

Communication

A Novel Self-assembled Supramolecular Complex $\{[\text{Cu}(\text{II})(\text{en})_2 \cdot \text{H}_2\text{O}][\text{Cu}(\text{I})_2(\text{CN})_4]\}_n$ with Honeycomb-like Structure and Its Adsorption Properties

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A novel supramolecular complex $\{[\text{Cu}(\text{II})(\text{en})_2 \cdot \text{H}_2\text{O}] \cdot [\text{Cu}(\text{I})_2(\text{CN})_4]\}_n$ (en = ethylenediamine), in which the cyanide-bridged Cu(I) forms the honeycomb-like skeleton host and the Cu(II) complex ion $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ is encapsulated in the center of the channel cavity of the skeleton, was synthesized by two different methods. The complex was also characterized by elemental analysis, ICP analysis, IR spectra and thermal analysis. The adsorption and desorption studies of the complex indicate that H_2O and NH_3 can be desorbed and re-adsorbed without collapse of the channel structure of the supramolecule.

Keywords crystal structure, cyano-bridged, copper complex, adsorption properties, supramolecular complex

Recently, there has been a growing interest in coordination polymers¹ with a one- (1-D), two- (2-D) or three-dimensional (3-D) structure. The unique physicochemical properties of these polymers, high thermal stability,² gas adsorption and desorption,³ small molecules occlusion,⁴ ion exchange⁵ and heterogeneous catalysis,⁶ have numerous applications. The synthesis of coordination polymers, however, has been proven to be a formidable challenge to both inorganic and polymer chemists. Poor solubility and the non-stoichiometric composition owing to adsorption of coexisting ions and solvent molecules have

been the main inconveniences. One of the successful cases is the cyanide-bridged polymers, which manifested in numerous recent reports⁷ and collectively revealed a remarkable diversity of structural types and properties. These polymers were assembled from the cyanometallates $[\text{M}(\text{CN})_n]^{m-}$ ion (building block) and a metal ion (connecting block) with polydentate ligands. These cyanometallates possess variable coordination entities, such as linear $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag}, \text{Au}$),^{7a-7c} trigonal $[\text{Cu}(\text{CN})_3]^{2-}$,^{7d} tetrahedral $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$),⁷ⁿ square planar $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Ni}, \text{Pt}, \text{Pd}$)^{7f} and octahedral $[\text{M}(\text{CN})_6]^{n-}$ ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$),^{7e-7l} so varieties of multidimensional structures such as 1-D zigzag chain,^{7h} 1-D rope-ladder,⁸ 2-D sheet,^{7i,9} honeycomb-like¹⁰ and 3-D network structure^{7e,7j} are developed. When a cyanometallate $[\text{M}(\text{CN})_n]^{m-}$ is linked to another coordination center M' by the nitrogen atom of its cyanide groups, the linear $\text{M}-\text{CN}-\text{M}'$ span has a length of 0.5—0.6 nm. The multidimensional structure formed by the successive $-\text{M}-\text{CN}-\text{M}'-$ linkages produces a void space with the dimension which is appropriate to accommodating a suitable molecule and it is necessary to stabilize the crystal structure. Recently, we have been interested in synthesizing cyanide-bridged supramolecular

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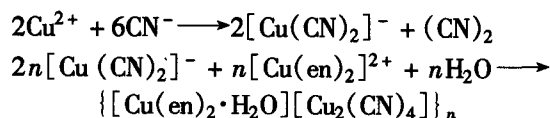
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assemblies containing a hexacyanomanganese ion $[\text{Mn}(\text{CN})_6]^{3-}$ (building blocking) and a complex cation $[\text{Cu}(\text{en})_2]^{2+}$ (en = ethylenediamine). Surprisingly, we found a special supramolecular complex $\{[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}][\text{Cu}_2(\text{CN})_4]\}_n$, in which the cyanide-bridged Cu(I) forms the honeycomb-like skeleton host and the Cu(II) complex ion $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ is encapsulated in the center of the channel cavity of the skeleton. To the best of our knowledge, it seems rare that a complex ion¹¹ acts as a guest in the three-dimensional cyanometallate supramolecular system.

