

# An interpenetrating primitive cubic net formed by hydrogen bonds and coordination bonds in *catena*-poly[[bis(methanol- $\kappa$ O)bis(thiocyanato- $\kappa$ N)iron(II)]- $\mu$ -1,2-bis(4-pyridyl-methylene)hydrazine- $\kappa^2$ N:N']

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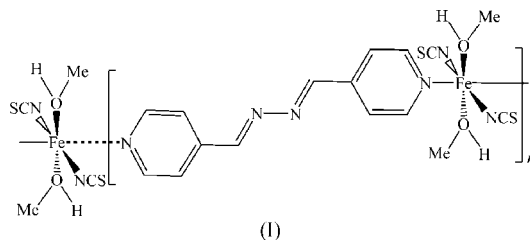
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In the title compound,  $[\text{Fe}(\text{NCS})_2(\text{C}_{12}\text{H}_{10}\text{N}_4)(\text{CH}_4\text{O})_2]_n$ , at 153 (2) K, the Fe atom is located on an inversion centre, as is the centre of the N—N bond in the ligand molecule. The structure contains a one-dimensional coordination polymer with an  $\text{Fe} \cdots \text{Fe}$  distance of 15.866 (7) Å and can be described as two interpenetrating six-connected primitive cubic (pcu) three-dimensional networks when additional intermolecular O—H $\cdots$ S hydrogen bonds are taken into account. The compound is not isostructural with the corresponding Mn<sup>II</sup> compound as they differ in the rotation around the M—O bond by 90°, giving rise to completely different hydrogen-bond patterns. This study demonstrates the impact of conformational differences on the final supramolecular arrangement.

## Comment

Great interest is currently devoted to exploring the versatility of coordination and hydrogen bonds with the aim of obtaining rational control over the creation of molecular framework materials (Delgado-Friedrichs *et al.*, 2007; Champness, 2006; Öhrström & Larsson, 2005). In this context, the monodentate rigid rod-like ligand 1,2-bis(4-pyridylmethylene)hydrazine has frequently been used, giving rise to one- and two-dimensional frameworks (Diskin-Posner *et al.*, 2002; Shi *et al.*, 2002; Patra & Goldberg, 2003; Kennedy *et al.*, 2005; Granifo *et al.*, 2006; Zhang *et al.*, 2006; Zhou *et al.*, 2006; Dong *et al.*, 2000; Shen, 2003). 1,2-Bis(4-pyridylmethylene)hydrazine and similar ligands have limited influence over network topology since in most complexes the ligand occupies only two metal coordination sites, offering a weak influence over the rest of the metal coordination environment. However, further support of the molecular architecture may be acquired through hydrogen

bonds. We reported recently on two different hydrogen-bonding motifs observed in compounds of this ligand, depending on the counter-ions (Ghazzali *et al.*, 2007), and we present here the structure of the title compound, (I), and show how conformational differences have a large impact on the final supramolecular arrangement in the crystal structure.



A perspective displacement ellipsoid drawing of (I) with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are summarized in Table 1. The Fe<sup>II</sup> centre exhibits a nearly ideal high-spin octahedral geometry with two *trans* N-isothiocyanate anions [maximum  $\text{SCN}^-$  deviation from linearity = 1.082 (2)°], two O atoms of two methanol molecules and the repeating 1,2-bis(4-pyridylmethylene)hydrazine ligands propagating in a perfect linear pattern, giving a one-dimensional chain topology with an  $\text{Fe} \cdots \text{Fe}$  distance of 15.866 (7) Å. The N1—N1<sup>ii</sup> single bond lies on a crystallographic centre of symmetry exhibiting a perfect antiperiplanar conformation (see Table 1 for symmetry code). As a result, the two pyridyl rings are parallel, with an interplanar distance of 0.417 (2) Å, and form a dihedral angle of 12.389 (1)° with the mean plane of the symmetrical —CH=N—N=CH— spacer.

There are quite a few isostructural Fe<sup>II</sup> and Mn<sup>II</sup> coordination polymers in the literature (see, for example, Abu-Youssef *et al.*, 2008) and although the structure presented here is topologically similar to that of the corresponding Mn<sup>II</sup> compound (Shen, 2003), exhibiting a similar chain architecture with a slightly longer  $M \cdots M$  distance of 16.036 (2) Å, the two compounds are not isostructural.

