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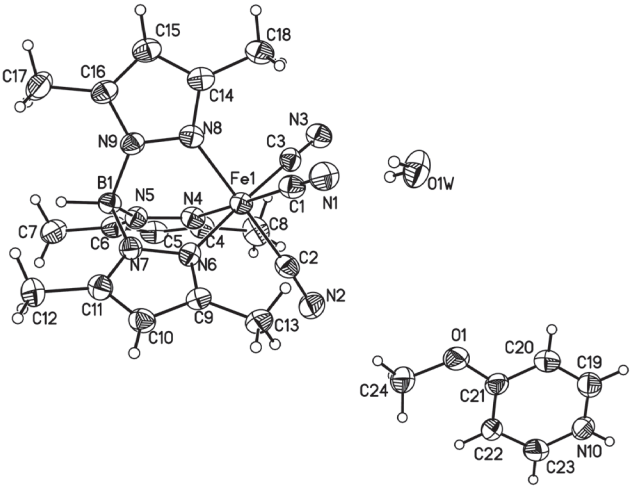
Zhong-Hai Ni* and Hao Sun

Crystal structure of tris(cyano-(hydrogen tris(3,5-dimethylpyrazolyl)borate))-iron(III) 4-methoxypyridinium monohydrate, $C_{24}H_{32}BN_{10}O_2Fe$



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Abstract

$C_{24}H_{32}BN_{10}O_2Fe$, orthorhombic, $Pca2_1$ (no. 29), $a = 19.053(4)$ Å, $b = 9.0666(18)$ Å, $c = 16.439(3)$ Å, $V = 2839.8(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0482$, $wR_{ref}(F^2) = 0.1194$, $T = 123(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Zhong-Hai Ni,** School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, People's Republic of China, e-mail: nizhonghai@cumt.edu.cn
Hao Sun : School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, People's Republic of China

Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.12 \times 0.08 \times 0.06$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.7 cm^{-1}
Diffractometer, scan mode:	Bruker APEXII, φ and ω-scans
$2\theta_{max}$, completeness:	52°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22002, 5551, 0.083
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3872
$N(param)_{refined}$:	359
Programs:	Bruker [1], SHELX [2], PLATON [3]

Source of material

The precursor $Bu_4N[Fe(Tp^*)(CN)_3]$ was synthesized according to the literature [4]. The title complex was obtained unexpectedly as follows: a methanol (MeOH) solution (10.0 ml) of cyanide-containing building block $Bu_4N[Fe(Tp^*)(CN)_3]$ (0.2 mmol) (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate) was subsequently added to a MeOH solution (10 ml) of $Fe(ClO_4)_3{\cdot}6H_2O$ (0.1 mmol). 4-methoxy-pyridine (MP) (0.4 mmol) was subsequently added to the above mixture. The mixture was then carefully filtered and the resulting solution was kept at room temperature for about three days, producing red block crystals of the title complex with a yield of 25.0%. Elemental analysis–calculated for $C_{24}H_{32}BN_{10}O_2Fe$: C, 51.55%; H, 5.77%; N, 25.05%; found: C,51.36%, H, 5.79%; N, 24.88%.

