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Crystal structure of the co-crystal *fac*-triaquatris-(thiocyanato-*κN*)iron(III)–2,3-dimethylpyrazine (1/3)

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In the crystal of the title compound, $[Fe(NCS)_3(H_2O)_3]\cdot3C_6H_8N_2$, the Fe[III] cation is located on a threefold rotation axis and is coordinated by three N atoms of the thiocyanate anions and three water molecules in a *fac* arrangement, forming a slightly distorted N_3O_3 octahedron. Stabilization within the crystal structure is provided by O—H⋯N hydrogen bonds; the H atoms from coordinating water molecules act as donors to the N atoms of guest 2,3-dimethylpyrazine molecules, leading to a three-dimensional supramolecular framework.

1. Chemical context

In the large family of coordination compounds, materials showing a tunable character of their physical properties (*e.g.*, electrical, magnetic, optical *etc*) are of special interest. Attempts to design compounds with such tunability have revealed the possibility to target the property of interest through the rational choice of ligands in transition metal complexes. For instance, variation of the aromatic *N*-donor ligand can lead to possible spin-state modulation of transition metals. In certain cases, these complexes can even possess spin crossover behaviour (transition between low and high spin states of a metal). The phenomenon of spin transition, which is one of the most known examples of molecular bistability, can be provoked by some external stimuli (temperature, pressure, light, magnetic field, absorption of some compounds) and is followed by a change of the optical, magnetic and electric properties (Gütlich & Goodwin, 2004).
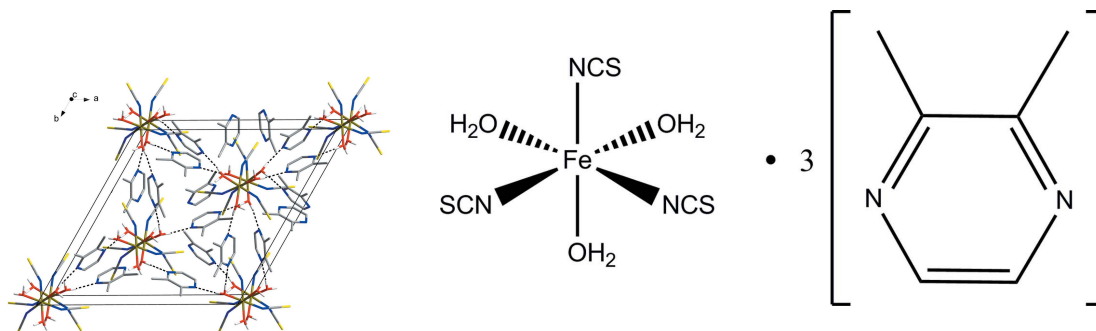

One of the simplest bridging *N*-donor ligands in the design of coordination polymers is pyrazine. This ligand is known for the formation of not only low-dimensional chains and sheets but also of some more complicated architectures, such as $[Ag(pz)](CB_{11}H_{12})$ [$CB_{11}H_{12}^-$ is the monocarba-*closo*-

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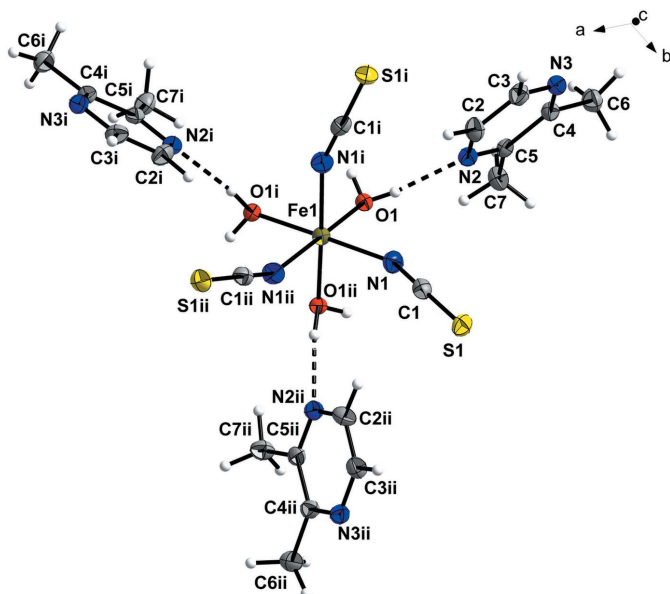
Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-y + 1$, $x - y + 1$, z; (ii) $-x + y$, $-x + 1$, z.]

