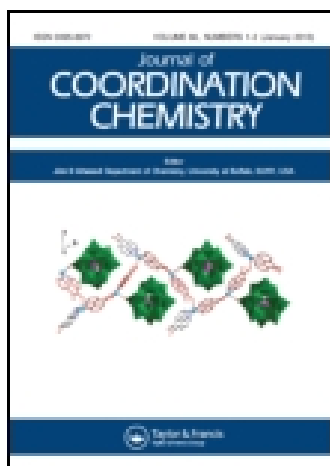


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Euni Kim^a, Doeon Kim^a, Young-A Lee^b & Ok-Sang Jung^a

^a Department of Chemistry, Pusan National University, Pusan, Republic of Korea

^b Department of Chemistry, Chonbuk National University, Jeonju, Republic of Korea

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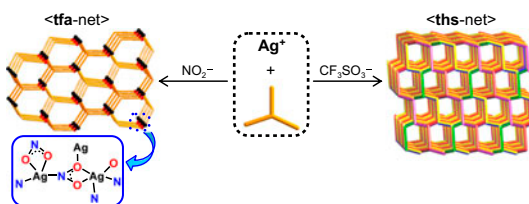
Coordinating ability of anions: 3-D silver(I) coordination polymers of C_3 -symmetric N,N',N'' -tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide

EUNI KIM[†], DOEON KIM[†], YOUNG-A LEE[‡] and OK-SANG JUNG^{*†}

[†]Department of Chemistry, Pusan National University, Pusan, Republic of Korea

[‡]Department of Chemistry, Chonbuk National University, Jeonju, Republic of Korea

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Reaction of AgX ($\text{X}^- = \text{NO}_2^-$ and CF_3SO_3^-) with C_3 -symmetric N,N',N'' -tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide (L) produces, respectively, an unusual nitrite-bridged 3-D coordination polymer, $[\text{Ag}_2(\text{NO}_2)_2\text{L}] \cdot \text{H}_2\text{O}$, with trinodal 3,3,4-connected **tfa** net topology and a unique 3-D coordination polymer, $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, with sixfold interpenetrating uninodal 3-connected **ths** net topology. Nitrite anions are two kinds of chelating and bridging ligands, whereas trifluoromethanesulfonate anions are simple counteranions. Structure-related thermal behavior, anion exchangeability, and photoluminescence have been investigated.

Keywords: Anion exchangeability; Nitrite; Silver(I); Trifluoromethanesulfonate; N,N',N'' -Tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide

1. Introduction

An area of interest in coordination chemistry is to design and construct coordination compounds with either structural diversities or potential applications such as gas-storage, adsorption, separation, catalysis, molecular and ion sensing, non-linear optics, biomedical imaging, solar cells, and drug delivery [1–9]. Achievement has been made through suitable combination of various geometrical metal ions and the appropriately designed organic ligands along with change of metal-to-ligand stoichiometry, solvent, temperature, and $p\text{H}$ [10–15]. Polyatomic anions also play significant roles in the construction of coordination

*Corresponding author. Email: oksjung@pusan.ac.kr

compounds [16–22]. Among various polyatomic anions, ambidentate nitrite has been much studied being capable of coordinating toward metal ions via the nitrogen lone pair to give nitro compounds $M\text{-NO}_2$ and via oxygen donors to yield nitrito complexes $M\text{-ONO}$ [23, 24]. Although nitrite coordination can occur in versatile modes including the two-atom O/N-bridging mode [25, 26]; the tridentate $1\kappa^2\text{-O}, O':2\kappa\text{-O}:3\kappa\text{-N}$ bridging mode has not yet been structurally established. The less coordinating trifluoromethanesulfonate, CF_3SO_3^- , has been used as ligands or counteranions for group 11 and 13 metal cations [20], and as an excellent leaving group in organic reactions such as nucleophilic substitution, Suzuki couplings, and Heck reactions [27].

