



## MÖSSBAUER SPECTROSCOPY, CRYSTAL AND MOLECULAR STRUCTURES OF THE ORGANIC-INORGANIC HYBRID SALT: 1,1'-METHYLENEDIPYRIDINIUM PENTACYANONITROSOFERRATE(II) PENTAHYDRATE

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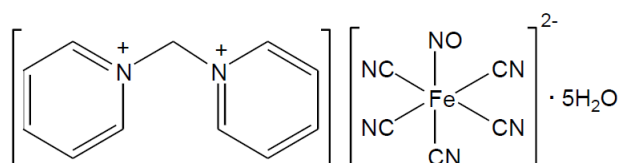
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To complete the characterization of ionic salt  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$ , its molecular and crystal structures were confirmed by powder X-ray diffraction study as well as the Mössbauer spectroscopy investigation was carried out. The molecular structure exhibits the distinctive organic dication  $[(C_5H_5N)_2CH_2]^{2+}$ , inorganic dianion  $[Fe(CN)_5NO]^{2-}$ , and five uncoordinated  $H_2O$  molecules occupying channels in the crystal lattice. The Fe(II) center of  $[Fe(CN)_5NO]^{2-}$  adopts a distorted octahedral geometry being coordinated by five C atoms from CN ligands and one N atom from the nitrosyl group. The Mössbauer spectrum of the complex was acquired at room temperature showing the expected quadruple splitting ( $\Delta Q$ ) and isomer shift ( $\delta$ ). The  $\Delta Q$  and ( $\delta$ ) are larger than their corresponding ones for the structurally related sodium pentacyanonitrosoferrate dihydrate  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ . This noticeable difference of Mössbauer spectra for  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  and  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$  is clearly due to different chemical, electrical and steric effects generated by the dication  $[(C_5H_5N)_2CH_2]^{2+}$  compared to cation  $Na^+$  at the environment of the iron center.



### INTRODUCTION

Designing of new complexes is always a big task facing chemists to support groups in various research domains. Organic-inorganic hybrid salts have currently a considerable interest as novel materials in different research fields such as materials sciences, crystal engineering and optical applications.<sup>1–4</sup> The salts containing  $[Fe(CN)_5NO]^{2-}$  anion have ongoing concern in biological and medical applications; for example the  $Na_2[Fe(CN)_5NO]$  is used as blood-pressure lowering.<sup>5</sup> To the best of our knowledge;

countable organic-inorganic hybrid complexes based on  $[Fe(CN)_5NO]^{2-}$  anion are reported.<sup>6–9</sup> The  $[Fe(CN)_5NO]^{2-}$  anion generates a variety of structures with different metal cations or complex cations for example bis[chloridobis(1,10-phenanthroline)copper(II)] pentacyanonitrosoferrate(II) dimethylformamide monosolvate  $[CuCl(C_{12}H_8N_2)_2][Fe(CN)_5(NO)] \cdot C_3H_7NO$ ,<sup>6</sup>  $\{[Cu((R)\text{-propane-1,2-diamine})_2][Fe(CN)_5(NO)] \cdot H_2O\}_n$ ,<sup>7</sup>  $(tmenH_2)[Fe(CN)_5NO] \cdot 2H_2O$ <sup>8</sup> ( $tmen = N,N,N',N'$ -tetramethylethylenediamine) and tetrabutylammonium pentacyanonitrosoferrate(II) dihydrate,  $[(C_4H_9)_4N]_2[Fe(CN)_5NO] \cdot 2H_2O$ .<sup>9</sup> In our

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previous publication, the synthesis, spectroscopic identifications and the optical nonlinearity investigation of the organic-inorganic ionic compound  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  were reported.<sup>10</sup> As we are interested to complete the characterization of this complex, in this article, we present the Mössbauer spectroscopy analysis, as well as the crystal and molecular structure of the complex  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  determined through powder X-ray diffraction.

## RESULTS AND DISCUSSION

As it is previously mentioned, the synthesis, spectroscopic identification and optical non-linear investigation of the complex (Fig. 1) were reported.<sup>10</sup> To complete the characterization of the complex, the molecular structure and its Mossbauer spectroscopy investigation are carried out.

