研究简报

一种含$[Ni(CN)_4]^{2-}$和$[Cu(pn)]^{2+}$构筑元组成的超分子配合物的合成、单晶结构和磁学性质

苏育志 刘兆清 董 文*
(广州大学化学化工学院,化学系,广州 510006)

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Synthesis, Crystal Structure and Magnetic Property of a Cyano-Bridged 3D Heterometallic Supramolecular Complex Containing $[Ni(CN)_4]^{2-}$ and $[Cu(pn)]^{2+}$ Tectons

SU Yu-Zhi LIU Zhao-Qing DONG Wen*
(*Department of Chemistry, School of Chemical Engineering and Technology, Guangzhou University, Guangzhou* 510006)

Abstract: A cyano-bridged heterometallic supramolecular complex $\{[Cu(pn)]_3[Ni(CN)_4]_3\}_n$ (**1**) has been synthesized and structurally characterized by single crystal X-ray diffraction. **1** displays an interesting 3D structure formed by μ_4, μ_3-$[Ni(CN)_4]^{2-}$ tectons bridging five-coordinated and six-coordinated Cu(Ⅱ) ions. The magnetic property shows that **1** behaves as weakly ferromagnetic interactions between the adjacent Cu(Ⅱ) ions through the diamagnetic spacer NC-Ni-CN. CCDC: 624387.

Key words: supramolecular complex; single crystal structure; magnetic property

In the pursuit of new molecule-based magnets, the cyano-bridged supramolecular complexes are good candidates and have been investigated extensively in the past decades [1~5]. 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 complexes possessing various degrees of dimensionality have been synthesized and characterized structurally as well as magnetically[6~17]. Currently, tetracyanometallates as good building blocks, are widely used to develop a various range of supramolecular complexes which exhibit various structures with interesting magnetic properties[18~20]. Here we report the synthesis, crystal structure and magnetic property of **1**. To our knowledge, the report of 3D heterometallic supramolecular complex bridged by $[Ni(CN)_4]^{2-}$ building block are very limit.

1 Experimental

1.1 Preparations

The blue crystals of **1** were obtained by slow diffusion method in a mixed solvent of H_2O-$CH_3CHOHCH_3$ (5∶1) using an H-shaped tube. The staring aqueous solution of of $K_2[Ni(CN)_4]\cdot H_2O$ (13 mg, 0.05 mmol) and 1,3-propanediamine (3.7 mg, 0.05

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*通讯联系人。E-mail:dw320@eyou.com
第一作者:苏育志,男,43 岁,教授;研究方向:功能材料。

mmol) was put in one arm and the solution $Cu(ClO_4)_2 \cdot 6H_2O$ (18.5 mg, 0.05 mmol) dissolved in a mixed solvent of H_2O-$CH_3CHOHCH_3$ (5∶1) was put in the other one. After a few weeks, blue crystals appeared. The crystal were handed picked, washed with a small amount of cold water and dried on filter paper.

Caution! Perchlorate salts of metal complexes with organic ligand are potentially explosive and should be handed in small quantities with care.

1.2 Measurements

Elemental analyses were carried out using a Perkin-Elmer analyzer model 240. The IR spectra were recorded as KBr discs on a Shimadzu IR408 infrared spectrophotometer in the 4 000 ~600 cm^{-1} region. The magnetic measurements of the sample were carried out in an applied field of 10 000 G using a SQUID magnetometer in the temperature range of 4~300 K. Effective magnetic moments were calculated by the equation $\mu_{eff}=2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility.

1.3 Crystal structure determination

Determination of the unit cell and data collection was performed on a Bruker Smart APEX Ⅱ diffractometer using graphite monochromatized Mo $K\alpha$ radiation (λ=0.710 7 nm) at 293(2) K. The structure was solved by direct methods and successive difference Fourier syntheses (SHELXS-97)[21] and refined by fullmatrix leastsquares procedure on F^2 with anisotropic thermal par-ameters for all non-hydrogen atoms (SHELXL-97)[21]. Crystal data collection and refinement parameters are given in Table 1. Table 2 list the selected bond lengths and angles for the complex.

