Inorganica Chimica Acta 376 (2011) 612–618

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Anion-controlled four silver coordination polymers with flexible bis(1,2,4-triazol-4-yl)ethane

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ARTICLE INFO

Article history:
Received 2 October 2010
Received in revised form 15 June 2011
Accepted 25 July 2011
Available online 2 August 2011

Keywords:
Silver complex
Anion role
1,2-Bis(1,2,4-triazol-4-yl)ethane
Coordination polymer
Anion exchange

ABSTRACT

The self-assembly reaction of the flexible ligand 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) and Ag salts with BF_4^-, SO_4^{2-}, NO_3^- and ClO_4^- gives novel coordination polymers $\{[Ag(btre)_2](BF_4)\}_n$ (**1**), $\{[Ag_2(btre)_{1.5}(H_2O)](SO_4)\cdot 5H_2O\}_n$ (**2**), $\{[Ag(btre)](NO_3)\cdot H_2O\}_n$ (**3**) and $\{[Ag(btre)](ClO_4)\}_n$ (**4**). The structure of **1** is a one-dimensional double chain through double bis-monodentate btre bridges. Compound **2** is a novel two-dimensional network containing the Ag_4 unit node and μ_4-btre building block. In **3** and **4**, adjacent two silver(I) atoms are linked through four nitrogen atoms of two N1/N2 atoms of two btre ligands and form Ag_2N_4 6-membered rings and construct a one-dimensional chain. The chains extends through btre bridges in four different directions alternatively to construct a novel three-dimensional network. The luminescences of **1**–**4** were observed in the solid state at room temperature. Compounds **3** and **4** are inversely transfered by the anion exchange procedure.

1. Introduction

The design and construction of the coordination polymers has attracted great attention for their potential applications, architectures, and topologies [1–5]. Design of effective ligands and the proper choice of metal centers are the keys to design and construct novel metal–organic frameworks. Many factors such as the coordination geometry of the central atom, the structural characteristics of the ligand molecule, the solvent system, and the counterions can play the key role in the construction of the coordination networks. The anions serve more than merely balancing the charges of a cationic complex and influence the structure of a supramolecular system through coordination to the metal [6–9]. Dunbar and coworkers reported that the reaction of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine with first-row transition metals could yield a molecular square and a pentagon with one anion accommodated in the cavities of the polygons. In this case, anions function as templates through anion–π interactions [10].

Silver coordination polymers have been widely studied not only for their applications in functional materials such as fluorescent materials but also for their fascinating structures derived from variable coordination numbers from 2 to 6 of silver atoms and different conformations around silver metal centers [11–23]. On the other hand, a large number of mononuclear, oligonuclear, and polynuclear transition metal complexes of 1- and 4-substituted 1,2,4-triazole derivatives have been synthesized and characterized because of their unique properties and novel topologies [24–39].

Few silver coordination polymers with flexible 1-substituted 1,2,4-triazole ligands bis(1,2,4-triazol-1-yl)methane (btm) [32,33] and 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) [34,35] were synthesized and structurally characterized. Recently, we reported a series of transition metal coordination polymers with the flexible ligand 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) [40–43]. The ligand 1,2-bis(1,2,4-triazol-4-yl)ethane (btre, Scheme 1) is a isomer of 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) but is not well studied [36–39]. In order to investigate the influence of the inorganic anions on the structures of silver coordination polymers with flexible ligand btre, four new silver coordination polymers $\{[Ag(btre)_2](BF_4)\}_n$ (**1**), $\{[Ag_2(btre)_{1.5}(H_2O)](SO_4)\cdot 5H_2O\}_n$ (**2**), $\{[Ag(btre)](NO_3)\cdot H_2O\}_n$ (**3**) and $\{[Ag(btre)](ClO_4)\}_n$ (**4**) were synthesized.

2. Experimental

2.1. Materials and physical measurements

All reagents were of analytical grade and used without further purification. 1,2-Bis(1,2,4-triazol-4-yl)ethane (btre) was synthesized according to literature method [36]. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. The luminescence measurements were carried out in the solid state at room temperature and the spectra were collected with a Perkin–Elmer LS50B spectrofluorimeter.

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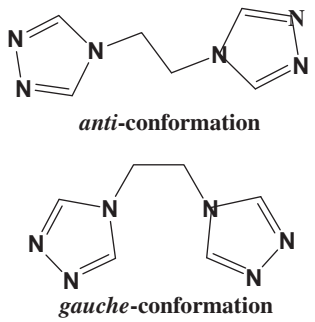
doi:10.1016/j.ica.2011.07.040



Scheme 1. The *anti* and *gauche* conformations of btre ligand.

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with extreme caution and only in very small quantities.

2.2. Synthesis of $\{[Ag(btre)_2](BF_4)\}_n$ (**1**)

A 5 mL aqueous solution of 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) (0.1 mmol) was added to a tube. Then 5 mL 1:1 (v/v) CH_3CH_2OH/H_2O solution was slowly added to the tube. Finally a 5 mL CH_3CH_2OH solution of $AgBF_4$ (0.2 mmol) was slowly added to the tube. Colorless crystals **1** (yield: 48% based on btre) were obtained after 5 days in a dark room at room temperature. *Anal.* Calc. for $C_{12}H_{16}AgBF_4N_{12}$ (**1**): C, 27.56; H, 3.08; N, 32.14. Found: C, 27.38; H, 3.01; N, 31.92%. IR data (cm^{-1}): 3101w, 1543m, 1454w, 1385m, 1327w, 1196s, 1076s, 1038s, 999m, 887w, 856w, 679w, 640m.