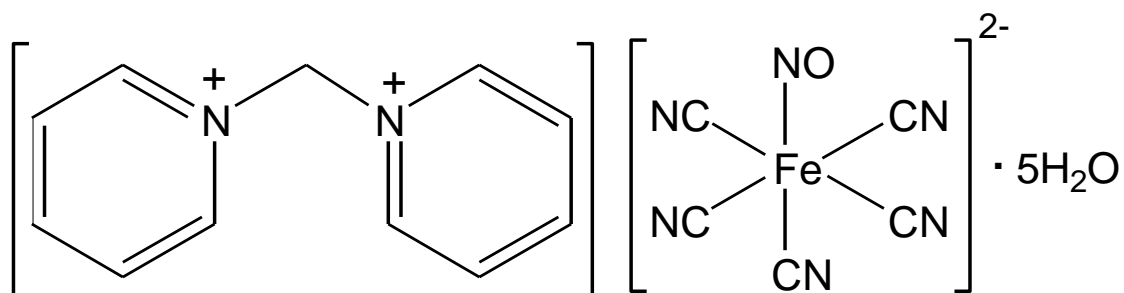


Fig. 1 – Molecular structure of  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  [according to ref. 10].

Although many attempts were performed, no crystals of good quality were obtained; therefore, the crystal and molecular structure are determined by powder X-ray diffraction study. The molecular

structure of the complex shows the distinctive independent organic dication  $[(C_5H_5N)_2CH_2]^{2+}$ , inorganic dianion  $[Fe(CN)_5NO]^{2-}$ , and five uncoordinated  $H_2O$  molecules (Fig. 2).

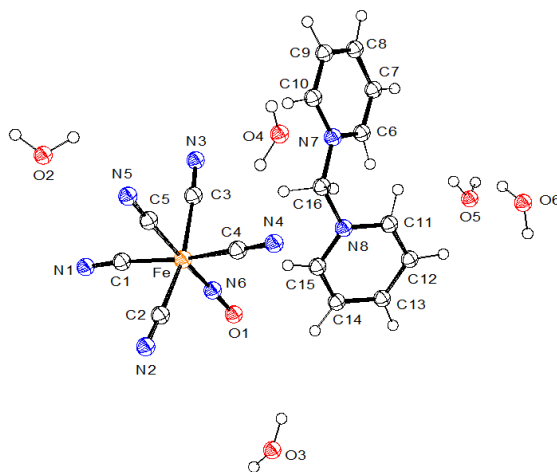


Fig. 2 – The asymmetric unit of crystal structure of  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$ , showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

The Fe(II) center of  $[Fe(CN)_5NO]^{2-}$  has a distorted octahedral geometry being coordinated by five C centers of CN ligands and one N atom of nitrosyl group. The Fe-C bond distances lie in the range 1.90(4)–1.97(4) Å with average Fe-C bond distance of 1.93(6) Å, while the Fe-N and N-O bond lengths are 1.64(2) Å and 1.13(1) Å,

respectively (Table 1). Both values are in their expected ranges, and in agreement with their corresponding ones in the structurally related complexes  $[(tmenH_2)][Fe(CN)_5NO] \cdot H_2O$ <sup>8</sup> and  $M^{II}[Fe(CN)_5NO] \cdot 3H_2O$  ( $M^{II} = Mn$  or  $Cd$ ).<sup>11</sup> The bond Fe-N-O angle is 172.55°, which is almost linear. The supportive indication of the linear

geometry of Fe–NO group was already mentioned by the distinctive FTIR absorption band at 1920.5  $\text{cm}^{-1}$ ,<sup>10</sup> where the relatively high absorption frequency of the nitrosyl group (in the range 1650–1900  $\text{cm}^{-1}$ ) indicates that NO is coordinated to the Fe center in a linear arrangement.<sup>12</sup> The Fe–C–N bond angles are almost linear (the largest

