

A new coordination complex based on a polynitrile ligand: bis(4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole)diaqua-iron(II) bis(1,1,3,3-tetracyano-2-methylsulfanylpropenide)

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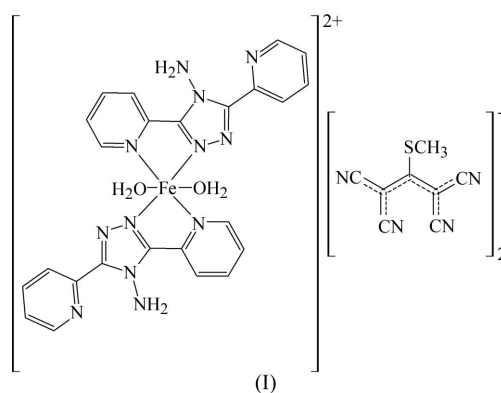
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The new high-spin iron(II) complex, $[\text{Fe}(\text{C}_{12}\text{H}_{10}\text{N}_6)_2(\text{H}_2\text{O})_2] \cdot (\text{C}_8\text{H}_3\text{N}_4\text{S})_2$ or $[\text{Fe}(\text{abpt})_2(\text{H}_2\text{O})_2](\text{tncsme})_2$ [where abpt is 4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole and tncsme is the 1,1,3,3-tetracyano-2-methylthiopropenide anion], consists of discrete $[\text{Fe}(\text{abpt})_2(\text{H}_2\text{O})_2]^{2+}$ dications, where the Fe^{II} ion is coordinated by two *N,N'*-bidentate chelating abpt ligands in the equatorial plane and two water molecules in *trans* positions, generating a distorted octahedral $[\text{FeN}_4\text{O}_2]$ environment. The cationic unit is neutralized by two polynitrile tncsme anions, in which the C–N, C–C and C–S bond lengths indicate extensive electronic delocalization. In the crystal structure, the dications and anions are linked through $\text{O} \cdots \text{H} \cdots \text{N}$ and $\text{N} \cdots \text{H} \cdots \text{N}$ hydrogen bonds involving the water H atoms and those of the NH_2 groups and the N atoms of the CN groups, leading to the formation of a three-dimensional network.

Comment

Polynitrile–transition metal compounds are of current interest for their magnetic properties and their rich architectures and topologies (Kaim & Moscherosch, 1994; Dunbar, 1996; Batten *et al.*, 1999; Thétiot *et al.*, 2003; Benmansour *et al.*, 2007). For geometric and electronic reasons, polynitrile anions are interesting ligands for the preparation of a large variety of magnetic materials displaying extended molecular architectures, because: (i) their geometry precludes the possibility of a chelate coordination mode, and therefore they can only act as terminal or bridging ligands through their nitrile groups; (ii) association of the π electron system of the CN groups with

the π system of the central fragment may allow electronic delocalization that facilitates the transmission of electronic effects between the metal centres (Batten *et al.*, 2000; Manson *et al.*, 2000; Triki *et al.*, 2005). Following these structural and electronic characteristics, several series of binary systems of the form polynitrile/ M^{II} (where M^{II} is a transition metal ion), with only polynitrile bridges, or ternary systems of the form polynitrile/co-ligand/ M^{II} involving an additional bridging or chelate co-ligand, have been reported. Most of them display one-, two- or three-dimensional polymeric assemblies, in which the polynitrile anions act as μ_2 -, μ_3 - and μ_4 -bridging ligands, and they exhibit interesting magnetic properties (Batten & Murray, 2003; Jones *et al.*, 2006; Setifi *et al.*, 2006, 2007; Yuste *et al.*, 2007). Given the crucial role of these anionic ligands, we are interested in using them in combination with other chelating or bridging neutral co-ligands to explore their structural and electronic characteristics in the large field of molecular materials exhibiting the spin crossover (SCO) phenomenon (Kunkeler *et al.*, 1996; Sheu *et al.*, 2008; Dupouy *et al.*, 2008, 2009). In an attempt to prepare such a complex, we obtained the title compound, $[\text{Fe}(\text{abpt})_2(\text{H}_2\text{O})_2](\text{tncsme})_2$, (I), where abpt is 4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole and tncsme is the 1,1,3,3-tetracyano-2-methylthiopropenide anion.



