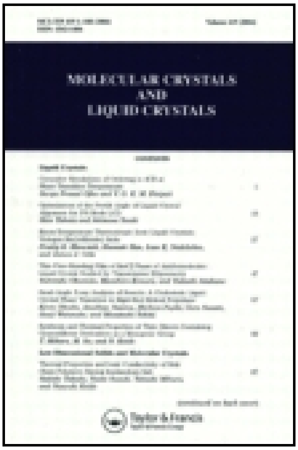

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Study By X-Ray Crystallography And Mössbauer Spectroscopy of The Layered Compounds with Two-Dimensional Metal Complex Iron(II) Tetracyanonic Kelate(II)

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STUDY BY X-RAY CRYSTALLOGRAPHY AND MÖSSBAUER SPECTROSCOPY OF THE LAYERED COMPOUNDS WITH TWO-DIMENSIONAL METAL COMPLEX IRON(II) TETRACYANONICKELATE(II)

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ABSTRACT A new layered compound, $Fe(H_2O)_2Ni(CN)_4{\cdot}2G$ (G=1,4-dioxane) has been characterized by single crystal X-ray analysis and ^{57}Fe Mössbauer spectroscopy. The host layer comprises a close-2D network of $[FeNi(CN)_4]_\infty$, from which a pair of water ligands protrude above and below the layer at Fe(II). The guest molecules, 1,4-dioxane, are accommodated in the interlayer space. The ^{57}Fe Mössbauer parameters indicate the iron atoms are in Fe(II) high-spin states. The X-ray and Mössbauer data imply the Fe(II) atom is surrounded by four N atoms of bridged cyano groups and two O atoms of water.

INTRODUCTION

Due to the bridging properties of cyano group the polynuclear transition metal cyanides build up versatile structures; infinite one, two, or three-dimensional framework structures have been found. For example, in Prussian Blue the cyano group acts as a bridging ligand to link the two structurally distinct octahedral iron ions. The sequence Fe(III)-N-C-Fe(II) is an essential unit built up of the infinite three dimensional framework structure.[1] X-ray diffraction has difficulties in assigning the carbon and nitrogen atoms of the bridging cyano groups. The orientation of cyano groups has been unambiguously established mainly by ^{57}Fe Mössbauer spectroscopy.[2,3] ^{57}Fe Mössbauer spectroscopy is useful for getting correct structural information on the orientation for cyanide in $Ln(III)Fe(III)(CN)_6{\cdot}nH_2O$ systems.[4] A new family of mineralomimetic inclusion structures have been developed, using cadmium cyanide and polycyanopolycadmate systems.[5-8] Disorder in the orientation of the cyanide group has been found by solid state ^{113}Cd NMR spectroscopy in $Cd(CN)_2$ host-guest materials.[9]

Although numerous investigations were carried out with the Hofmann-type and related compounds,[7,10-15] fundamental knowledge of the layered compounds with iron(II) tetracyanonickelate(II) is relatively sparse. Thus we prepared a new clathrate compound $Fe(H_2O)_2Ni(CN)_4 \cdot 2C_4H_8O_2$ to extend the Fe(II)-Ni(II) polycyanide systems and carried out single crystal X-ray determination. We also measured ^{57}Fe Mössbauer spectra to obtain the structural information on the orientation of the cyano group.

EXPERIMENTAL SECTION

Preparation Although Iwamoto *et al.* prepared iron(II) tetracyanonickelate(II) benzene clathrate $Fe(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ in a nitrogen stream in order to avoid the air oxidation of Fe^{2+} ions,[15] we obtained single crystals of the new 1,4-dioxane clathrate in the ambient atmosphere by a method similar to that for the cadmium(II) tetracyanonickelate(II) layered compounds.[13,14] Into 60 mL of water 1.57 g of Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_20$ and 1.04 g of $K_2[Ni(CN)_4] \cdot H_2O$ were added to form a precipitate immediately. This was dissolved by adjusting to pH ca. 5.7 with 5.00 g of citric acid and 1,3-diaminopropane. Good single crystals were obtained by vapor diffusion method using a 1:15 (v/v) 1,4-dioxane-water mixture as a source of the guest molecules. 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, 33.36; H, 4.50; N, 13.11%; $Fe(H_2O)_2Ni(CN)_4 \cdot 2C_4H_80_2$ requires C, 33.45; H, 4.68; N, 13.00%.

