研究简报

三维超分子[Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$][Ni(SCN)$_2$(H$_2$O)$_4$](H$_2$O)$_2$的自组装,晶体结构及磁性质(hmt=六次甲基四胺)

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Self-Assembly, Crystal Structure and Magnetic Properties of Three-Dimensional Supramolecular Complex [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$][Ni(SCN)$_2$(H$_2$O)$_4$](H$_2$O)$_2$ (hmt = hexamethylenetetramine)

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Compound [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$][Ni(SCN)$_2$(H$_2$O)$_4$](H$_2$O)$_2$ (hmt = hexamethylenetetramine) was prepared and structurally characterized by means of X-ray single crystal diffraction. The two neutral units [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$] and [Ni(SCN)$_2$(H$_2$O)$_4$] are joined together through hydrogen bonds N···H-O, O···H-O and S···H-O. In the solid state, the compound has three-dimensional network structure. The determination of its variable-temperature magnetic susceptibilities (5~300K) shows that the magnetic behavior obeys the Curie-Weiss law over the whole temperature ranges.

Keywords: self-assembly supramolecular complex hydrogen bonds magnetic properties

0 Introduction

Recently, strong interest has been focused on the crystal engineering of supramolecular architectures organized by coordinate covalent bonds[1] or hydrogen bonds and π-π interactions[2, 3]. In the latter methodology the hydrogen bond has attracted most interest due to its relative strength and directionality[4]. The presence of hydrogen bonds in some supramolecular compounds can influence coordination geometry[5]. The self-assembly is currently the most efficient approach towards the design of novel metal-organic supramolecular compounds. Using small molecular units as building blocks to form noncovalently bonded supramolecules is a subject of continuous interest[6]. In order to prepare the potential functional materials such as molecu-

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lar-based magnets and desired networks, nickel (Ⅱ) is a good candidate as magnetic center in L-M-L network, and hexamethylenetetramine (hmt) as a potential tetradentate ligand seems quite suitable in self-assembly systems. Severial groups have reported[7, 8] that Co (Ⅱ) or Mn (Ⅱ) ions with KSCN and hmt form two-dimensional or three-dimensional networks and also described the thermal and non-linear optical properties of these complexes. We are currently interested in searching new magnetic materials. Herein we report the hmt as terminal ligands coordinating to the Ni (Ⅱ) ions and several neutral units interacting through hydrogen bonds to form three-dimensional supuramolecular complex $[Ni(hmt)_2(SCN)_2(H_2O)_2][Ni(SCN)_2(H_2O)_4](H_2O)_2$. Magnetic measurements indicate that the magnetic behavior obeys the Curie-Weiss law over the whole temperature ranges.

1 Experimental

1.1 General

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Infrared spectra were recorded on a SHIMADZU IR-435 spectrophotometer as KBr pellets in the 400 ~ 4000cm^{-1} region. Elemental analyses were carried out on a Carlo-Erba1106 Elemental Analyzer. Variable-temperature magnetic susceptibility data were obtained on a Quantum Design MPMS-5 SQUID magnetometer in the temperature range of 5.0 ~ 300K with an applied field of 10000G. Diamagnetic corrections were calculated from Pascal's constants[9].

1.2 Synthesis of $[Ni(hmt)_2(SCN)_2(H_2O)_2][Ni(SCN)_2(H_2O)_4](H_2O)_2$

An amount of 5mL of a methanolic solution of hmt (0.1402g; 1mmol) was added dropwise to 3mL of an aqueous solution of $Ni(SCN)_2$ (0.1748g; 1mmol). The resulting solution was left at room temperature. Green crystals suitable for X-ray single crystal analysis were formed after several days. It shows characteristic infrared absorption peaks at 3375m, 2102s, 1243s, 1233m, 1004s, 827m, 690m, 684m, 516m; Anal. Calc. for $C_{16}H_{40}Ni_2N_{12}O_8S_4$: C, 24.80; H, 5.17; N, 21.70%. Found: C, 24.85; H, 5.28; N, 21.66%.

