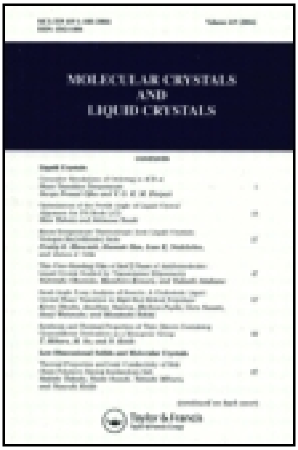

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Crystal Structure and ^{57}Fc Mössbauer Spectra of Hofmann-Type Pyrrole Clathrate, $Fe(NH_3)_2Ni(CN)_4.2C_4H_5N$

Takafumi Kitazawa [a] , Yoshiyuki Sato [a] , Yuji Gomi [a] , Masashi Takahashi [a] & Masuo Takeda [a]
[a] Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba, 274, Japan

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CRYSTAL STRUCTURE AND ^{57}Fe MÖSSBAUER SPECTRA OF HOFMANN-TYPE PYRROLE CLATHRATE, $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$

TAKAFUMI KITAZAWA, YOSHIYUKI SATO, YUJI GOMI,
MASASHI TAKAHASHI AND MASUO TAKEDA

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

ABSTRACT The host framework of $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ **2** is isostructural with those of the other Hofmann-type clathrates. The pyrrole molecules in the interlayer space display the orientation disorder associated with the location of the nitrogen atom. The ^{57}Fe Mössbauer spectra show that the iron atoms are in Fe(II) high-spin states at both RT and 78 K.

INTRODUCTION

The Hofmann-type clathrates have been developed in not only the structural chemistry but also the theoretical studies on the host-guest interactions.[1-7] The iron(II) intercalation compound $Fe(H_2O)_2Ni(CN)_4 \cdot 2G$ (G = 1,4-dioxane) was recently characterized by ^{57}Fe Mössbauer spectroscopy and X-ray crystallography.[2] More recently, the spin-crossover behaviour of the coordination polymer $Fe(C_5H_5N)_2Ni(CN)_4$ has been found by ^{57}Fe Mössbauer spectra and the magnetic data obtained by the SQUID technique.[3] The iron(II) spin state of the Hofmann pyridine complex $Fe(C_5H_5N)_2Ni(CN)_4$ changes from a paramagnetic state to a diamagnetic state when temperature is lowered, while that of the Hofmann-type benzene clathrate $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ **1** does not. The magnetic susceptibilities of $M(NH_3)_2Ni(CN)_4 \cdot 2G$, where M has octahedral coordination, indicate that the square-planar Ni(II) is in the diamagnetic state.[8,9] Although the X-ray single crystal data for the Hofmann-type benzene clathretes $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ are available, those of Hofmann-type pyrrole clathrate $M(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ have not been obtained.[1] For the pyrrole molecule, the X-ray single crystal data of $Cd(en)Ni(CN)_4 \cdot 2C_4H_5N$ were reported.[10]

We have now examined the effect on the two-dimensional host $Fe(NH_3)_2Ni(CN)_4$ of using pyrrole as guest, whose property, size, shape and symmetry are different from those of the benzene molecule. The pyrrole molecule contains a basic heteroatom, which may influence on the host framework.[6,7] We report here the crystal structure and the ^{57}Fe Mössbauer spectra of the Hofmann-type pyrrole clathrate $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ **2**.

EXPERIMENTAL SECTION

Preparation of $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ 2

While Iwamoto and coworkers prepared the powdered crystals of $Fe(NH_3)_2Ni(CN)_4 \cdot 2G$ (G= C_6H_6, $C_6H_5NH_2$) in a nitrogen stream,[9] the preparation was made in a similar manner to that of $Fe(H_2O)_2Ni(CN)_4 \cdot 2G$ (G = 1,4-dioxane).[2] To a 180 cm^3 aqueous solution of 4.71 g $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and 3.12 g $K_2[Ni(CN)_4] \cdot H_2O$, 15 g of citric acid was added. After the pH was adjusted at ca. 8.0 with ammonia, the solution was filtered through a membrane (Milipore 4 μm) and covered with pyrrole in mesitylene. Yellow plate-like crystals were obtained at room temperature after a few weeks. 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 almost 1:1. (Iron atoms were slightly more than nickel atoms.) The elemental analysis for C, H, N was carried out with a Perkin-Elmer Model 2400. Found : C, 37.2; H, 3.5; N, 27.7%; $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ requires C, 37.3; H, 4.2; N, 28.9%. The differences in elemental analysis appear to be due to the release of guest molecules at room temperature and the minor component found by ^{57}Fe Mössbauer spectra. Although the formation of the three aniline clathrate materials depends on the pH of the mother aqueous solution,[11] water ligand clathrate $Fe(H_2O)_2Ni(CN)_4 \cdot 2C_4H_5N$ has not been obtained yet probably since the pyrrole is less polar than the aniline. The color of the products in the solution changed from yellow to black for several months maybe as polypyrrole would be produced in the hostframework.[12]