Fe–C–N angle is 179.5(3) $^\circ$  and the smallest angle is 171.6(5) $^\circ$ ) with average C–N bond length of 1.13(8) Å. Both of them lie in their normal ranges and they are comparable to their counterparts in the related complexes  $[(\text{tmenH}_2)][\text{Fe}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$ <sup>8</sup> and  $\text{M}^{\text{II}}[\text{Fe}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mn}$  or  $\text{Cd}$ ).<sup>11</sup>

Table 1

Selected bond lengths (Å) and angles ( $^\circ$ ) for  $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2][\text{Fe}(\text{CN})_5\text{NO}] \cdot 5\text{H}_2\text{O}$ 

Bond	Bond length (Å)	Angle	Bond angle ( $^\circ$ )
Fe—C1	1.93(4)	C1—Fe—C2	88.0(2)
Fe—C2	1.97(1)	C1—Fe—C3	88.8(9)
Fe—C3	1.97(4)	C1—Fe—N6	97.1(5)
Fe—C4	1.93(6)	C2—Fe—C3	164.3(4)
Fe—C5	1.90(4)	C2—Fe—C4	88.8(5)
Fe—N6	1.64(2)	C2—Fe—C5	83.7(0)
C1—N1	1.13(7)	C2—Fe—N6	97.5(1)
C2—N2	1.13(8)	C3—Fe—C4	90.7(6)
C3—N3	1.13(8)	C3—Fe—C5	80.7(6)
C4—N4	1.13(8)	C3—Fe—N6	98.1(1)
C5—N5	1.13(8)	C4—Fe—C5	82.5(6)
N6—O1	1.13(1)	C4—Fe—N6	95.7(4)
		C5—Fe—N6	177.9(1)

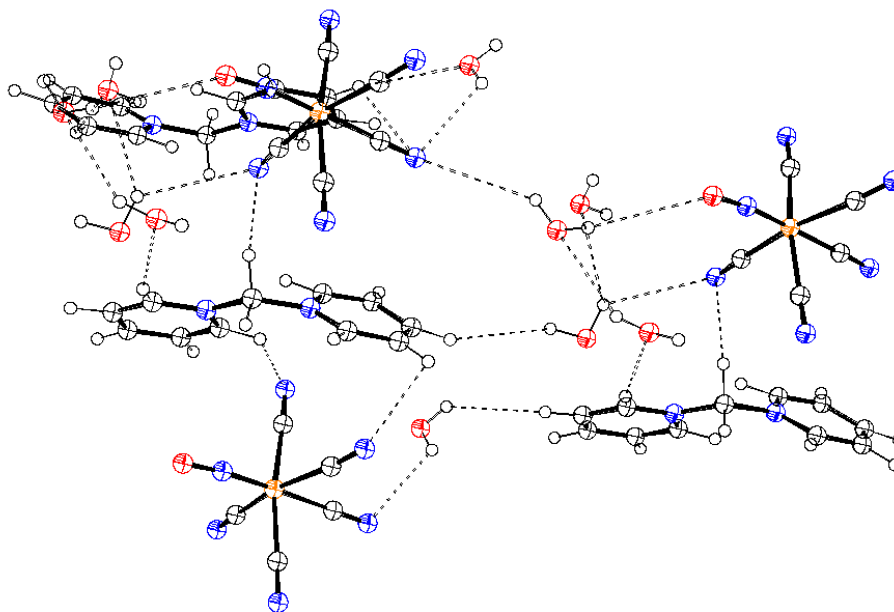


Fig. 3 – Portion of the packing diagram of  $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2][\text{Fe}(\text{CN})_5\text{NO}] \cdot 5\text{H}_2\text{O}$ . Dashed lines indicate hydrogen bonds between water molecules,  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ , and  $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2]^{2+}$ . Symmetry code: (i)  $-x, -y, -z$ ; (ii)  $-x, y + 1/2, -z$ .

In the crystal packing of the complex, five uncoordinated  $\text{H}_2\text{O}$  molecules occupy the channels within the crystal lattice. The water molecules are involved in hydrogen bonding with both nitrile and nitrosyl groups and among each other (C–N $\cdots$ H–O, N–O $\cdots$ H–O, and O–H $\cdots$ O–H). Moreover, weak intermolecular C–H $\cdots$ O and C–H $\cdots$ N

contacts are observed. Those standard and nonstandard hydrogen bonds are linking the dications  $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2]^{2+}$  and dianions  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  to form three dimensional network structure (Fig. 3). These hydrogen bonds are more probably very effective in the stabilization of the crystal packing of the complex (Table 2).