1.3 Crystallography

A crystal having approximate dimensions of 0.30 × 0.30 × 0.20mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$Å). The two structures were solved by the direct method and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All data were collected at a temperature of 293(2) K using the ω-2θ scan technique and correction was applied for Lorenz-po- larization effects. A correction for secondary extinction was applied. The final cycle of the full-matrix least-squares refinement was based on 2944 observed reflections and 226 variable parameters. All calculations were performed using the SHELXL-97 crystallographic software package[10]. Crystal data: triclinic, space group $P\bar{1}$, with $a = 7.9228(16)$, $b = 9.0376(18)$, $c = 12.849(3)$ Å; $\alpha = 94.18(3)$, $\beta = 96.76(3)$, $\gamma = 115.77(3)°$; $Z = 1$; $D_{calc} = 1.579$Mg · m^{-3}; final $R = 0.0324$, w$R^2 = 0.0755$. Selected bond lengths and bond angles are listed in Table 1. The data of hydrogen bonds are listed in Table 2.

2 Results and Discussion

2.1 Structure of $[Ni(hmt)_2(SCN)_2(H_2O)_2][Ni(SCN)_2(H_2O)_4](H_2O)_2$

The structure unit consists of neutral group $[Ni(hmt)_2(SCN)_2(H_2O)_2]$, $[Ni(SCN)_2(H_2O)_4]$ and two crystallization water. In $[Ni(hmt)_2(SCN)_2(H_2O)_2]$ group, the Ni (Ⅱ) center coordinates to four nitrogen atoms from two hmt groups and two SCN^- anions, and two oxygen atoms from two H_2O. The equatorial plane is constituted by two nitrogen atoms [N6 and N6A] belonging to the thiocyanate groups and two oxygen atoms [O1 and O1A], while the axial positions are occupied by two nitrogen atoms [N1 and N1A] of hmt ligands. The Ni-N bond lengths involving the SCN^- groups, 2.0028(16) Å are shorter than those involving the hmt ligands, 2.2812(15) Å. The Ni-O distances are

Table 1　Selected Bond Distances (Å) and Bond Angles (°)

Ni(1)-N(1)	2.2812(15)	Ni(2)-O(2)	2.0526(15)	Ni(1)-N(6)	2.0028(16)
Ni(2)-N(5)	2.0470(16)	Ni(1)-O(1)	2.0861(14)	Ni(2)-O(3)	2.0891(15)
N(1)#1-Ni(1)-N(1)	180.00(7)	O(1)#1-Ni(1)-O(1)	180.00(9)	N(6)-Ni(1)-N(6)#1	180.00(12)
N(6)#1-Ni(1)-O(1)	90.10(7)	N(6)-Ni(1)-O(1)	89.90(7)	O(1)-Ni(1)-N(1)	88.28(6)
O(1)-Ni(1)-N(1)#1	91.72(6)	N(6)-Ni(1)-N(1)	91.49(7)	N(6)#1-Ni(1)-N(1)	88.51(7)
O(3)#2-Ni(2)-O(3)	180.00(8)	N(5)-Ni(2)-N(5)#2	180.00(9)	O(2)#2-O(2)-O(2)	180.00(1)
O(3)#2-Ni(2)-O(2)	91.05(7)	O(3)-Ni(2)-O(2)	88.95(7)	O(3)-Ni(2)-N(5)#2	87.94(7)
O(3)-Ni(2)-N(5)	92.06(7)	N(5)-Ni(2)-O(2)	91.17(7)	N(5)#2-Ni(2)-O(2)	88.83(7)

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

Table 2　Geometry of Hydrogen Bonds with $d(H-A) < r(A)+2.000$Å and $\angle DHA > 110°$