X-ray Diffraction Study A single crystal of dimension 0.45 x 0.45 x 0.15 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. Crystal data : $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$, M = 386.86; tetragonal, $P4/m$ (No. 10), a = 7.299(2), c= 7.941(6) Å, U = 423.0(4) Å^3 , Z = 1, D_m = 1.51(1), D_x = 1.52 g/cm^3, μ(Mo-Kα) = 19.83 cm^{-1} , 612 reflections observed, 339 used; 34 parameters refined: R = 0.034, Rw = 0.038, goodness of fit (gof) = 2.98. The structure was solved using the TEXSAN[13] software package including ORTEP[14] 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 obtiained by a spectrometer comprising an MVT-1000 velocity transducer, an MDU-1200 driving unit, and an DEG-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) ^{57}Co(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. The powdered crystals from the same batch for the X-ray determination were used for Mössbauer measurement.

RESULTS AND DISCUSSION

The Crystal structure of $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ 2

The positional parameters refined for **2** are listed in Table I. The structures are illustrated in Figures 1 and 2. The space group of **2** is *P*4/m, although that of $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$ **1** is *P*4/mmm due to the two orientations of benzene molecules related by a (100) or (010) mirror plane.[3] The host framework of **2** is isostructural with that of **1**. The both host frameworks possess the *P*4/mmm symmetry. The host layers are based on 2D-cross network of square-planar nickel(II) and octahedral iron(II) ions linked by cyanide ligands. The distance between Fe and Ni atoms is 5.161(2) Å. The carbon atoms of the cyanide are bound to the nickel ions, the nitrogen atoms to the six-coordinate iron 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 2.159(6), 2.182(9) and 1.873(7) Å. The guest pyrrole molecules are located between the host layers. The lattice constants of **2** (a = 7.299(2) Å, c =7.941(6)Å) are shorter than those of **1** (a = 7.353(2)Å, c = 8.316(2) Å)[3]. The decrease of the lattice constants are associated with the size of pyrrole molecule. The pyrrole is smaller than the benzene. The pyrrole aromatic plane is inclined by an angle of 68° with respect to the (100) or (010) plane (Figure 2), while an inclination angle of $Cd(en)Ni(CN)_4{\cdot}2C_4H_5N$ is 90°.[10] The pyrrole molecules of **2** have the orientational disorder with the nitrogen atom pointing upward and downward as the same in $Cd(en)Ni(CN)_4{\cdot}2C_4H_5N$. The N3 of the pyrrole is located at position with the 2.. site symmtry with the 0.5 occupancy. The unusually short distances (N3-C3, 1.17(1); C3-C3, 1.29(2) Å) and the considerably large temperature factors are related to the disorder of the pyrrole molecules. There remains the possibility of locating the nitrogen atom on the position of C3. The reorientaional motions of pyrrole are observed in the other pyrrole clathare $Cd(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ by wide-line ^{1}H NMR.[15] Spectroscopic methods will be helpful to investigate the dynamic behavior of the pyrrole molecules in **2**.[16]

Mössbauer Spectra The ^{57}Fe Mössbauer spectra obtained at room temperature and 78 K are shown in Figure 3. Each spectrum is not able to be fitted by assuming only one site but two sites. The spectral parameters are given in Table II. The peak area ratios of the major component and the minor component are 8:1 (RT) and 30:1(78 K). The major component is attributed to $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ **2**. The Mössbauer spectra at RT and 78 K for **2**

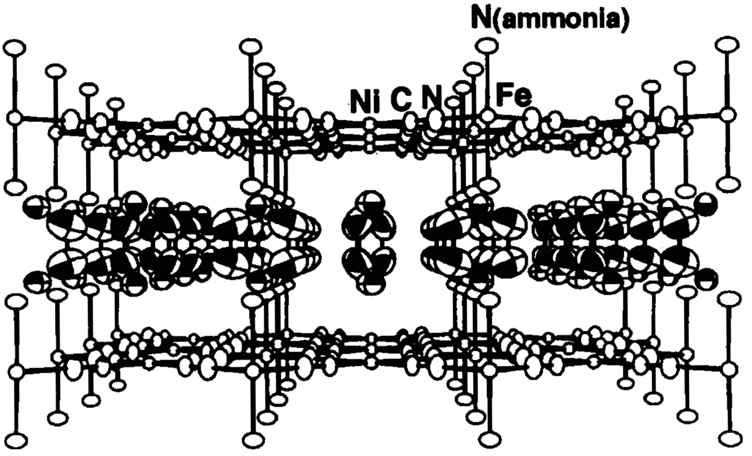

Figure 1. Perspective view of $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ **2** along the *a*-axis: the view along the host layers. The guest pyrrole molecules are disordered.