Table 2  
Hydrogen bond distances (Å) and bond angles (°) for the complex

	$d(D-H)$	$d(H\cdots A)$	$d(D\cdots A)$	$Angle(D-H\cdots A)$
O3–H16 $\cdots$ O1	0.934	3.278	4.018	137.80
O2–H14 $\cdots$ N5	0.978	2.551	2.974	106.08
O4–H18 $\cdots$ O3	0.975	2.730	3.485	134.73
O4–H17 $\cdots$ N4	0.982	2.143	2.949	138.20
O6–H12 $\cdots$ O5	1.002	2.794	3.611	139.09
C12–H8 $\cdots$ O5	1.074	2.443	3.235	129.55
C10–H5 $\cdots$ O4	1.092	2.253	3.799	143.22
C15–H10 $\cdots$ O1	0.918	2.107	2.839	135.85
C15–H10 $\cdots$ N6	0.918	2.454	3.333	160.31
C16–H12 $\cdots$ N3	1.095	2.656	3.657	151.85

Symmetry code: (i)  $-x, -y, -z$ ; (ii)  $-x, y + 1/2, -z$ .

The Mössbauer spectrum was fitted to a sum of Lorentzians using WinNormos<sup>13-15</sup> that uses nonlinear optimization with least-squares statistics (a  $\chi^2$ -method). The Mössbauer Spectrum of  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  sample at room temperature is shown in Fig. 4. In this figure, most of the nitroprussides have a well-resolved symmetric quadrupole doublet. The asymmetry that can be caused by the Goldanskii-Karyagin effect (GKE)<sup>16</sup> or oriented texture in the absorber was not observed.

As shown in the figure 4 we found that  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  has a quadrupole splitting ( $\Delta Q$ ) and isomer shift ( $\delta$ ) equal to  $1.890 \pm 0.003 \text{ mm} \cdot \text{s}^{-1}$  and  $-0.370 \pm 0.003 \text{ mm} \cdot \text{s}^{-1}$  (r.t.

$\alpha$ -Fe) respectively, with line width ( $\Gamma$ ) equal to  $0.249 \pm 0.005 \text{ mm} \cdot \text{s}^{-1}$  and  $c^2 = 1.066$ , at room temperature. As in the references;<sup>17-19</sup> it is noticed that the  $\Delta Q$  and  $|\delta|$  are larger than its idem for sodium pentacyanonitrosferrate dihydrate  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$  ( $1.7015, 0.000 \text{ mm} \cdot \text{s}^{-1}$ , respectively) and the line width less than its idem for sodium pentacyanonitrosferrate dihydrate ( $0.28 \text{ mm} \cdot \text{s}^{-1}$ ).<sup>17</sup> This is readily due to the presence of 1,1'-methylenedipyridinium dication, which generates a distinct electrical and chemical environment at the iron center in  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  compared to the environment at the iron centre produced by cations  $Na^+$  in  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ .

