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catena-Poly[[diaquadiisothiocyanatoiron(II)]-μ-4,4′-bi-1,2,4-triazole]: a one-dimensional coordination polymer

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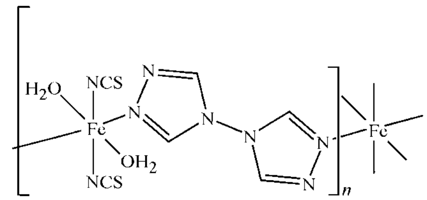
In the title complex, $[Fe(NCS)_2(C_4H_2N_6)_2(H_2O)_2]_n$, the Fe^{II} atom is on an inversion centre and the 4,4′-bi-1,2,4-triazole (btr) group is bisected by a twofold axis through the central N—N bond. The coordination geometry of the Fe^{II} atom is elongated distorted FeN_4O_2 octahedral, where the cation is coordinated by two N atoms from the triazole rings of two btr groups, two N atoms from NCS^- ligands and two water molecules. Btr is a bidentate ligand, coordinating one Fe^{II} atom through a peripheral N atom of each triazole ring, leading to a one-dimensional polymeric (chain) structure extending along [101]. The chains are further connected through a network of O—H···N and C—H···S hydrogen bonds.

Comment

Recently, considerable interest has been paid to iron coordination complexes which exhibit a large variety of magnetic behaviour ranging from purely high spin (S = 2) to low spin (S = 0) and solid-state spin-crossover. In general, the difference in electron configuration of the central Fe atom parallels large structural modifications of the coordination geometry, especially the Fe–ligand bond lengths. In the case of spin-crossover materials, the characteristics of the spin transition (*e.g.* transition temperature, transition abruptness or hysteresis) are closely related to the structural features, such as Fe^{II} coordination geometry, crystal packing, or the presence of solvent molecules or counter-ions in the voids of the structure (Gütlich *et al.*, 1994). Co-operative interactions in the solid are a prerequisite for practical applications of these materials in nanotechnology and molecular electronics, since co-operativity may govern hysteretic spin transitions. One strategy for designing highly co-operative systems relies on the use of polydentate bridging ligands with the hope of creating a polymeric structural organization in the solid state. Numerous Fe spin-crossover materials exhibit an extended polymeric structure, and among these infinite chains, planar and three-dimensional networks built up from 4-substituted 1,2,4-triazole units have been described. We report here the crystal structure analysis of the title polymeric Fe^{II} coordination complex, $[Fe(NCS)_2(btr)_2(H_2O)_2]_n$ (btr is 4,4′-bi-1,2,4-triazole), (I), with a one-dimensional topology.



(I)

The Fe atom in (I) lies on an inversion centre and the btr group is bisected by a twofold axis through the central N—N bond. The coordination geometry of the cation is an elongated distorted FeN_4O_2 octahedron involving two N atoms from two triazole rings, two N atoms from thiocyanate ligands and two water molecules (Fig. 1). The coordination polyhedron is highly elongated in the triazole directions, with similar Fe—N1 and Fe—O1 bond lengths in the basal plane, which are typical for $[Fe(NCS)_2(L)_2(H_2O)_2]$ complexes in the high-spin electron configuration. In contrast, the Fe—N2 bond of 2.2319 (5) Å is the longest observed for any 4-substituted 1,2,4-triazole ligand. For comparison, values from 2.180 (3) to 2.223 (3) Å have been reported for the layer systems $[Fe(NCS)_2(btre)_2]$ [btre is 1,2-bis(1,2,4-triazol-4-yl)ethane] (Garcia *et al.*, 2005) and $[Fe(NCS)_2(btr)_2]\cdot H_2O$ (Vreugdenhil *et al.*, 1990), and from 2.151 (3) to 2.164 (3) Å for the three-dimensional complex $[Fe(btr)_3](ClO_4)_2$ (Garcia *et al.*, 1999). Considerably shorter Fe—N bonds, in the range 1.950 (2)–1.994 (5) Å, are observed for the corresponding low-spin states (Pillet *et al.*, 2004; Garcia *et al.*, 1999).

According to the coordination geometry in (I), it is expected that the electron configuration of the central Fe atom is high spin, with an attempted assignment of the quantum axis as x and y along N1 and O1 and z along N2, as a result of the pseudo-$D4h$ distortion. The high-spin electron configuration would also be in agreement with the colourless aspect of the crystals at room temperature and even at 120 K; the lowest

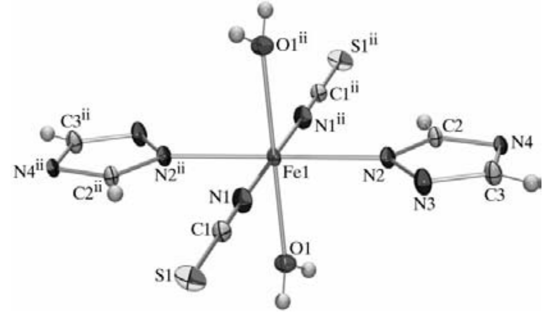


Figure 1
The coordination environment of atom Fe1 in (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. [Symmetry code: (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

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energy d–d spin-allowed transition ($^5T_{2g} \rightarrow ^5E_g$) generally occurs in the near-IR for this class of compound. In addition, several other complexes for which the central Fe^{II} ion is FeN_4O_2-coordinated by two water molecules and four btr ligands have been reported and their high-spin state confirmed by magnetic and Mössbauer measurements (Garcia *et al.*, 2001).

