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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

^{57}Fe Mössbauer Spectra and Crystal Structure of Hofmann-type Thiophene Clathrate, $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$

Takafumi Kitazawa^a, Yuji Gomi^a, Masashi Takahashi^a & Masuo Takeda^a

^a Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba, 274, Japan

Version of record first published: 04 Oct 2006

To cite this article: Takafumi Kitazawa, Yuji Gomi, Masashi Takahashi & Masuo Takeda (1998): ^{57}Fe Mössbauer Spectra and Crystal Structure of Hofmann-type Thiophene Clathrate, $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 167-172

To link to this article: <http://dx.doi.org/10.1080/10587259808042383>

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⁵⁷Fe Mössbauer Spectra and Crystal Structure of Hofmann-type Thiophene Clathrate, Fe(NH₃)₂Ni(CN)₄·2C₄H₄S

TAKAFUMI KITAZAWA, YUJI GOMI, MASASHI TAKAHASHI,
and MASUO TAKEDA
Department of Chemistry, Faculty of Science, Toho University, Funabashi,
Chiba 274, Japan

The crystal structure of Fe(NH₃)₂Ni(CN)₄·2C₄H₄S **3** has been determined by single crystal X-ray determination. The thiophene molecules in the interlayer space display the orientational disorder associated with the location of the S atom. The ⁵⁷Fe Mössbauer spectrum at RT (before cooling to 78 K) indicates one kind of high spin iron(II) site, while that at 78 K shows two kinds, suggesting that the phase transition or the decomposition of the host framework occurs on cooling. There still exist two kinds of sites at RT (after heating from 78 K) probably due to the irreversible phase transition.

Keywords: intercalation; ⁵⁷Fe Mössbauer spectroscopy; cyanides

INTRODUCTION

Considerable progress has been made in the Hofmann-type clathrates and related intercalation compounds.^[1-10] There remains still much to be developed in not only the structural chemistry but also the theoretical studies on the host-guest interactions. We have demonstrated the wide varieties of the 2D coordination polymer compounds based on iron(II) tetracyanonickelate(II).^[3-6] Recently the spin crossover behaviour of the coordination polymer Fe(C₅H₅N)₂Ni(CN)₄ has been reported.^[4] The iron(II) spin state of the Hofmann pyridine complex Fe(C₅H₅N)₂Ni(CN)₄ changes from a paramagnetic state to a diamagnetic state when temperature is lowered, while those of the Hofmann-type benzene and pyrrole clathrates Fe(NH₃)₂Ni(CN)₄·2G (G = C₆H₆ **1**, C₄H₅N **2**) do not.

We have set out to examine the effect on the 2D host framework

$\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ of using thiophene as a guest, whose property, size, shape and symmetry are different from those of the previously reported guest molecules. We report here the ^{57}Fe Mössbauer spectra and the crystal structure of the Hofmann-type thiophene clathrate compound $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$ **3**.

EXPERIMENTAL SECTION

Preparation of $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$ **3**

Crystals of the compound **3** were prepared according to the method applied to $\text{Fe}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$ ($\text{G} = 1,4\text{-dioxane}$).^[3] To a 180 cm^3 aqueous solution of 4.71 g $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and 3.12 g $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$, 15 g of citric acid was added. After the pH of the solution was adjusted to ca. 7.7 with a dilute ammonia, the solution was filtered through a membrane (Milipore $4\text{ }\mu\text{m}$) and covered with thiophene. Yellow plate-like crystals were obtained by standing the flask in a refrigerator at $5\text{ }^\circ\text{C}$ for a few months. The relative amounts of metal constituents were determined by an X-ray fluorescent analysis. The compounds contained nickel and iron atoms in a ratio of 1:1. The elemental analysis for C, H, N was carried out with a Perkin-Elmer Model 2400. Found : C, 34.45; H, 2.67; N, 19.94%; $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$ requires C, 34.24 H, 3.35; N, 19.96%.

