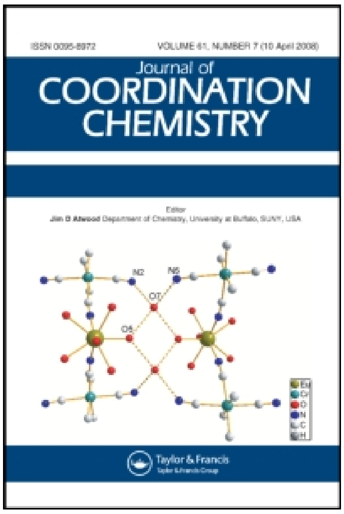

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A 2-D Ag(I) complex with μ_4-bte containing infinite tubes (bte = 1,2-*bis*(1,2,4-triazole-1-yl)ethane)

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Using the flexible ligand 1,2-*bis*(1,2,4-triazole-1-yl)ethane (bte) and corresponding Ag(I) salts, a new two-dimensional (2-D) silver(I) complex $\{[Ag_4(\mu_4\text{-bte})(\mu_2\text{-}H_2O)_2](SiF_6)_2\}_n$ (**1**) has been isolated. **1** crystallizes in the orthorhombic Pcca space group. The bte adopts an unusual μ_4-tetradentate coordination mode to link neighboring Ag^I atoms forming infinite 1D Ag-bte tubular structures. Further neighboring Ag-bte tubes are inter-connected by relatively long Ag-(μ_2-H_2O) bonds forming a 2-D layered structure. Solid-state fluorescence spectrum of **1** shows that the excitation peak is at 320 nm while the maximum emission peak is at 425 nm.

Keywords: 1,2-*Bis*(1,2,4-triazole-1-yl)ethane; Tubular; Tetradentate; Fluorescence

1. Introduction

Metal-organic coordination polymers are of interest due to their versatile coordination motifs and potential applications in areas such as light-emitting diodes (LEDs), catalysis, magnetic materials, etc. [1–4]. Construction of coordination polymers depends on the selection of ligands and coligands. Flexible ligands with variable *trans*- and *cis*-configurations generate many interesting structure motifs [5, 6].

As a flexible ligand 1,2-*bis*(1,2,4-triazole-1-yl)ethane (L) contains an ethane spacer and two triazole groups to construct metal-organic frameworks. Li *et al*. have made a systemic investigation on Cd^{II} and Co^{II} frameworks based on L [7]. We have also been interested in metal-triazole systems and reported a series of Zn(II) and Cd(II) frameworks [8]. As a continuation of previous work, herein a 2-D silver(I) complex $\{[Ag_4(\mu_4\text{-bte})(\mu_2\text{-}H_2O)_2](SiF_6)_2\}_n$ (**1**) is isolated, in which infinite 1-D Ag-bte tubes are interconnected by coordinated water. Interestingly, bte adopts the μ_4-coordination mode, and such tubular structures are rare. Solid state luminescence of **1** also has strong emission centered at 425 nm.

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2. Experimental

2.1. *Materials and general methods*

Reagents were purchased commercially and used without further purification. The ligand bte was prepared according to the literature method [9]. The solvents were distilled from the appropriate drying agents prior to use. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. FT-IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer in the range 4000–400 cm^{-1}. The luminescence spectrum was measured by a MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source.

2.2. *Synthesis of* $\{[Ag_4(\mu_4\text{-}bte)(\mu_2\text{-}H_2O)_2](SiF_6)_2\}_n$ *(1)*

A solution of bte (4.76 mg, 0.020 mmol) in MeOH (10 mL) was carefully layered onto a solution of Ag_2SiF_6 (7.16 mg, 0.0230 mmol) in H_2O (10 mL) and left for 7 days at room temperature to give colorless crystals. The product was collected after washing by H_2O and ether in 35% yield based on Ag. Elemental analysis (%) Calcd for **1**: C, 12.94; H, 1.99; N, 15.09. Found: C, 13.15; H, 2.05; N, 15.34. IR data (cm^{-1}): 3410(br), 3110(m), 3022(w), 1520(m), 1253(m), 1224(m), 1163(m), 1018(m), 976(m), 635(m), 498(w). Parallel preparation experiment using mixed solutions containing Ag_2SiF_6 and bte evaporating in a beaker gave only microcrystals not suitable for single crystal X-ray analysis. Crystallization speed should be key for obtaining suitable crystals of **1**.