Recently, we demonstrated suprachannel formation via a molecular array of 2-D networks consisting of $[\text{Ag}_3\text{L}_2](\text{X})_3$ ($\text{L} = N,N',N''\text{-tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide}$; $\text{X}^- = \text{NO}_2^-$ and NO_3^-) [28]. In order to scrutinize the coordination chemistry and related properties of significantly different anions, self-assembly of AgX ($\text{X}^- = \text{NO}_2^-$ and CF_3SO_3^-) with C_3 -symmetric L was carried out. Such C_3 -symmetric ligands with conformational non-rigidity have enabled a variety of coordination modes, which provide a balance between the desirable properties (e.g. binding and selectivity, and ease of synthesis and characterization) [29, 30]. We report herein the syntheses, crystal structures, coordination modes, and physicochemical properties of 3-D coordination polymers, $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ and $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$. Specifically, anion coordination effect on formation of the skeletal structure along with unprecedented $\mu^3\text{-}1\kappa^2\text{-O}, O':2\kappa\text{-O}:3\kappa\text{-N}$ coordination of nitrite will be discussed. Silver(I) has been used as an angular components in linear or T-geometric arrangement [31].

2. Experimental

2.1. Materials and measurements

All chemicals including silver(I) nitrite and silver(I) trifluoromethanesulfonate were purchased from Aldrich and were used without purification. $N,N',N''\text{-Tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide}$ (L) was prepared according to the literature procedure [32]. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer with samples prepared as KBr pellets. Elemental microanalyses (C, H, and N) were performed on crystalline samples by using a Vario-EL analyzer at Pusan center, KBSI. Thermal analyses were performed under N_2 at a scan rate of $10\text{ }^\circ\text{C}/\text{min}$ using a Labsys TGA-DSC 1600. Scanning electron microscope image was obtained on a Tescan VEGA 3. Absorption and photoluminescence (PL) spectra were acquired on a Shimadzu UV-1800 and Hitachi F-7000, respectively. Powder X-ray diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu $\text{K}\alpha$.

2.2. Synthesis of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$

A mixed water (4 mL) and ethanol (20 mL) solution of AgNO_2 (0.15 g, 1.0 mM) was slowly diffused into a mixture of dichloromethane (20 mL) and dimethyl sulfoxide (5 mL) solution of L (0.26 g, 0.5 mM). Colorless crystals of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ formed at the interface, are obtained in six days in a 63% yield. M.p. $172\text{ }^\circ\text{C}$ (dec.). Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{N}_8\text{O}_8\text{Ag}_2$ (%): C, 42.47; H, 3.80; and N, 13.21. Found: C, 42.30; H, 3.68; and N,

13.20. IR (KBr, cm^{-1}): 3266, 3074, 2925, 1643, 1598, 1544, 1479, 1436, 1290, 1265(s, NO_2^-), 1224, 1155, 1010, 769, and 703.

2.3. Synthesis of $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

An ethanol solution (15 mL) of AgCF_3SO_3 (0.15 g, 0.6 mM) was slowly diffused into a dichloromethane solution (15 mL) of L (0.21 g, 0.4 mM). Colorless crystals of $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ formed at the interface, are obtained in six days in a 81% yield. M.p. 231 °C (dec.). Anal. Calcd for $\text{C}_{64}\text{H}_{64}\text{N}_6\text{O}_{25}\text{F}_9\text{S}_3\text{Cl}_2\text{Ag}_3$ (%): C, 38.84; H, 3.26; and N, 8.64. Found: C, 38.50; H, 3.33; and N, 8.55. IR (KBr, cm^{-1}): 3354, 3077, 2943, 1663, 1594, 1533, 1478, 1431, 1270(s, CF_3SO_3^-), 1163, 1034, 766, and 636.

2.4. Anion exchange of $[\text{Ag}_2(\text{NO}_2)_2\text{L}] \cdot \text{H}_2\text{O}$ with NaCF_3SO_3

An aqueous solution (0.5 mL) of NaCF_3SO_3 (both 1.7 mg, 0.01 mM and 3.4 mg, 0.02 mM) was added into a suspension of microcrystalline $[\text{Ag}_2(\text{NO}_2)_2\text{L}] \cdot \text{H}_2\text{O}$ (8.5 mg, 0.01 mM) in water (3 mL) at room temperature. The reaction mixture was stirred for 2 h, and the precipitate was filtered and washed with water several times. Chemical analyses of the exchanged species were satisfactory.