dodecaborate($-$) anion], which exhibits a three-dimensional structure made up of checkerboard sheets of silver cations and anions connected by pillars of bridging pyrazine ligands (Cunha-Silva *et al.*, 2006). In addition, pyrazine is able to construct Hofmann clathrates – spin crossover compounds with general formula $[Fe^{II}M^{II}(pz)(CN)_4]_\infty$ where M = Ni, Pd or Pt (Niel *et al.*, 2001). A combination of pyrazine ligands with thiocyanates instead of tetracyanidometalates leads to the two-dimensional coordination polymer $[Fe(pz)_2(NCS)_2]_\infty$ with an antiferromagnetic exchange between the metal cations (Real *et al.*, 1991). In this context, we attempted to synthesize an Fe^{II} thiocyanate complex with 2,3-dimethylpyrazine;
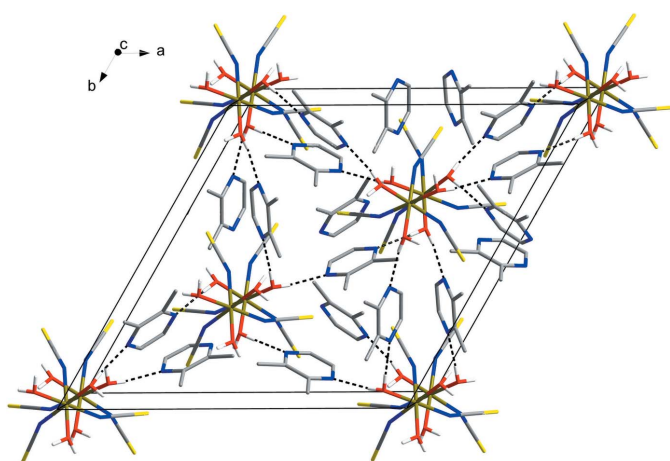
Figure 2
Crystal structure of the title compound, showing hydrogen bonds as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. Colour key: bronze Fe, yellow S, blue N, grey C and red O.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1A\cdots N2$	0.80 (3)	1.95 (3)	2.745 (4)	172 (8)

however, the exposure of the starting material $[Fe(OTs)_2]\cdot 6H_2O$ (OTs = *p*-toluenesulfonate) to the oxygen in the air led to the oxidation of Fe^{II} and to the formation of the title compound.

2. Structural commentary

In the crystal structure of the title compound, the Fe^{III} cation is located on a threefold rotation axis and is in an octahedral coordination environment formed by three N atoms of the thiocyanate anions and three O atoms of water molecules arranged in a *fac* configuration (Fig. 1). The distance between the Fe^{III} ion and the N atoms [2.025 (4) Å] is longer than that between the Fe^{III} ion and the O atoms [2.034 (3) Å] and therefore the FeN_3O_3 octahedron is slightly distorted. These structural features are typical for related compounds (Shylin *et al.*, 2013, 2015). The thiocyanate ligands are bound through

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Fe(NCS)_3(H_2O)_3]\cdot 3C_6H_8N_2$
M_r	608.57
Crystal system, space group	Trigonal, $R3c$
Temperature (K)	133
a, c (Å)	16.9383 (12), 17.6259 (13)
V (Å^3)	4379.5 (7)
Z	6
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.77
Crystal size (mm)	$0.16 \times 0.12 \times 0.1$
Data collection	
Diffractometer	Stoe IPDS II
Absorption correction	Numerical (*X-RED*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.908, 0.939
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5784, 1903, 1716
R_{int}	0.058
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.633
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.070, 1.07
No. of reflections	1903
No. of parameters	120
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, -0.28
Absolute structure	Flack x determined using 685 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	-0.03 (3)

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2002), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

nitrogen atoms and are quasi-linear [N1—C1—S1 = 179.5 (4)°], while the Fe–NCS linkages are bent [C1—N1—Fe1 = 157.0 (4)°]. Previously reported complexes with an N-bound NCS group possess similar structural features (Petrusenko *et al.*, 1997).

3. Supramolecular features

In the title compound, the crystal packing is stabilized by O—H$\cdots$N hydrogen bonds (Table 1): the H atoms from coordinating water molecules act as donors to the N atoms of guest 2,3-dimethylpyrazine molecules. The compound contains three guest molecules of pyrazine per Fe[III] cation. In the crystal lattice, each molecule of the complex is attached to six molecules of pyrazine, while each pyrazine is connected with two water molecules of the host complexes, leading to the formation of a three-dimensional network (Fig. 2).

4. Synthesis and crystallization

Crystals of the title compound were obtained by the slow-diffusion method between three layers, the first layer being a solution of [Fe(OTs)$_2$]·6H$_2$O (0.096 g, 0.2 mmol) and NH$_4$SCN (0.046 g, 0.6 mmol) in water (10 ml), the second being a water/methanol mixture (1/1, 10 ml) and the third a solution of 2,3-dimethylpyrazine (0.065 g, 0.6 mmol) in methanol (3 ml). After two weeks, red plates grew in the second layer; they were collected, washed with water and dried in air, yield 0.028 g (23%).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms connected to C and O atoms were placed in their expected calculated positions and refined as riding with C—H = 0.98 (CH$_3$), 0.95 (C$_{arom}$), O—H = 0.80 (3) Å, and with $U_{iso}(H) = 1.2U_{iso}(C)$ with the exception of methyl hydrogen atoms, which were refined with $U_{iso}(H) = 1.5U_{eq}(C)$.