Experimental details

The coordinates of the H atoms bound to boron atom and water molecule and pyridine nitrogen were found from difference Fourier maps and refined freely; distance restraints were used for water H atoms. All H atoms bond to C atoms were introduced using the HFIX command in the SHELX program [2], with the value of 0.93 Å or 0.96 Å for C—H bonds distances. All H atoms were allowed for as riding atoms with $U_{iso}(H) = 1.5U_{eq}$(methyl carrier and water) and $U_{iso}(H) = 1.2U_{eq}$(C, B) for all other hydrogen atoms.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.33587(2)	1.18721(6)	0.25840(5)	0.04476(16)
B1	0.3343(2)	0.8469(5)	0.2539(5)	0.0442(10)
H1	0.3320(16)	0.722(4)	0.252(3)	0.053*
C1	0.3191(2)	1.3115(5)	0.3512(3)	0.0532(11)
C2	0.4147(2)	1.3075(5)	0.2299(3)	0.0551(11)
C3	0.2791(2)	1.3220(5)	0.1974(3)	0.0500(10)
C4	0.3617(2)	1.0841(5)	0.0802(3)	0.0549(11)
C5	0.3677(2)	0.9495(5)	0.0407(3)	0.0599(12)
H5	0.3749	0.9349	−0.0147	0.072*
C6	0.3608(2)	0.8420(5)	0.0990(3)	0.0558(12)
C7	0.3662(2)	0.6764(5)	0.0904(3)	0.0692(14)
H7A	0.4066	0.6416	0.1195	0.104*
H7B	0.3706	0.6511	0.0339	0.104*
H7C	0.3247	0.6312	0.1123	0.104*
C8	0.3676(3)	1.2361(6)	0.0426(3)	0.0743(14)
H8A	0.3217	1.2711	0.0283	0.111*
H8B	0.3963	1.2310	−0.0053	0.111*
H8C	0.3886	1.3025	0.0811	0.111*
C9	0.45096(19)	1.0750(5)	0.3775(3)	0.0476(10)
C10	0.4751(2)	0.9371(5)	0.4029(3)	0.0557(11)
H10	0.5109	0.9197	0.4401	0.067*
C11	0.4365(2)	0.8320(5)	0.3630(3)	0.0530(11)
C12	0.4414(3)	0.6673(4)	0.3659(3)	0.0708(14)
H12A	0.3952	0.6263	0.3723	0.106*
H12B	0.4702	0.6383	0.4110	0.106*
H12C	0.4617	0.6318	0.3162	0.106*
C13	0.4779(2)	1.2225(5)	0.4037(3)	0.0621(12)
H13A	0.5064	1.2638	0.3613	0.093*
H13B	0.5056	1.2114	0.4522	0.093*
H13C	0.4391	1.2870	0.4146	0.093*
C14	0.1860(2)	1.0862(5)	0.3050(2)	0.0515(10)
C15	0.1519(2)	0.9500(5)	0.3124(3)	0.0587(12)
H15	0.1048	0.9357	0.3248	0.070*
C16	0.2008(2)	0.8408(5)	0.2980(3)	0.0548(11)
C17	0.1933(3)	0.6764(5)	0.2989(4)	0.0797(16)
H17A	0.2085	0.6370	0.2477	0.120*
H17B	0.1450	0.6508	0.3079	0.120*
H17C	0.2216	0.6360	0.3418	0.120*
C18	0.1548(2)	1.2358(5)	0.3164(3)	0.0630(12)
H18A	0.1756	1.2821	0.3630	0.095*
H18B	0.1051	1.2268	0.3246	0.095*
H18C	0.1636	1.2946	0.2689	0.095*
C19	0.5767(3)	1.1592(6)	0.1148(3)	0.0681(13)
H19	0.5568	1.2496	0.1283	0.082*
C20	0.5432(2)	1.0325(5)	0.1366(3)	0.0653(13)
H20	0.5005	1.0362	0.1641	0.078*
C21	0.5736(2)	0.8971(5)	0.1170(3)	0.0619(12)
C22	0.6371(2)	0.8945(5)	0.0748(3)	0.0665(14)
H22	0.6581	0.8057	0.0602	0.080*
C23	0.6679(2)	1.0270(6)	0.0554(4)	0.0759(16)
H23	0.7108	1.0272	0.0284	0.091*
C24	0.5659(3)	0.6335(5)	0.1207(4)	0.0905(19)
H24A	0.5634	0.6173	0.0630	0.136*
H24B	0.5389	0.5595	0.1483	0.136*
H24C	0.6139	0.6279	0.1381	0.136*
N1	0.3091(2)	1.3853(5)	0.4071(3)	0.0696(11)
N2	0.4644(2)	1.3736(4)	0.2116(3)	0.0750(12)
N3	0.24658(19)	1.4036(4)	0.1596(2)	0.0612(10)
N4	0.35136(17)	1.0605(4)	0.1600(2)	0.0513(9)
N5	0.35062(17)	0.9086(4)	0.1703(2)	0.0492(8)
N6	0.39866(16)	1.0533(3)	0.3230(2)	0.0462(8)
N7	0.39031(16)	0.9042(4)	0.3148(2)	0.0470(8)
N8	0.25457(17)	1.0603(4)	0.28588(19)	0.0483(8)
N9	0.26258(16)	0.9093(4)	0.2814(2)	0.0493(9)
N10	0.6376(2)	1.1561(4)	0.0745(3)	0.0648(11)
H10A	0.6575	1.2375	0.0606	0.078*
O1	0.53791(16)	0.7784(4)	0.1397(2)	0.0781(10)
O1W	0.3072(2)	0.5851(4)	0.5372(2)	0.0781(10)
H1WB	0.301(4)	0.525(5)	0.577(3)	0.117*
H1WA	0.314(3)	0.531(6)	0.494(3)	0.117*