2.5. Crystal structure determination

X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation and a CCD detector at $-25 \text{ }^\circ\text{C}$. Thirty-six frames of 2-D diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the multi-scan method (SADABS) [33]. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix

Table 1. Crystal data and structure refinement for $[\text{Ag}_2(\text{NO}_2)_2\text{L}] \cdot \text{H}_2\text{O}$ and $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

	$[\text{Ag}_2(\text{NO}_2)_2\text{L}] \cdot \text{H}_2\text{O}$	$[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$
Empirical formula	$\text{C}_{30}\text{H}_{32}\text{N}_8\text{O}_8\text{Ag}_2$	$\text{C}_{64}\text{H}_{70}\text{N}_{12}\text{O}_{19}\text{F}_9\text{S}_3\text{Cl}_2\text{Ag}_3$
Formula weight	848.38	1973.01
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$C2/c$
Unit cell dimensions (\AA , $^\circ$)		
a	30.2619(4)	30.0954(4)
b	4.7197(1)	15.5048(2)
c	24.7223(4)	35.4843(5)
α	90	90
β	115.820(2)	107.185(1)
γ	90	90
Volume (\AA^3 , Z)	3178.50(9), 4	15,818.6(4) 8
Calculated density (g cm^{-3})	1.773	1.657
Absorption coefficient (mm^{-1})	1.296	0.977
Completeness (%)	99.8 ($\theta = 26.99^\circ$)	99.9 ($\theta = 26.50^\circ$)
Data/restraints/parameters	6274/2/433	16,397/6/1009
Goodness-of-fit on F^2	1.020	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0290$, $wR_2 = 0.0532$	$R_1 = 0.0737$, $wR_2 = 0.1901$
R indices (all data)	$R_1 = 0.0384$, $wR_2 = 0.0564$	$R_1 = 0.1346$, $wR_2 = 0.2305$

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{(\sum [w(F_o^2 - F_c^2)^2])^{1/2}}{\sum [w(F_o^2)^2]^{1/2}}$$

least-squares techniques (SHELXL 97) [34]. The non-hydrogen atoms were refined anisotropically, and hydrogens were placed in calculated positions and refined only for isotropic thermal factors. The crystal parameters and procedural information corresponding to data collection and structure refinement are listed in table 1.

3. Results and discussion

3.1. Synthesis and characterization

Self-assembly of AgNO_2 and AgCF_3SO_3 with N,N',N'' -tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide (L) produced single crystals of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ and $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$, respectively, suitable for single-crystal X-ray diffraction in high yield. The reaction was originally conducted in a 1 : 1 M ratio, but the compositions of the products were slightly affected by the change of reactants mole ratio and concentration, indicating that the skeletal structures are thermodynamically stable. However, L/Ag(I) ratios of the products are dependent on the coordinating nature of the polyatomic anions. The ratios are exactly coincident with the order of coordinating ability of anions as established in our previous results [20]. The crystalline solids are air-stable and insoluble in common organic solvents such as acetone, methanol, chloroform, diethyl ether, and tetrahydrofuran, but are dissociated in strong polar solvents such as acetonitrile, DMSO, and DMF.

3.2. Crystal structures

As depicted in figure 1, $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ crystal consists of 3-D coordination polymers. Relevant bond lengths and angles are listed in table 2. The asymmetric unit contains two

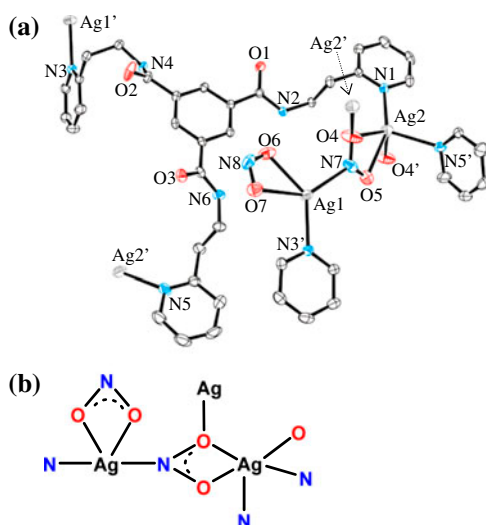


Figure 1. (a) ORTEP drawing and (b) coordinating environments for two nitrites of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$. Hydrogens and solvate water were omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ and $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$.

