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Effect of the Schiff-base-containing triazole ligand and counter anion on the construction of dimeric silver and polynuclear copper complexes

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ABSTRACT

Five new complexes, namely $[Ag_2(tmat)_2(MeCN)_2](PF_6)_2$ (**1**), $[Ag_2(tmat)_4](PF_6)_2$ (**2**), $[Ag_2(tmat)_4](CF_3SO_3)_2$ (**3**), $[Cu_3(tmat)_6(H_2O)_6](ClO_4)_6\cdot 4H_2O$ (**4**) and $[Cu_4(OH)_2(OAc)_6(tmat)_2]\cdot 2H_2O$ (**5**), have been obtained from the reactions of silver(I) or copper(II) salts with (*E*)-(thiophen-2-yl)-*N*-(4*H*-1,2,4-triazol-4-yl)methanimine (tmat). Complexes **1**–**3** are based on Ag dimers and have extended solid-state structures formed by different weak interactions. The Ag(I) atoms exhibit a *Y*-shape coordination geometry in dimeric **1**, in which Ag–π and Ag···S weak interactions can be found. Complex **2** is constructed from dinuclear $[Ag_2(tmat)_4]^{2+}$ cations and PF_6^- anions, which are further connected to form a quasi-3D structure by C–H···F hydrogen bonds. In **3**, the Ag(I) atoms exhibit a distorted tetrahedral geometry and rich non-classical weak interactions, such as F···S, sustain the packing structure. Complexes **4** and **5** are linear trinuclear and planar tetranuclear complexes, respectively. Complex **5** is an antiferromagnetic complex with $J_{wb} = -77.5\ cm^{-1}$, $J_{bb} = -33.8\ cm^{-1}$ ($g = 2.0$). A discussion of the crystal structures, as well as the coordination properties of the tmat ligands with different counter anions, has been provided.

1. Introduction

Recently, the development of coordination complexes based on 1,2,4-triazole and its derivatives has led to an active discussion of their versatile intriguing architectures and topologies as well as their applications in various molecular magnets with unique magnetic properties [1]. Central to this research has been the goal of revealing magneto-structural correlations and developing their potential applications in molecular switches and molecular devices, especially when 1,2,4-triazole and its derivatives are used as linkers in spin-crossover polynuclear iron(II) molecular systems [2,3]. In particular, the employment of 4-substituted 4*H*-1,2,4-triazoles as bridging ligands has allowed the isolation and investigation of various Fe(II)-triazole compounds that are devoted to find new valuable spin crossover molecular materials [4], and Ag and Cu-triazole compounds for designing metal–organic frameworks (MOFs) [5]. Crystal engineering principles provide a facile approach to the assembly of Ag and Cu complexes with Schiff-base-containing ligands and help predict theoretically the topology and geometries of the structures to produce useful functional materials in the areas of magnetism, electrochemistry and biology [6]. However, to establish precise principles for the construction of desirable geometries is still a major challenge, and only a few transition metal complexes with Schiff-bases-containing 4-substituted 4*H*-1,2,4-triazoles have been reported [7]. As far as we know, the compound (*E*)-(thiophen-2-yl)-*N*-(4*H*-1,2,4-triazol-4-yl)methanimine (tmat, Scheme 1) was first prepared and screened for anticonvulsant activity by Popp in 1989 [8] and from then on, it has hardly ever been touched in the field of coordination chemistry. We chose tmat as a multifunctional ligand with respective to its multiple coordination sites and its thiophen rings side group, that can more readily accommodate the steric demands for the formation of a non-bonded S···X (X refers to some other close atom) interaction, which is favorable for the consolidation of multidimensional solid-state structures [9]. On the other hand, this ligand is facile to tune to a certain extent and occupies much more space than a simple ligand (such as 4*H*-1,2,4-triazoles) [2], allowing small terminal or bridging ligands to be coordinated to the metal center.