2.3. Synthesis of $\{[Ag_2(btre)_{1.5}(H_2O)](SO_4)\cdot 5H_2O\}_n$ (**2**)

The H_2O (4 mL) and CH_3CN (1 mL) solution of Ag_2SO_4 (0.2 mmol) was slowly added to a tube. Then 5 mL 1:1 (v/v) CH_3OH/H_2O solution was slowly added to the tube. Finally a 5 mL CH_3OH solution of btre (0.1 mmol) was slowly added to the tube. Colorless crystals **2** (yield: 43% based on btre) were obtained after 3 days in a dark room at room temperature. *Anal.* Calc. for $C_9H_{24}Ag_2N_9O_{10}S$ (**2**): C, 16.23; H, 3.63; N, 18.93. Found: C, 16.12; H, 3.54; N, 18.76%. IR data (cm^{-1}): 3458m, 3101m, 1541m, 1450w, 1385w, 1326w, 1195m, 1109s, 1082m, 999m, 856w, 682w, 639m, 618m.

2.4. Synthesis of $\{[Ag(btre)](NO_3)\cdot H_2O\}_n$ (**3**)

A 5 mL aqueous solution of 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) (0.1 mmol) was added to a tube. Then 5 mL 1:1 (v/v) CH_3CH_2OH/H_2O solution was slowly added to the tube. Finally a 5 mL CH_3CH_2OH solution of $AgNO_3$ (0.2 mmol) was slowly added to the tube. Colorless crystals **3** (yield: 35% based on btre) were obtained after 7 days in a dark room at room temperature. *Anal.* Calc. for $C_6H_{10}AgN_7O_4$ (**3**): C, 20.47; H, 2.86; N, 27.85. Found: C, 20.34; H, 2.74; N, 27.76%. IR data (cm^{-1}): 3448m, 3108m, 1544m, 1391s, 1184m, 1072w, 1001w, 968w, 860w, 686w, 641m.

2.5. Synthesis of $\{[Ag(btre)](ClO_4)\}_n$ (**4**)

A 5 mL aqueous solution of 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) (0.1 mmol) was added to a tube. Then 5 mL CH_3OH was slowly added to the tube. Finally a CH_3OH (4 mL) and CH_3CN (1 mL) solution of $AgClO_4$ (0.2 mmol) was slowly added to the tube above the CH_3OH solution. Colorless crystals **4** (yield: 37% based on btre) were obtained after 3 days in a dark room at room temperature. *Anal.* Calc. for $C_6H_8AgClN_6O_4$ (**4**): C, 19.40; H, 2.17; N, 22.63. Found: C, 19.28; H, 2.06; N, 22.49%. IR data (cm^{-1}): 3128w, 1538w, 1474w, 1345w, 1196m, 1096s, 922m, 866m, 685w, 640m.

2.6. X-Ray data collection and structure determinations

Suitable single crystals of compounds **1**–**4** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were collected by the ω scan technique. The structures were solved by direct methods and refined with full-matrix least-squares technique (SHELXTL-97) [44]. The positions of hydrogen atoms of btre were determined with theoretical calculation. The parameters of the crystal data collection and refinement of **1**–**4** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

2.7. Anion exchange of $\{[Ag(btre)](NO_3)\cdot H_2O\}_n$ with $NaClO_4$

A 10 mL aqueous solution of $NaClO_4$ (132 mg, 1.0 mmol) was added to an aqueous suspension (5 mL) of microcrystalline

Table 1
Crystallographic data for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{12}H_{16}AgBF_4N_{12}$	$C_9H_{24}Ag_2N_9O_{10}S$	$C_6H_{10}AgN_7O_4$	$C_6H_8AgClN_6O_4$
Formula weight	523.05	666.17	352.08	371.50
Crystal system	tetragonal	orthorhombic	orthorhombic	orthorhombic
Space group	*P4/nc*	*Pccn*	*Cccm*	*Cccm*
T (K)		223(2)	223(2)	223(2)
a (Å)	12.333(2)	11.411(2)	7.816(2)	8.701(1)
b (Å)	12.333(2)	27.955(4)	21.283(4)	20.857(2)
c (Å)	12.123(2)	14.887(2)	8.342(2)	8.287(1)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
V (Å^3)	1843.8(3)	4748.9(11)	1387.7(4)	1503.9(3)
Z	4	8	4	4
ρ_{calc} (g cm^{-3})	1.884	1.864	1.685	1.641
μ (mm^{-1})	1.162	1.798	1.471	1.532
F(0 0 0)	1040	2648	696	728
Reflections collected	9445	16 395	2084	4863
Unique reflections (R_{int})	1062 (0.0270)	5416 (0.0583)	818 (0.0355)	926 (0.0310)
Parameters	81	293	61	59
Goodness-of-fit (GOF) on F^2	1.084	1.079	1.088	1.095
R_1 [$I > 2\sigma(I)$]	0.0441	0.0722	0.0766	0.0569
wR_2 (all data)	0.1372	0.2291	0.2416	0.1718