X-ray Diffraction Study

A single crystal of dimension $0.25 \times 0.25 \times 0.15\text{ mm}$ was coated with epoxy resin in order to reduce decomposition and evaporation of the guest molecules. The collection of X-ray diffraction intensity data was carried out on a Rigaku AFC-5S automated four-circle diffractometer at 295 K . Crystal data : $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$, $M = 386.86$; tetragonal, $P4/m$ (No. 10), $a = 7.333(4)$, $c = 8.174(6)\text{ \AA}$, $U = 439.6(4)\text{ \AA}^3$, $Z = 1$, $D_m = 1.59(1)$, $D_x = 1.59\text{ g/cm}^3$, $\mu(\text{Mo-K}\alpha) = 21.33\text{ cm}^{-1}$, 630 reflections observed, 550 used; 34 parameters refined: $R = 0.037$, $R_w = 0.034$, goodness of fit (gof) = 2.98. The structure was solved using the TEXSAN^[11] software package installed on the diffractometer system. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not inserted in the refinement.

Mössbauer Measurements

^{57}Fe Mössbauer spectra were obtained by a spectrometer comprising an MVT-1000 velocity transducer, an MDU-1200 driving unit, and an DFG-1200 digital function generator, all from Wissenschaftliche Elektronik GmbH., and an N-5500 multichannel analyzer from EG&G ORTEC. An

1.48 GBq (40 mCi) ⁵⁷Co(Rh) source was obtained from Amersham International plc. The spectra were fitted to Lorentzian curves with a least-squares fitting program. The isomer shifts are referred to the centroid of the Mössbauer spectrum of α -iron at room temperature.

RESULTS AND DISCUSSION

The Crystal structure of $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_5\text{S}$ **3** at RT

The positional parameters refined for **3** are listed in Table I. The structure is illustrated in Figure 1. The space group of **3** is $P4/m$, the same as that of $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_5\text{N}$ **2**,^[6] although that of $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ **1** is $P4/mmm$ due to the two orientations of benzene molecules related by a (100) or (010) mirror plane.^[4] The host framework of **3** is isostructural with those of **1** and **2**. The host framework is built up by 2D-cross network of square-planar tetracyanonickelate(II) and octahedral iron(II) ion. The carbon atoms of the cyanide are coordinated to the nickel ions, the nitrogen atoms to the octahedral iron(II) ions, which also have two trans NH_3 ligands oriented perpendicular to the plane of the host layers. The bond distances of Fe-N1, Fe-N2 and Ni-C1 are 2.170(5), 2.203(8) and 1.869(5) Å respectively. The guest thiophene molecules are located between the host layers. The thiophene molecule appears to be a hexagon ring due to the disorder of the guest molecule. The lattice constants of **3** ($a = 7.333(4)$ Å, $c = 8.174(3)$ Å) are intermediate between those of **1** ($a = 7.353(2)$ Å, $c = 8.316(2)$ Å)^[4] and **2** ($a = 7.299(2)$ Å, $c = 7.941(6)$ Å)^[6]. The variation of the lattice constants are associated with the size of thiophene molecule. The thiophene is smaller than the benzene and larger than the pyrrole. Thermal motions of the guest molecules are other factors to be considered.

Mössbauer Spectra

The ⁵⁷Fe Mössbauer spectra obtained at RT (before cooling to 78 K), 78 K and, RT (after heating from 78 K), are shown in Figure 2. The spectral parameters are given in Table II. The spectrum of RT (before cooling to 78 K) contains one kind of high spin iron(II) site as in $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$ ($\text{G} = \text{C}_6\text{H}_6$ **1**,^[4] $\text{C}_4\text{H}_5\text{N}$ **2**,^[6] $\text{C}_6\text{H}_5\text{NH}_2$ **4**^[5]). Although the values of the isomer shifts for **3** are almost the same as those of **1**, **2** and **4**, the quadrupole splitting values of **3** are different. The quadrupole splitting values are associated with the asymmetry of the coordinating atoms around the iron(II) ions. The measurement at 78 K shows that the compound **3** has two kinds of high spin iron(II) sites. In cases of **1** and **2**, the spectra at 78 K still

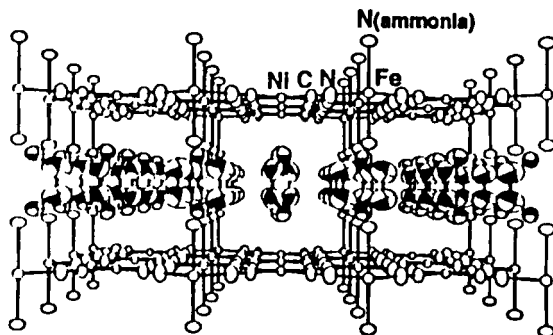


Figure 1. Perspective view of $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}_3$ along the a -axis: the view along the host layers. The guest molecule appears to be a hexagon skeleton due to the disorder of the thiophene.

