

Mössbauer Spectroscopic Study on Hofmann-like Coordination Polymer $\text{Fe}(4\text{-Clpy})_2[\text{Ni}(\text{CN})_4]$

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THIS PAPER IS DEDICATED TO DR. SVETOZAR MUSIĆ ON THE OCCASION OF HIS 70TH BIRTHDAY

Abstract: ⁵⁷Fe Mössbauer spectroscopic results on the 2D Hofmann-like coordination polymer $\text{Fe}(4\text{-Clpy})_2\text{Ni}(\text{CN})_4$ (sample **1**) indicate that iron(II) ions are in a high spin state both at R.T. and $T = 80$ K, showing that the compound exhibits no spin crossover (SCO) behavior. Mössbauer spectra at R.T. and $T = 80$ K show one major doublet which corresponds to the HS1 is due to high spin iron(II) sites coordinated by four N atoms of cyano groups and two N atoms of 4-Clpy ligand in the sample **1**. Two minor doublets coexisted in sample **1**. One minor doublet with a large quadrupole splitting can be explained by the presence of defects in the coordination polymer frameworks. Another minor doublet is with a small quadrupole splitting, indicating the presence of iron(III) high spin species or iron(II) low spin species.

Keywords: ⁵⁷Fe Mössbauer spectroscopy, coordination polymer, high spin state.

INTRODUCTION

SPIN state switching behavior in iron(II) coordination polymer compounds have become most attractive in recent years and are extensively investigated by chemists and physicists.^[1] Special attention is currently much paid to Hofmann-like coordination polymer iron(II) spin crossover (SCO) compounds such as $\text{FeL}_2\text{M}(\text{CN})_4$ (L = monodentate pyridine derivatives, M = Ni^{II}, Pd^{II}, Pt^{II}) and $\text{FeLM}(\text{CN})_4$ (L = bridging pyridine and bi-pyridine derivatives, M = Ni^{II}, Pd^{II}, Pt^{II}) acting cooperative behavior due to sensory and memory functions.^[2–46] Some Hofmann-like coordination polymer compound are SCO compounds, however others are not due to properties of pyridine derivatives and environments of octahedral iron(II) ions. ⁵⁷Fe Mossbauer spectroscopy is a very powerful tool for investigations on iron(II) SCO compounds and related materials whose spin states are high spin states under all temperature ranges. Recently ⁵⁷Fe Mössbauer spectroscopy has provided very powerful information on re-appearance of cooperativity in ultra-small spin crossover Hofmann-type $\text{Fe}(\text{pz})[\text{Ni}(\text{CN})_4]$ nanoparticles.^[2] ⁵⁷Fe Mössbauer spectroscopy and SQUID

technique in 1996 revealed that the original Hofmann pyridine coordination polymer $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ shows iron(II) SCO with one step transition containing hysteresis.^[7] It should be noted that iron(II) ions in the Hofmann-type clathrate $\text{Fe}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ are in high spin states at R.T. and $T = 78$ K, showing the clathrate exhibits no SCO behavior.^[7] Details of history about Hofmann-type and Hofmann-related compounds before the discovery of SCO $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ were reviewed by Iwamoto.^[8,9]

A brief history after the discovery of SCO $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ is listed in Table 1. Pressure tuning Raman spectroscopy of the prototype compound $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ has been reported, indicating the pressure induced SCO behavior.^[10] Emission Mössbauer spectroscopic study on ⁵⁷Co-labelled analogous $\text{Co}(\text{py})_2\text{Ni}(\text{CN})_4$ demonstrates the nuclear-decay-induced excited spin state trapping (NIESST), indicating NIESST is also important in Hofmann-type compounds.^[11] Recently the investigation for the prototype $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ using temperature-dependent EXAFS has been carried out.^[12] The effects on the SCO behaviors of Cl and CH₃ replacements located at different positions on the

Table 1. Brief History of Hofmann-like Spin Crossover (SCO) Coordination Polymers.