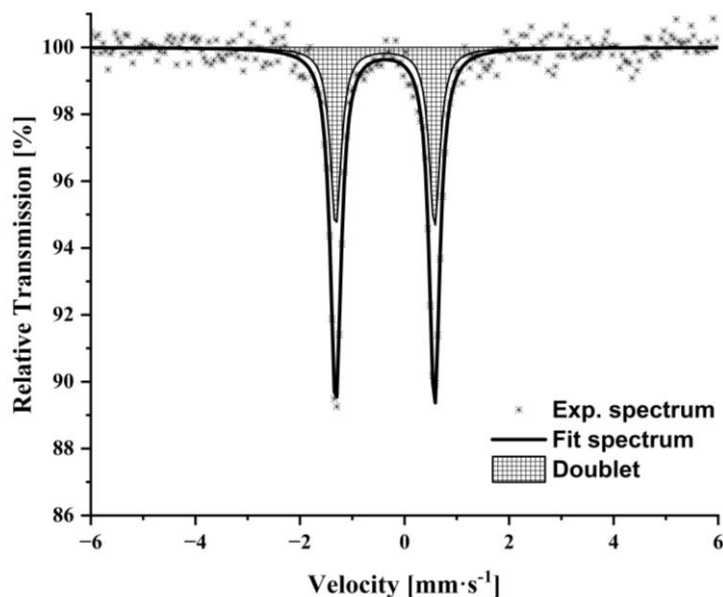


Fig. 4 – Mössbauer spectrum and its fit using one doublet for  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  at room temperature.

## EXPERIMENTAL

Reactions and manipulations were conducted in air with reagent grade solvents.

$[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  was prepared according to literature method.<sup>10</sup> Microanalysis was performed using EURO EA (Italy). The characterization data of the complex are

summarized in Table 3. Powder X-ray diffraction was performed on a *Stoe Transmission diffractometer* (Stadi P) (Stoe & CIE, Germany). Mössbauer spectrum was collected with a constant acceleration transmission mode setup, with a  $\sim 100$  mCi  $^{57}\text{Co}/\text{Rh}$  gamma-ray source (April 2017, Ritverc Co.), and was obtained with a spectrometer equipped with a Mössbauer Velocity transducer (WissEl GmbH model MA-260S) controlled by a linear function driving (WissEl

GmbH Mössbauer Drive Unit model MR-360). Value of Mössbauer isomer shift is quoted relatively to  $\alpha\text{-Fe}$  foil (30  $\mu\text{m}$ , Ritverc Co.). The Mössbauer spectrum is fitted to a sum of Lorentzians by means of a least-squares procedure using software package WinNormos for Igor (written by R. A. Brand, at Laboratorium für Angewandte Physik, Universität Duisburg, D-47048, Duisburg-Germany). All Mössbauer measurements were achieved at room temperature.

Table 3

Basic characterization data for  $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2][\text{Fe}(\text{CN})_5\text{NO}]\cdot 5\text{H}_2\text{O}$ 

Formula	Molecular Weight	Elemental analysis			Yield %	M.p. °C	
		C	H	N			
$\text{C}_{16}\text{H}_{22}\text{FeN}_8\text{O}_6$	478.25	$w_i(\text{calc.})/\%$	40.18	4.64	23.43	63	200 (dec)
		$w_i(\text{found})/\%$	41.04	5.20	23.28		

### Crystal structure determination for $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2][\text{Fe}(\text{CN})_5\text{NO}]\cdot 5\text{H}_2\text{O}$ by powder X-ray diffraction

The crystal structure was determined using the powder X-ray diffraction data which is collected using the transmission diffractometer (*STADI-P STOE*, Darmstadt, Germany), with Cu  $K_\alpha$  radiation ( $\lambda = 1.54059$  Å) and a germanium monochromator operated at 50 kV and 30 mA. The scanning angle was from  $5^\circ$  to  $75^\circ$  with a scanning rate of  $1^\circ$  per minute. In order to solve the material structure, a direct calculation method was applied, using the software package *EXPO2014*.<sup>20</sup> A Triclinic cell with satisfactory figure of merit [ $M(22) = 15.5$ ] was found for the

material and weighted profile R-factor ( $R_{wp} = 0.042$ ). The structure can be described as belonging to the space group  $P\bar{1}$ . The crystal parameters are  $a = 12.735(4)$  Å,  $b = 11.934(4)$  Å,  $c = 9.805(3)$  Å,  $\alpha = 103.373^\circ$ ,  $\beta = 98.524^\circ$ ,  $\gamma = 95.901^\circ$ . The structure could be further refined using Rietveld method as implemented in *GSAS-II* package.<sup>21</sup> The figure of merit [ $M(22) = 16.26$ ] becomes better and the goodness of fit (GOF = 1.04). The final values of the crystallographic data and refinement goodness factors are shown in Table 4. Where we can see the weighted profile R-factor ( $R_{wp} = 0.032$ ) is improved. The final Rietveld plots of the X-ray diffraction patterns are given in Fig. 5.