Table 1 Crystal data and structure refinement for 1

Formula	$C_{21}H_{30}Cu_3N_{18}Ni_3$	Z	4
Formula weight	901.38	D_c / ($g \cdot cm^{-3}$)	1.762
Crystal system	Monoclinic	μ(Mo $K\alpha$) / mm^{-1}	3.515
Space group	$C2/c$	F(000)	1 812
a / nm	2.6549(10)	θ range / (°)	1.93~25.02
b / nm	0.960 1(4)	Reflections collected / unique	6 499 / 2 902 (R_{int}=0.028 7)
c / nm	0.960 1(4)	Completeness to θ=25.020/%	96.6
α / (°)	90	Goodness-of-fit on F^2	0.954
β / (°)	127.260(5)	Final indices [$I>2\sigma(I)$]	R_1=0.039 3, wR_2=0.078 2
γ / (°)	90	R indices (all data)	R_1=0.060 2, wR_2=0.087 4
V / nm^3	0.127 26(5)	Largest diff. peak / hole / ($e \cdot nm^{-3}$)	1.166 and −1.740

[a] $R_1=||F_o| - |F_c||/|F_o|$; [b] $wR_2=w(F_o^2-F_c^2)^2]/[w(F_o)^2]^{1/2}$.

Table 2 Selected bond lengths (nm) and angles (°) for 1

Cu(1)-N(1)	0.199 8(4)	Cu(2)-N(9)	0.194 8(4)	Ni(1)-C(1)	0.187 6(5)
Cu(1)-N(5)	0.200 5(4)	Cu(2)-N(9)#1	0.194 8(4)	Ni(2)-C(5)	0.185 2(5)
Cu(1)-N(8)	0.200 7(4)	Cu(2)-N(3)	0.198 2(5)	Ni(2)-C(6)	0.186 1(6)
Cu(1)-N(7)	0.201 7(4)	Cu(2)-N(3)#1	0.198 2(5)	N(1)-C(1)	0.113 2(6)
Cu(1)-N(4)	0.220 7(5)	Ni(1)-C(2)	0.183 8(6)		
C(2)-Ni(1)-C(3)	8.87 (2)	N(8)-Cu(1)-N(7)	89.53(17)	N(9)-Cu(2)-N(3)	177.2(2)
N(1)-Cu(1)-N(5)	90.67(17)	N(1)-Cu(1)-N(4)	92.52(18)	N(9)#1-Cu(2)-N(3)	88.1(2)
N(1)-Cu(1)-N(8)	171.03(18)	N(5)-Cu(1)-N(4)	103.53(17)	N(9)-Cu(2)-N(3)#1	88.1(2)
N(5)-Cu(1)-N(8)	86.16(17)	N(8)-Cu(1)-N(4)	96.38(18)	N(3)-Cu(2)-N(3)#1	90.5(3)
N(1)-Cu(1)-N(7)	90.50(17)	N(7)-Cu(1)-N(4)	97.11(17)	N(5)-Cu(1)-N(7)	159.25(18)
N(9)-Cu(2)-N(9)#1	93.4(3)				

Symmetry transformations used to generate equivalent atoms: x, y, z; $-x$, y, $-z+1/2$; $x+1/2$, $y+1/2$, z; $-x+1/2$, $y+1/2$, $-z+1/2$; $-x$, $-y$, $-z$; x, $-y$, $z-1/2$; $-x+1/2$, $-y+1/2$, $-z$; $x+1/2$, $-y+1/2$, $z-1/2$.

CCDC: 624387.