1996	2D Hofmann-like SCO $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$ was found. ^[7]
1997	Nuclear decay Induced Excited Spin State Trapping (NIESST) effect in $\text{Co}(\text{py})_2\text{Ni}(\text{CN})_4$ was found. ^[11]
1999	2D Hofmann-like SCO $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ was found. ^[13]
2001	3D Hofmann-like SCO $\text{Fe}(\text{pz})\text{M}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ (M = Ni, Pd, Pt) were found. ^[42]
2002	$\text{Fe}(\text{II})\text{-}[\text{Ag}(\text{CN})_2]^-$ SCO system was found. ^[43]
2003	$\text{Fe}(\text{II})\text{-}[\text{Au}(\text{CN})_2]^-$ SCO system was found. ^[44]
2003	$\text{Fe}(\text{II})\text{-}[\text{Cu}(\text{CN})_2]^-$ SCO system was found. ^[45]
2007	2D SCO $\text{Fe}(\text{py})_2[\text{Ag}(\text{CN})_2]$ was found. ^[32]
2008	2D SCO $\text{Fe}(\text{py})_2[\text{Au}(\text{CN})_2]$ was found. ^[46]
2009	Guest-dependent 3D Hofmann-like SCO $\text{Fe}(\text{pz})\text{M}(\text{CN})_4\text{G}$ (M = Ni, Pd, Pt) were found. ^[23,24]

pyridine ring were also found.^[13,14] ^{57}Fe Mössbauer spectroscopic study of the SCO polymer complex, $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ was reported with the SQUID data.^[13] Due to the physical and chemical properties of 2D and 3D frameworks, the related Hofmann-like SCO coordination polymer compounds have been developed extensively.^[15–46] Some of them contain 3D pillared Hofmann-type-organic frameworks with guest molecules associated with SCO behaviors.^[22–28,41] Recently an interconversion of nuclear-spin isomers for hydrogen molecule H_2 adsorbed in a Hofmann-type porous coordination polymers (PCPs), by the temperature dependence of Raman spectra has been reported.^[33]

Three types of 2D coordination polymer iron(II) spin crossover complexes containing 3,5-lutidine as ligands and guest molecules were reported with a general formula $\text{Fe}(\text{3,5-lutidine})_2\text{Ni}(\text{CN})_4 \cdot n(\text{H}_2\text{O})m(\text{3,5-lutidine})$.^[15,16] Hofmann-like spin crossover coordination compound $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ with thermal-, pressure- and light-induced SCO behaviors were described in details.^[17,18] Recently Mössbauer spectroscopic study on $\text{Fe}(\text{3-Clpy})_2\text{Pd}(\text{CN})_4$ has been reported.^[47]

We report here ^{57}Fe Mössbauer spectroscopic study on the new coordination polymer $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ (sample **1**), which showed that this compound exhibits no SCO down to at least $T = 80$ K. Mössbauer spectra at R.T. and $T = 80$ K show one major doublet which correspond to the site1, which is a iron(II) high spin state, and two minor doublets with a large and a small quadrupole splitting, the site 2 and the site 3. In the site 1, iron(II) ions are coordinated by four N atoms of cyano groups and two N atoms of 4-Clpy ligand. The minor site 2 with the large quadrupole splitting is due to the presence of defects in the coordination polymer frameworks. The other minor site 3 with the small quadrupole splitting is probably due to the presence of iron(III) high spin states or iron(II) low spin states.