The silver ion is apt to form various structural motifs for its different coordination numbers, ranging from 2 to 6, as well as its positive coordination tendency with various hard donor atoms (N or O) or soft donor atoms (S, P) atoms, being a favorable and fashionable building block for MOFs [9–11]. Furthermore, short Ag···Ag interactions as well as ligand unsupported interactions are important factors to form one-dimensional to three dimensional (1–3D) compounds with special properties, such as an antibacterial function [10c,12,13]. It is somewhat interesting that the Ag···Ag interaction is often just found in compounds with simple 1,2,4-triazole

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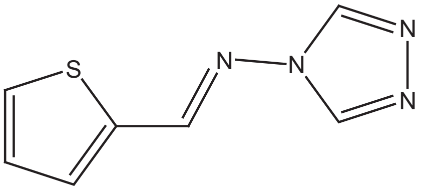

Scheme 1. The structure of the(*E*)-(thiophen-2-yl)-N-(4*H*-1,2,4-triazol-4-yl)methanimine ligand (tmat).

or 3- or 5-substituted 1,2,4-triazoles, meaning that a larger substituent at the 4-position of the triazole has a much greater steric restriction to stop the Ag···Ag interaction [5,14]. Besides this, large substituents may affect the nuclearity of the metal cluster. For copper(II) complexes featuring triazole with a substituent, such as mononuclear, dinuclear, non-linear or linear trinuclear, or tetrahedral tetranuclear cluster, have been reported. However, few structures and magnetic properties of planar tetranuclear Cu(II) complexes with a Schiff-base-containing 4-substituted 4*H*-1,2,4-triazole have been reported to date [15].

Herein, we report the syntheses and structures of three Ag(I) dimers and two polynuclear Cu(II) complexes formulated as $[Ag_2(tmat)_2(MeCN)_2](PF_6)_2$ (**1**), $[Ag_2(tmat)_4](PF_6)_2$ (**2**), $[Ag_2(tmat)_4](CF_3SO_3)_2]$ (**3**), $[Cu_3(tmat)_6(H_2O)_6](ClO_4)_6{\cdot}4H_2O$ (**4**) and $[Cu_4(OH)_2(OAc)_6(tmat)_2]{\cdot}2H_2O$ (**5**). Each Ag atom in complex **1** is coordinated to two tmat units and one terminal acetonitrile ligand in a *Y*-shaped geometry [16]. A similar geometry of the Ag(I) ions appears in complexes **2** and **3**, and just an additional triazole ligand is bound to the Ag(I) ion replacing acetonitrile in a terminal monodentate fashion [7a]. Because all the tmat ligands are coordinated in a near-planar *E* configuration, the resulting dinuclear unit can be described as an X-shaped dimer, and this kind of dimer once appeared in two dimeric copper(I) complexes, which were reported by Drabent et al. [7a]. Moreover, the close distance between Ag and the O from $CF_3SO_3^-$ in **3** strongly influences the packing of the discrete units in the crystal. As for Cu(II), appropriate to tetra-, penta- and hexa-coordination numbers, it adopts a distorted octahedral coordination geometry in **4**, which is a linear compound with its six tmat ligands in a snowflake-shape arrangement. **5** is a tetranuclear copper cluster with four copper atoms in a planar arrangement and there are two coordination geometries for Cu(II). Systematic studies were conducted to gain a better understanding of the geometric effects of the Schiff-base-containing 4-substituted 4*H*-1,2,4-triazole and the differentiations of predetermined reaction conditions, *i.e.* solvent type, counter anions and the molar ratio of starting materials. The magnetic property of **5** is also discussed.

2. Experimental

2.1. Materials and methods

The reagents and solvents employed were commercially available and used as received without further purification. The two primary materials, 2-thiophene carboxaldehyde and 4-amino-1,2,4-triazole, that prepared tmat were bought from the Multisovent Stock Company (J&K Chemical). The C, H, N and S microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRD) intensities for **1**–**5** were measured at 293 K on a Rigaku D/max-IIIA diffractometer (Cu Kα, λ = 1.54056 Å). The crushed single-crystalline powder samples were prepared by crushing the crystals and were scanned from 5° to 55° with a step of 0.1°/s. Magnetic susceptibilities were obtained from powdered samples using a Quantum-Design MPMSR-5S SQUID magnetometer equipped with a 0.5 tesla magnet in the range 300 to 2 K. The diamagnetic correction of the sample was estimated from Pascal's constants.

2.2. Synthesis of complexes 1–5

Complexes **1**–**5** were synthesized by the reaction of tmat with silver(I) salts AgX (X^- = PF_6^-, $CF_3SO_3^-$) or hydrated copper(II) salts CuY_2 (Y = ClO_4^-, OAc^-) in different ratios. Complexes **1** and **2** provide remarkable structural diversity, depending on the stoichiometry of the reactants. Prismatic colorless crystals of complex **1** were obtained in high yields by the stoichiometric reaction of tmat and $AgPF_6$. Increasing the tmat:$AgPF_6$ reaction ratio to more than 1:1 gave rhombic-like colorless crystals of complex **2** in lower yields with the existence of a byproduct that proved to be complex **1**.

