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Two Mn(II)–Au(I) supramolecular assemblies bonded by coordination, aurophilicity and hydrogen-bonding, π–π interactions and their magnetic properties

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Abstract

Two Mn(II)–Au(I) supramolecular assemblies {{Mn[Au(CN)$_2$]$_2$(H$_2$O)$_4$} [Au(CN)$_2$]$_2$(H$_2$bpy) · H$_2$O}(bpy = 4,4′-bipyridine) **1** and {Mn(4,4′-dmbpy) [Au(CN)$_2$]$_2$(CH$_3$OH)} (4,4′-dmbpy = 4,4′-dimethyl-bipyridine) **2** have been synthesized and magnetic properties have been investigated The interplay of aurophilicity, coordination, hydrogen-bonding and π–π interactions in two complexes result in three-dimensional network.

Keywords: Aurophilicity; Hydrogen-bonding; Magnetic properties; Three-dimensional network

Recently, a considerable effort on crystal engineering has been devoted to the research of supramolecular assemblies because they show abundant topologic structures and offer possibilities for potential applications of functional materials in catalysis, host–guest chemistry, molecule-based magnets, optical materials, ion-exchange and gas absorption, etc. [1]. In the design of new cyano-bridged supramolecular architectures, the formation of coordinate M–CN–M′bonds between dicyanometalates, tetracyanometalates, hexacyanometalates, octacyanometalates etc and 3d or 4f metal tectons, has been widely used in the strategy of self-assembly and lots of supramolecular assemblies possessing various degrees of dimensionality have been obtained [2]. In general, hydrogen-bonding interactions, accompanied by weaker π–π stacking, and electrostatic interactions between moieties into supramolecular system are perhaps the well-developed methods for increasing structural dimensionality [3,4]. On the other hand, the closed-shell d^{10} M–M interactions such as between gold(I) ions, sometimes called aurophilicity, are also useful tools in controlling supramolecular structure and dimensionality [5,6]. The strength of the aurophilic interactions is comparable to hydrogen bonds (ca. 7–11 kca/mol) [7]. Several studies have shown that Au···Au interactions are not dependent on ligand types and may have a considerable influence on the orientation of supramolecular system in the crystalline state [8]. The linear dicyanometalate anion [Au(CN$_2$)]$^-$ is an ideal tecton because it possesses the ability to link various central atoms by formation of coordination Au–CN–M′ and the Au(I) ions of dicyanometalate groups can be involved in bonding aurophilic interactions for the construction of multidimensional frameworks [9–13]. Some studies have shown that the [Au(CN)$_2$]$^-$ anions can aggregate under a variety of conditions in both the solid state and in solution and the aggregates show variations in their luminescence [14–17]. The luminescence in aqueous solution is of special importance, because this

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may allow for monitoring and probing biological processes associated with the luminescent material [18–20]. Using $[Au(CN)_2]^-$ anion and metal ions as tectons, new supramolecular assemblies with novel topologic structures and properties are expected to be obtained [21–28]. Since the self-assembly of supramolecular architectures is highly influenced by factors such as the solvent system, templates and counterion, the exploration of synthetic routes is a long-term challenge [29]. As part of our contribution to the study of supramolecular architectures involving $[Au(CN)_2]^-$ anion and metal ions tectons, we report the syntheses and crystal structures of two novel self-assembled supramolecular assemblies **1**–**2**.

All reagents used in the syntheses were of analytical grade and used without further purification. Elemental analyses were carried out using a Perkin–Elmer analyzer model 240. The IR spectra were recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} region. The magnetic measurements of the sample were carried out in an applied field of 5000G using a SQUID magnetometer in the temperature range of 4–293 K.

Synthesis of the single crystal of $\{Mn[Au(CN)_2]_2(H_2O)_4\}[Au(CN)_2]_2\ (H_2bpy)\cdot H_2O\}$ **1**. A solution of 6.6 mg (0.0425 mmol) 4,4′-dipyridine in 5 mL of methanol was added dropwise under stirring to a solution of 15.4 mg (0.0425 mmol) of $Mn(ClO_4)_2\cdot 6H_2O$ in 5 mL of water. After the solution was stirred for a few minutes, a solution of 50 mg (0.17 mmol) of potassium dicyanoaurate in 10 mL of water was further added dropwise. The light yellow reaction mixture was filtered. By slow evaporation of the solvent, colorless crystals of the product suitable for X-ray crystallography were formed. The yield was 53.9 mg (Au, 41.9%). Anal. Calcd for $C_{18}H_{20}Au_4MnN_{10}O_5$: C, 16.62; H, 1.54; N, 10.77. Found: C, 16.47; H, 1.75; N, 10.53.

