

HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF $(C_6H_5N_2)(FeBr_4)$

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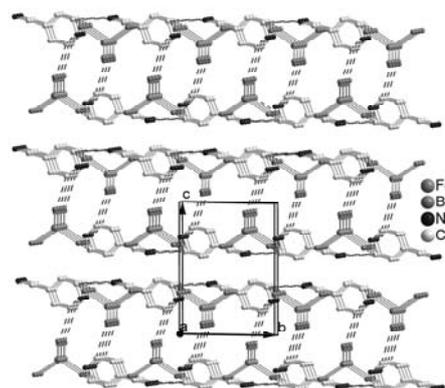
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$(C_6H_5N_2)(FeBr_4)$ (**1**) has been synthesized via a hydrothermal reaction and characterized by X-ray single crystal diffraction. Compound **1** crystallizes in the space group $P\bar{1}$ of the triclinic system with two formula units in a cell: $a = 7.416(3)$, $b = 7.807(3)$, $c = 11.381(4)$ Å, $\alpha = 90.579(4)$, $\beta = 104.623(5)$, $\gamma = 93.705(6)^\circ$, $V = 636.0(4)$ Å³, $C_{6H_5Br_4FeN_2}$, $M_r = 480.61$ g/mol, $D_c = 2.510$ g/cm³, $S = 0.995$, $\mu(MoK\alpha) = 13.711$ mm⁻¹, $F(000) = 442$, $R = 0.0409$, $wR = 0.0759$. The title compound features an isolated structure, based on discrete $(C_6H_5N_2)^+$ and $(FeBr_4)^-$ moieties. The Fe(III) atom is surrounded by four terminal bromine atoms to form a tetrahedron. The $(C_6H_5N_2)^+$ and $(FeBr_4)^-$ moieties are held together via hydrogen bonding interactions to yield a two-dimensional (2-D) supramolecular structure.



INTRODUCTION

Recently, supramolecular chemistry has gained increasing attention to synthesize new solid state compounds because it makes use of self-assembly to build new compounds in virtue of weak intermolecular cooperative interactions like hydrogen bonding interactions, aromatic π - π stacking interactions, ion-dipole interactions, ion-ion interactions, and dipole-dipole interactions to interconnect building units together and a great number of supramolecular compounds have so far been prepared.^{1,2} Cyanopyridine is a quite interesting building block in forming supramolecu-

lar and extended structures due to its unsymmetrical divergent feature and it is able to interlink metal atoms with its nitrogen atoms. In recent years, we aim at the supramolecular compounds containing both magnetically active metal centers like Fe(III) atom and bifunctional ligands, such as cyanopyridine. Herein, we report the hydrothermal synthesis and X-ray single-crystal structure of $(C_6H_5N_2)(FeBr_4)$ (**1**) which is characteristic of a 2-D supramolecular structure. To our knowledge, it is the first example containing both FeX_4 ($X = F, Cl, Br$ or I) and 4-cyanopyridine, although some 4-cyanopyridine-containing iron compounds have been documented thus far.³⁻⁵

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EXPERIMENTAL

Synthesis of $(C_6H_5N_2)(FeBr_4)$ (1): All reactants of A.R. grade were commercially obtained and used without further purification. $FeBr_3$ (1 mmol, 296 mg), 4-cyanopyridine (2 mmol, 208 mg), hydrobromic acid (1 mL) and distilled water (10 mL) were loaded into a Teflon-lined stainless steel autoclave (23 mL) and kept at 423 K for 8 days. After being slowly cooled down to room temperature at a rate of 6 K/h, brown crystals suitable for X-ray analysis were obtained. Yield: 43% (based on iron).