The reddish violet crystals were obtained by vaporization of the reaction solution containing $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ and $(\text{Et}_4\text{N})_3\text{Mn}(\text{CN})_6$ in the 5:1 methanol/water mixture solvent at the room temperature for several days. The title complex is stable in air and insoluble in common solvents. IR spectra, element analysis, inductively coupled plasma atomic emission spectrum (ICP)¹² and crystal structure determination¹³ confirm the composition and structure of the title supramolecular complex. Two cyanide stretching bands at 2091 cm^{-1} and 2076 cm^{-1} are very close to those in $[\text{Cu}(\text{CN})_3]^{2-}$ (2094 cm^{-1}) and $[\text{Cu}(\text{CN})_4]^{3-}$ (2076 cm^{-1}),¹⁴ and differ from that of $[\text{Mn}(\text{CN})_6]^{3-}$ (2112 cm^{-1}).¹⁵ The result of ICP data shows that only one kind of metal of copper exists in the title complex. These results indicate that the complex is a cyanide-bridged copper complex. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in N_2 atmosphere within the temperature range of $20\text{--}500\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Three big sharp endothermic peaks have been found at 125 , 225 and $275\text{ }^\circ\text{C}$ respectively. The weight loss corresponding to the coordinating water molecules was observed at $120\text{--}130\text{ }^\circ\text{C}$ (weight lost 4.17% , calcd 4.16%). The second and third endothermic peaks corresponds to a 76% loss of ethylenediamine (weight lost 21.1% , calcd 27.77%). Upon further heating, the skeleton of the title supramolecular complex broke down.

It is known that the aqueous solution of $(\text{Et}_4\text{N})_3[\text{Mn}(\text{CN})_6]$ is unstable at the room temperature. Decomposition generates cyanide ions. The oxidation-reduction reaction with bivalent copper ions in the solution to produce the more stable Cu(I) complex ions $[\text{Cu}(\text{CN})_2]^-$ can take place. Only now the supramolecular complex $\{[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}][\text{Cu}_2(\text{CN})_4]\}_n$ is formed via a one-step self-assembly process with the complex ion $[\text{Cu}(\text{en})_2]^{2+}$

which acts both as a template and a counter-ion:



In order to prove above reaction mechanism, the aqueous solution of KCN, CuCl_2 and $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$ with the molar ratio of $6:2:1$ was heated to $100\text{ }^\circ\text{C}$ for 15 min and then placed at the room temperature for a few days, the reddish violet crystals appeared. The X-ray crystal structure analysis showed that its structure is the same as the title complex.

The ORTEP diagram of the title complex with the atom numbering scheme is shown in Fig. 1 and the packing diagram along the b -axis is shown in Fig. 2. The asymmetric unit consists of a $[\text{Cu}_2(\text{CN})_4]^{2-}$ anion and a $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ cation. The coordination geometry of the Cu(3) ion in $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ units is an elongated square pyramid where the basal plane is composed of four nitrogen atoms from two diamine ligands [Cu(3)—N(11) $0.1994(2)\text{ nm}$, Cu(3)—N(12) $0.2017(2)\text{ nm}$, Cu(3)—N(13) $0.20178(13)\text{ nm}$ and Cu(3)—N(14) $0.19969(14)\text{ nm}$] and the axial position is occupied by the oxygen atom O(1w) from H_2O molecular [Cu(3)—O(1w) $0.24336(14)\text{ nm}$]. The Cu—N distances in the $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ cation are quite close to those in the complex $\text{Cu}(\text{en})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (0.198 , 0.200 , 0.202 nm),¹⁶ which confirms that Cu(3) ion is bivalent copper ion. According to the charge neutralization of the complex

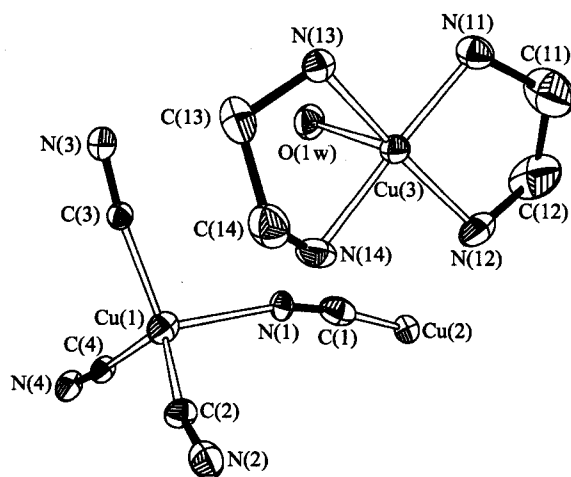


Fig. 1 ORTEP diagram of the title complex with the atom numbering scheme.