$[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$		$[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$	
Ag(1)–N(3) ^{#1}	2.304(3)	Ag(1)–N(1)	2.137(6)
Ag(1)–N(7)	2.429(4)	Ag(1)–N(9) ^{#5}	2.139(6)
Ag(1)–O(6)	2.367(3)	Ag(2)–N(5)	2.213(6)
Ag(1)–O(7)	2.671(3)	Ag(2)–N(7)	2.212(6)
Ag(2)–N(1)	2.432(4)	Ag(3)–N(3) ^{#6}	2.171(7)
Ag(2)–N(5) ^{#2}	2.261(3)	Ag(3)–N(11)	2.175(7)
Ag(2)–O(4)	2.521(3)		
Ag(2)–O(5)	2.433(3)	N(1)–Ag(1)–N(9) ^{#5}	168.0(2)
Ag(2)–O(4) ^{#3}	2.659(3)	N(5)–Ag(2)–N(7)	165.6(2)
		N(3) ^{#6} –Ag(3)–N(11)	161.7(3)
N(3) ^{#1} –Ag(1)–N(7)	124.8(1)		
O(6)–Ag(1)–O(7)	48.3(1)		
N(1)–Ag(2)–N(5) ^{#2}	115.2(1)		
O(4)–Ag(2)–O(5)	49.4(1)		
Ag(2)–O(4)–Ag(2) ^{#4}	131.3(2)		

^{#1} $x - 1/2, y + 1/2, z$; ^{#2} $x, -y + 2, z + 1/2$; ^{#3} $x, y - 1, z$; ^{#4} $x, y + 1, z$; ^{#5} $x - 1/2, y - 3/2, z$; ^{#6} $x + 1/2, -y + 1/2, z + 1/2$.

Ag(I) ions, two nitrite anions, one L, and one water. Ag(1) has a distorted tetrahedral arrangement with two oxygen donors from a nitrite (Ag–O = 2.367(3), 2.671(3) Å; O–Ag–O = 48.3(1)°), a nitrogen donor from L (Ag–N = 2.304(3) Å), and one nitrogen donor from another nitrite anion (Ag–N = 2.429(4) Å; N–Ag–N = 124.8(1)°). The dihedral angle between the two planes defined by O–Ag–O and N–Ag–N is 51.9(1)°. By contrast, the local geometry around Ag(2) is a severely distorted square-pyramidal (SP) arrangement with three oxygen donors from two nitrites (Ag–O = 2.433(3)–2.659(3) Å) and a nitrogen donor from L (Ag–N = 2.261(3) Å) in a basal plane and with additional nitrogen donor from L (Ag–N = 2.432(4) Å) in an apical position. In order to evaluate the SP contributions, the τ values were calculated: $\tau = 1$ for an idealized trigonal bipyramidal arrangement and $\tau = 0$ for a SP [35]. The τ value for Ag(2) is 0.41, indicating that the coordinating geometry around Ag(2) ion can be described as a square pyramid rather than a trigonal bipyramid. Ag(2) ion is displaced from the least-squares plane defined by the basal donors in the direction of the apical atom by 0.63 Å. The dihedral angles between each pyridyl moiety and central benzene ring of L are 4.6(3)°, 7.8(2)°, and 84.78(9)°. The most interesting feature for the Ag(I) coordination polymer is that the nitrite anions adopt two coordination modes, as described in figure 1(b). One nitrite is chelated to one Ag(I) through the two oxygen donors ($\kappa^2\text{-O}, \text{O}'$ mode), while another nitrite bridges three Ag(I) ions through two oxygen donors, a nitrogen donor, and one of the chelating oxygen atoms ($1\kappa^2\text{-O}, \text{O}': 2\kappa\text{-O}: 3\kappa\text{-N}$ mode), respectively. In order to simplify the structural representation of the 3-D coordination polymer, topological analysis was employed. As depicted in figure 2, both L and the bridging NO_2^- are 3-connected nodes and the Ag(2) can be defined as a 4-connected node, resulting in the **tfa** net topology with the point symbol of $(8^3)_2(8^6)$ [36].