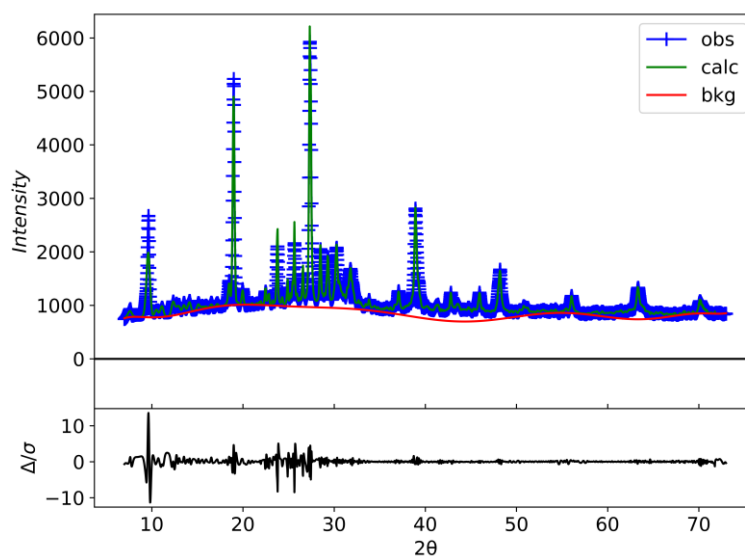


Fig. 5 – The final Rietveld pattern for  $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2][\text{Fe}(\text{CN})_5\text{NO}]\cdot 5\text{H}_2\text{O}$ . The (+) is the observed values and (–) are the fitted ones. The black line is the difference between the observed and the fitted values.

Table 4

Crystallographic data and refinement parameters for  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$ 

CCDC number	2391097
Chemical formula	$C_{16}H_{22}FeN_8O_6$
<i>Mr</i>	478.25
Powder colour	Green
Crystal system	Triclinic
Space group	$P\bar{1}$
Temperature (K)	300
Unit cell parameters	
<i>a</i> (Å)	12.735 (4)
<i>b</i> (Å)	11.934 (4)
<i>c</i> (Å)	9.805 (3)
$\alpha$ (°)	103.373 (5)
$\beta$ (°)	98.524 (5)
$\gamma$ (°)	95.901 (7)°
<i>V</i> (Å <sup>3</sup> )	1419.0 (9)
<i>Z</i>	2
Radiation type	Cu $K\alpha_1$
$\lambda$	1.54059 Å
Specimen shape, size	Fine powder
<b>Data collection</b>	
Diffractometer	STOE transmission STADI-P
Specimen mounting	powder loaded between two Mylar foils
Data collection mode	transmission
Scan method	step
<i>2θ</i> min	5.0°
<i>2θ</i> max	75.0°
<i>2θ</i> step =	0.02°
<b>Refinement</b>	
R factors and goodness of fit $R_p$	0.018
$R_{wp}$	0.035
$R_{exp}$	0.031
$\chi^2$	1.279
Number of data points	3401
Number of parameters	29

## CONCLUSION

The molecular structure of the organic-inorganic ionic complex  $[(C_5H_5N)_2CH_2][Fe(CN)_5NO] \cdot 5H_2O$  was confirmed by powder X-ray diffraction study and its Mössbauer spectroscopy at room temperature. The molecular structure shows the distinctive organic dication  $[(C_5H_5N)_2CH_2]^{2+}$ , dianion  $[Fe(CN)_5NO]^{2-}$ , and five uncoordinated water molecules. The  $H_2O$  molecules are occupying channels linking the dication  $[(C_5H_5N)_2CH_2]^{2+}$  and anions  $[Fe(CN)_5NO]^{2-}$  in the crystal lattice to form three dimensional network. The Mössbauer spectrum of the complex shows the expected doublet with different quadruple splitting ( $\Delta Q$ ) and isomer shift ( $\delta$ ) comparing to the parent salt  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ .

### Supplementary information.

CCDC 2391097 contains the supplementary crystallographic data for this paper. This data can be

obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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