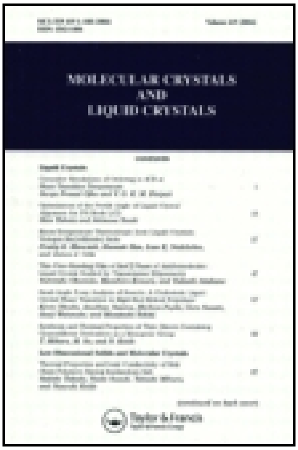

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Crystal Structures of Two-Dimensional Coordination Polymer Fe(Methylpyridine)$_2$Ni(CN)$_4$

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Two-dimensional coordination polymer compounds FeL$_2$Ni(CN)$_4$ (L: 2, 3, or 4-methylpyridine) have been synthesized and characterized by single crystal X-ray diffraction method.

Keywords: coordination polymer; spin crossover; cyanides

INTRODUCTION

Two-dimensional (2D) coordination polymers related with Hofmann-type clathrates and Hofmann pyridine complexes have been developed, using various metal ions, organic guest molecules and guest ligands.[1-11] The complex layers of the Hofmann-pyridine complex Fe(pyridine)$_2$Ni(CN)$_4$ **1** consist of a square-meshed network of the square-planar Ni(II) and the octahedral Fe(II) atoms alternately linked by the bridged cyano groups. The octahedral iron(II) ion is coordinated by the four N-terminals of cyano ligands and the two N atoms of pyridine ligands in a trans configuration. Recently the temperature-dependent spin crossover behavior of the Hofmann-pyridine complex Fe(pyridine)$_2$Ni(CN)$_4$ **1** and Fe(3-chloropyridine)$_2$Ni(CN)$_4$ has been reported.[1,2] Molecular interactions between the spin crossover molecules may be different between the discrete molecular systems and the two-dimensional coordination polymer systems, thus causing potential differences in the spin transition mechanism. This has stimulated us to study the two-dimensional coordination polymer compounds based on iron(II) tetracyanonickelate (II).

Three 2D coordination polymer compounds based on iron(II) tetracyanonickelate (II) have been obtained using three kinds of methylpyridine ligands. We report here crystal structures of the two-dimensional polymer compounds $FeL_2Ni(CN)_4$ (L: 2-methylpyridine **2**, 3-methylpyridine **3**, and 4-methylpyridine **4**), where L acts as a guest ligand in the host framework. The crystal structures of **2**, **3** and **4** have been found to be similar to that of $Fe(pyridine)_2Ni(CN)_4$ **1** .

Experimental

$Fe(2,3$ or $4\text{-methylpyridine})_2Ni(CN)_4$ **2**, **3** and **4** were prepared by a method similar to that for $Fe(pyridine)_2Ni(CN)_4$ **1** with bubbling N^2 gas.[11] To 60 mL of water, 1.04 g of $K_2[Ni(CN)_4]{\cdot}H_2O$ and 1.57 g of $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ were added to form a light blue precipitate immediately. This precipitate was dissolved to turn into a yellow solution by adding cirtric acid(3.5 - 5.0 g) and 1,3-diaminopropane successively with stirring. The pH of the solution was between 4.5 and 8.0, depending on the amount of cirtric acid and 1,3-diaminopropane. (caution: when the pH is higher than 8.5, crystals of $Ni(1\text{-}3\text{-diaminopropane})_2Ni(CN)_4$ were obtained. The crystal structure is similar to the reported $Ni(en)_2Ni(CN)_4$. [12]) The vapor diffusion method using methylpyridine-water mixture as a source of the ligand molecules provided yellow polycrystaline crystals of **2**, **3** and **4**. It is most diffucult to obtain single crystal of **3**. The single crystal quality of **3** was rather poor. The elemental analysis for C, H, N was carried out with a Perkin-Elmer Model 2400. Found **2** : C, 47.04; H, 3.24 ; N, 20.80 %; **3** : C, 47.45; H,2.95 ; N, 20.37 %; **4** : C, 47.17; H, 3.39 ; N, 20.21 %; $Fe(metylepyridine)_2Ni(CN)_4$requires C, 47.46; H, 3.48 ; N, 20.75 %. The diffrences in elemtntal analysis appear to be due to the non-stoichiometric character of the coordination polymer and the defects in the polymer structure.

Table 1 lists the crystallographic and experimental data for the compounds studied. The collection of X-ray diffraction intensity data were carried out on a Rigaku AFC-5S automated four-circle diffractometer at room temperature.

Table 1. Crystallographic and Experimental data for **2**-**4**

	2	**3**	**4**
formula	$FeNiN_6C_{16}H_{14}$	$FeNiN_6C_{16}H_{14}$	$FeNiN_6C_{16}H_{14}$
crystal system	orthorhombic	orthorhombic	monoclinc
space group	*Cmmm*	*Cmmm*	*C2/m*
fw	404.87	404.87	404.87
a, Å	7.342(2)	7.200(4)	18.67(3)
b, Å	15.578(4)	16.063(7)	7.436(3)
c, Å	7.257(3)	7.400(9)	6.841(6)
β, deg	90	90	109.95(9)
V, $Å^3$	829.9(4)	856(2)	893(2)
Z	2	2	2
μ(Mo-Kα) cm^{-1}	20.23	19.61	18.81
crystal size/mm	0.25x0.25x0.15	0.20x0.20x0.15	0.20x0.20x0.15
Dcalc g/cm^3	1.620	1.571	1.506
R, Rw	0.031, 0.034	0.129, 0.137	0.062, 0.066
GOF	2.39	2.84	2.71

