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Bis(thiocarbohydrazide)dithiocyanato-iron(II)

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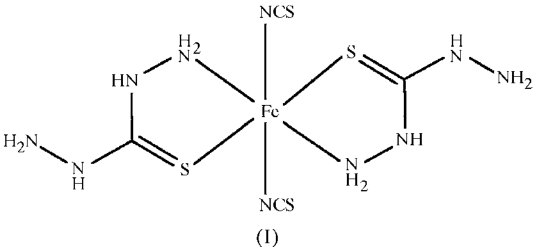
In the title compound, [Fe^{II}(NCS)$_2$(CH$_6$N$_4$S)$_2$], the Fe^{II} cation is surrounded by two S atoms and two N atoms from thiocarbohydrazide groups and by two N atoms from thiocyanate groups. The geometry around the Fe^{II} cation, which is located on a center of inversion, is distorted octahedral. The thiocarbohydrazide molecule assumes a *cis–trans* conformation, which is reinforced by an N—H$\cdots$N hydrogen bond. Molecules of the title compound are connected *via* intermolecular N—H$\cdots$S and N—H$\cdots$N hydrogen bonds to form a three-dimensional network structure.

Comment

We previously synthesized bis[4-amino-3-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione]dichlorocopper(II) dihydrate in our laboratory (Cai *et al.*, 2004). In a similar tentative synthetic procedure, FeCl$_3$ was used instead of CuCl$_2$ to prepare iron compounds of the ligand. Unexpectedly, the title compound, (I), was synthesized, where the thiocarbohydrazide (TCH) ligand and thiocyanate anion may result from reaction of 4-amino-1,2,4-triazole-5-thione (ATT). From a search of the Cambridge Structural Database (Allen, 2002), it is known that only five crystal structures of TCH compounds (Braibanti *et al.*, 1969, 1971, 1972; Bigoli *et al.*, 1971, 1972) have been reported so far. In this paper, we study the structure of (I).



(I)

In (I) (Fig. 1 and Table 1), the Fe^{II} ion is located on an inversion center. Owing to the obvious differences of bond lengths and bond angles around the Fe^{II} ion, the coordination is distorted octahedral. The equatorial plane consists of two amine N atoms and two S atoms from two TCH ligands, and the axial positions are filled by two N atoms from thiocyanate anions. The bond lengths in the thiocyanate anions agree with data reported previously (Petrucenko *et al.*, 1997; Wharf & Simard, 1998). The Fe^{II} ion is located in the C1/N1/N2/S1/Fe plane, which has an r.m.s. deviation of 0.041 (3) Å. The structure is similar to that of bis(TCH)dichlorocadmium, except for the fact that in the latter the Cd atom lies out of the equivalent plane (Bigoli *et al.*, 1971).

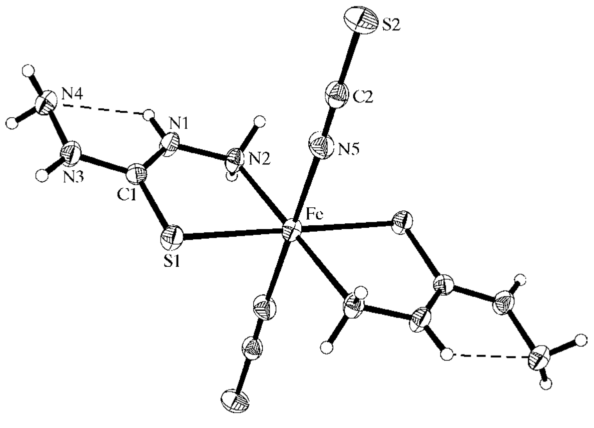
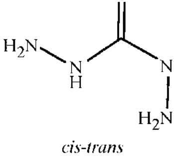
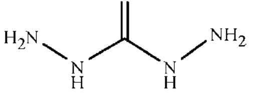


Figure 1
The formula unit of (I), with atom labels, showing 40% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

TCH molecules may assume *cis–trans* or *cis–cis* conformations (see scheme below). In the title compound, TCH assumes a *cis–trans* conformation, which has also been found in neutral TCH (Braibanti *et al.*, 1969), bis(TCH)dichlorocadmium (Bigoli *et al.*, 1971) and TCH hemihydrochloride (Braibanti *et al.*, 1972). Conversely, the *cis–cis* conformation has been observed in TCH dihydrochloride dihydrate (Braibanti *et al.*, 1971) and TCH sulfate (Bigoli *et al.*, 1972). Interestingly, the *cis–trans* conformation is reinforced by an N1—H1$\cdots$N4 hydrogen bond [2.590 (3) Å; Fig. 1 and Table 2).



