A)\cdots O(1)$	2.16	2.993(4)	162		
$N(5)-H(5A)\cdots N(3)^{\#2}$	2.32	3.168(5)	170		
$N(5)-H(5B)\cdots O(1)$	2.13	2.960(5)	162		

**Table 2.** Important hydrogen-bonding interactions presentin compounds I and II\*

Note: \* Symmetry transformations used to generate equivalent atoms:  ${}^{\#1}x + 1/2, -y + 3/2, z + 1/2; {}^{\#2}x - 1/2, -y + 3/2, z + 1/2; {}^{\#3}x - 1/2, -y + 3/2, z - 1/2; {}^{\#4}x + 1/2, -y + 3/2, z - 1/2$  for I;  ${}^{\#1}x - 1/2, -y - 1/2, -z - 1/2; {}^{\#2}x + 1/2, -y - 1/2, -z - 1/2; {}^{\#2}x + 1/2, -y - 1/2, -z - 1/2$  for II.

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