2.2.1. Synthesis of $[Ag_2(tmat)_2(MeCN)_2](PF_6)_2$ (1)

Tmat (0.036 g, 0.2 mmol) dissolved in 5 mL MeCN was dropped slowly into a suspension of $AgPF_6$ (0.051 g, 0.2 mmol) in MeCN/H_2O (20 ml, V/V = 1:1) with magnetic stirring over 45 min. The resultant solution was allowed to slowly diffuse in darkness at room temperature over several days and colorless needle-like crystals for X-ray crystallography were obtained (yield: ca. 72%). Elemental *Anal.* Calc. for $C_{18}H_{18}Ag_2P_2F_{12}S_2N_{10}$ (**1**): C, 22.90; H, 1.92; N, 14.83; S, 6.79. Found: C, 22.94; H, 2.08; N, 14.72; S, 6.95%. IR data (KBr) (400–4000 cm^{-1}): 3450w, 3114w, 1614m, 1597m, 1509m, 1431m, 1390vw, 1347vw, 1223w, 1166m, 1059m, 838vs, 722m, 623m, 602vw, 562s.

2.2.2. Synthesis of $[Ag_2(tmat)_4](PF_6)_2$ (2)

This was prepared as described for **1** by changing the molar ratio of $AgPF_6$ and tmat ligand from 1:1 to 1:2. Colorless rhombic-like crystals were isolated (yield: ca. 30%). Elemental *Anal.* Calc. for $C_{28}H_{24}Ag_2N_{16}S_4P_2F_{12}$ (**2**): C, 27.60; H, 1.99; N, 18.39; S, 10.53. Found: C, 27.70; H, 1.92; N, 18.36; S, 10.50%. IR data (KBr) (400–4000 cm^{-1}): 3421w, 3120m, 1595m, 1527m, 1430w, 1389w, 1311w, 1255vw, 1222m, 1176w, 1056m, 962vw, 838vs, 734m, 626m, 601w, 558m.

2.2.3. Synthesis of $[Ag_2(tmat)_4](CF_3SO_3)_2$ (3)

This was prepared as described for **1** by only changing the reagent $AgPF_6$ to $Ag(CF_3SO_3)$. Colorless rectangle-like crystals were isolated and dried in the air (yield: ca. 80%). Elemental *Anal.* Calc. for $C_{30}H_{24}Ag_2N_{16}O_6S_6F_6$ (**3**): C, 29.37; H, 1.97; N, 18.27; S, 15.68. Found: C, 29.61; H, 2.129; N, 18.38; S, 15.84%. IR data (KBr) (400–4000 cm^{-1}): 3432vw, 3106s, 2965vw, 1715vw, 1593s, 1526s, 1505s, 1469w, 1429s, 1388w, 1345w, 1280vs, 1250vs, 1224vs, 1086w, 1057s, 1026s, 970m, 867m, 802m, 732s, 635s, 600m, 573m, 516w, 485m.

2.2.4. Synthesis of $[Cu_3(tmat)_6(H_2O)_6](ClO_4)_6$ (4)

$Cu(ClO_4)_2{\cdot}6H_2O$ (0.559 g, 1.5 mmol) was dissolved in 35 ml MeCN/H_2O (1:1) and a solution of tmat (0.089 g, 0.5 mmol) in MeCN was added with vigorous stirring to afford a viridescent solution. After an hour, the solution was filtrated and left undisturbed at room temperature. Four weeks later, rectangle-like crystals of **4** for X-ray crystallography were obtained in a poor yield (ca. <2%). *Caution:* Perchlorate salts are potentially explosive and should be handled with care! Elemental *Anal.* Calc. for $C_{42}H_{68}Cl_6Cu_3N_{24}O_{34}S_6$ (**4**): C, 24.62; H, 3.35; N, 16.41; S, 9.39. Found: C, 24.60; H, 3.37; N, 16.48; S, 9.37%. Selected IR data (KBr, cm^{-1}): 3444s, 3128s, 2029w, 1593s, 1542s, 1430m, 1392m, 1354w, 1319w, 1260w, 1227m, 1080s, 967w, 868w, 804w, 725m, 626s, 488w.