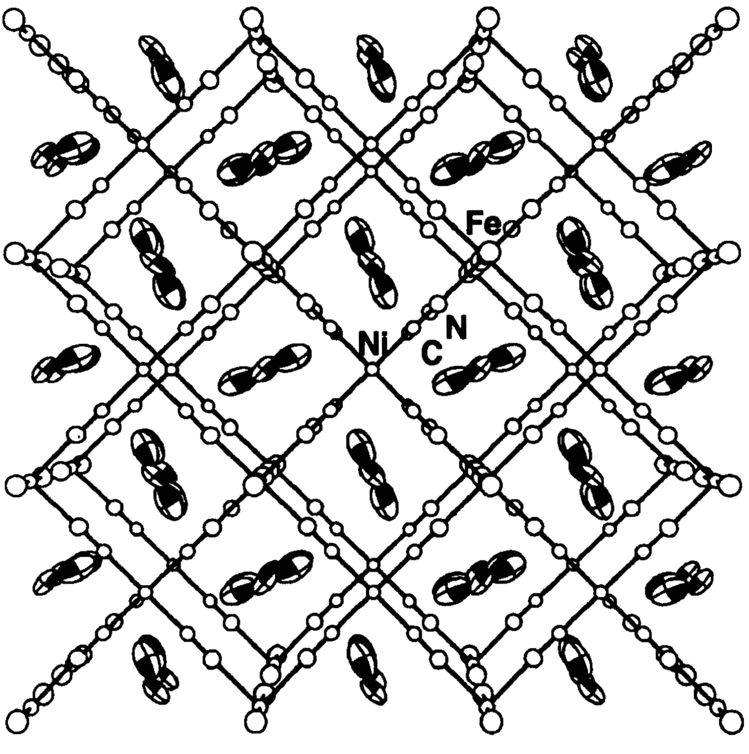

Figure 2. Perspective view of $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ **2** along the *c*-axis: the view normal to the host layers.

Table I. The positional parameters for $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ **2**

atom	x	y	z	B(eq)
Fe	0	0	0	1.71(7)
Ni	0.5	0.5	0	1.45(6)
C1(CN)	0.320(1)	0.3171(9)	0	2.1(3)
N1(CN)	0.2118(8)	0.2065(8)	0	3.0(4)
N2(NH_3)	0	0	0.275(1)	3.0(2)
N3(C_4H_5N)*	0	0.5	0.343(2)	5(1)
C3(C_4H_5N)	0.127(1)	0.446(1)	0.419(1)	9.4(6)

*N3 atom is disordered. The occupancy is 0.5.

Table II. Mössbauer parameters for $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ **2**

component	Temperature	IS (mm/s)	QS (mm/s)	Γ(mm/s)
major	78 K	1.20	2.33	0.30, 0.30
	RT	1.09	1.24	0.26, 0.26
minor	78 K	0.19	0.73	0.22, 0.22
	RT	0.18	0.45	0.52, 0.52

The major component is due to $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ **2**.

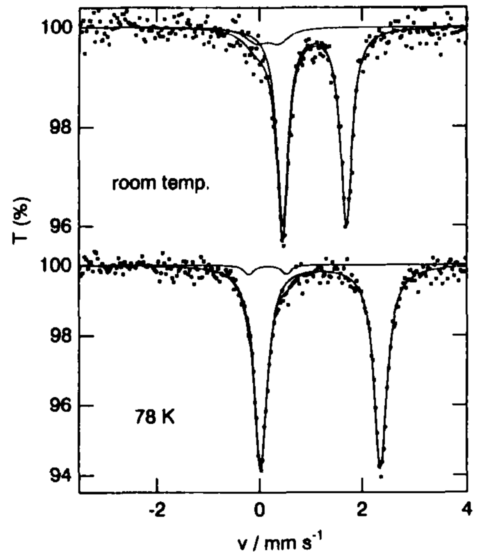

Figure 3. ^{57}Fe Mössbauer spectra for $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_4H_5N$ **2**

indicate that iron(II) atoms are in a high-spin state as in $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$ **1**. It should be noted that the spin state of iron (II) atom in the Hofmann pyridine complex $Fe(C_5H_5N)_2Ni(CN)_4$ changes from high spin to low spin when temperature is lowered.[3] Although the values of the isomer sifts for **2** are almost the same as those of **1** (IS =1.10 mm/s at RT; 1.22 mm/s at 78K), the quardrupole splitting values of **2** are different from those of **1** (QS = 0.89 mm/s at RT; 1.24 mm/s at 78K)[3]. The quardrupole splitting values are associated with the asymmetry of the coordinating atoms around the iron(II) ions.

An unambiguous assignment for the minor component cannot be given, as iron(II) low spin and iron (III) high spin are not distinguished from those Mössbauer parameters. The one possibility is that iron(III) high spin materials would be produced by an air oxidation during the preparation or powdering process before the Mössbauer measurement. The other possibility is that the square-planar $[Ni(CN)_4]^{2-}$ moiety would be replaced with the octahedral $[Fe(NH_3)_2(CN)_4]^{2-}$ moiety.

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