X-ray structure determination: X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens

SHELXTL™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2 . All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths are listed in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 904864. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 1

Summary of Crystallographic Data and Structure Analysis for **1**

Empirical formula	$C_6H_5Br_4FeN_2$
Formula weight	480.61
X-rays	MoK α
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.416(3)$ Å $b = 7.807(3)$ Å $c = 11.381(4)$ Å $\alpha = 90.579(4)^\circ$ $\beta = 104.623(5)^\circ$ $\gamma = 93.705(6)^\circ$
Z	2
V	$636.0(4)$ Å ³
D_c	2.510 Mg/m ³
Absorption coefficient	13.711 mm ⁻¹
Crystal size	$0.22 \times 0.12 \times 0.10$ mm
No. of reflections collected/unique	4199/2193 [$R_{(int)} = 0.0763$]
Refinement	full matrix least squares on F^2
Goodness-of-fit on F^2	0.995
Final R indices	$R_1 = 0.0409$, $wR_2 = 0.0759$
R indices (all data)	$R_1 = 0.0479$, $wR_2 = 0.0774$
Index ranges	$-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $-9 \leq l \leq 13$
Measurement	Rigaku Mercury CCD diffractometer
Monochromator	graphite
Largest difference peak($e \cdot \text{Å}^{-3}$)	1.235, -1.127
$(\Delta/\sigma)_{max}$	0

Table 2

Selected Bond Lengths (Å) and Bond Angles (°) of **1**

Fe(1)-Br(1)	2.347(1)	Br(1)-Fe(1)-Br(2)	109.54(5)
Fe(1)-Br(2)	2.333(1)	Br(1)-Fe(1)-Br(3)	108.67(5)
Fe(1)-Br(3)	2.334(1)	Br(1)-Fe(1)-Br(4)	108.66(4)
Fe(1)-Br(4)	2.345(1)	Br(2)-Fe(1)-Br(3)	110.43(5)
C(1)-N(1)	1.154(9)	Br(2)-Fe(1)-Br(4)	110.44(5)
		Br(3)-Fe(1)-Br(4)	109.05(5)

RESULTS AND DISCUSSION

An ORTEP drawing of compound **1** with atomic label is shown in Fig. 1. X-ray single crystal diffraction analyses reveal that the title compound is characteristic of an isolated structure, consisting discrete $(C_6H_5N_2)^+$ cations and $(FeBr_4)^-$ anions. The Fe(III) atom is surrounded by four terminal bromine atoms to yield a tetrahedron, as shown in Fig. 1. The bond lengths of Fe(1)-Br(1), Fe(1)-Br(2), Fe(1)-Br(3) and Fe(1)-Br(4) are 2.347(1), 2.333(1), 2.334(1) and 2.345(1) Å, respectively, with an average value of 2.340(1) Å

which is comparable with those reported.^{7,8} The bond angles of Br-Fe-Br are between $108.66(4)^\circ$ and $110.44(5)^\circ$ with a mean value of $109.47(5)^\circ$, which is close to the value for a right tetrahedron. As for the 4-cyanopyridine, the bond length of the C(1)-N(1) of the cyanide group is 1.154(9) Å which is typical for a cyanide group. Because the charge of the $(FeBr_4)$ group is -1, in order to keep charge balance, the charge of the $(C_6H_5N_2)$ group must be +1, indicating that the nitrogen atom of the pyridine should be protonated, as the cases found in the literature.⁹⁻¹²

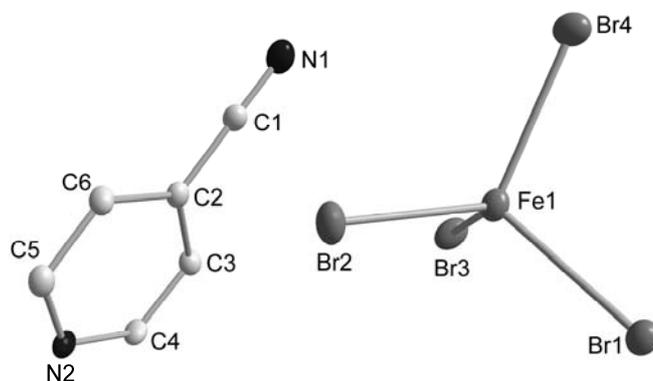


Fig. 1 – ORTEP drawing of **1** with 35% thermal ellipsoids. Hydrogen atoms were omitted for clarity.

