

Investigating the effect of anion substitutions on the structure of silver-based coordination polymers



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ABSTRACT

Five silver(I) compounds namely, $[\text{Ag}(\text{tdmpp})(\text{NO}_3)]_n$ (**1**), $[\text{Ag}_2(\text{SeCN})_2(\text{tdmpp})]_n$ (**2**), $[\text{Ag}(\text{tdmpp})]\text{PF}_6$ (**3**), $[\text{WS}_4\text{Ag}_3\text{Cl}(\text{tdmpp})_{1.5}]\cdot 2\text{CH}_3\text{CN}$ (**4**) and $[\text{WS}_4\text{Ag}_4\text{I}_2(\text{tdmpp})]1.5\text{CH}_3\text{CN}$ (**5**) were prepared by the reactions of 1,1,3,3-tetrakis(3,5-dimethyl-1-pyrazolyl)propane (tdmpp) with various silver(I) salts in order to investigate the impact of the variation of the inorganic anions on the structure of these complexes. In the chain structures of **1** and **2**, each tdmpp ligand acts as a bridge between a pair of adjacent silver(I) centers. In the structure of **1**, the nitrate ion act as a terminal, monodentate ligand, while in compound **2** the SeCN anion functions as bidentate-bridging ligand between two neighboring Ag(I) centers. The parallel adjacent chains in **1** and **2** are linked together by means of non-covalent interactions to generate two-dimensional structures. In contrast to the distorted AgN_4O square-pyramidal structure of **1**, in the structure of **2** each of the silver ions possesses a distorted tetrahedral with an AgN_3Se coordination geometry. Crystals of compounds **3–5** were not suitable for X-ray diffraction studies.

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1. Introduction

The rational design and synthesis of silver(I) coordination polymers have been widely studied. This study was motivated not only by the possibility of their application as functional materials i.e. fluorescent materials, but also by the prospect of obtaining fascinating structures that can be accessed by the variable coordination numbers from 2 to 6 and different conformations adopted by the silver ions [1–19]. The study of the coordination chemistry with the pyrazole-based ligands began in 1889 with a report of the polymeric $[\text{Ag}(\text{pz})]_n$ complex [20]. Much later, Trofimenko stimulated further research with the introduction of poly(pyrazol-1-yl)borate chelating ligands in coordination chemistry [21–24]. Following the discovery that chelating poly(pyrazol-1-yl)borate ligands formed strong interactions with metal centers, the coordination chemistry of these ligands became the focus of considerable attention [25–27]. These ligands may be used as synthetic analogs of imidazole and mimic the coordinating sites found in metal enzymes or metalloproteins [28]. Unlike monodentate pyrazole and the rigid poly(pyrazol-1-yl)borate chelating ligands [29–32], flexible pyrazole-based ligands, offer the prospect of conformations that will

lead to variation in coordination geometries, influenced by the spacer length and the orientations of the donor atoms of the organic bridging ligands. The flexibility of these ligands can lead to the generation of structures with interesting properties. Architectures with specific structural motifs can be achieved by careful selection of organic ligands with the suitable coordinating groups, metal centers with preferred coordination geometries and variation of reaction conditions [33–36]. As a part of our research devoted to the synthesis, structural and spectroscopic characterization of the coordination chemistry of pyrazole ligands, here we report the synthesis and structural characterization of five new silver(I) coordination polymers formed by the reaction of tdmpp ligand (Scheme 1) with appropriate silver(I) salts. It is anticipated that this investigation will provide insights into the effect of different inorganic anions on the structures of the silver (I) coordination polymers.

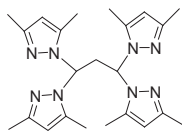
2. Experimental

2.1. Materials and physical measurements

All synthetic procedures were performed without precautions to exclude air. Starting materials were purchased from commercial sources and used without further purification. The tdmpp [36] and

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Scheme 1. Structure of the tdmpp ligand used in this work.

$(\text{NH}_4)_2\text{WS}_4$ [37] were prepared from them by published methods. The infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on KBr disks with an FT-IR model BOMEN MB102 spectrometer. The UV–Vis spectra ($700\text{--}270\text{ nm}$) of $[\text{WS}_4]^{2-}$ anion and complexes **4** and **5** were recorded on a GBC Cintral 101 spectrophotometer from freshly made samples in acetonitrile solution. X-ray powder diffraction patterns were recorded on a Philips X'PertPro diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54184\text{ \AA}$) in the 2θ range $5\text{--}50^\circ$. The elemental analyses for C, H and N were performed on a Costech-ECS 4010 CHNSO analyzer.