The octahedral angular distortion in (I), defined as the sum of the deviations from 90° of the 12 X—Fe—Y angles (Σ = 13°), is at the lower limit of all the other bitriazole (btr and btre) complexes listed above (14.8–21.2°) and is small compared with typical high-spin Fe^{II} complexes (Guionneau *et al.*, 2004).

The NCS group of (I) adopts a quasi-linear geometry with respect to the Fe atom, with an Fe—N—C angle of 175.48 (6)°. The triazole rings are oriented in an almost planar configuration with respect to the Fe atom and NCS groups, induced by a weak C2—H2···N1^{ii} hydrogen bond [symmetry code: (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$]; the r.m.s. deviation of all the atoms concerned from the mean plane is 0.04 Å. As for the btr group, the C—N and N—N bond lengths, and especially the differences between the longest (C2—N4 and C3—N4) and shortest (C2—N2 and C3—N3) bonds, are consistent with those reported in the literature (Domiano, 1977; Garcia *et al.*, 1999; Vreugdenhil *et al.*, 1990; Pillet *et al.*, 2004) and indicative of the main mesomeric form depicted in the chemical scheme and discussed recently in the light of electron-density results for $[Fe(NCS)_2(btr)_2]\cdot H_2O$ (Legrand *et al.*, 2006). On the other hand, the dihedral angle between the two symmetry-related (symmetry code: $-x, y, -z + \frac{1}{2}$) triazole rings of one btr fragment [72.58 (2)°] is clearly lower than in all other btr-containing materials, with dihedral angles ranging from 90° in crystalline btr (Domiano, 1977) to 77.35° in $[Fe(btr)_3](ClO_4)_2$ (Garcia *et al.*, 1999). Free rotation of the two triazole rings around the central N4—N4^{i} bond [symmetry code: (i) $-x, y, -z + \frac{1}{2}$] is hindered by the potential H···H close contact that would arise if the dihedral angle were too low.

The crystal packing of compound (I) consists of Fe atoms bridged by btr ligands to form infinite parallel chains running along the [101] crystallographic direction. The corresponding Fe···Fe separation along the chains [9.1937 (3) Å] is in the same range as the separation in the high-spin crystal structure of $[Fe(NCS)_2(btr)_2]\cdot H_2O$ at room temperature [9.30 (2) Å] and is much longer than that in the high-spin structure of $[Fe(btr)_3](ClO_4)_2$ at 260 K (8.67 Å). The chains are connected through a network of O—H···N and C—H···S hydrogen bonds in the (010) plane and in the perpendicular [010] direction, leading to a three-dimensional network with corresponding shortest inter-chain Fe···Fe separations of 6.6559 (1) and 5.8299 (1) Å, respectively (Fig. 2). The shortest hydrogen bond, O1—H5···N3^{iii}, occurs in the [010] direction [symmetry code: (iii) $x, y - 1, z$]. Even though the C2—H2···S1^{v} hydrogen bond [symmetry code: (v) $x - \frac{1}{2}, y - \frac{1}{2}, z$] might seem rather long at first sight, we suspect it is nevertheless involved in the stabilization of the chain packing, as can be judged in Fig. 2(b).

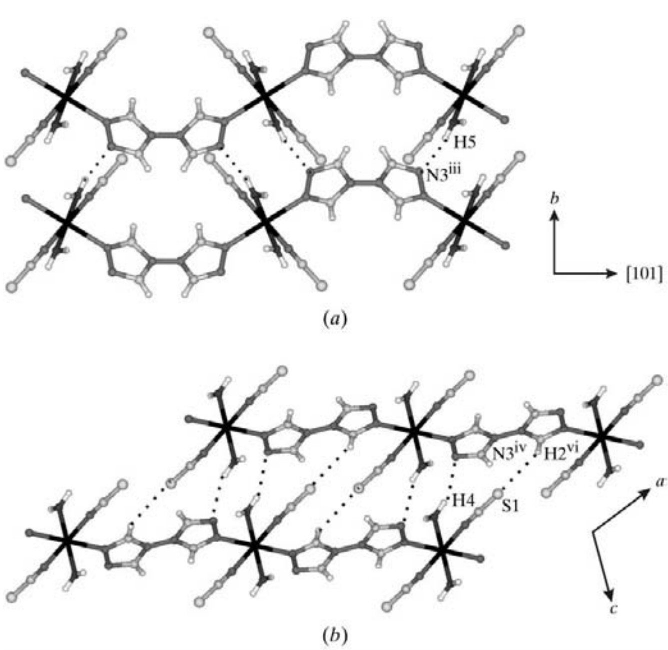

Figure 2
Two views of the packing of chains at right angles to one another around the [101] chain direction and showing hydrogen-bond contacts. (a) A view normal to the b axis and (b) a view along the b axis. [Symmetry codes: (iii) $x, y - 1, z$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x + \frac{1}{2}, y - \frac{1}{2}, z$.]