Discussion

The design and synthesis of molecule-based magnetic materials have been the subject of several investigations in the past several decades because of their interesting properties and their novel molecular topological structures [5–7]. As one of the most well-known bridging groups for magnetic complexes, the cyanide ligand exhibits unique advantages for the assembly of new molecular magnetic materials, not only because the resulting structures can be easily predicted but also because mediation of magnetic coupling between (heterospin) metal centres can be expected. Up to date, a large number of cyanide-bridged complexes with interestingly magnetic properties have been obtained [8–13]. Among the many cyanide-containing building blocks, tricyanide-containing building blocks of $[Fe(Tp)(CN)_3]^-$ (Tp = hydrogen tris(pyrazolyl)borate) and its derivatives have been extensively exploited for assemblying low-dimensional cyanide-bridged complexes [14]. Herein, we report the synthesis and crystal strucure of such a cyanide-containing building block, $C_{24}H_{32}BN_{10}O_2Fe$, in a solvated and monohydrate form, which was obtained serendipitously when assembling cyanide-bridged complex with alternating low-spin and high-spin Fe(III) ions.

The title compound consists of the $[Fe(Tp^*)(CN)_3]^-$ unit, one 4-methoxypyridinium cation 4-methoxy-pyridin and one free water molecule. The $[Fe(Tp^*)(CN)_3]^-$ unit resembles a three-bladed propeller, using Fe(III) and B atoms as the fixed points and three pyrazole rings as the paddles. The central metal Fe(III) cation of the title complex is six-coordinated by three nitrogen atoms from the capping ligand Tp* and three cyanide nitrogen atoms at the other three *fac* positions, forming a slightly distorted octahedral coordination geometry. The $Fe—N_{pyrozle}$ bond lengths are very similar and located within

the 1.982(3) to 2.008(3) Å range, and are significantly longer than the Fe—$C_{cyanide}$ distances (1.915(5)–1.923(5) Å). The C—$N_{cyanide}$ bond distances range from 1.148(5) to 1.161(5) Å. The B—N bond distances within the Tp* ligand range from 1.517(8) to 1.552(7) Å. The Fe—C—N bond angles are nearly linear and located within the narrow range of 176.4(4)–179.6(5)°. The dihedral angles between the three pyrazole rings are different due to the presence of 4-methoxypyridinium cationic units and the above three dihedral angles are 55.3(3)°, 56.8(3)° and 67.9(3)°, respectively. O—H···N and N—H···O hydrogen bonds give rise to a zigzag one-dimensional (1D) supramolecular construct where $[Fe(Tp^*)(CN)_3]^-$ units and protonated 4-methoxy-pyridine molecules are located at the opposite sides of the 1D chains.

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