2.2. Preparation of coordination polymers

2.2.1. Synthesis of $[\text{Ag}(\text{tdmpp})(\text{NO}_3)]_n$ (**1**)

A mixture of AgNO_3 (0.190 g, 1 mmol) and tdmpp (0.420 g, 1 mmol) in acetonitrile (20 mL) was stirred at room temperature for 2 h. The precipitate was centrifuged and filtered off. The residue was washed with ethanol ($2 \times 2\text{ mL}$) and diethyl ether ($2 \times 3\text{ mL}$) and dried in vacuum to give a white powder of the product (439 mg, yield: 74% based on Ag). Colorless needle-shaped single crystals suitable for X-ray diffraction studies were obtained after 2 days by diffusion of diethyl ether into an acetonitrile solution of **1**. *Anal.* Calc. for $\text{AgC}_{23}\text{H}_{32}\text{N}_9\text{O}_3$: C, 46.8; H, 5.5; N, 21.3. Found: C, 46.3; H, 5.1; N, 21.1%. IR (KBr, cm^{-1}): 3126 (m) and 2918 (m) ($-\text{CH}_2-$ of spacer), 1635 (m), 1559 (s) (C=N of tdmpp), 1450 (m), 1415 (m) and 1320 (s) (ν_3 of NO_3), 1030 (m), 781 (m), 572 (m).

2.2.2. Synthesis of $[\text{Ag}_2(\text{SeCN})_2(\text{tdmpp})]_n$ (**2**)

KSeCN (0.228 g, 2 mmol) and AgNO_3 (0.340 g, 2 mmol) were added to DMSO (20 mL) and the mixture was stirred and heated under reflux conditions at $80\text{ }^\circ\text{C}$ for 1 h. To this solution, tdmpp (0.420 g, 1 mmol) was added and the mixture was stirred for another 4 h. The reaction mixture was filtered and colorless supernatant was decanted off. The precipitate was washed with ethanol ($2 \times 2\text{ mL}$) and diethyl ether ($2 \times 3\text{ mL}$) and dried in vacuo to give the required product as a white powder (526 mg, yield: 70% based on Ag). Colorless hexagonal-shaped single crystals suitable for X-ray crystallography were obtained by slow evaporation of the filtrate after 5 days. *Anal.* Calc. for $\text{Ag}_2\text{C}_{25}\text{H}_{32}\text{N}_{10}\text{Se}_2$: C, 35.5; H, 3.8; N, 16.6. Found: C, 35.3; H, 3.3; N, 16.7%. IR (KBr, cm^{-1}): 3124 (m) and 2917 (m) ($-\text{CH}_2-$ of spacer), 2100 (s) (CN of SeCN), 1636 (m), 1558 (s) (C=N of tdmpp), 1460 (s), 1417 (s), 1387 (m), 1316 (m), 1300 (m), 1032 (s), 789 (s), 680 (m), 565 (m).

2.2.3. Preparation of $[\text{Ag}(\text{tdmpp})]\text{PF}_6$ (**3**)

NH_4PF_6 (0.163 g, 1 mmol) and AgNO_3 (0.170 g, 1 mmol) were added to an acetonitrile solution (20 mL) and the mixture was stirred at room temperature for 30 min. To this solution, tdmpp (0.420 g, 1 mmol) was added and the mixture was stirred for another 4 h. The reaction mixture was filtered off and the colorless supernatant was decanted. The precipitate was washed with ethanol ($2 \times 2\text{ mL}$) and diethyl ether ($2 \times 3\text{ mL}$) and dried in vacuo to give the required product as a white powder (437 mg, yield: 65% based on Ag). *Anal.* Calc. for $\text{AgC}_{23}\text{H}_{32}\text{N}_8\text{PF}_6$: C, 41.0; H, 4.7; N, 16.6. Found: C, 40.8; H, 4.0; N, 17.3%. IR data (cm^{-1}): 3129 (m) and 2918 (m) ($-\text{CH}_2-$ of spacer), 1558 (s) (C=N of tdmpp), 1458

(s), 1420 (s), 1387 (m), 1319 (m), 1297 (m), 1034 (s), 843 (vs) (P-F of PF_6), 791 (s), 680 (m), 557 (s) (P-F of PF_6).