2.3. *X-ray crystallography*

Structural data of **1** were obtained on a computer controlled Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation at 0.71073 Å by using ω-scan technique. Semi-empirical absorption corrections using SADABS were applied. The structure was solved by direct methods and refined with full-matrix least-squares using SHELXS-97 and SHELXL-97 programs [10]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Organic hydrogen atoms were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths and angles are listed in table 1 and table 2, respectively. CCDC-**1** 670967 contains the supplementary crystallographic data for this article. The data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

3. Results and discussion

Single crystal X-ray analysis shows that the asymmetrical structural unit of **1** contains one silver(I), half of a μ_4-bte ligand, two μ_2-bridged water molecules and half of an

Table 1. Crystallographic data and structure refinement summary.[a]

Formula	$C_3H_{5.50}AgF_3N_3OSi_{0.50}$
Fw ($g\,mol^{-1}$)	557.04
Wavelength (Å)	0.71073
Crystal size (mm^3)	0.24 × 0.20 × 0.12
Crystal system	Orthorhombic
Space group	*Pcca*
Unit cells and dimensions (Å, °)	
a	12.575(2)
b	6.2874(9)
c	17.436(3)
V ($Å^3$)	1378.6(4)
Z	4
θ range (°)	2.34 to 26.41
Limiting indices	$-15 \le h \le 13$ $-6 \le k \le 7$ $-18 \le l \le 21$
ρ ($g\,cm^{-3}$)	2.684
μ (mm^{-1})	3.017
Reflections collected/unique	7156/1415
R (int)	0.0592
Data/restraints/parameters	1415/2/107
GoF	1.075
F (000)	1068
T (K)	294(2)
R_1^a/wR_2^b ($I > 2\sigma(I)$)	0.0270/0.0633
R_1/wR_2 (all data)	0.0395/0.0682
Largest diff. peak and hole ($e\,Å^{-3}$)	0.443 and −0.559

[a] $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$. [b] $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)]^{1/2}$.

Table 2. Selected bond distance (Å) and angles (°).[a]

Ag(1)–N(3)#1	2.173(3)	Ag(1)–N(1)	2.205(3)
Ag(1)–O(1)	2.5525(19)	Ag(1)–O(2)	2.567(2)
N(3)#1–Ag(1)–N(1)	159.01(10)	N(3)#1–Ag(1)–O(1)	107.16(8)
N(1)–Ag(1)–O(1)	91.63(7)	N(3)#1–Ag(1)–O(2)	103.26(8)
N(1)–Ag(1)–O(2)	90.14(8)	O(1)–Ag(1)–O(2)	75.79(6)

[a] Symmetry transformations used to generate equivalent atoms: #1: $x + 1/2$, y, $-z$.

uncoordinated SiF_6^{2-}. There only exists one crystallographic independent Ag(I) (Ag1) with tetrahedral geometry and from two nitrogens of two bte ligands and two μ_2-bridged waters (figure 1). The Ag–N distances [2.173(3) and 2.205(3) Å] are shorter than Ag–O distances [2.552(2) and 2.570(2) Å]. Ag ··· Ag separations by water or bte ligands are 3.579(4) and 6.383(3) Å, respectively. The five-membered triazole ring is almost coplanar with a mean deviation of 0.0029(3) Å. The dihedral angle of the two triazole rings within the bte is 34.3(4)°.

As shown in figure 2(a), Ag^I ions are linked by bte ligands forming infinite 1-D tubes with dimensions of 3.579(4) × 7.902(6) $Å^2$. Adjacent 1-D tubes are extended by Ag-(μ_2-H_2O) coordination bonds forming a 2-D corrugated layered structure. A DFT study of Ag–(H_2O) coordination bonds indicates they can release enough energy to allow framework distortion through hydrogen bonds of coordinated water [11].

The uncoordinated SiF_6^{2-} anions are located between neighboring layers. Strong intermolecular classical O–H ··· F and non-classical C–H ··· F hydrogen bonds are observed between the free SiF_6^{2-} anions and bridged water molecules or bte carbons.

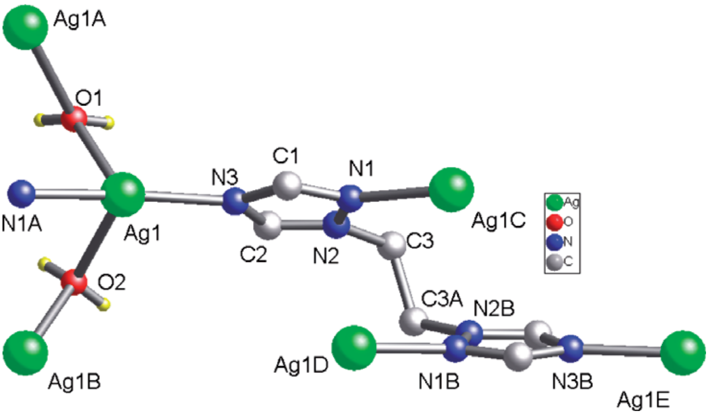

Figure 1. An ORTEP drawing of **1** showing the coordination environment of Ag^I ion.