D-H···A	d(D-H)	d(H···A)	∠DHA	d(D···A)	A	
O4-H4E	0.742	2.673	150.75	3.340	S1	[x+1, y, z]
O4-H4F	0.874	1.961	176.13	2.834	N4	
O3-H3F	0.920	1.892	172.58	2.807	N2	[x+1, y, z]
O1-H1E	0.945	1.813	172.38	2.752	O4	[x, y+1, z]
O2-H2E	0.822	2.053	167.38	2.861	N3	[x+2, y+1, z]
O2-H2F	0.706	2.103	176.88	2.808	O4	[x+1, y+1, z]
O3-H3E	0.752	2.673	150.22	3.347	S2	[x+1, y, z]

2.0861(14)Å. The bond angles around Ni are 180.00° or about 90°, giving rise to a slightly elongated octahedral environment.

In [Ni(SCN)$_2$(H$_2$O)$_4$] group, the distances between axial positional O atoms and Ni (Ⅱ) center are 2.0891(15) Å; The average distance between equatorial atoms and Ni is 2.0498Å; The bond angles of N5-Ni2-N5A, O2-Ni2-O2A and O3-Ni2-O3A are all 180.00°, thus around the Ni (Ⅱ) center is close to an ideal octahedral geometry.

In the solid-state structure of the compound, [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$], [Ni(SCN)$_2$(H$_2$O)$_4$] and H$_2$O are joined together by hydrogen bonds forming a three-dimensional supramolecule. Fig. 1 shows the hydrogen bonding systems of the compound. As can be seen, in the compound there are six kinds of hydrogen bonds. One hydrogen bond is arising from the interaction of O2HE (or O3HF) from [Ni(SCN)$_2$(H$_2$O)$_4$] group with atom N3 (or N2) of hmt from [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$] group [O2···N3 = 2.861, H2E···N3 = 2.053Å, O2 - H2E···N3 = 167.38° or O3···N2 = 2.807, H3F ··· N2 = 1.892Å, O3 - H3F ··· N4 = 172.58°]. Two hydrogen bonds are between O2H2F and O3H3E from [Ni(SCN)$_2$(H$_2$O)$_4$] group and O4 from crystallization water and S2 atom from another

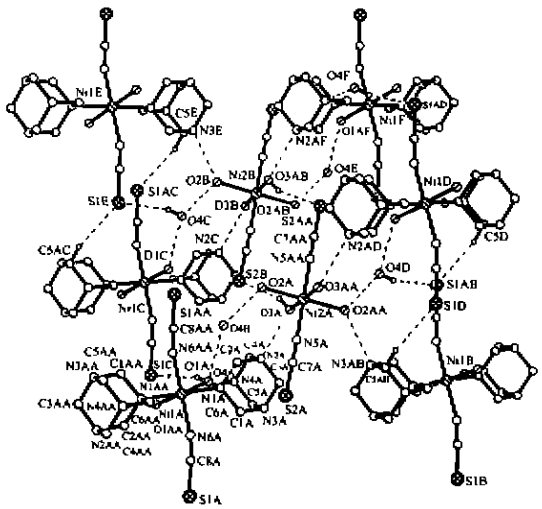

Fig. 1　Hydrogen bonding systems of [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$] [Ni(SCN)$_2$(H$_2$O)$_4$](H$_2$O)$_2$

[Ni(SCN)$_2$(H$_2$O)$_4$] group respectively [O2···O4 = 2.808, H2F ··· O4 = 2.103Å, O2 - H2F ··· O4 = 176.88°; O3 ··· S2 = 3.347, H3E ··· S2 = 2.673Å, O3 - H3E···S2 = 150.22°]. Two originate from O4H4E and O4H4F units from crystallization water with S1 atom and N4 atom from [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$] group respectively [O4···S1 = 3.340, H4E···S1 = 2.673Å, O4 - H4E···S1 = 150.75°; O4···N4 = 2.834, H4F···N4 = 1.961Å, O4 - H4F···N4 = 176.13°]. One result from O1H1E from [Ni(hmt)$_2$(SCN)$_2$(H$_2$O)$_2$]