2.2.4. Preparation of $[\text{WS}_4\text{Ag}_3\text{Cl}(\text{tdmpp})]_{1.5} \cdot 2\text{CH}_3\text{CN}$ (**4**)

$(\text{NH}_4)_2\text{WS}_4$ (0.348 g, 1 mmol) and AgCl (0.429 g, 3 mmol) were added to acetonitrile solution (30 mL). After stirring for 30 min at room temperature, tdmpp (0.630 g, 1.5 mmol) was added to this solution. The mixture was stirred for another 3 h and then filtered. The yellow precipitate was washed with ethanol ($2 \times 2\text{ mL}$) and diethyl ether ($2 \times 3\text{ mL}$) and dried in vacuo to give the required product as a yellow-orange powder (595 mg, yield: 43% based on W). *Anal.* Calc. for $\text{Ag}_6\text{C}_{77}\text{H}_{108}\text{N}_{28}\text{Cl}_2\text{W}_2\text{S}_8$: C, 33.4; H, 3.9; N, 14.2. Found: C, 32.8; H, 3.3; N, 14.5%. IR data (cm^{-1}): 3132 (m) and 2918 (m) ($-\text{CH}_2-$ of spacer), 2253 (m) (CN of acetonitrile), 1559 (s) (C=N of tdmpp), 1460 (s), 1377 (m), 1319 (m), 1278 (m), 1034 (s), 448 (s) (W- μ_2 -S), 439 (s) (W- μ_3 -S).

2.2.5. Preparation of $[\text{WS}_4\text{Ag}_4\text{I}_2(\text{tdmpp})] 1.5\text{CH}_3\text{CN}$ (**5**)

$(\text{NH}_4)_2\text{WS}_4$ (0.348 g, 1 mmol) and AgI (0.936 g, 4 mmol) were added to an acetonitrile solution (30 mL). After stirring at room temperature for 30 min, tdmpp (0.420 g, 1 mmol) was added to this solution. The mixture was stirred for another 3 h and filtered. The yellow precipitate was washed with ethanol ($2 \times 2\text{ mL}$) and diethyl ether ($2 \times 3\text{ mL}$) and dried in vacuo to give the required product as a yellow powder (562 mg, yield: 38% based on W). *Anal.* Calc. for $\text{Ag}_8\text{C}_{52}\text{H}_{73}\text{N}_{19}\text{I}_4\text{W}_2\text{S}_8$: C, 21.1; H, 2.5; N, 9.0. Found: C, 21.3; H, 2.4; N, 8.5%. IR data (cm^{-1}): 3127 (m) and 2920 (m) ($-\text{CH}_2-$ of spacer), 2250 (m) (CN of acetonitrile), 1559 (s) (C=N of tdmpp), 1460 (s), 1377 (m), 1320 (m), 1281 (m), 1038 (s), 439 (s) (W- μ_3 -S).

2.3. X-ray crystallography

The crystallographic data for compounds **1** and **2** were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Data collection, cell refinement, data reduction and absorption correction were performed using multi scan methods with BRUKER software [38]. The structures were solved by direct methods using SIR2004 [39]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [40]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The title compounds were prepared by the reactions of (1)–(5) in DMSO for **2** and in acetonitrile for the rest of compounds.

Table 1
Crystal data for compounds **1** and **2**.

Compound	1	2
Chemical formula	$\text{AgC}_{23}\text{H}_{32}\text{N}_9\text{O}_3$	$\text{Ag}_2\text{C}_{25}\text{H}_{32}\text{N}_{10}\text{Se}_2$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
<i>a</i> (Å)	9.8422(5)	22.4987(10)
<i>b</i> (Å)	13.7187(6)	7.9464(2)
<i>c</i> (Å)	19.3258(9)	20.5755(8)
α ($^\circ$)	90.00	90.00
β ($^\circ$)	96.488(2)	126.699(8)
γ ($^\circ$)	90.00	90.00
<i>z</i>	4	4
<i>R</i> -factor (%)	2.89	2.37
ν (Å^3)	2592.7	2950.57

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