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supporting information

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

fac-Triaquatris(thiocyanato-*κN*)iron(III)–2,3-dimethylpyrazine (1/3)

Crystal data

[Fe(NCS)$_3$(H$_2$O)$_3$]·3C$_6$H$_8$N$_2$	$F(000) = 1902$
$M_r = 608.57$	$D_x = 1.384$ Mg m^{-3}
Trigonal, $R3c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 16.9383$ (12) Å	$\mu = 0.77$ mm^{-1}
$c = 17.6259$ (13) Å	$T = 133$ K
$V = 4379.5$ (7) Å^3	Block, red
$Z = 6$	$0.16 \times 0.12 \times 0.1$ mm

Data collection

Stoe IPDS II diffractometer	1903 independent reflections
φ scans and ω scans with κ offset	1716 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (*X-RED*; Stoe & Cie, 2002)	$R_{int} = 0.058$
	$\theta_{max} = 26.8°$, $\theta_{min} = 2.4°$
$T_{min} = 0.908$, $T_{max} = 0.939$	$h = -18 \rightarrow 21$
5784 measured reflections	$k = -21 \rightarrow 15$
	$l = -18 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.038$	
$wR(F^2) = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1903 reflections	$(\Delta/\sigma)_{max} < 0.001$
120 parameters	$\Delta\rho_{max} = 0.27$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -0.28$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack x determined using 685 quotients [$(I^+)-(I^-)$]/[$(I^+)+(I^-)$] (Parsons *et al.*, 2013)
Secondary atom site location: difference Fourier map	Absolute structure parameter: -0.03 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.3333	0.6667	0.99891 (7)	0.0201 (2)
S1	0.29300 (8)	0.86373 (8)	1.16318 (7)	0.0300 (3)
N1	0.2860 (3)	0.7347 (3)	1.0611 (2)	0.0297 (9)
O1	0.2256 (2)	0.62277 (19)	0.92686 (19)	0.0221 (6)
C1	0.2893 (3)	0.7891 (3)	1.1041 (3)	0.0238 (9)
N2	0.0562 (2)	0.5854 (2)	0.9750 (2)	0.0250 (8)
N3	−0.1220 (2)	0.5016 (2)	1.0276 (2)	0.0254 (8)
C2	0.0336 (3)	0.5471 (3)	1.0439 (3)	0.0299 (10)
H2	0.0796	0.5481	1.0753	0.036*
C3	−0.0543 (3)	0.5064 (3)	1.0704 (3)	0.0288 (10)
H3	−0.0674	0.4812	1.1201	0.035*
C4	−0.1008 (3)	0.5385 (3)	0.9586 (2)	0.0235 (9)
C5	−0.0099 (3)	0.5815 (3)	0.9318 (3)	0.0229 (9)
C6	−0.1766 (3)	0.5322 (3)	0.9107 (3)	0.0322 (10)
H6A	−0.2345	0.4977	0.9379	0.048*
H6B	−0.1795	0.5010	0.8630	0.048*
H6C	−0.1655	0.5936	0.8996	0.048*
C7	0.0144 (3)	0.6246 (3)	0.8553 (3)	0.0304 (10)
H7A	0.0795	0.6484	0.8459	0.046*
H7B	0.0012	0.6747	0.8531	0.046*
H7C	−0.0214	0.5791	0.8166	0.046*
H1A	0.179 (3)	0.617 (5)	0.943 (4)	0.080*
H1B	0.206 (5)	0.572 (3)	0.912 (4)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0197 (3)	0.0197 (3)	0.0209 (5)	0.00986 (13)	0.000	0.000
S1	0.0320 (6)	0.0293 (5)	0.0316 (6)	0.0175 (5)	0.0009 (5)	−0.0061 (5)
N1	0.030 (2)	0.031 (2)	0.029 (2)	0.0157 (18)	0.0031 (17)	−0.0024 (18)
O1	0.0180 (14)	0.0201 (14)	0.0283 (17)	0.0096 (13)	−0.0011 (13)	−0.0021 (13)
C1	0.022 (2)	0.030 (2)	0.022 (2)	0.0141 (18)	0.0019 (17)	0.0053 (18)
N2	0.0234 (18)	0.0234 (17)	0.028 (2)	0.0119 (15)	−0.0004 (16)	−0.0026 (15)
N3	0.0236 (17)	0.0233 (17)	0.029 (2)	0.0113 (15)	0.0027 (15)	0.0001 (15)
C2	0.027 (2)	0.037 (2)	0.030 (3)	0.019 (2)	−0.0040 (19)	−0.001 (2)
C3	0.032 (2)	0.029 (2)	0.028 (3)	0.018 (2)	0.0022 (19)	0.0030 (19)
C4	0.021 (2)	0.023 (2)	0.027 (2)	0.0113 (16)	0.0008 (18)	−0.0022 (18)
C5	0.023 (2)	0.0203 (19)	0.027 (2)	0.0121 (17)	0.0023 (17)	−0.0028 (17)
C6	0.027 (2)	0.036 (3)	0.035 (3)	0.017 (2)	−0.002 (2)	−0.002 (2)

