研究简报

一种由$[Ag(CN)_2]^-$和 Mn(Ⅱ)建筑块组装的三个三维网穿插的超分子配合物的结构和荧光性质

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Three Interpenetrating 3D Related Networks and Luminescence of a Supramolecular Assembly Containing $[Ag(CN)_2]^-$ and Mn(Ⅱ) Tectons

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Abstract: Three interpenetrating 3D related networks of a cyano-bridged heterometallic supramolecular complex $\{KMn[Ag(CN)_2]_3\cdot H_2O\}_n$ (**1**) have been synthesized, and characterized by single crystal X-ray diffraction. The solid state of **1** displays interesting luminescence determined by argentophilicity at room temperature. CCDC: 197205.

Key words: supramolecular complex; argentophilicity; luminescence

0 Introduction

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[1~4]. In the design of new cyano-bridged supramolecular architectures, the formation of coordinate M-CN-M′ bonds between dicyanometalates, tetracyanometalates, hexacyanometalates, octacyanometalates etc and 3*d* or 4*f* 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[5~12]. In general, the noncovalent interactions containing hydrogen bonding interactions in particular, π-π stacking and electrostatic interactions between moieties into supramolecular system are perhaps the well-developed methods for increasing structural dimensionality[13,14]. On the other hand, the closed-shell d^{10} M-M interactions such as between Ag(I) ions, sometimes called argentophilicity, are also useful tools in controlling supramolecular structure and dimensionality[15~19]. The strength of the M-M interactions is comparable to hydrogen bonds (*ca.* 29~46 kJ·mol^{-1})[20,21]. Several studies have shown that Ag⋯Ag interactions are not dependent on ligand types and may have a considerable influence on the orientation of supramolecular system in the crystalline state[22]. The linear dicyanometalate anion of $[Ag(CN_2)]^-$ is an ideal tecton for the construction of multidimensional frameworks because it possesses the ability to link various

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central atoms by formation of coordination Ag-CN-M′ and the Ag(I) ions of dicyanometalate groups can be involved in bonding argentophilic interactions[23]. Some studies have shown that the $[Ag(CN)_2]^-$ anions can aggregate under a variety of conditions in both the solid state and in solution and the aggregates show variations in their luminescence[24~27]. As part of our contribution to the study of supramolecular architectures involving dicyanometalate groups and metal ions tectons, here, the elaborate structure and interesting luminescence of **1** are reported and discussed, though the crystal structure of **1** has been reported in our previous paper[26].

1 Experimental

1.1 Synthesis of 1

15 mL aqueous solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (36.2 mg, 0.1 mmol) was added dropwise to 20 mL stirred aqueous solution of $K[Ag(CN)_2]$ (59.7 mg, 0.3 mmol). After the solution was stirred for half hour, the solution was filtered. By slow evaporation of the solvent for several days, colorless crystals suitable for X-ray crystallography were obtained. Anal. calcd for $C_6H_2Ag_3KMnN_6O$(%): C, 12.17; H, 0.33; N, 14.19. Found(%): C, 12.47; H, 0.75; N, 14.53. IR: 2 285.5s, 2 229.2m and 2 156.2s cm^{-1} for ν(CN).

1.2 Physical measurements

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 4 000~600 cm^{-1} region. Conventional fluorescence excitation and emission spectra were recorded on a Perkin Elmer LS50B luminescence spectrophotometer.

1.3 Crystal structure determination

For the complex, determination of the unit cell and data collection was performed on a Bruker Smart 1000 area detector diffractometer using graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293(2) K. The structure was solved by using direct

Table 1 Crystal data and structure refinement for compound 1

Formula	$C_6H_2Ag_3MnN_6O$	D_c / ($g \cdot cm^{-3}$)	2.911
F_w	591.79	μ(Mo $K\alpha$) / mm^{-1}	5.502
Crystal system	Trigonal	F(000)	273
Space group	$P\bar{3}$	θ range / (°)	2.50 to 26.323
a / nm	0.692 21(10)	Reflections collected / unique	1 378 / 412 [R(int)=0.029 1]
b / nm	0.692 21(10)	Completeness to θ_{max}	89.20%
c / nm	0.813 4(2)	Goodness-of-fit on F^2	1.182
γ / (°)	120	Final indices [$I>2\sigma(I)$]	R_1=0.036 6, wR_2=0.095 3
V / nm^3	0.337 054(12)	R indices (all data)	R_1=0.038 2, wR_2=0.096 1
Z	1	Largestdiff.peak and hole / ($e \cdot nm^{-3}$)	734 and −2 767

Table 2 Bond lengths (nm) and angles (°)