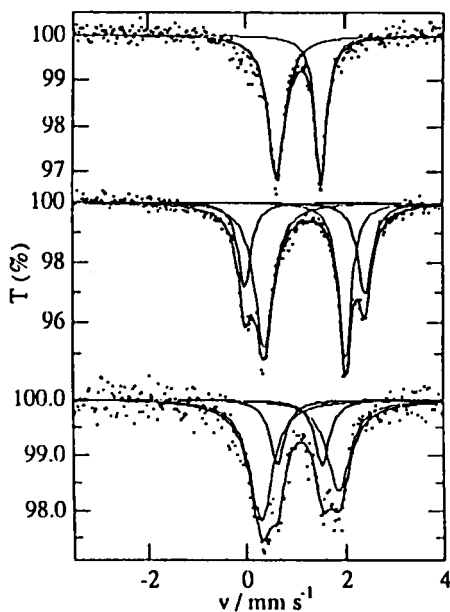


Figure 2. ^{57}Fe Mössbauer spectra for $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}_3$. top: RT (before cooling to 78 K), middle : 78 K, bottom: RT (after heating from 78K)

Table I. The positional parameters for $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$ **3**

atom	x	y	z	B(eq)
Fe	0	0	0	1.78(6)
Ni	0.5	0.5	0	1.58(5)
C1(CN)	0.3190(7)	0.3205(7)	0	2.6(3)
N1(CN)	0.2077(6)	0.2108(8)	0	2.6(3)
N2(NH ₃)	0	0	0.269(1)	3.1(2)
CS1(C ₄ H ₄ S)*	0	0.5	0.349(2)	9.4(6)
CS2(C ₄ H ₄ S)*	0.1626(8)	0.5587(7)	0.4425(7)	8.3(3)

*The atoms of the disordered thiophene molecule were refined by assuming the relevant C and S atoms have 4:1 probability of being C and S. The disordered atoms are denoted as CS and the occupancy is 0.8.

Table II. Mössbauer parameters for $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_4\text{S}$ **3**

Temperature	site	IS (mm/s)	QS (mm/s)	Γ (mm/s)	
RT(before cooling)		1.09	0.89	0.41,	0.28
78K	outer doublet	1.22	2.44	0.31	0.35
	inner doublet	1.20	1.64	0.46	0.31
RT(after cooling)					
	outer doublet	1.09	1.56	0.50	0.47
	inner doublet	1.09	0.89	0.34	0.34
rf. $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ 1 ^[4]					
RT		1.10	0.89		
78K		1.22	1.47		
rf. $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_5\text{N}$ 2 ^[6]					
RT		1.09	1.24		
78K		1.20	2.33		
rf. $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ 4 ^[5]					
RT		1.12	1.44		

possess one kind of high spin iron(II) site. The appearance of the second doublet at 78 K in **3** indicates that the phase transition of the host framework happens on cooling. The temperature-dependent motional effect of the thiophene on the host framework in **3** is greater than those of the benzene in **1** and the pyrrole in **2**. At even RT after heating from 78 K, the two kinds spin iron(II) sites still remain. The difference between two RT measurements suggests the phase transition is irreversible. There is possibility that the some parts of the host framework are decomposed on cooling and the restoring do not occur completely on heating again to RT. The peak area ratio of the outer and inner doublets at 78 K and RT (after heating from 78 K) are 1:2 and 2:1 respectively. Although it is not easy to explain the difference in the ratio, the motions of thiophene may be associated with restoring of host structure. The powder X-ray pattern of **3** at RT(before cooling to 78 K) is consistent with single crystal X-ray determination data, while that at RT(after heating from 78 K) contains additional peaks. These results agree with those of the Mössbauer spectra.

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