EXPERIMENTAL

We prepared the 2D coordination polymer $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ sample **1** in the ambient atmosphere by a method similar to that for the prototype $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$. 2.10 g (8.11 mmol) of $\text{K}_2[\text{Ni}(\text{CN})_4]$ were added into 120 ml of water. To the water solution, 3.15 g (8.11 mmol) Mohr's salt ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), and 7.95 g of citric acid were added. Then a light white blue precipitate formed immediately. The precipitate was dissolved by adding 4.0 ml of 1,3-diaminopropane dropwise, adjusting the pH of the solution to 5.2. 4-Cl-pyridine was added to the mixture solution. Pale light yellow solid particles were formed after several days as the sample **1**. The sample **1** was characterized by ^{57}Fe Mössbauer and infrared (IR), X-ray diffraction (XRD) and elemental analysis. The C, H and N elemental analysis for the sample **1** was carried out with a Perkin-Elmer Model 2400 CHNS/O analyser and suggested the formation of $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ (Found C, 37.16; H, 1.24; N, 18.50. Calcd. C, 37.72; H, 1.81; N, 18.86).

^{57}Fe Mössbauer spectra were obtained using WissEl Mössbauer system consisting of MVT-1000, MR-260A, DFG-500 and CMCA-550. The temperature dependence of the spectra in the range of 80–295 K were measured by keeping the sample in a gas-flow type cryostat (Advanced Research System LT-3-100 Helitran System) and the source was kept at room temperature. The temperature of the sample was controlled by a 9620-1 digital temperature controller from Scientific Instruments. A silicon diode was used to measure the temperature. The spectra were computer-fitted using a MossWinn 3.0i software. The values of the isomer shift (δ) are given relative to α -iron foil at room temperature.

IR spectra were recorded on JASCO FT/IR-4100 in Nujol mulls between KBr windows. X-ray powder diffraction studies were performed on a RIGAKU RINT-2500VHF with $\text{Cu K}\alpha$ radiation.

RESULTS AND DISCUSSION

In the present preparation of $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ (sample **1**), citric acid and 1,3-diaminopropane were used to adjust pH of the mother aqueous solution containing $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2[\text{Ni}(\text{CN})_4]$. The precipitation rate of the sample **1** depends on the pH of the mother aqueous solution, and fine particles were precipitated due to the direct contact method. Powder XRD patterns for sample **1** (Figure 1S) are almost similar to those of $\text{Fe}(\text{4-methyl-pyridine})_2\text{Ni}(\text{CN})_4$ which was determined by single crystal X-ray determination.^[38] The proposal structure of sample **1** is shown in Figure 1. The layer consists of a square-meshed network of square-planar Ni(II) ion and octahedral iron(II) ions alternately linked by the bridged

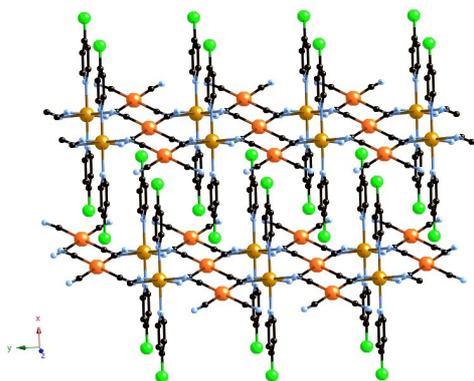


Figure 1. The proposal structure of $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$.

cyno groups. The geometry of iron(II) is accomplished by four N terminals of cyano groups and two N atoms of the 4-Clpy ligands in a trans configuration. The solid state IR for sample **1** was measured at room temperature in Nujol mulls between KBr windows (Figure 2S). The IR vibration from the Ni-CN-Fe sheet structure is due to 2148 cm^{-1} . This strongly suggests that the CN groups acts as bidentate bridging ligands. 1593 cm^{-1} is due to a strong band of the pyridine ring. Considering the analytical studies, the powder XRD patterns and IR spectra of sample **1**, sample **1** contains CN bridged 2D sheet framework structures as shown Figure 1.