The asymmetric unit of (I) is composed of a discrete $[\text{Fe}(\text{abpt})_2(\text{H}_2\text{O})_2]^{2+}$ dication with two crystallographically independent abpt ligands (ligand *A* containing atoms N1–N6/C1–C12 and ligand *B* containing atoms N7–N12/C13–C24), two water molecules and two noncoordinated tncsme anions (Fig. 1). The coordination geometry of the metal centre is distorted octahedral $[\text{FeN}_4\text{O}_2]$, with four equatorial N atoms (N1 and N2, and N7 and N8) belonging to the pyridine and triazole rings of the two abpt chelating ligands. The remaining axial positions are occupied by atoms O1 and O2 from two water molecules. The Fe1–N bond lengths [Fe1–N1 = 2.176 (3) Å, Fe1–N2 = 2.163 (3) Å, Fe1–N7 = 2.170 (3) Å and Fe1–N8 = 2.162 (3) Å] are similar to the Fe–N distances reported previously for high-spin (HS) iron(II) complexes (Moliner *et al.*, 1999, 2001; Dupouy *et al.*, 2009; Sheu *et al.*, 2009). The coordinated pyridine and triazole rings of the *A* and *B* abpt ligands are almost coplanar [dihedral angles = 1.9 (2) and 2.9 (2)°, respectively], while the uncoordinated pyridine groups and the chelate pyridine–triazole systems define dihedral angles of 6.77 (17) and 11.68 (16)° for ligands *A* and *B*, respectively. The angles involving the *cis*-N atoms,

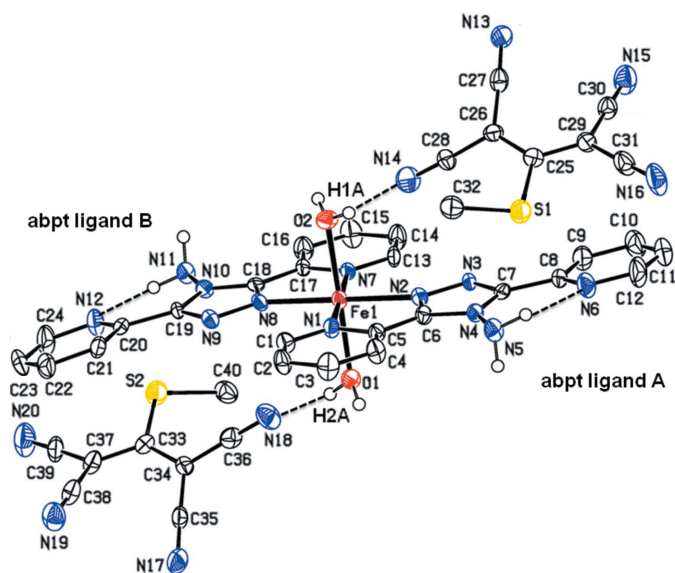


Figure 1

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular O—H···N and N—H···N hydrogen bonds are shown as dashed lines (details are given in Table 1).

lying in the plane defined by the two abpt ligands, differ considerably from 90°, with the N1—Fe—N2 and N7—Fe—N8 bite angles being 75.74 (11) and 75.77 (10)°, respectively. The remaining bond angles involving the *cis*-N atoms (N2—Fe1—N7 and N1—Fe1—N8) are 104.20 (11) and 104.29 (10)°, respectively, while those involving the *trans*-N atoms (N1—Fe1—N7 and N2—Fe1—N8) are 179.94 (11) and 179.91 (13)°, respectively.

The distances of atoms O1, O2 and Fe1 from the mean plane through atoms N1/N2/N7/N8 are 2.124 (2), −2.130 (2) and 0.0008 (6) Å, respectively. This is similar to the situation observed in other mononuclear abpt compounds (Moliner *et al.*, 1999; Dupouy *et al.*, 2008; Gaspar *et al.*, 2003). The two ligands are in the same plane, since the mean planes through both coordinating triazole rings make an angle of 2.0 (2)°. The dihedral angle defined by the triazole ring and the noncoordinated pyridine ring is 6.3 (2)° in ligand A and 10.0 (2)° in ligand B. The same feature has been observed previously in the other mononuclear abpt compounds mentioned above. It appears that a triazole–pyridine twist angle of 6–15° is required to bring the ligand into the favoured conformation to form the intramolecular N(NH₂)—H···N(pyridine) hydrogen bond, which contributes to this almost planar conformation (Fig. 1 and Table 1). The abpt ligand is considerably more planar on coordinating bidentately to metal ions.

Examination of the intermolecular contacts in the crystal structure of (I) reveals that the main contacts are associated with O—H···N and N—H···N hydrogen bonds involving the water H atoms and those of the NH₂ groups, and the N atoms of the CN groups of the anions (Table 1 and Fig. 2). In the crystal structure, this leads to the formation of a three-dimensional hydrogen-bonded network, as shown in Fig. 3.