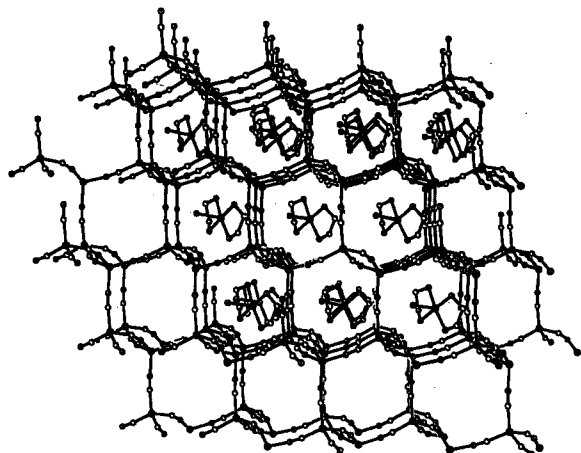


Fig. 2 Projection along the *b*-axis for the title complex, showing a 3-D honeycomb-like structure.

$\{[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}][\text{Cu}_2(\text{CN})_4]\}_n$, other two copper ions [Cu(1) and Cu(2)] in the unit cell are cuprous ions. They are surrounded by four cyanide groups and formed a distorted tetrahedron. We suppose, however it is difficult to determine which atom (carbon or nitrogen atom) of the cyanide group coordinating to either the Cu(1) ion or Cu(2) ion. It may be distinguishable from the little difference between two bond lengths: Cu(I)—C and Cu(I)—N, since the distance of Cu(I)—C is slightly shorter than that of Cu(I)—N, which had been reported in the linear cyanide-bridged polymer $[\text{KCu}(\text{CN})_2]_n$ [Cu(I)—C 0.192 nm and Cu(I)—N 0.205 nm].¹⁷ According to this, we consider that Cu(1) ion in the unit $[\text{Cu}_2(\text{CN})_4]^{2-}$ is surrounded by three carbon atoms [C(2), C(3), C(4)] and one nitrogen atom [N(1)] [the bond lengths: Cu(1)—C(3) 0.1964(2) nm, Cu(1)—C(4) 0.19683(14) nm, Cu(1)—C(2) 0.1952(2) nm, Cu(1)—N(1) 0.2077(2) nm], while Cu(2) ion is coordinated by three nitrogen atoms [N(2c), N(3b), N(4a)]¹⁸ and one carbon atom [C(1)] [the bond lengths: Cu(2)—N(3b) 0.20153(14) nm, Cu(2)—N(4a) 0.19869(14) nm, Cu(2)—N(2c) 0.2044(2) nm, Cu(2)—C(1) 0.1971(2) nm].

As already mentioned, each cuprous ion is surrounded by four cyanide groups with tetrahedron coordination geometry. These four cyanide groups act as a bridged ligand to link four adjacent cuprous ions forming a 3-D honeycomb-like structure and a one-dimensional channel (Fig. 2). Six cuprous ions and six cyanide groups compose a hexagonal-like cavity. In the unit, the Cu...Cu distances between two adjacent cuprous ions are in the range of

0.5047—0.5100 nm, the distances between two alternated cuprous ions are in the range of 0.739—0.833 nm and the distances between two opposite cuprous ions are in the range of 0.891—1.041 nm. The size of the cavity is already close to that of zeolite and can accommodate $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ cations. Also, the charge of the skeleton cavity matches to that of the guest $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ cations. Undoubtedly, the $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ cation lying in the center of the channel cavity plays an important role in the self-assembly reaction. It acts not only as a counter-ion to balance the charge of the supramolecule, but also as a template to form the porous supramolecular frameworks. In fact, the framework can not be formed unless the $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}]^{2+}$ cations exist in the self-assembly reaction. There was a similar phenomenon in a previous report,¹⁹ where it was found that when the small guest $\text{CMe}_{4-n}\text{Cl}_n$ ($n = 0-4$) with tetrahedral or pseudotetrahedral geometry was present, the $\text{Cd}(\text{CN})_2$ moiety formed an adamantane-like structure, while $\text{Cd}(\text{CN})_2$ formed a H-tridymite structure ($P6_3/mmc$) when Bu_2O as a guest.