In the present Fe<sup>II</sup> case, the chains are interconnected with O—H $\cdots$ S hydrogen bonds between MeOH and  $\text{SCN}^-$  groups, supporting the molecular arrays with a C(6) chain pattern at

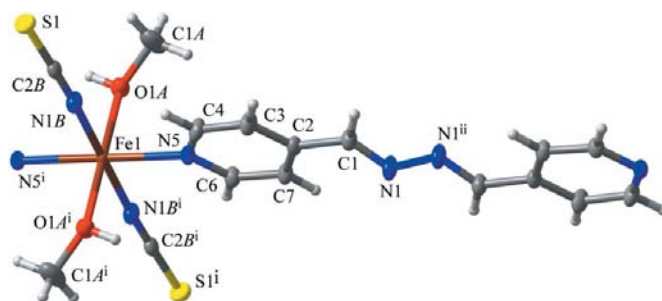
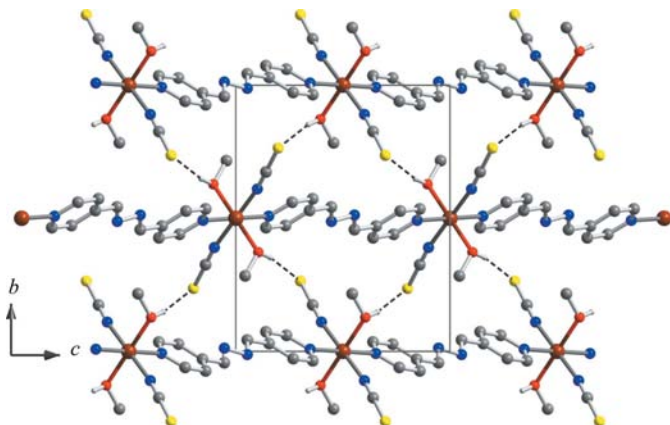


Figure 1

A perspective drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. For symmetry codes, see Table 1.

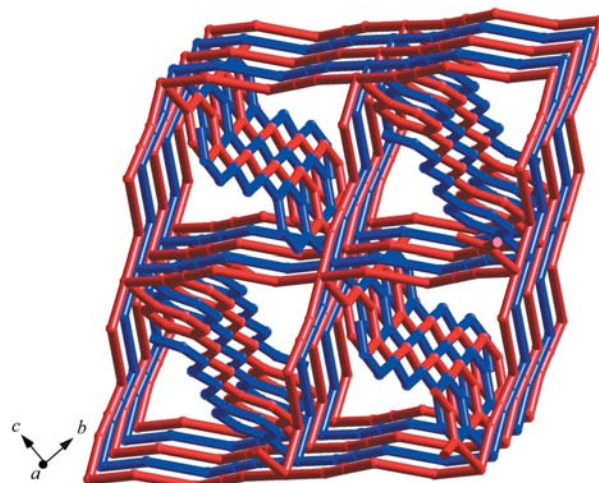

**Figure 2**

The O—H...S hydrogen-bond pattern (dashed lines) in (I), viewed in projection along the *a* direction. For details, see Table 2. H atoms not involved in O—H...S hydrogen bonds have been omitted.

the first-level graph-set, as defined by Bernstein *et al.* (1995) and Grell *et al.* (1999) (Table 2). The supramolecular architecture can be described as a two-dimensional ( $8.4 \times 8.4$  Å) square grid based on hydrogen bonds (Fig. 2), combined with the one-dimensional coordination polymer, giving a three-dimensional net with primitive cubic (pcu) topology (O’Keeffe *et al.*, 2008), the most common of the six-connected three-dimensional nets. The complete structure can then be described as two interpenetrating networks (Fig. 3). In contrast, the corresponding Mn<sup>II</sup> compound (Shen, 2003) contains O—H...N hydrogen bonds to the diaza unit, giving a (4,4)-grid consolidating a sheet structure.

The striking difference between the Fe and Mn structures may be traced to the different orientations of the MeOH ligand. In the Fe<sup>II</sup> compound, the O—H bond is nearly parallel to the Fe—N(pyridine) bond (dihedral angle =  $12^\circ$ ). In the Mn<sup>II</sup> compound, the O—H bond is parallel to the Mn—NCS link. Probably the slightly longer metal–ligand bond distances in the Mn<sup>II</sup> compound (average Mn—L = 2.23 Å *versus* average Fe—L = 2.17 Å) mean that the ligands are too far from each other to interact, giving rise to another conformation, and thus the resulting supramolecular arrangement in the crystal structure of the Fe<sup>II</sup> compound is determined by the ligand–MeOH interactions.