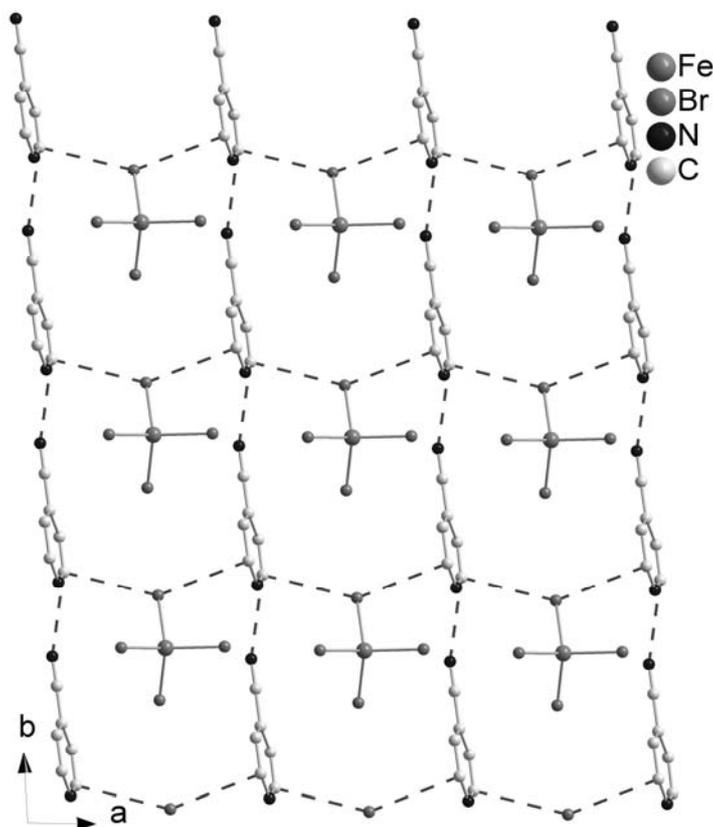


Fig. 2 – A monolayer of **1** with the dashed lines representing hydrogen bonding interactions.

In the title compound, there is no $\pi \dots \pi$ stacking interactions established between the pyridine rings. The $(C_6H_5N_2)^+$ cations interlink to each other via C-H \dots N hydrogen bonding interactions to give a one-dimensional (1-D) chain running along the *b* axis. The 1-D chains are connected by $(FeBr_4)^-$ anions via C-H \dots Br hydrogen bonding interactions to yield a monolayer extending along the *ab* plane, as shown in Figure 2. The monolayer then further

interconnects to a neighbouring one to form a double layer structure through C-H \dots Br hydrogen bonding interactions (Fig. 3). To our knowledge, such a double layer is rare for cyanopyridine-containing compounds. The double layers stack together via static interactions and Van der waal's force to construct a 3-D supramolecular structure, as shown in Fig. 4.

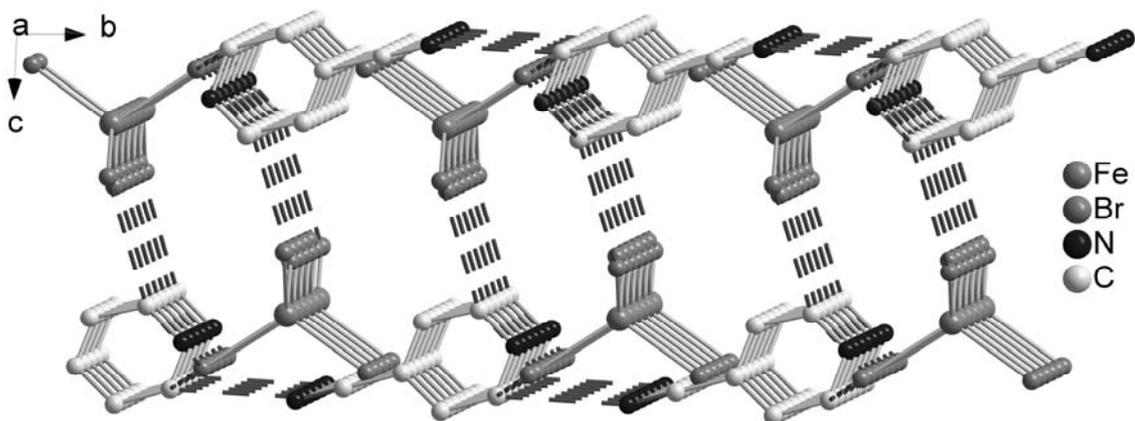


Fig. 3 – A double layer of **1** with the dashed lines representing hydrogen bonding interactions.