2 Results and discussion

2.1 Crystal structure

The structure schemeof **1** is shown in Fig.1. The structure determination of **1** discloses a novel 3D structure. In **1** there are two coordinated models of Cu (Ⅱ) ions. The Cu (1A) ion is five-coordinated, with a square pyramidal geometry, by means of two nitrile nitrogen atoms from two μ_4, μ_3-$[Ni(CN)_4]^{2-}$ bridging ligands and two nitrogen atoms from a propanediamine in planar position and a nitrogen atom of a μ_3-$[Ni(CN)_4]^{2-}$ bridging ligand in axial position. The Cu(2A) ion is six-coordinated, with a prolonged octahedral geometry. The basal plane is formed by two nitrile nitrogen atoms from two μ_3-$[Ni(CN)_4]^{2-}$ bridging ligands and the other two nitrogen atoms from a propanedia-mine. The axial positions are filled by two nitrogen atoms from two μ_4-$[Ni(CN)_4]^{2-}$ bridging ligands with the Cu-N distances of 0.277 2 nm. In **1**, $Ni(CN)_4^{2-}$ building block acts as two different μ_4 and μ_3 bridges. The uncoordinated nitrile nitrogen atom of μ_3-$[Ni(CN)_4]^{2-}$ bridge connects to the nitrogen atom of a propanediamine through N⋯N hydrogen bond with the distance of N⋯N of 0.294 9 nm. Each Cu(1A) ion is connected to the other three by two μ_3-$[Ni(CN)_4]^{2}$ bridges and a μ_4-$[Ni(CN)_4]^{2}$ bridge and each Cu(2) ion is connected to the other four by two μ_3-$[Ni(CN)_4]^{2}$ and two μ_4-$[Ni(CN)_4]^{2}$ bridges, leading to a 3D network(Fig.2).

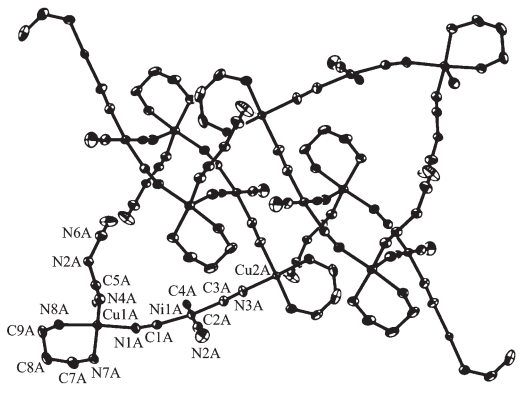


Fig.1　Structure scheme of **1**

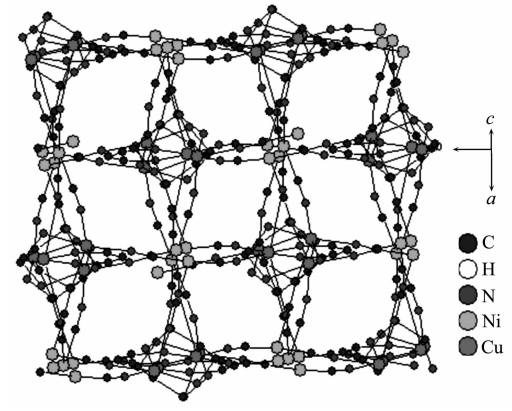


Fig.2　A 3D packing scheme of **1**

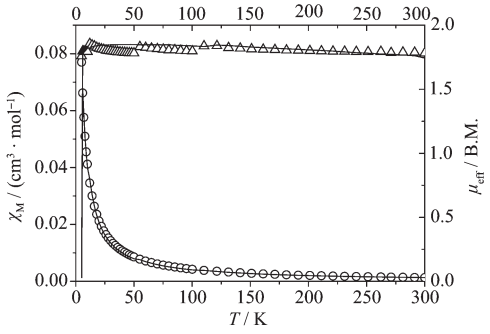
2.2 IR Spectra and elemental analyses

The IR spectra of **1** shows one sharp ν_{CN} band around 2 154 cm^{-1}, which is at a higher wavenumber than that of $K_2[Ni(CN)_4]\cdot H_2O$, indicating that the $[Ni(CN)_4]^{2}$ ions acts as a bridge. Anal. Calc. Calcd for $C_{21}H_{30}Cu_3N_{18}Ni_3$ (%): C, 37.96; H, 3.32; N, 27.96. Found(%): C, 37.65; H, 3.54; N, 27.68