cis-trans



cis-cis

There are six kinds of intramolecular N—H$\cdots$S hydrogen bonds with H$\cdots$S distances shorter than 2.9 Å (the sum of the van der Waals radii of H and S atoms; Allen *et al.*, 1997). As shown in Fig. 2, molecules of (I) are connected by N4—H4$B\cdots$S1$^{\rm iii}$ and N4—H4$A\cdots$S2$^{\rm iv}$ hydrogen bonds to form one-dimensional chains along the [001] direction (Fig. 2 and Table 2). Neighboring chains are associated with one another by an N1—H1$\cdots$S2$^{\rm i}$ hydrogen bond and are interrelated by translation to produce a supramolecular layer parallel to (100). There are various hydrogen-bonded rings embedded in

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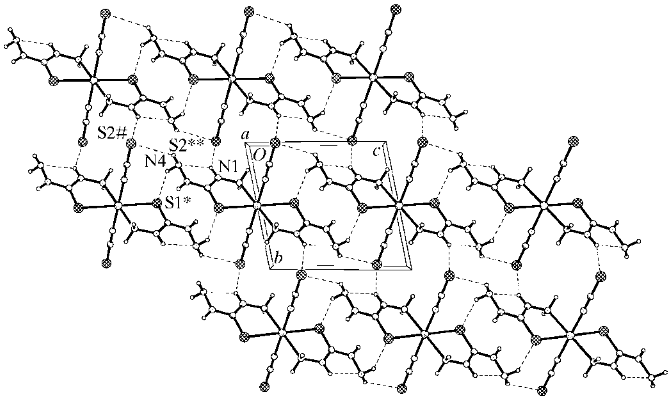

Figure 2
Part of the crystal structure, showing a supramolecular layer of N—H···S hydrogen bonds, which is built up from N—H···S hydrogen-bonded chains. Hydrogen bonds are shown as dashed lines. Atoms labeled with a hash (#), an asterisk (*) or two asterisks (**) are at the symmetry positions (x, y, $z-1$), ($-x$, $-y+1$, $-z-1$) and ($-x$, $-y$, $-z$), respectively.

the layer (Fig. 2), which can be described in graph-set notation (Etter, 1990; Grell *et al.*, 2000) as $R_1^1(5)$, $R_2^2(8)$, $R_2^2(10)$, $R_2^2(14)$ and $R_4^4(8)$. The layers are associated by N2—H2A···S2$^{\rm ii}$, N2—H2B···S1$^{\rm ii}$ and N3—H3···S1$^{\rm v}$ hydrogen bonds.

Experimental

The title compound was synthesized by a hydrothermal method from a mixture of ATT (4 mmol, 0.76 g), $FeCl_3$ (1 mmol, 0.16 g) and water (20 ml) in a 30 ml Tefon-lined stainless steel reactor. The solution was heated to 415 K for 3 d. After the reaction system had been cooled slowly to room temperature, pale-blue block-shaped crystals were collected and washed with distilled water.

Crystal data

$[Fe(NCS)_2(CH_6N_4S)_2]$
M_r = 384.37
Triclinic, $P\overline{1}$
a = 5.2176 (6) Å
b = 8.0061 (9) Å
c = 8.7683 (10) Å
α = 78.662 (2)°
β = 84.150 (2)°
γ = 88.891 (2)°
V = 357.26 (7) Å^3

Z = 1
D_x = 1.786 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 856 reflections
θ = 2.6–24.3°
μ = 1.64 mm^{-1}
T = 273 (2) K
Block, pale blue
0.37 × 0.16 × 0.12 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\rm min}$ = 0.729, $T_{\rm max}$ = 0.824
1926 measured reflections

1299 independent reflections
1240 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.009
$\theta_{\rm max}$ = 25.3°
$h = -6 \rightarrow 5$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 9$

Table 1
Selected geometric parameters (Å, °).

Fe—N5	2.118 (2)	Fe—S1	2.5699 (6)
Fe—N2	2.187 (2)		
N5—Fe—N2	87.93 (8)	N2—Fe—S1	79.18 (5)
N5—Fe—S1	89.91 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N4	0.92	2.21	2.590 (3)	104
N1—H1···S2$^{\rm i}$	0.92	2.60	3.397 (2)	145
N2—H2A···S2$^{\rm ii}$	0.95	2.65	3.510 (2)	151
N2—H2B···S1$^{\rm ii}$	0.93	2.57	3.443 (2)	157
N4—H4B···S1$^{\rm iii}$	0.92	2.70	3.482 (2)	143
N4—H4A···S2$^{\rm iv}$	0.89	2.89	3.597 (2)	138
N3—H3···S1$^{\rm v}$	0.90	2.68	3.565 (2)	167

Symmetry codes: (i) $-x, -y, -z$; (ii) $x-1, y, z$; (iii) $-x, -y+1, -z-1$; (iv) $x, y, z-1$; (v) $-x+1, -y+1, -z-1$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.080
S = 1.07
1276 reflections
88 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.3522P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.29 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.48 e Å^{-3}

All H atoms were located in a difference Fourier map and were allowed for at these positions with $U_{\rm iso}$(H) values set at 0.08 Å^2.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; 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: AV1233). Services for accessing these data are described at the back of the journal.

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