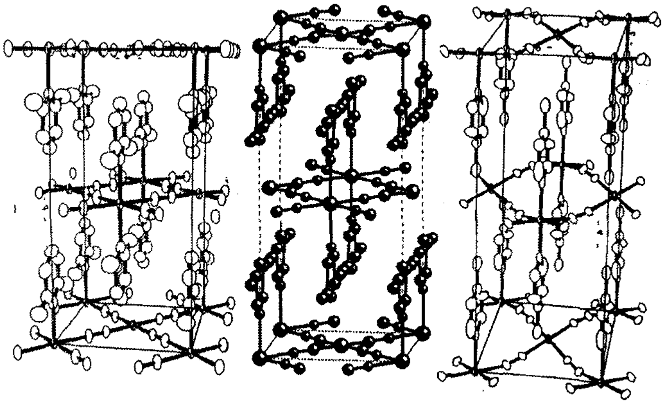

Figure 1. Perspective views of **2** (left), **3** (center) and **4** (right). The methyl group of **2** and **3** is disordered.

Table 2. The positional parameters for **2** -**4**.

atom	x	y	z
	Fe(2-methylpyridine)$_2$Ni(CN)$_4$ **2**		
Fe	0	0	0
Ni	1/2	0	1/2
C(1)	0.3202(6)	0	0.3202(7)
N(1)	0.2113(6)	0	0.2079(5)
N(2)	0	0.1464(4)	0
C(2)	0	0.1915(4)	0.160(1)
C(3)	0	0.2804(5)	0.164(1)
C(4)	0	0.3255(7)	0
C(5)	0	0.163(1)	0.352(2)
	Fe(3-methylpyridine)$_2$Ni(CN)$_4$ **3**		
Fe	0	0	0
Ni	1/2	0	1/2
C(1)	0.328(6)	0	0.340(6)
N(1)	0.207(3)	0	0.202(3)
N(2)	0	0.140(2)	0
C(2)	0	0.181(2)	0.134(6)
C(3)	0	0.276(3)	0.186(7)
C(4)	0	0.300(5)	0
C(5)	0	0.269(7)	0.42(1)
	Fe(4-methylpyridine)$_2$Ni(CN)$_4$ **4**		
Fe	0	0	0
Ni	0	1/2	1/2
N(1)	0.0323(5)	0.207(1)	0.234(1)
C(1)	0.0243(6)	0.317(1)	0.337(1)
N(2)	0.1164(8)	0	-0.015(2)
C(2)	0.180(1)	0	0.156(2)
C(3)	0.257(1)	0	0.149(3)
C(4)	0.262(1)	0	-0.037(3)
C(5)	0.201(1)	0	-0.212(3)
C(6)	0.130(1)	0	-0.205(3)
C(7)	0.344(1)	0	-0.041(4)

The structure was solved using the TEXSAN[13] software package installed on the diffractometer system. All the non-hydrogen atoms were refined. Hydrogen atoms were not inserted in the refinement.

Results and Discussion

The refined atomic coordinates for compound **2**-**4** are listed in Table 2. As shown in Figure 1, the X-ray crystal structures of **2**-**4** are similar to that of Fe(pyridine)$_2$Ni(CN)$_4$ **1**.[1] The complex layers consist of a square-meshed network of the square-planar Ni(II) and the six-coordinate Fe(II) atoms alternately linked by the bridged cyano ligands. The six-coordination of iron(II) is accomplished by four N terminals of cyano groups and two N atoms of the methylpyridine ligands in a trans configuration. While the space group of **2** and **3** is *Cmmm*, that of **4** is *C2/m*. The distances of Fe-N1(cyanide), Fe-N2(methylpyridine) and Ni-C1(cyanide) were 2.164(4), 2.280(7) and 1.856(5) Å for **2**; 2.11(2), 2.25(4) and 1.71(4) Å for **3**; 2.151(9), 2.21(1) and 1.91(1) Å for **4** respectively. The data for **3** should be considered with some care because of the low accuracy of this structure determination due to the poor quality of the single crystal. The low accuracy of the distances for **3** may be associated with the thermal motion of the 3-methylpyridine. The distances between layers for **2**, **3** and **4** are 7.789 Å (half of cell dimension b), 8.032 Å (half of cell dimension b) and 9.34 Å (half of cell dimension a) respectively. The location of methyl group is associated with the distances between layers. The neighboring layers are shifted by the symmetry operation of *Cmmm* or *C2/m*. The shift is associated with the large size of methylpyridine ligand because an eclipsed layer stacking pattern would make large void space.

While **1** and **3** act spin-crossover behavior, **2** and **4** do not.[1,14] The 2D frameworks of the all three kinds of methylpyridine complexes have topologies identical to that of Fe(pyridine)$_2$Ni(CN)$_4$ **1**. The spin crossover behavior in the polymeric iron(II) tetracyanonikelate(II) system depends on the substituent effect including the electronic and sthe teric effect of the pyridine derivative ligand [1,2,14] oriented perpendicular to the 2D iron(II) tetracyanonikelate(II) layers.

The methyl groups of **2** and **3** are disordered due to the symmetry operation of the space group. The coordination polymer of **2** and **3** has location disorder concerning the methyl groups. Four kinds of iron(II) atoms probably exist in the polymer structure of **2** and **3** in the same way as in Fe(3-chloropyridine)$_2$Ni(CN)$_4$. [12] These disorder may link to the difficulties in obatining their good single crystals. The disorder concerning **3** may be associated with the behavior of the spin crossover : on cooling about half of the high spin iron(II) fraction in **3** still remain in almost the same way as in Fe(3-chloropyridine)$_2$Ni(CN)$_4$[12], which is diffrent from that of **1**.[14]

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