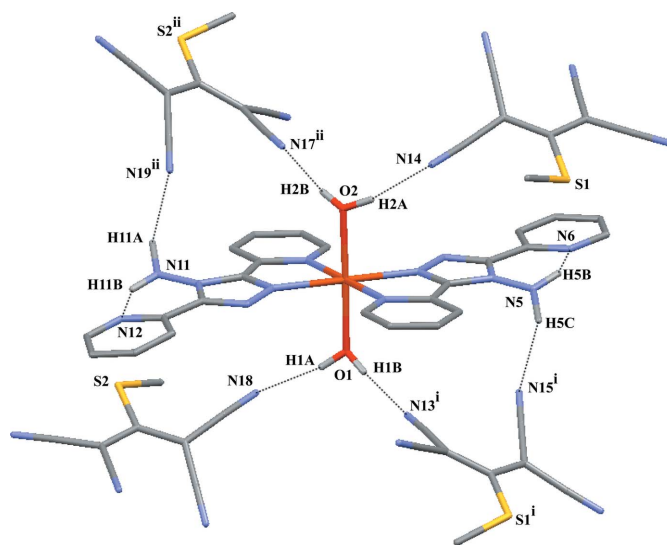


Figure 2

A view of the [Fe(abpt)₂(H₂O)₂]²⁺ dication, surrounded by the hydrogen-bonded tcnsmc anions. O—H···N and N—H···N hydrogen bonds are shown as dashed lines [details are given in Table 1; symmetry codes: (i) $x + \frac{1}{2}, -y + 1, z$; (ii) $x - \frac{1}{2}, -y + 2, z$].

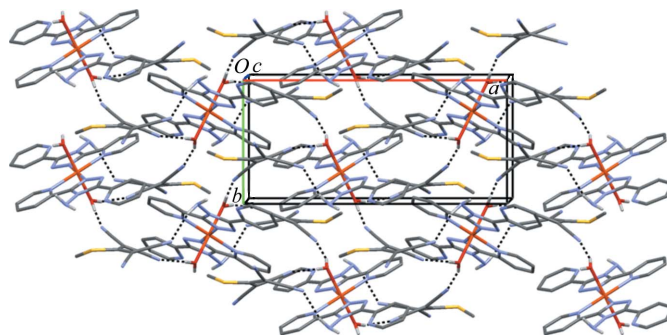


Figure 3

A view, along the *c* axis, of the crystal packing in (I). O—H···N and N—H···N hydrogen bonds are shown as dashed lines (details are given in Table 1).

Due to the presence of the supplementary π electron systems of the cyano groups, the tcnsmc ligands of (I) present a strong electronic delocalization, as indicated by the six almost equivalent C—C bond lengths in the two anions [1.395 (5)–1.428 (5) Å]. The tcnsmc anion can thus be considered as a resonance hybrid of the different canonical structures, giving rise to the mean electronic structure of Fig. 4, which agrees well with the bond lengths and angles. However, it is noteworthy that, despite this high conjugation, the anions deviate significantly from planarity, since the two almost planar $-C(CN)_2$ wings are tilted out of the plane containing the central C25/C26/C29/S1 and C33/C34/C37/S2 fragments. For the tcnsmc anion involving atom S1, the tilt angles, namely the angles between the central C25/C26/C29/S1 plane and the C26/C27/C28 and C29/C30/C31 planes, are 24.0 (4) and 12.3 (4)°, respectively, although the dihedral angle between the two wings is 33.9 (6)°. For the tcnsmc anion involving atom S2, the tilt angles, namely the angles between the central C33/C34/C37/S2 plane and the C34/C35/C36 and C37/C38/C39

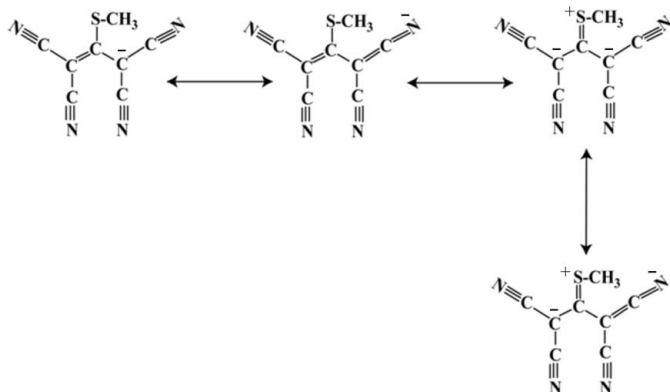


Figure 4
The different canonical structures of the tcnsmc anion.

planes, are 24.0 (4) and 16.4 (4)°, respectively. Here, the dihedral angle between the two wings is 37.0 (6)°.