Further evidence for this argument comes from quantum mechanical density functional theory (DFT) calculations. The bridging ligand was replaced by pyridine molecules and two single-point calculations were carried out for each compound to probe the effects of the different MeOH orientations. The results show that, while changing the conformation of MeOH in the Mn<sup>II</sup> compound is only slightly unfavourable from an energetic point of view (31 kJ mol<sup>-1</sup>), the energy of the Fe<sup>II</sup> compound is strongly dependent on the orientation of the MeOH ligand: a 90° rotation around the Fe—O bond to give a similar conformation to the Mn<sup>II</sup> compound gives an energy increase of 141 kJ mol<sup>-1</sup>. In the latter case, this corresponds to the loss of up to six hydrogen-bond interactions between the methanol and the other ligands (Table 2). Summing over six weak interactions with average bond energies of 17 kJ mol<sup>-1</sup>


**Figure 3**

The two interpenetrating (red and blue in the electronic version of the paper) six-connected three-dimensional pcu nets in (I) formed by hydrogen and coordination bonds.

(Jeffrey, 1997; Emsley, 1980) yields 100 kJ mol<sup>-1</sup>, which can be considered an upper-limit estimate. Thus, the calculated value is of a reasonable magnitude, although probably exaggerated.

In conclusion, these results suggest that seemingly minor conformational changes may have a large effect on the overall topology of the network.

## Experimental

**Caution:** Perchlorate salts of metal complexes are potentially explosive. Only small quantities of the compound should be prepared and it should be handled with care! 1,2-Bis(4-pyridylmethylene)hydrazine (1 mmol) was prepared as described previously (El-Rayyes & Katrib, 1983). A methanol solution of 1,2-bis(4-pyridylmethylene)hydrazine (0.2 mmol, 0.04 g) was added dropwise to a stirred solution of iron(II) perchlorate hydrate (0.2 mmol, 0.05 g) and potassium thiocyanate (0.3 mmol, 0.03 g) in MeOH/EtOH/MeCN (15 ml, 1:1:1 *v/v*). The solution was stirred under N<sub>2</sub> for 1 h at room temperature and then filtered. Uniform red–orange prisms were collected after one week and dried in air. IR ( $\nu$ , cm<sup>-1</sup>, KBr): 496 (*m*,  $\nu_{\text{MN}}$ ), 687 (*m*, SCN<sup>-</sup>), 810 (*m*, SCN<sup>-</sup>), 1012 (*m*,  $\nu_{\text{MeOH}}$ ), 1310 (*s*,  $\nu_{\text{OH}}$ ), 1427 (*s*,  $\delta_{\text{C}=\text{N}}$ ), 2070 (*s*, SCN<sup>-</sup>), 3274 (*m*, *b*, OH<sub>stretching</sub>). DFT calculations were performed using the B3LYP function (Lee *et al.* 1988; Becke, 1993) as implemented in SPARTAN06 (Wavefunction, 2007) with the 6-31G\*\* basis set.

### Crystal data

[Fe(NCS) <sub>2</sub> (C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> )(CH <sub>4</sub> O) <sub>2</sub> ]	$V = 1022.73$ (10) Å <sup>3</sup>
$M_r = 446.33$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.6903$ (4) Å	$\mu = 0.96$ mm <sup>-1</sup>
$b = 12.8591$ (7) Å	$T = 153$ (2) K
$c = 10.8707$ (6) Å	$0.09 \times 0.08 \times 0.04$ mm
$\beta = 107.9410$ (10)°	

### Data collection

Siemens SMART CCD area-detector diffractometer	14356 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2549 independent reflections
$T_{\text{min}} = 0.871$ , $T_{\text{max}} = 0.962$	1950 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.054$

**Table 1**

Selected geometric parameters (Å, °).

Fe1–N1 <i>B</i>	2.1105 (17)	Fe1–N5	2.2381 (15)
Fe1–O1A <sup>i</sup>	2.1659 (14)	N1–N1 <sup>ii</sup>	1.415 (3)
N1 <i>B</i> –Fe1–O1A <sup>i</sup>	91.66 (6)	O1A <sup>i</sup> –Fe1–N5	88.44 (6)
N1 <i>B</i> <sup>i</sup> –Fe1–N5	89.38 (6)		

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $-x - 1, -y, -z$ .**Table 2**

Hydrogen-bond and short-contact geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1A–H1A···S1 <sup>iii</sup>	0.84	2.42	3.2451 (15)	169
C4–H4···N1 <i>B</i>	0.95	2.47	3.092 (3)	123
C6–H6···N1 <i>B</i> <sup>i</sup>	0.95	2.52	3.123 (3)	121

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (iii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.035$	126 parameters
$wR(F^2) = 0.084$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\max} = 0.38 \text{ e } \text{Å}^{-3}$
2549 reflections	$\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$

H atoms were constrained to ideal geometry using an appropriate riding model, with C–H = 0.95–0.98 Å and O–H = 0.84 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{aryl}})$ ,  $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$  or  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2005) and *CrystalMaker* (Palmer, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3226). Services for accessing these data are described at the back of the journal.

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