^{57}Fe Mössbauer spectra of the sample **1** obtained at $T = 80\text{ K}$ and R.T. are shown in Figure 2. ^{57}Fe Mössbauer parameters for sample **1** are listed in Table 2. Spectra of **1** indicate the sample **1** does not have SCO behavior. As shown in Figure 2, ^{57}Fe Mössbauer spectra of the sample **1** show one major doublet which corresponds to the site 1 (blue lines) and two minor doublets (the site 2 green lines and the site 3 red lines). The site 1 and the site 2 are in iron(II) high spin states. Considering both the Mössbauer parameters and/or the structural data for $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$,^[7,19] $\text{Fe}(\text{3-Cl-py})_2\text{Ni}(\text{CN})_4$,^[13] $\text{Fe}(\text{3-Methyl-py})_2\text{Ni}(\text{CN})_4$,^[14] $\text{Fe}(\text{3-F-py})_2\text{Ni}(\text{CN})_4$ ^[17,20] and other related compounds,^[2,15,16,21,27,31,32,47] the iron(II) ions in the site 1 of the sample **1** have six

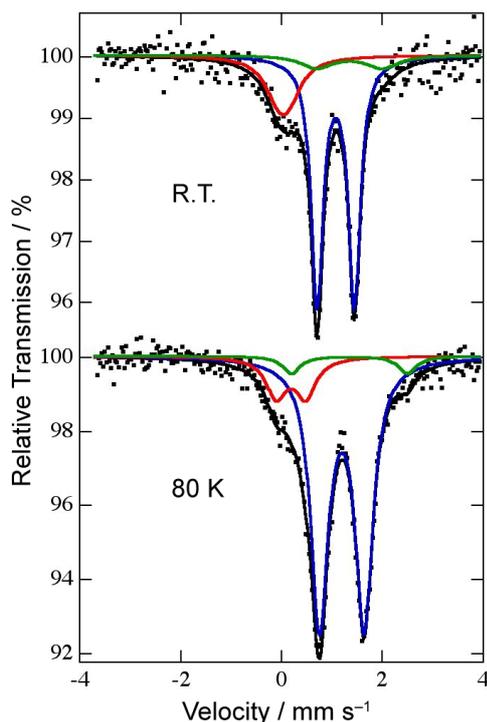


Figure 2. ^{57}Fe Mössbauer spectra of the $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ sample **1** at $T = 80\text{ K}$ and R.T.

coordination with four nitrogen atoms of cyano groups and two nitrogen of 4-Cl-pyridine ligands. The quadrupole splitting of the major site 1 in the sample $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ at R.T. is smaller than that of the sample $\text{Fe}(\text{3-Cl-py})_2\text{Ni}(\text{CN})_4$ at R.T. because the symmetry around iron(II) in $\text{Fe}(\text{4-Cl-py})_2\text{Ni}(\text{CN})_4$ is higher than that in $\text{Fe}(\text{3-Cl-py})_2\text{Ni}(\text{CN})_4$. The position-4 substituents of the pyridine ring have higher symmetry than the position-3 substituents.

The site 2 species in **1** with large quadrupole splitting (ΔE_Q) can be also explained by the presence of defects in the coordination polymer frameworks.^[2] The minor site 2 parameters with a large ΔE_Q value as 1.31 mm s^{-1} at R.T. is also probably due to the $\text{FeN}_5(\text{OH}_2)$ or $\text{FeN}_4(\text{OH}_2)_2$ environment. The FeN_5O core consists of an octahedral iron(II)

Table 2. ^{57}Fe Mössbauer parameters for the sample $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ **1**.

	site	$\delta / \text{mm s}^{-1}$	$\Delta E_Q / \text{mm s}^{-1}$	$\Gamma / \text{mm s}^{-1}$	Area / %
R.T.	site_1	1.076(3)	0.740(8)	0.28(1)	70
	site_2	1.35(16)	1.31(33)	0.75(32)	9
	site_3	0.037(33)	0.22 (17)	0.63(17)	21
80 K	site_1	1.197(3)	0.885(5)	0.419(7)	81
	site_2	1.35(4)	2.30(8)	0.42(14)	5
	site_3	0.19(2)	0.59(4)	0.50(6)	14