X-ray Diffraction Study A single crystal of dimension 0.20 x 0.20 x 0.05 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: $Fe(H_2O)_2Ni(CN)_4 \cdot 2C_4H_8O_2$, M = 430.85; monoclinic, *P*2/m (No. 10), a = 7.222(1), b= 7.470(1), c= 8.008(2) Å, β = 94.11(1)°, U = 430.9(2) Å^3, Z = 1, Dm = 1.65(1), Dx = 1.66 g/cm^3, μ(Mo-Kα) = 19.73

cm^{-1}, 1161 reflections observed, 560 used; 63 parameters refined: R = 0.101, Rw = 0.113, goodness of fit (gof) = 5.85. The structure was solved using the TEXSAN[16] software package including ORTEP[17] installed on the diffractometer system. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not inserted in the refinement. After the refinement of the host framework, difference map indicated that the 1,4-dioxane molecules displayed positional disorder due to a thermal motion and a pseudosymmetry of the structure. Although the crystals whose c dimension of unit cell were two and six times (16.006(2), 48.00(2)Å) were found by single crystal X-ray method, the structural features of the host framework were common to all structures. This fact would be resulted from the different mode of the orientation of the guest molecules.[18]

Mössbauer measurements ^{57}Fe Mössbauer spectra were measured by using 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 powdered crystals from the same batch for the X-ray determination were used for Mössbauer measurement. The spectra obtained 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

X-ray Diffraction Study The structure is illustrated in Figures 1 and 2. The atomic parameters and selected bond distances and angles are listed in Tables 1 and 2. The X-ray crystal structure shows that it is built of the two-dimensionally extended iron(II) tetracyanonikelate(II) sheets(close-2D network[7]), from which the water ligands protrude above and below the layer at iron(II). The iron atom thus exhibits six-coordination with four nitrogen of cyano groups and two oxygen of water. The assignment of the carbon and nitrogen ends of cyano group are based on chemical principles, the behavior of the thermal parameters and contact distances.

While crystals of $Cd(NH_3)_2Ni(CN)_4{\cdot}2G$ (G=C_6H_6,[19] $C_4H_8O_2$ [20]) crystallize in the tetragonal space group *P*4/m, the present inclusion compound is monoclinic and space group *P*2/m. There are two kinds of cavities which accommodate 1,4-dioxane between the host layers. The conformation of 1,4-dioxane is chair-like rather than boat-like form. The X-ray results indicate that one of the two crystallographically different 1,4-dioxane has hydrogen bonds to the water ligands of the host.

Mössbauer Spectra The Mössbauer spectra measured at room temperature and 80 K are shown in Figure 3. The Mössbauer spectrum cannot be fitted by assuming only one component but two sites: i.e., site A (major component) and site B (minor component), whose peak area ratios are 10:1 (RT) and 14:1 (80 K). The Mössbauer parameters for the site A are isomer shift, δ = 1.16 mm s^{-1};quadrupole splitting, Δ = 2.56 mm s^{-1} at RT and δ =1.28 mm s^{-1}, Δ = 3.30 mm s^{-1} at 80 K. The site A is attributed to the one in $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$. The values of isomer sifts indicate the iron atoms in $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$ are in iron(II) high-spin states and the cyano groups are coordinated to iron(II) atom by nitrogen atoms. If the cyano carbon atoms are coordinated to iron(II) atoms, iron(II) atoms would be in low-spin states. The assignment of orientation for cyanide by Mössbauer spectra is consistent with the results of the X-ray determination. The quadrupole splitting value at RT is larger than that of $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$ (Δ=0.95 mm s^{-1} at RT)[21], suggesting the symmetry of the 3d electron distribution of the Fe^{2+} ion is lower in $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$. This is quite reasonable because coordination sphere for $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$ and $Fe(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$ are FeN_4O_2 and FeN_6 respectively.

The Mössbauer parameters for the site B are δ = 0.23 mm s^{-1}, Δ = 0.29 mm s^{-1} at RT and δ = 0.32 mm s^{-1}, Δ = 0.44 mm s^{-1} at 80 K. Since iron(II) low spin and iron(III) high spin are not distinguished from those Mössbauer parameters, we cannot give an unambiguous assignment. Two considerations may be reported. The one possibility is due to iron(III) high spin species which would be produced by an air oxidation during the synthesis or powdering process before the Mössbauer measurement. The other is formation of iron(II) low spin species which might be resulted from a disorder introduced by replacing the $Ni(CN)_4$ moieties by $Fe(CN)_4(H_2O)_2$ moieties, where the carbon atoms of cyano groups are coordinated to the introduced Fe^{2+} atoms. Since an X-ray fluorescent analysis suggests the relative amount of iron is slightly larger than that of nickel, such an replacement might occur. The further details should be investigated in order to solve the above problem, although we have not yet explored this.