Synthesis of the single crystal of $\{Mn(4,4'\text{-dmbpy})[Au(CN)_2]_2\cdot(CH_3OH)\}$ **2**. A solution of 7.82 mg (0.0425 mmol) of 4,4′-dimethyl-bipyridine in 10 mL of methanol was added dropwise under stirring to an aqueous solution of 15.4 mg (0.0425 mmol) of $Mn(ClO_4)_2\cdot 6H_2O$ dissolved in 5 mL of water. After the solution was stirred for a few minutes, an aqueous solution of 50 mg (0.17 mmol) of potassium dicyanoaurate dissolved in 10 mL of water was further added dropwise. The reaction mixture was filtered. By slow evaporation of the solvent, colorless crystals of the product suitable for X-ray crystallography were obtained. The yield was 39.2 mg (Au, 51%). Anal. Calcd for $C_{17}H_{16}Au_2MnN_6O$: C, 26.53; H, 2.08; N, 10.92. Found: C, 26.17; H, 2.11; N, 10.62.

For two complexes, determination of the unit cell and data collection was performed on a Bruker Smart 1000 area detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Their structures were solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [30].

$\{\{Mn[Au(CN)_2]_2(H_2O)_4\}[Au(CN)_2]_2(H_2bpy)\cdot H_2O\}$ **1**. The atomic labeling scheme of **1** is shown in Fig. 1a. **1** contains two neutral supramolecular moieties of $\{Mn[Au(CN)_2]_2(H_2O)_4\}$ and $[Au(CN)_2]_2(H_2bpy)\cdot H_2O$. Each Mn(II) ion coordinates to two nitrile nitrogen atoms from two terminal $[Au(CN)_2]^-$ ligands in axial positions and four H_2O molecules in the equatorial plane to form a distorted octahedron geometry. The Mn–O bond lengths range from 2.177(9) to 2.210(8) Å, and Mn–N bond lengths are equal to 2.156(9) and 2.166(10) Å, respectively. The bond angles around Mn(II) ion do not deviate much from 90° to 180°. The monodentate $[Au(CN)_2]^-$ anion is almost linear with the bond angle C(1)–Au(1)–C(2) of 175.9(5)°. The another uncoordinated nitrile nitrogen atom of each monodentate $[Au(CN)_2]^-$ ligand links to two coordinated

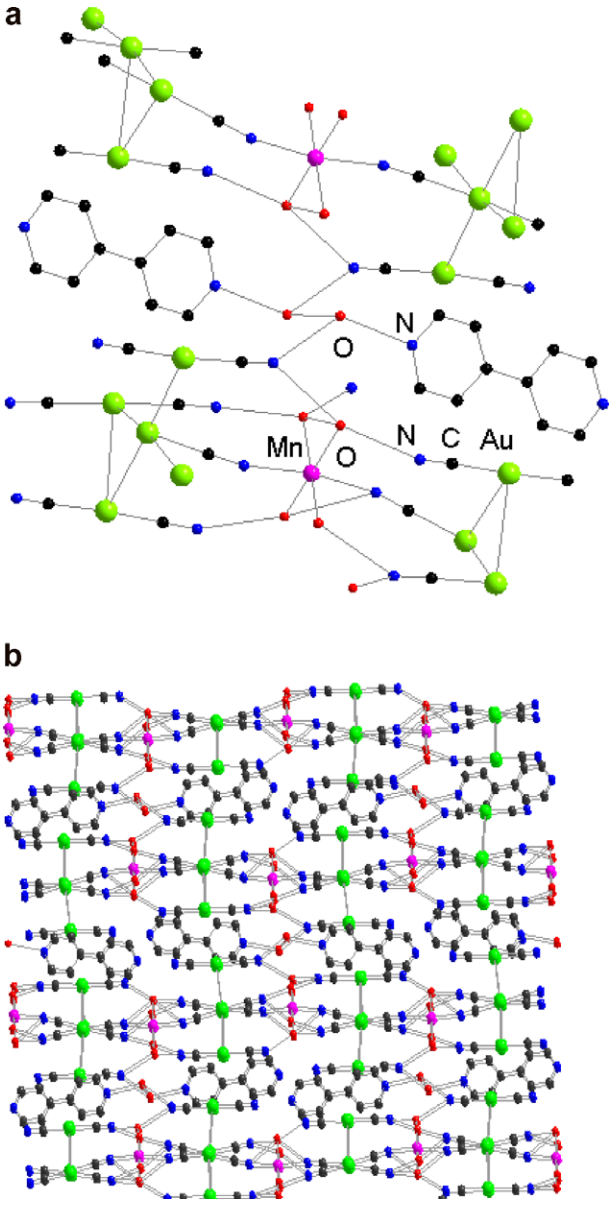

Fig. 1. (a) The atomic labeling of **1**. Hydrogen atoms are omitted for clarity. (b)The three-dimensional scheme of **1**.