A number of mononuclear SCO complexes with the formula $[\text{Fe}(\text{abpt})_2\text{X}_2]$ have been synthesized (Kunkeler *et al.*, 1996; Moliner *et al.*, 1998, 1999, 2001; Sheu *et al.*, 2008, 2009; Dupouy *et al.*, 2008, 2009). They have two bidentate abpt ligands in equatorial positions and two axial anion ligands, such as $X = \text{N}(\text{CN})_2$ (dicyanamide), NCS (isothiocyanate), NCSe (isoselenocyanate), TCNQ (7,7,8,8-tetracyanoquinodimethane), $\text{C}(\text{CN})_3$ (tricyanomethanide), tcnocet (1,1,3,3-tetracyano-2-ethoxypropenide) and tcpd (2-dicyanomethylene-1,1,3,3-tetracyanopropanediide). Examination of the molecular structure of these complexes reveals compact molecules in the lattice with π - π stacking interactions, and shows rather planar abpt ligands with a small dihedral angle between the uncoordinated pyridine and the triazole rings. In the present study, no π - π stacking interactions were observed. This is probably due to the fact that the axial N atoms are replaced by water molecules in (I), which may provide a reason for the stabilization of the HS state and may also be responsible for the absence of the SCO phenomenon.

Experimental

All reagents were purchased from commercial sources and used as received. Potassium 1,1,3,3-tetracyano-2-methylthiopropenide (Ktensme) was synthesized according to a published procedure (Edwards & Kendall, 1950). To an aqueous solution of FeCl_2 (0.025 g, 5 ml) was added dropwise an ethanolic solution of 4-amino-3,5-di-2-pyridyl-1,2,4-triazole (0.093 g, 10 ml), resulting in a red suspension. Ktensme was dissolved in water (0.089 g, 10 ml) and added quickly to the mixture. The final solution was filtered and the filtrate allowed to evaporate in air for a week, giving red crystals of (I) suitable for X-ray diffraction analysis.

Crystal data

$[\text{Fe}(\text{C}_{12}\text{H}_{10}\text{N}_6)_2(\text{H}_2\text{O})_2](\text{C}_8\text{H}_3\text{N}_4\text{S})_2$	$V = 4297.66$ (16) Å ³
$M_r = 942.81$	$Z = 4$
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
$a = 17.0060$ (4) Å	$\mu = 0.51$ mm ⁻¹
$b = 7.9570$ (2) Å	$T = 170$ K
$c = 31.7600$ (5) Å	$0.45 \times 0.30 \times 0.25$ mm

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 N18	0.84 (3)	2.02 (3)	2.847 (4)	167 (3)
O1–H1B \cdots N13 ⁱ	0.81 (3)	2.10 (3)	2.888 (4)	166 (4)
O2–H2A \cdots N14	0.85 (3)	2.00 (3)	2.824 (4)	161 (3)
O2–H2B \cdots N17 ⁱⁱ	0.82 (3)	2.09 (3)	2.899 (4)	169 (3)
N5–H5B \cdots N6	0.91	2.18	2.852 (5)	130
N5–H5C \cdots N15 ⁱ	0.91	2.16	3.008 (5)	154
N11–H11A \cdots N19 ⁱⁱ	0.91	2.16	3.004 (5)	155
N11–H11B \cdots N12	0.91	2.15	2.847 (4)	132

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

Data collection

Oxford Xcalibur 2 CCD diffractometer	91385 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	9408 independent reflections
$T_{\min} = 0.859, T_{\max} = 1.000$	6273 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.103$	$\Delta\rho_{\text{max}} = 0.62$ e Å ⁻³
$S = 1.12$	$\Delta\rho_{\text{min}} = -0.32$ e Å ⁻³
9408 reflections	Absolute structure: Flack (1983), with 4478 Friedel pairs
603 parameters	Flack parameter: 0.546 (17)
5 restraints	

The crystal structure was refined as an inversion twin, with the major twin fraction refining to a value of 0.546 (17). The H atoms of the water molecules and NH_2 groups could all be located in difference Fourier maps. The water H atoms were refined with a distance restraint of $\text{O}-\text{H} = 0.84$ (2) Å. The difference maps showed that the NH_2 H atoms were arranged pyramidally and they were subsequently allowed for using tetrahedral NH_3 -type constraints (AFIX 137; *SHELXL97*; Sheldrick, 2008) ($\text{N}-\text{H} = 0.91$ Å), with the occupancy of the third H atom set to zero. C-bound H atoms were placed in geometric positions and allowed for using a riding model, with $\text{C}-\text{H} = 0.95$ or 0.98 Å for aromatic and methyl H atoms, respectively. For all H atoms, $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{O,N,C})$, with $k = 1.5$ for the water molecule, the NH_2 group and the methyl H atoms, and $k = 1.2$ for all other H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* and *pubCIF* (Westrip, 2010).

The X-ray data were collected at the University of Bretagne Occidentale (UBO; UMR CNRS 6521). FS thanks Professor S. Triki for providing access to the X-ray diffraction facilities, and the Université Ferhat Abbas de Sétif, Algeria, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3192). Services for accessing these data are described at the back of the journal.

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