atom coordinated by four nitrogen atoms of cyano group, one nitrogen atom of the lutidine and one oxygen atom of the water ligand. The FeN_4O_2 core completes an octahedral iron(II) atom by coordinating two water molecules at the axial position. However, the Mössbauer parameter ΔE_Q values for $\text{Fe}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ which contains the $\text{FeN}_4(\text{OH})_2$ environment ($\delta = 1.16$, $\Delta E_Q = 2.56 \text{ mm s}^{-1}$ at R.T. and $\delta = 1.28$, $\Delta E_Q = 3.30 \text{ mm s}^{-1}$ at $T = 80 \text{ K}$) are larger than those of the site 2.^[36] Taking into account of particle sizes of sample **1**, the site 2 doublet may be ascribed to the iron(II) units located at the nanocrystals edge as they must have coordinative defects, that is, coordinatively unsaturated sites or coordinated terminal water molecules.^[20]

As listed in Table 1, the ratio of the site 1 to the site 2 and the site 3 at R.T. is 70:9:21%, that at $T = 80 \text{ K}$ is 81:5:14, respectively. The recoil-free fraction of the site 1 is different of that of the site 2 and the site 3 due to different octahedral iron(II) environments. The other minor site 3 with a small quadrupole splitting is probably due to iron(III) high spin state species. Iron(III) high spin species would be produced by an air oxidation during the synthesis or treatment process before the Mössbauer measurements. Since iron(III) high spin and iron(II) low spin are distinguished from those Mössbauer parameters, we cannot give an unambiguous assignment. ^{57}Fe Mössbauer spectra of the $\text{Fe}[\text{Ni}(\text{CN})_4] \cdot 2\text{pz}$ (= $\text{Fe}(\text{pz})_2\text{Ni}(\text{CN})_4$) sample which is not a SCO material contain iron(II) low spin state atoms as the minor phase.^[37]

CONCLUSION

This study shows an example of ligand-dependence of SCO behavior in Hofmann-like SCO compounds. Mössbauer study for the sample **1** indicates $\text{Fe}(\text{4-Clpy})_2\text{Ni}(\text{CN})_4$ does not have SCO behavior, while both 3-methyl-pyridine Hofmann complex $\text{Fe}(\text{3-Methyl-py})_2\text{Ni}(\text{CN})_4$ and 3-chloropyridine Hofmann complex $\text{Fe}(\text{3-Clpy})_2\text{Ni}(\text{CN})_4$ show incomplete spin crossover behavior.^[13,14] The $\text{Fe}(\text{4-Methyl-py})_2\text{Ni}(\text{CN})_4$ coordination polymer is not a SCO compound.^[14,38] The position-3 substituent of pyridine ring is associated with SCO behavior, while the position-4 substituents of pyridine ring do not allow SCO behavior. However, Ligand 4-X pyridine (X = Cl, Br, I) dependence in Hofmann-type spin crossover complexes: $\text{Fe}(\text{4-Xpyridine})_2[\text{Au}(\text{CN})_2]_2$ has been reported.^[39] Different properties between $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Au}(\text{CN})_2]^-$ are associated with SCO behaviors in Hofmann-like Coordination polymer systems. Ligand effects on SCO behaviors are different from guest molecule effects.^[40,41]

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Supplementary Information. Supporting information to the paper is enclosed to the electronic version of the article at: <http://dx.doi.org/10.5562/cca2758>.