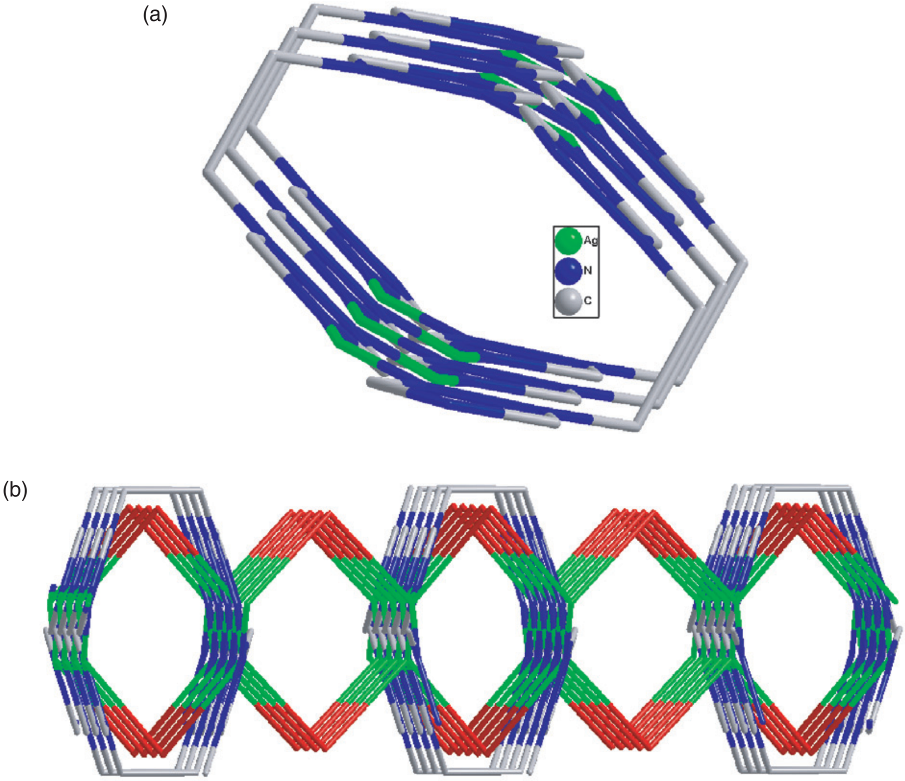

Figure 2. (a) 1-D infinite Ag-bte tube-like structural motif. (b) 1-D Ag-bte tube-like structures linked via coordinated water forming a 2-D corrugated layered structure.

These strong hydrogen bonds further assemble the 2-D structure into a 3-D supramolecular structure (figure 3). Hydrogen bond distances and angles are listed in table 3. Supramolecular contacts play crucial roles in directing and regulating the framework structure, helping to stabilize the coordinated waters.

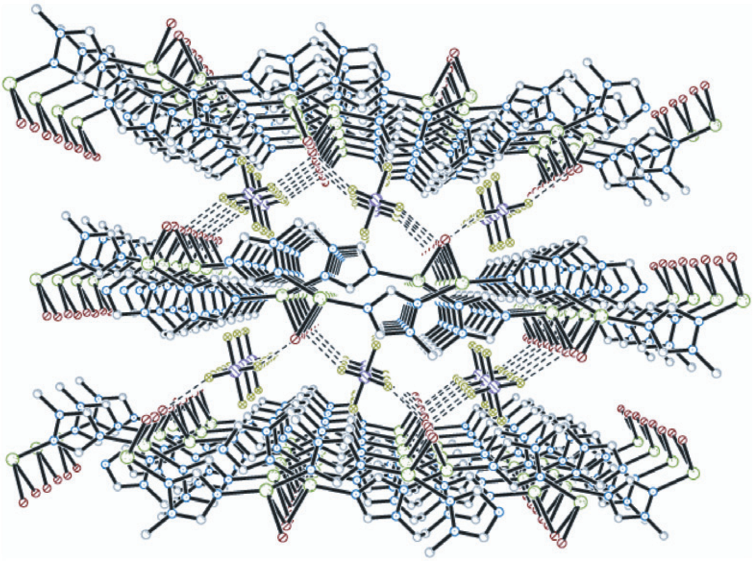

Figure 3. The free SiF_6^{2-} anions reside between 2-D layers, further consolidating the 3-D supramolecular architecture of **1** through hydrogen bonds.