As depicted in figure 3, the structure of $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$ revealed that L is coordinated with three Ag(I) ions, and each Ag(I) ion connects to two nitrogen donors from two L with linear arrangement (Ag–N = 2.137(6)–2.213(6) Å; N–Ag–N = 161.7(3)°–168.0(2)°) to form a 3-D coordination polymer. The slight deviation from the ideal linear geometry around the Ag(I) ions is presumably due to weak interaction with the oxygens of the carbonyl moieties (Ag \cdots O = 2.690(5)–3.027(5) Å). From the topological point of

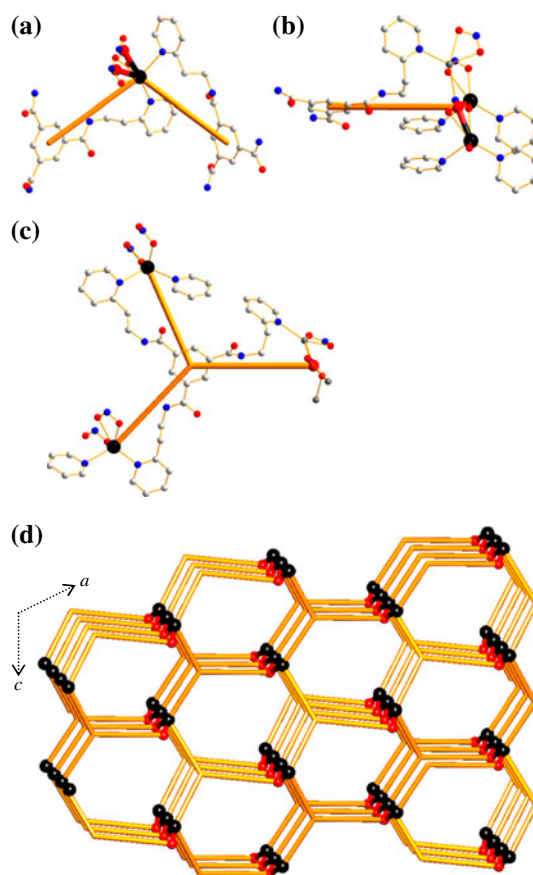


Figure 2. Topological representation of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$. Ball-and-stick diagrams of (a) 4-connected $\text{Ag}(2)$ ion, (b) 3-connected NO_2^- , and (c) 3-connected L with schematic connectivity. (d) Top view of a schematic drawing of the 3-D **tfa** net. The large black and red circles denote the $\text{Ag}(2)$ ion and the center of bridging NO_2^- , respectively (see <http://dx.doi.org/10.1080/00958972.2014.966702> for color version).

view, as depicted in figure 3, L is a 3-connected node to construct a uninodal **ths** net topology with a point symbol of 10^3 [36]. The significant feature is that the 3-D **ths** net is a sixfold interpenetrating structure based on 160-membered metallamacrocyclic rings. In contrast to nitrite, the trifluoromethanesulfonate is a simple counteranion (the shortest distance $\text{Ag}\cdots\text{OSO}_2\text{CF}_3 = 2.876(9) \text{ \AA}$).

3.3. Bonding mode and anion exchangeability

Anion characteristics such as metallophilicity, size, geometry, and solubility seem to play pivotal roles in construction of the present skeletons. The formation might be attributed to a suitable combination of the skewed conformer of tridentate L and silver(I) coordination geometries. For $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$, the nitrites have two coordination modes, $\kappa^2\text{-O,O'}$ and $1\kappa^2\text{-O,O'}:2\kappa\text{-O}:3\kappa\text{-N}$. As depicted in figure S1 (see online supplemental material at <http://dx.doi.org/10.1080/00958972.2014.966702>), the simple chelating $\kappa^2\text{-O,O'}$ nitrite can be