group with O4 from a crystallization water [O1···O4 = 2.752, H1E ··· O4 = 1.813Å, O1 – H1E ··· O4 = 172.38°]. Viewed from the b-axis, each $[Ni(SCN)_2(H_2O)_4]$ unit links adjacent $[Ni(SCN)_2(H_2O)_4]$ unit leading to an infinite chain $[Ni(SCN)_2(H_2O)_4]_n$ (A) through intermolecular S ··· H – O hydrogen bonds; Another infinite chain $[Ni(hmt)_2(SCN)_2(H_2O)_2]_n$ (B) was formed by S ··· H – O and O ··· H – O hydrogen bonds. The O···H – O and N···H – O hydrogen bonds serve to link the chains A and B into sheets. On the other hand, the four coordinated water in $[Ni(SCN)_2(H_2O)_4]$ group link four hmt of different $[Ni(hmt)_2(SCN)_2(H_2O)_2]$ groups through hydrogen bonds (N··· H – O), while the two water in axial position of $[Ni(SCN)_2(H_2O)_4]$ link two crystallization water through hydrogen bonds O ··· H – O also. These hydrogen bonds lead the neutral groups into 3-D supramolecular structure. Fig. 2 shows its solid-state structure along b-axis.

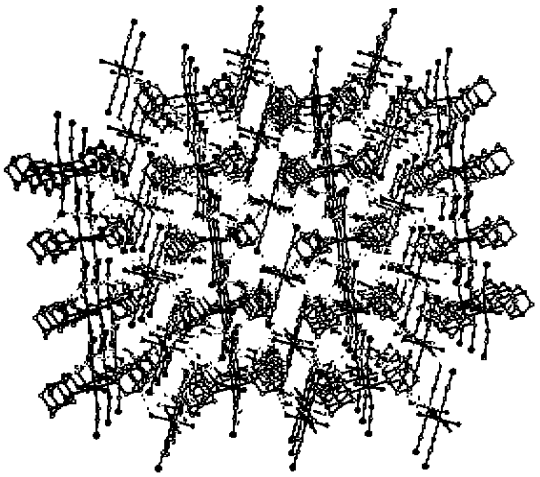

Fig. 2 Solid state structure along *b*-axis directions

2.2 Magnetic Properties

The variation of the inverse of the magnetic susceptibility, χ_m^{-1} and $\chi_m T$ of the compound are shown in Fig. 3. The thermal evolution of χ_m^{-1} obeys Curie-Weiss law, $\chi_m = C/(T - \theta)$ over the whole temperature ranges with $C_m = 2.623 cm^3 \cdot K \cdot mol^{-1}$ and $\theta = -4.523K$. The μ_{eff} is 4.616μ_B at rt. From Fig. 3 it can be seen that the $\chi_m T$ magnitude slowly decreases as temperature is lowered, rapidly decreasing upon further cooling below 29K, which could be associated with the occurrence of antiferromagnetic interactions and a zero splitting effect, or a zero field splitting effect, only[9].

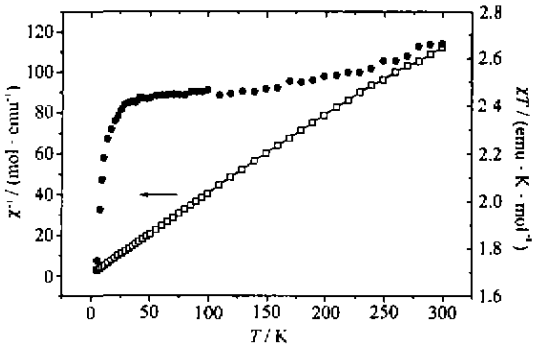

Fig. 3 Thermal variation for the $\chi_m T$ and χ_m^{-1} for the compound

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