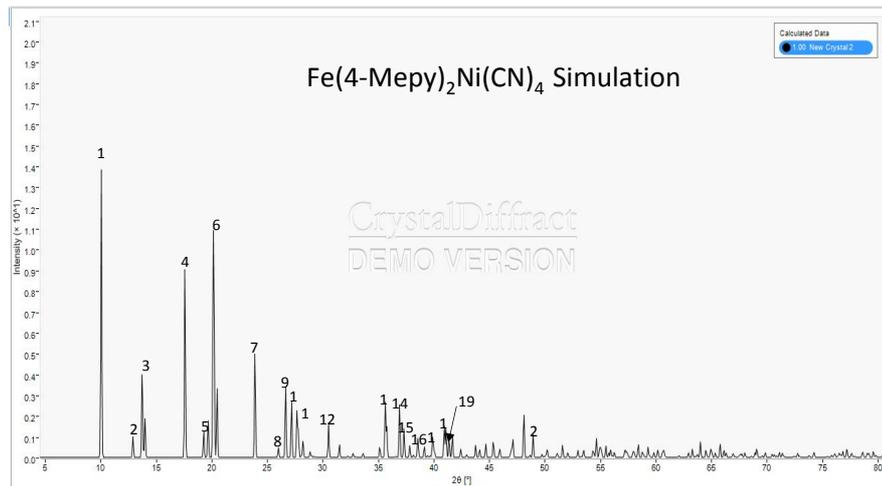
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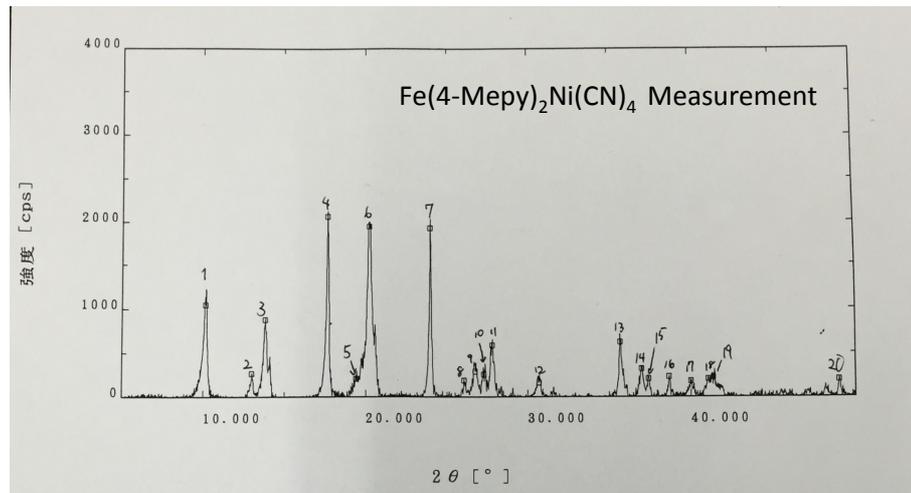
Fe(4-Mepy)₂Ni(CN)₄ Simulation

peak No.	2θ(°)	d Value (Å)
1	10,07	8,775
2	12,92	6,847
3	13,76	6,430
4	17,60	5,034
5	19,29	4,598
6	20,22	4,387
7	23,91	3,718
8	26,01	3,423
9	26,66	3,340
10	27,20	3,276
11	27,69	3,219
12	30,54	2,925
13	35,64	2,517
14	36,93	2,432
15	37,33	2,407
16	38,60	2,330
17	39,90	2,257
18	40,95	2,202
19	41,39	2,179
20	48,95	1,859



Fe(4-Mepy)₂Ni(CN)₄ Measurement

peak No.	2θ(°)	d Value (Å)
1	10,150	8,7077
2	12,980	6,8148
3	13,800	6,4117
4	17,660	5,0180
5	19,410	4,5694
6	20,240	4,3838
7	23,990	3,7064
8	26,070	3,4152
9	26,760	3,3287
10	27,290	3,2652
11	27,800	3,2065
12	30,680	2,9117
13	35,710	2,5123
14	37,020	2,4263
15	37,430	2,4007
16	36,680	2,3259
17	40,000	2,2522
18	41,050	2,1969
19	41,360	2,1812
20	49,020	1,8568



Fe(4-Clpy)₂Ni(CN)₄ Measurement

peak No.	2θ(°)	d Value (Å)
1	9,500	9,3020
2	10,280	8,5979
3	14,380	6,1544
4	20,500	4,4249
5	20,870	4,2529
6	24,160	3,6807
7	26,570	3,3520
8	28,200	3,1619
9	31,170	2,8670
10	38,010	2,3670
11	49,440	1,8420