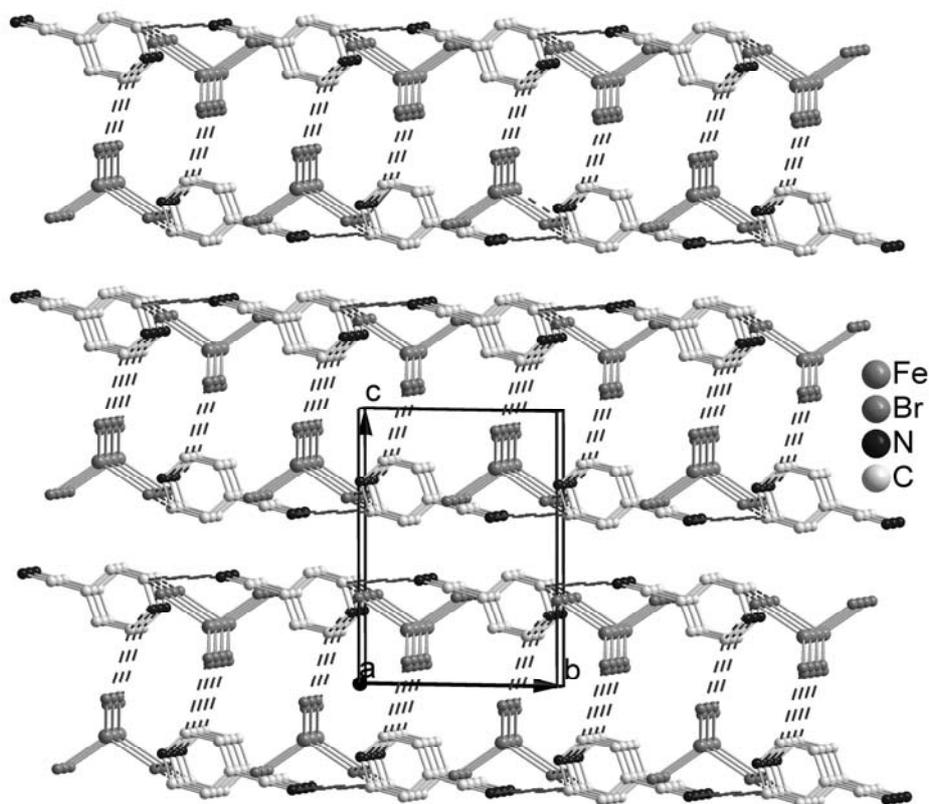


Fig. 4 – Packing diagram of **1** with the dashed lines representing hydrogen bonding interactions. Hydrogen bonds (Å): C(4)-H(4A) \dots Br(3)(2-x, 1-y, -z) 3.505(6), C(4)-H(4A) \dots Br(4)(-1+x, -1+y, z) 3.559(6), C(5)-H(5A) \dots Br(4)(x, -1+y, z) 3.525(7), and C(5)-H(5A) \dots N(1)(x, -1+y, z) 3.100(1).

A search from the Cambridge Crystallographic Data Centre (CCDC) shows that there are many 4-cyanopyridine-containing iron compounds have been reported thus far.³⁻⁵ However, no one contains both FeX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) and 4-cyanopyridine moieties. Therefore, compound **1** is the first example containing both FeX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) and 4-cyanopyridine moieties.

CONCLUSIONS

In conclusion, a new iron compound, $(\text{C}_6\text{H}_5\text{N}_2)(\text{FeBr}_4)$ (**1**) which is characteristic of a 2-D supramolecular structure, has been synthesized via a hydrothermal reaction and characterized by X-ray single crystal diffraction. It is the first example containing both FeX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) and 4-cyanopyridine.

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