| C7 | 0.026 (2) | 0.037 (2) | 0.028 (3) | 0.016 (2) | 0.0020 (19) | 0.0020 (19) |

Geometric parameters (Å, º)

Fe1—N1	2.025 (4)	N3—C4	1.333 (6)
Fe1—N1^i	2.025 (4)	C2—H2	0.9500
Fe1—N1^{ii}	2.025 (4)	C2—C3	1.372 (6)
Fe1—O1	2.034 (3)	C3—H3	0.9500
Fe1—O1^i	2.034 (3)	C4—C5	1.415 (6)
Fe1—O1^{ii}	2.034 (3)	C4—C6	1.495 (6)
S1—C1	1.615 (5)	C5—C7	1.491 (6)
N1—C1	1.172 (6)	C6—H6A	0.9800
O1—H1A	0.80 (3)	C6—H6B	0.9800
O1—H1B	0.80 (3)	C6—H6C	0.9800
N2—C2	1.339 (6)	C7—H7A	0.9800
N2—C5	1.329 (5)	C7—H7B	0.9800
N3—C3	1.340 (6)	C7—H7C	0.9800
N1—Fe1—N1^i	93.42 (17)	N2—C2—C3	121.9 (4)
N1—Fe1—N1^{ii}	93.42 (17)	C3—C2—H2	119.0
N1^i—Fe1—N1^{ii}	93.42 (16)	N3—C3—C2	121.2 (5)
N1—Fe1—O1^{ii}	90.67 (14)	N3—C3—H3	119.4
N1^{ii}—Fe1—O1^{ii}	90.47 (14)	C2—C3—H3	119.4
N1^{ii}—Fe1—O1^i	90.67 (14)	N3—C4—C5	120.9 (4)
N1^i—Fe1—O1^{ii}	174.17 (17)	N3—C4—C6	117.6 (4)
N1—Fe1—O1	90.47 (14)	C5—C4—C6	121.5 (4)
N1^i—Fe1—O1^i	90.47 (14)	N2—C5—C4	120.5 (4)
N1^{ii}—Fe1—O1	174.17 (17)	N2—C5—C7	118.3 (4)
N1^i—Fe1—O1	90.67 (14)	C4—C5—C7	121.2 (4)
N1—Fe1—O1^i	174.17 (17)	C4—C6—H6A	109.5
O1—Fe1—O1^{ii}	85.15 (14)	C4—C6—H6B	109.5
O1^{ii}—Fe1—O1^i	85.15 (14)	C4—C6—H6C	109.5
O1—Fe1—O1^i	85.15 (14)	H6A—C6—H6B	109.5
C1—N1—Fe1	157.0 (4)	H6A—C6—H6C	109.5
Fe1—O1—H1A	118 (6)	H6B—C6—H6C	109.5
Fe1—O1—H1B	115 (6)	C5—C7—H7A	109.5
H1A—O1—H1B	98 (7)	C5—C7—H7B	109.5
N1—C1—S1	179.5 (4)	C5—C7—H7C	109.5
C5—N2—C2	117.7 (4)	H7A—C7—H7B	109.5
C4—N3—C3	117.7 (4)	H7A—C7—H7C	109.5
N2—C2—H2	119.0	H7B—C7—H7C	109.5
N2—C2—C3—N3	1.5 (7)	C3—N3—C4—C6	179.4 (4)
N3—C4—C5—N2	0.4 (6)	C4—N3—C3—C2	−0.7 (7)
N3—C4—C5—C7	−178.7 (4)	C5—N2—C2—C3	−1.2 (6)
C2—N2—C5—C4	0.3 (6)	C6—C4—C5—N2	−179.2 (4)

C2—N2—C5—C7	179.5 (4)	C6—C4—C5—C7	1.7 (6)
C3—N3—C4—C5	−0.2 (6)		

Symmetry codes: (i) −*y*+1, *x*−*y*+1, *z*; (ii) −*x*+*y*, −*x*+1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···N2	0.80 (3)	1.95 (3)	2.745 (4)	172 (8)