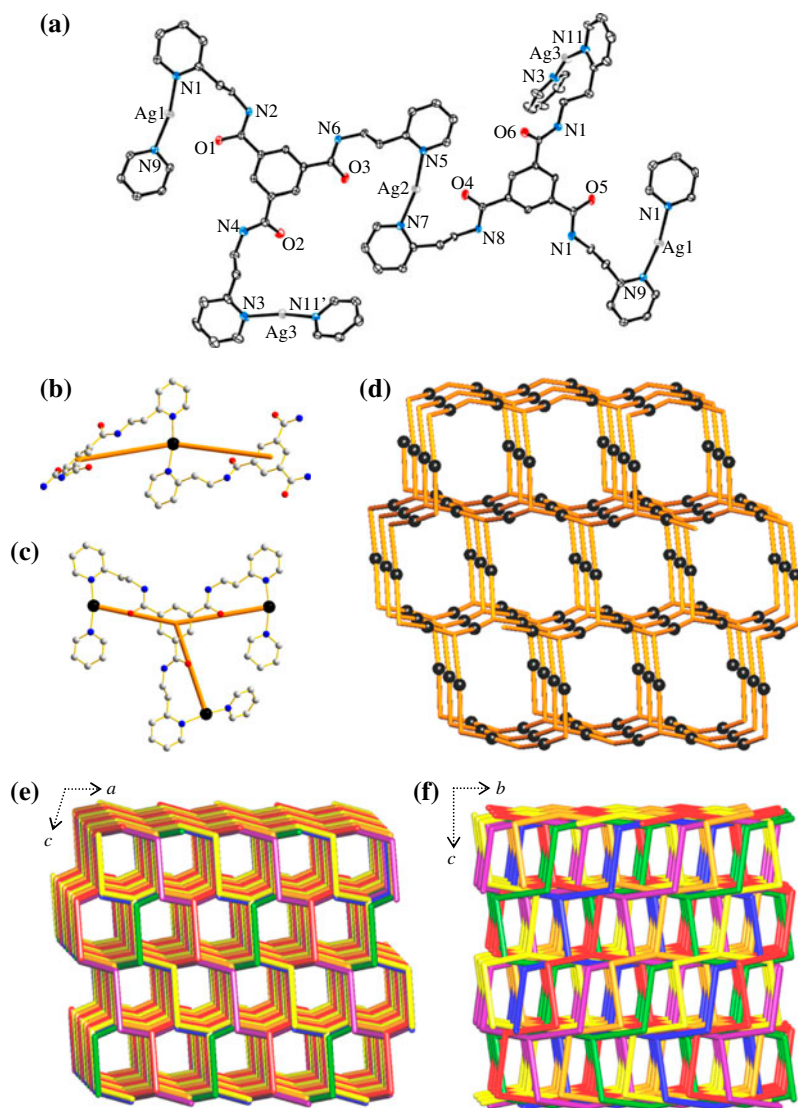


Figure 3. (a) ORTEP drawing and topological representation of the (d) individual 3-D **ths** net for [Ag₃L₂] (CF₃SO₃)₃·CH₂Cl₂·4H₂O. Ball-and-stick diagrams of (b) Ag(I) ion and (c) 3-connected L with schematic connectivity. Illustrations of the sixfold interpenetrating **ths** net in (e) *b*-axis and (f) *a*-axis views. In (a), trifluoromethanesulfonates, hydrogens, and solvate molecules were omitted for clarity.

exchanged upon addition of NaCF₃SO₃ in a 1 : 1 ratio in aqueous media [22]. Its powder XRD pattern is similar to that of [Ag₂(NO₂)₂L]·H₂O, suggesting partial anion exchange with retention of the skeleton. Upon addition of NaCF₃SO₃ in a 1 : 2 ratio, not surprisingly, the skeletal structure of the compound seems to disassemble, presumably due to the removal of the bridging nitrite. The IR peak corresponding to CF₃SO₃⁻ at 638 cm⁻¹ appears, while the NO₂⁻ band at 1265 cm⁻¹ disappears. By contrast, anion exchange of [Ag₃L₂] (CF₃SO₃)₃·CH₂Cl₂·4H₂O with three equivalents of NaNO₂ can be smoothly achieved, and

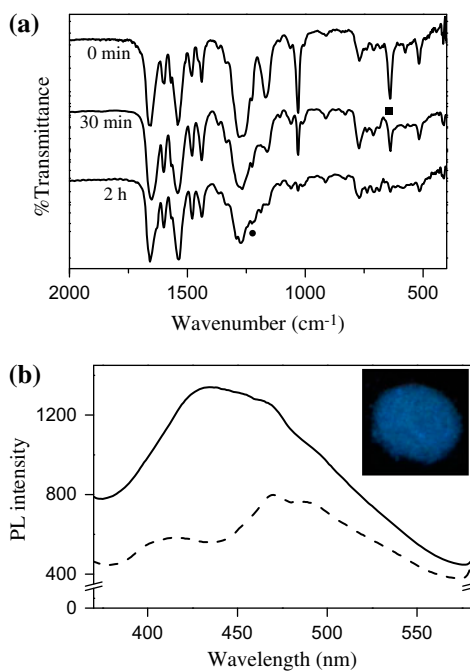


Figure 4. (a) IR spectra during the anion exchange of $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ with three equivalents of NaNO_2 . Circle and square denote the characteristic IR bands for NO_2^- and CF_3SO_3^- , respectively. (b) PL spectra for $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (solid line) and the anion exchanged species, $[\text{Ag}_3\text{L}_2](\text{NO}_2)_3$ (dashed line). Inset in (b): photographic image of $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ under UV irradiation at 365 nm.