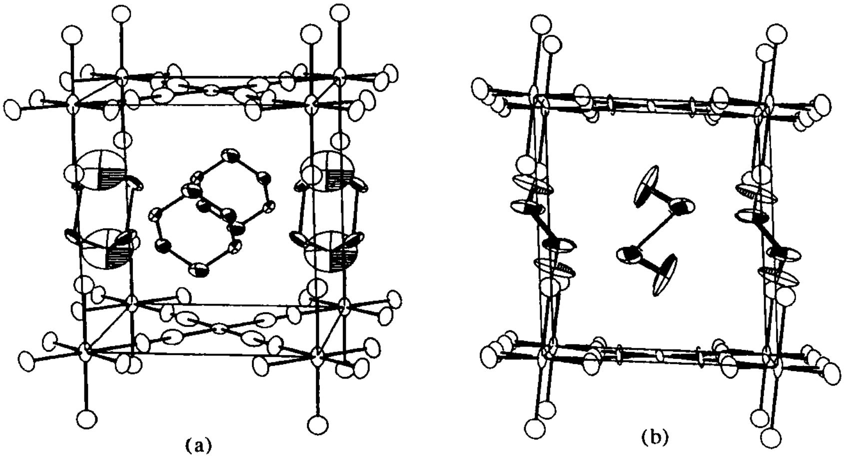

Figure 1. A view of $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$ along the layered host. The unit cell is outlined. Anisotropic sections are shown for the guest molecules. (a) a view along approximately the a axis. (b) a view along approximately the b axis.

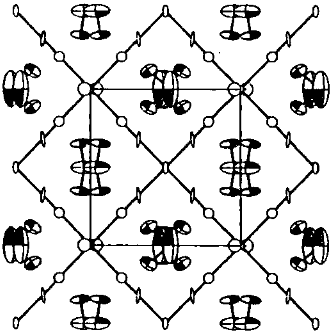

Figure 2. A view of $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$ normal to the layered host.

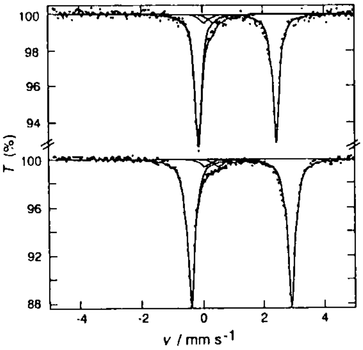

Figure 3. Mössbauer spectra for $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$ at room temprature(top) and 80 K(bottom)

Table 1. Atomic parameters and isotropic temperature factors for $Fe(H_2O)_2Ni(CN)_4{\cdot}2C_4H_8O_2$

atom	x	y	z	B(eq)
host				
Ni	0.5	0.5	0	1.5(3)
Fe	0	0	0	1.8(4)
N	0.211(2)	0.209(2)	-0.005(2)	2(1)
C(1)	0.319(3)	0.321(4)	-0.001(3)	2.4(8)
O(1)	0.040(2)	0	0.269(2)	3.1(8)
guest				
C(2)	0.067(3)	0.346(2)	0.427(2)	3.7(9)
O(2)	0.041(5)	0.5	0.334(3)	7(1)
C(3)	0.387(3)	0.117(3)	0.403(2)	3.6(8)
O(3)	0.533(4)	0	0.327(5)	14(3)

Table 2.
Selected bond distances (Å) and angles (°)

Ni	-	C(1)	1.87(2)
Fe	-	N	2.18(2)
Fe	-	O(1)	2.15(2)
C(1)	-	N	1.15(2)

C(1)	Ni	C(1')	91(1)
C(1)	Ni	C(1")	89(1)
O(1)	Fe	N	91.5(6)
O(1)	Fe	N'	88.5(6)
N	Fe	N'	88.8(8)
N	Fe	N"	91.2(8)
Fe	N	C(1)	177(1)
Ni	C(1)	N	178(2)

CONCLUSIONS

Now we are successful in preparing a novel clathrate $Fe(H_2O)_2Ni(CN)_4 \cdot 2C_4H_8O_2$. The host layer is constructed of a close-2D network of $[FeNi(CN)_4]_\infty$, from which a pair of water ligands coordinated to iron(II) protrude above and below the layer. The guest species of 1,4-dioxane intercalate the interlayer space. Diffraction technique depends on lattice symmetry, and hence, long range order, space averaging is inherent in this technique. ^{57}Fe Mössbauer spectroscopy can provide valuable information about the short range environment around the iron site. The X-ray diffraction and ^{57}Fe Mössbauer data imply the iron(II) atom is surrounded by four N-terminals of cyanide and two O atoms of water.

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