The adsorption and desorption properties of the supramolecular complex have been determined using Sartorius supermicro S3D-S Electronic Vacuum Ultramicro Balances Installation and Operating Instructions Elektronische Vakuum-Ultramikrowaagen Aufstellungs-Und Betriebsanleitung. The water molecules coordinated to the copper ions are lost at 80 °C and 5 Pa pressure. The color of the title crystal turns to dark violet from reddish violet while the sample loses all its coordinating water molecules. It can re-absorb H_2O up to about 93% of original amount of water adsorbed, under saturation vapor pressure of H_2O at 25 °C. Color almost restores to original during the re-adsorption. The dried sample can also re-adsorb ammonia molecules which coordinate to the copper cations, up to the amount of 97% of the copper cations at 25 °C. The color changes from dark violet to green after adsorbing ammonia. All ammonia molecules coordinated to copper ions may be desorbed under 5 Pa at 60 °C. The X-ray diffraction patterns of the title complex, the sample after desorbing water and that after adsorbing ammonia (Fig. 3) are very similar, indicating that these three samples have the same skeleton structure. It is quite a unique property for this supramolecular complex to reversibly desorb and adsorb water and ammonia without the collapse of the cavity or channel structures.

Most of the inclusion coordination compounds that irreversibly lose their crystallinity, undergo a phase change, or alter their morphology when their guests are lost. In the title supramolecular complex, there is an ionic interaction between the guest and host species. A little effect on the main structure of the guest and host was observed when desorption and adsorption of H₂O and NH₃, which coordinated to the copper ion occurred. This means that the skeleton network structure did not collapse in the course of adsorption and desorption of coordinating water and ammonia molecules.

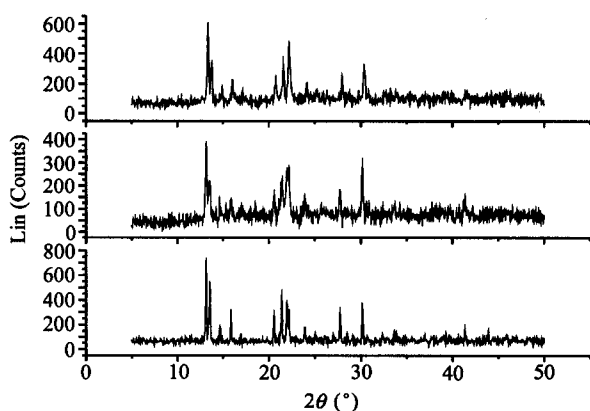


Fig. 3 Powder X-ray diffraction patterns of the title complex (bottom), the sample after desorbing water (middle) and the sample after adsorbing ammonia (top).

In conclusion, self-assembled supramolecular complex $\{[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_4]\}_n$ with a novel honeycomb-like structure was synthesized using $[\text{Cu}(\text{CN})_2]^-$ as a building unit and $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ as a template in a one-pot reaction. Water and ammonia molecules coordinated to copper ions can be desorbed and re-adsorbed at least several times accompanying a color change. It is a unique example of the three-dimensional porous framework supramolecular complex in which some molecules such as H₂O and NH₃ can be desorbed and re-adsorbed without collapse of the channel structure of the supramolecule. The further study is in progress.

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- 13 Reddish violet crystals of $[\text{Cu}(\text{en})_2 \cdot \text{H}_2\text{O}][\text{Cu}_2(\text{CN})_4]$ were analyzed at (293 ± 2) K: $\text{C}_8\text{H}_{18}\text{N}_8\text{Cu}_3\text{O}$, $M_r = 432.92$, monoclinic, space group Cc (# 9) with $a = 1.4759(3)$ nm, $b = 0.7734(2)$ nm, $c = 1.4247(3)$ nm, $\beta = 112.65(3)^\circ$, $V = 1.5009(5)$ nm³, $Z = 4$, $D_c = 1.916$ Mg/m³ and μ (Mo K α) = 4.220 mm⁻¹. Data were collected on an Enraf Nonius CAD4 diffractometer. The structure was solved by direct method (SHELXS-86). All non-hydrogen atoms were refined anisotropically (SHELXL-93). Final full-matrix least-squares refinement on F^2 with 1504 observed reflections ($I > 2\sigma(I)$) and 187 variables converged to $R_1 = 0.0267$, $wR_2 = 0.0633$.
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