monitored by both the appearance of the NO_2^- band at 1229 cm^{-1} and disappearance of the CF_3SO_3^- band at 640 cm^{-1} [figure 4(a)]. The other peaks of the IR spectrum remain virtually unchanged, indicating that the 3-D skeletal structure is retained during the anion exchange.

3.4. PL and thermal properties

The PL properties of the present compounds were investigated in the solid state at room temperature, as shown in figures 4(b) and S1. L displays an emission band at 467 nm along with a slight shoulder at 433 nm ($\lambda_{\text{ex}} = 324 \text{ nm}$) originating from intraligand $\pi^* \rightarrow n$ and $\pi^* \rightarrow \pi$ transitions (figure S2). In contrast, PL spectra of authentic $[\text{Ag}_2(\text{NO}_2)_2\text{L}] \cdot \text{H}_2\text{O}$ appear at 400 and 468 nm ($\lambda_{\text{ex}} = 312 \text{ nm}$) corresponding to metal-to-ligand charge transfer [37] and intraligand transition, respectively. The anion exchange of $[\text{Ag}_2(\text{NO}_2)_2\text{L}] \cdot \text{H}_2\text{O}$ with CF_3SO_3^- significantly increases the emission band at 431 nm and decreases the emission band at 400 nm. Enhancement of PL band at 431 nm might be responsible for ligand-centered transition perturbed by the presence of disassembled species including nitrite and trifluoromethanesulfonate anions. On the other hand, $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ exhibits an emission band at 434 nm and a shoulder at 466 nm upon excitation at 312 nm, whereas PL spectrum of the anion exchanged species $[\text{Ag}_3\text{L}_2](\text{NO}_2)_3$ is quite different from that of $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

For $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$, the framework skeleton started to decompose at 172 °C. Above 400 °C, the residue consisted of Ag(0) material along with a trace amount of organic species (figure S3). For $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$, the basic skeletal structure is stable at 231 °C, indicating that $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$ is thermally more stable than $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$; solvate dichloromethane and water evaporated in the range of 30–90 °C (calcd 7.9%, found 5.1%).

4. Conclusion

Two 3-D Ag(I) coordination polymers, $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ and $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$, have been synthesized via assembly of C_3 -symmetric tridentate L with Ag(I) salts. The skeletal structures of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ and $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$ exhibit trinodal 3,3,4-connected **tfa** net topology and sixfold interpenetrating uninodal 3-connected **ths** net topology. The L/M ratios of the products significantly depend on the coordinating ability of anions: trifluoromethanesulfonates are simple counteranions, whereas nitrites take part in coordination. $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ shows the unprecedented coordination of nitrite anions with both a $\mu^{3-1}\kappa^2-O,O'$: $2\kappa-O$: $3\kappa-N$ mode and a κ^2-O,O' mode. The κ^2-O,O' nitrite was more easily exchanged than $\mu^{3-1}\kappa^2-O,O'$: $2\kappa-O$: $3\kappa-N$ nitrite. Thermal stability and photoluminescent properties of the Ag(I) complexes are discussed. Further research on coordination of nitrite to a metal ion can provide important information for the understanding of anion coordination chemistry.

Supplementary material

IR, powder XRD patterns, and PL spectra during the anion exchange of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ with CF_3SO_3^- , solid-state PL spectrum of L, TGA curves of the present silver(I) complexes, and X-ray crystallographic data, in CIF format, for the structure determination of $[\text{Ag}_2(\text{NO}_2)_2\text{L}]\cdot\text{H}_2\text{O}$ and $[\text{Ag}_3\text{L}_2](\text{CF}_3\text{SO}_3)_3\cdot\text{CH}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$ are deposited with the Cambridge Crystallographic Data Center, CCDC, under supplementary publication number CCDC 999639 and 999640, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk].

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