Ag(1)-O(1)#1	1.998 4(11)	Ag(1)-O(1)	1.998 4(12)	Ag(1)-C(1)	2.046(7)
Ag(1)-C(1)#1	2.046(7)	Mn(1)-N(1)#2	2.222(6)	Mn(1)-N(1)#3	2.222(6)
Mn(1)-N(1)#4	2.222(6)	Mn(1)-N(1)#5	2.222(6)	Mn(1)-N(1)#6	2.222(6)
Mn(1)-N(1)	2.222(6)	N(1)-C(1)	1.155(10)		
O(1)#1-Ag(1)-O(1)	180.0	O(1)#1-Ag(1)-C(1)	91(2)	O(1)-Ag(1)-C(1)	89(2)
O(1)#1-Ag(1)-C(1)#1	89(2)	O(1)-Ag(1)-C(1)#1	91(2)	C(1)-Ag(1)-C(1)#1	180.0(5)
N(1)#2-Mn(1)-N(1)#3	180.000(1)	N(1)#2-Mn(1)-N(1)#4	93.3(2)	N(1)#3-Mn(1)-N(1)#4	86.7(2)
N(1)#2-Mn(1)-N(1)#5	86.7(2)	N(1)#4-Mn(1)-N(1)	93.3(2)	N(1)#4-Mn(1)-N(1)#5	180.000(1)
N(1)#6-Mn(1)-N(1)	180.0	N(1)#3-Mn(1)-N(1)#6	86.7(2)	N(1)#3-Mn(1)-N(1)	93.3(2)
N(1)-C(1)-Ag(1)	178.6(7)	N(1)#5-Mn(1)-N(1)	86.7(2)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1, -z$; #2: $-x+y, -x, z$; #3: $x-y, x, -z+1$; #4: $y, -x+y, -z+1$; #5: $-y, x-y, z$; #6: $-x, -y, -z+1$.

methods and successive difference Fourier 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)[28]. The crystallographic data of **1** were given in Table 1, and Table 2 lists the selected bond lengths and angles.

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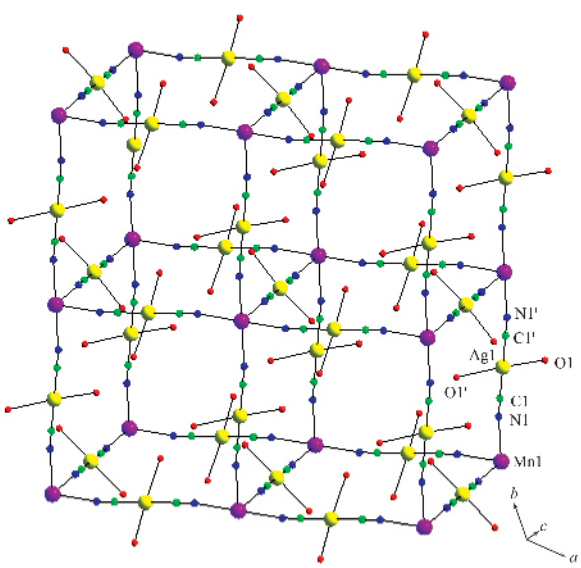
2 Results and discussion

2.1 Crystal structure

$\{KMn[Ag(CN)_2]_3 \cdot H_2O\}_n$ (**1**). The atomic labeling scheme of **1** is shown in Fig.1. In **1**, each Mn(Ⅱ) ion is six-coordinated, with a distorted octahedron geometry, by means of six nitrile nitrogens atoms from six (2-bridging $[Ag(CN)_2]^-$ anions completing the coordination environment. The bond length of Mn(1)-N(1) is 0.222 2(6) nm and the bond angle of N(1)#6-Mn(1)-N(1) is 180°. Each Mn(Ⅱ) ion is connected to six others by six different (2-bridging $[Ag(CN)_2]^-$ anions, resulting from a three-dimensional open microporous network. The $[Ag(CN)_2]^-$ anions act as (2-bridging ligands and each Ag(I) ion coordinates to two oxygen atoms of two water molecules to form a square structure. The Ag(I)-O distance is 0.199 84(12) nm. The Mn(Ⅱ)…Mn(Ⅱ) distance is 1.068 1 nm. The large pore formed by a single 3D network allow incorporation of two other identical networks thus giving three 3D interpenetrating triple networks, as shown in Fig.2(a). The Ag(I)-Ag(I) distance is 0.346 1 nm, less than the sum of the van der Waals radii of Ag (0.360 nm), indicating argentophilic interactions in **1**. Each Ag(I) ion connects to three others by argentophilic interactions, giving a planar Ag(I) layer with hexagonal and triangle alternating arrangement (Fig.2(b)). The water molecules locate at the centre of triangle and each water molecule coordinates to three Ag(I) ions. Fig.3 gives the 3D packing diagram of 1 viewed along the crystallographic a axis. The K ions act as counterion ions and occupy the vacancy of the 3D network. The incorporation of coordinative linkage, argentophilic, accompanied by electrostatic interactions result from the elaborate 3D network of **1**.