Table 3. Hydrogen bonds for **1** [(Å) and (°)].[a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(1)–H(1A)···F(3)[a]	0.849	1.815	2.661(3)	174.88
O(2)–H(2A)···F(1)[b]	0.843	1.934	2.768(3)	170.11
C(1)–H(1)···F(2)[c]	0.930	2.261	3.120(4)	150.36
C(3)–H(3B)···F(2)[d]	0.970	2.313	3.239(4)	159.27

[a] Symmetry transformations used to generate equivalent atoms: a: $-x+1$, $-y+1$, $-z$; b: $-x+1$, $-y$, $-z$; c: $1/2-x$, y, $-1/2+z$; d: $1-x$, y, $1/2-z$.

Such assembly of silver(I) ions and bis(triazole) is unique in metal-triazole systems [12]. In general, solvent molecules are terminal ligands and L are bridging ligands. This structural motif is somewhat similar to previously reported Ag(tcm)(Me_4pyz)$_{1/2}$ (tcm = tricyanomethanide, Me_4pyz = tetramethylpyrazine) by Batten *et al.* [13], in which rectangular tubes of Ag(tcm) are bridged by Me_4pyz ligands.

A 2-D Ag(I) compound $\{[Ag(\mu_2\text{-bte})_2](NO_3)\}_n$ has been isolated, in which four-coordinate Ag(I) atoms are extended via four bridging μ_2-bte ligands forming a 2-D layered structure [7b]. The structural motif variation for **1** can be attributed to anion tuning and incorporation of water, revealing potential applications in constructing framework structures with such flexible ligands.

3.1. *FT-IR spectrum of 1*

FT-IR spectroscopy can be used as a diagnostic tool for identifying the coordination modes of triazole derivatives, which may be monodendate, bidendate or tridendate [14]. FT-IR spectrum of **1** shows a broad strong band at 3410 cm^{-1} indicating –OH

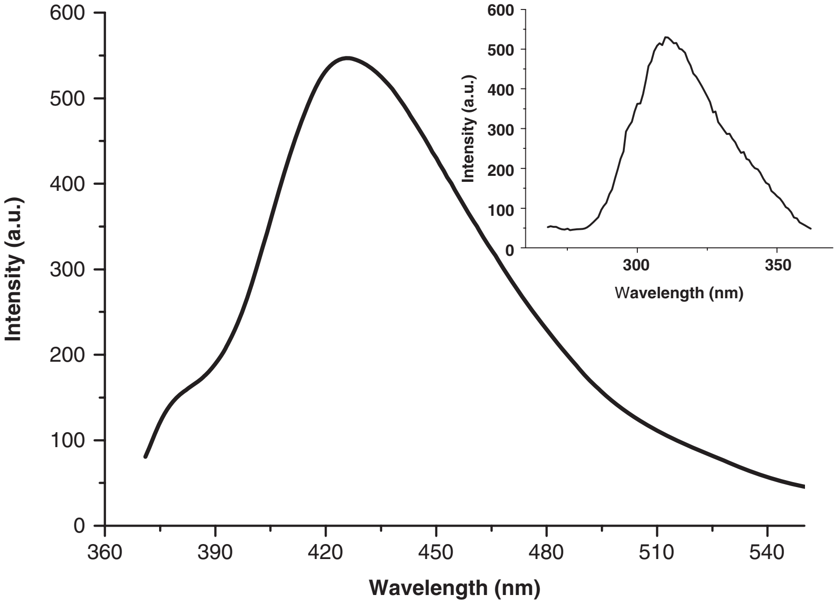

Figure 4. Solid-state fluorescence spectrum of **1**.

stretching vibration from the presence of coordinated water. The medium or weak broad bands at 3110 and 3022 cm^{-1} can be attributed to N–H stretching bands. The triazole out of plane ring absorption can be observed at 635 cm^{-1} [15]. The FT-IR results agree with the single crystal X-ray results.

3.2. *Solid-state fluorescence spectrum of 1*

Inorganic-organic coordination polymers, by judicious choice of organic spacers and transition metal centers, can give new types of electroluminescent materials [16]. The luminescent properties of ligand and **1** were investigated in the solid state. The fluorescence spectrum of **1** is shown in figure 4 with strong emission bands centered at 425 nm upon excitation at 320 nm. No fluorescence bands can be observed for free ligand, therefore the emission band for **1** can be attributed to metal-to-ligand charge transfer. The rigid framework structure may also facilitate strong fluorescence bands of **1** [17].

4. Conclusion

Using the flexible ligand 1,2-*bis*(1,2,4-triazole-1-yl)ethane (bte), a new 2-D silver(I) complex $\{[Ag_4(\mu_4\text{-bte})(\mu_2\text{-}H_2O)_2](SiF_6)_2\}_n$ (**1**) with the rare μ_4-bte is obtained, in which 1-D tubular Ag-bte structures are extended by bridged water molecules. Solid-state fluorescence of **1** was also investigated. The structural motif of **1** indicates potential in constructing new functional polymers with such flexible ligands.

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