2.3 Magnetic property

Fig.3 shows the temperature dependence of the magnetic susceptibility of **1**. The μ_{eff} value is 1.76μ_B at room temperature, slightly larger than the spin-only value 1.73μ_B of an isolated Cu(Ⅱ) ion (S=1/2) interacting with a diamagnetic Ni(Ⅱ) ion (S=0). On cooling from room temperature, the μ_{eff} value smoothly increases, achieving the maximum value of 1.86μ_B at 18 K, suggesting a weakly ferromagnetic interaction between adjacent Cu(Ⅱ) ions through the diamagnetic spacer NC-Ni-CN. Upon further cooling, the μ_{eff} decreases below 18 K presumably due to the antiferromagnetic interaction between chains. The μ_{eff} versus T plot in the range from 300 K to 18 K obeys the Curie-Weiss law ($\chi=C/(T-\theta)$) with a Weiss constant θ of 5.04 K (Fig.4). The small positive Weiss constant further indicates an weakly ferromagnetic interaction between the adjacent Cu(Ⅱ) ions through the diamagnetic spacer NC-Ni-CN. The magnetic data of **1** can be analyzed by means of the theoretical expression (**1**) for ferromagnetically coupled uniform chain of local spin S=1/2[22]:

$$\chi=\{Ng^2\beta^2/[4K(T-\theta)]\}(A/B)^{2/3}$$
$$A=1.0+5.797\,991\,6Y+16.902\,653Y^2+29.376\,885Y^3+29.832\,959Y^4+14.036\,918Y^5$$
$$B=1.0+2.797\,991\,6Y+7.008\,678\,0Y^2+8.653\,864\,4Y^3+4.574\,311\,4Y^4$$
$$Y=J/(2KT) \qquad (1)$$



Continuous lines represent the best fit to the theoretical models

Fig.3 Thermal variation of χ_M and μ_{eff} for complex **1**

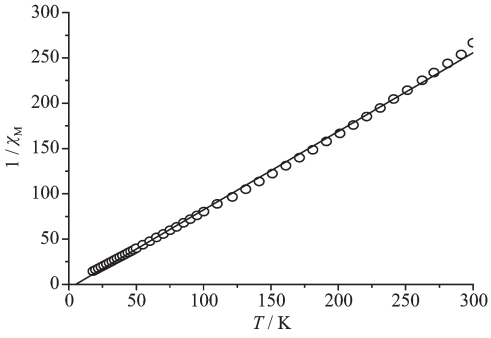


Fig.4 Plot of χ_M^{-1} vs T for **1** in the temperature range of 18~300 K

The best fitting parameters are J=0.92 cm^{-1}, θ= −0.89 K, g=2.03 and R=2.14 × 10^{-2}, where R is the agreement factor: $R=\sum(\chi_{obsd}-\chi_{calcd})^2/\sum\chi_{obsd}^2$. The small positive J value further indicates a weak ferromagnetic interaction between the adjacent Cu(Ⅱ) ions through the diamagnetic spacer NC-Ni-CN.

3 Conclusion

A novel 3D heterometallic supramolecular complex **1** has been synthesized and structurally characterized. In **1** the $[Ni(CN)_4]^{2-}$ tecton shows μ_4- and μ_3-bridging models and Cu(Ⅱ) ions exhibit five-coordinated and six-coordinated structure. The magnetic properties have shown that **1** behaves as weakly ferromagnetic interactions between the adjacent Cu(Ⅱ) ions through the diamagnetic spacer NC-Ni-CN.

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