Hydrogen atoms are omitted for clarity

Fig.1 Atomic labeling scheme of **1**

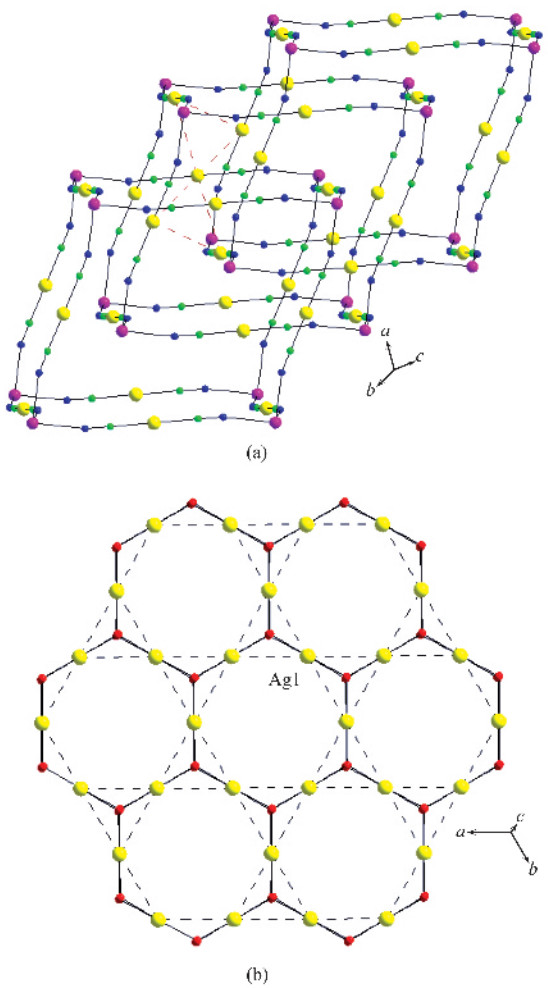


Fig.2 (a) Three interpenetrating 3D related nertworks of **1**, (b) The packing diagram of Ag…Ag interactions

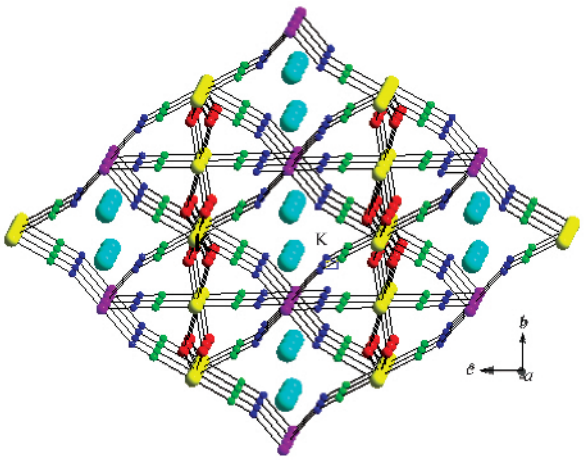


Fig.3 3D packing diagram of **1** viewed along the crystallographic *a* axis

2.2 Luminescent properties

Fig.4 shows the emission and excitation spectra of solid sample of **1** at room temperature. The emission spectrum obtained with excitation at 288 nm exhibits three peak bands with the maxima of 327, 428 and 472 nm. The resulting luminescence should be attributed to the argentophilic interactions. The oligomeric forms of Ag(I)···Ag(I) from $[Ag(CN)_2]^-$ anions allow the overlap of the occupied argent 4d orbitals to produce filled bands of orbitals and the overlap of the empty argent 5*p* orbitals to produce correspongding bands of unoccupied orbitals. When elections are excited from the filled 4*d* bands to the empty 5*p* bands, the reverse process related to excited electrons from the 5*p* bands back to the 4*d* band results from emission[25,26].

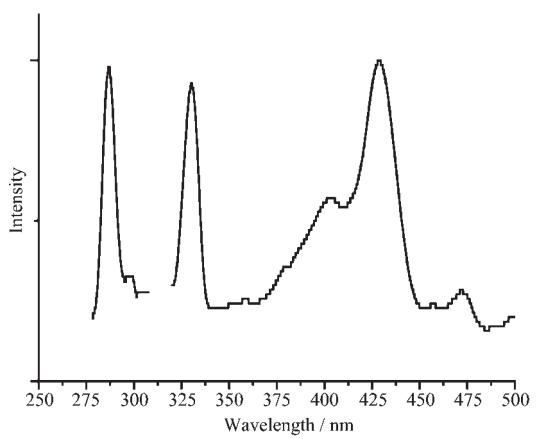


Fig.4 Emission (right) and excitation (left, λ_{ex}=288 nm) spectra of the solid of **1**

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