Experimental

The ligand 4,4′-bi-1,2,4-triazole (btr) was synthesized as described by Haasnoot & Groeneveld (1979). A solution containing btr (0.40 g, 2.94 mmol) dissolved in a mixture of water (5 ml) and methanol (5 ml) was warmed to 333 K and added to a solution containing $[Fe(H_2O)_6](ClO_4)_2$ (0.35 g, 0.96 mmol) and ascorbic acid (1 mg) dissolved in water (10 ml) warmed to 333 K. The resulting solution was layered on top of dichloromethane (10 ml) in a closed test tube. Large colourless single crystals of (I) grew at the water–methanol/dichloromethane interface over a period of several weeks. The crystals were air sensitive.

Crystal data

$[Fe(NCS)_2(C_4H_2N_6)_2(H_2O)_2]$
M_r = 343.85
Monoclinic, $C2/c$
a = 19.2178 (4) Å
b = 5.82990 (10) Å
c = 11.9673 (2) Å
β = 112.287 (2)°
V = 1240.63 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.56 mm^{-1}
T = 120 (2) K
0.19 × 0.14 × 0.09 mm

Data collection

Oxford Xcalibur CCD area-detector diffractometer
Absorption correction: Gaussian (*CrysAlis RED*; Oxford Diffraction, 2003)
T_{min} = 0.69, T_{max} = 0.83
13719 measured reflections
3829 independent reflections
3300 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.073
S = 1.09
3829 reflections
102 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 1.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	2.0928 (6)	C3—N3	1.3074 (8)
Fe1—N2	2.2319 (5)	C2—N4	1.3584 (8)
Fe1—O1	2.1192 (5)	C3—N4	1.3633 (9)
N1—C1	1.1671 (8)	N2—N3	1.3898 (8)
C1—S1	1.6293 (7)	N4—N4^{i}	1.3728 (10)
C2—N2	1.3006 (8)		
N1—Fe1—N2	91.36 (2)	Fe1—N1—C1	175.48 (6)
N1—Fe1—O1	88.58 (2)	N1—C1—S1	179.40 (6)
O1—Fe1—N2	90.47 (2)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H4···N3^{iv}	0.837 (19)	2.42 (2)	3.1989 (9)	155.1 (16)
O1—H5···N3^{iii}	0.835 (19)	2.021 (19)	2.8435 (8)	168.4 (17)
C2—H2···N1^{ii}	0.923 (14)	2.523 (13)	3.0625 (9)	117.7 (10)
C2—H2···S1^{v}	0.923 (14)	2.875 (14)	3.5000 (6)	126.2 (10)

Symmetry codes: (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $x, y - 1, z$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

H atoms were located in a difference Fourier synthesis and refined freely [C—H = 0.908 (14)–0.923 (14) Å and O—H = 0.835 (19)–0.837 (19) Å], with (different) global isotropic displacement parameters for C- and O-bound H atoms. The highest positive residual electron-density peak is located at the Fe site, on the centre of inversion.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3030). Services for accessing these data are described at the back of the journal.

References

Domiano, P. (1977). *Cryst. Struct. Commun.* **6**, 503–506.
Farrugia, L. J. (1999). *WinGX*. Version 1.64.02. University of Glasgow, Scotland.
Garcia, Y., Bravic, G., Gieck, C., Chasseau, D., Tremel, W. & Gütlich, P. (2005). *Inorg. Chem.* **44**, 9723–9730.
Garcia, Y., Kahn, O., Rabardel, L., Chansou, B., Salmon, L. & Tuchagues, J. P. (1999). *Inorg. Chem.* **38**, 4663–4670.
Garcia, Y., Ksenofontov, V. & Gütlcih, P. (2001). *C. R. Acad. Sci.* **4**, 227–233.
Guionneau, P., Marchivie, M., Bravic, G., Létard, J.-F. & Chasseau, D. (2004). *Topics in Current Chemistry*, Vol. 234, *Spin Crossover in Transition Metal Compounds II*, edited by P. Gütlich & H. A. Goodwin, pp. 97–128. Berlin: Springer-Verlag.
Gütlich, P., Hauser, A. & Spiering, H. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 2024–2054.
Haasnoot, J. G. & Groeneveld, W. L. (1979). *Z. Naturforsch. Teil B*, **34**, 1500–1506.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Legrand, V., Pillet, S., Souhassou, M., Lugan, N. & Lecomte, C. (2006). *J. Am. Chem. Soc.* **128**, 13921–13931.
Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.170. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Pillet, S., Hubsch, J. & Lecomte, C. (2004). *Eur. Phys. J. B*, **38**, 541–552.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Vreugdenhil, W., Van Diemen, J. H., De Graaff, R. A. G., Haasnoot, J. G., Reedijk, J., Van Der Kraan, A. M., Kahn, O. & Zarembowitch, J. (1990). *Polyhedron*, **9**, 2971–2979.