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Crystal structure of poly[tetra-μ_2-cyanido-1:2κ^8*N*:*C*-bis(dimethyl sulfoxide-1κ*O*)-diargentate(I)iron(II)]

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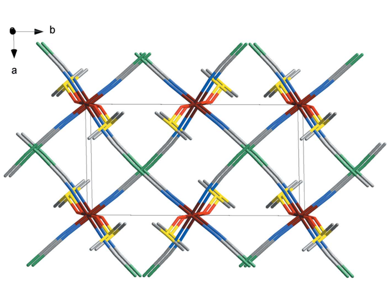
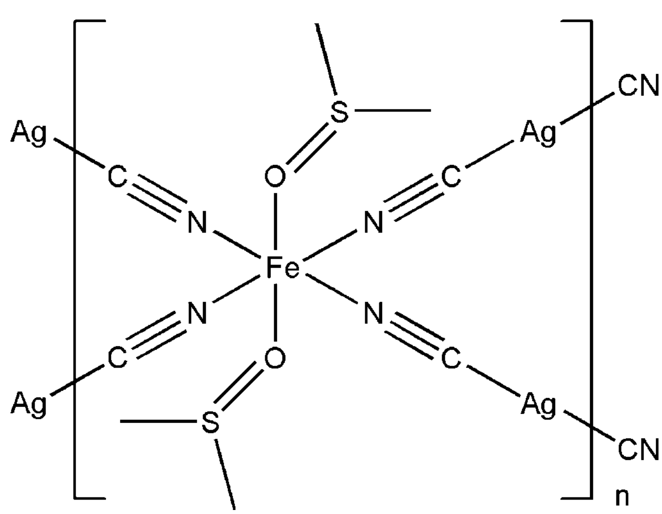
In the title polymeric complex, $[Fe\{OS(CH_3)_2\}_2\{Ag(CN)_2\}_2]$, the Fe^{II} cation is located at an inversion centre and is coordinated by four cyanide (CN^-) anions and two dimethyl sulfoxide molecules in a slightly compressed N_4O_2 octahedral geometry, the Ag^I cation is C-coordinated by two CN^- anions in a nearly linear geometry. The CN^- anions bridge the Fe^{II} and Ag^I cations to form a two-dimensional polymeric structure extending parallel to (102). In the crystal, the nearest Ag$\cdots$Ag distance between polymeric sheets is 3.8122 (12) Å. The crystal studied was a twin with a contribution of 0.2108 (12) for the minor component.

1. Chemical context

Metal–organic frameworks (MOFs), also known as porous coordination polymers, form a group of compounds that consist of metal ions and organic ligand linkers (Zhou & Kitagawa, 2014). MOFs have attracted considerable attention over the past decades due to the ability to tune their porosity, structure and other properties by a rational choice of the metal and linkers. Despite the fact that the most investigated properties of MOFs are gas storage and separation, it has been shown that the incorporation of corresponding building blocks or guests into MOFs can provoke specific functional magnetic, chiral, catalytic, conductive, luminescence and other properties.





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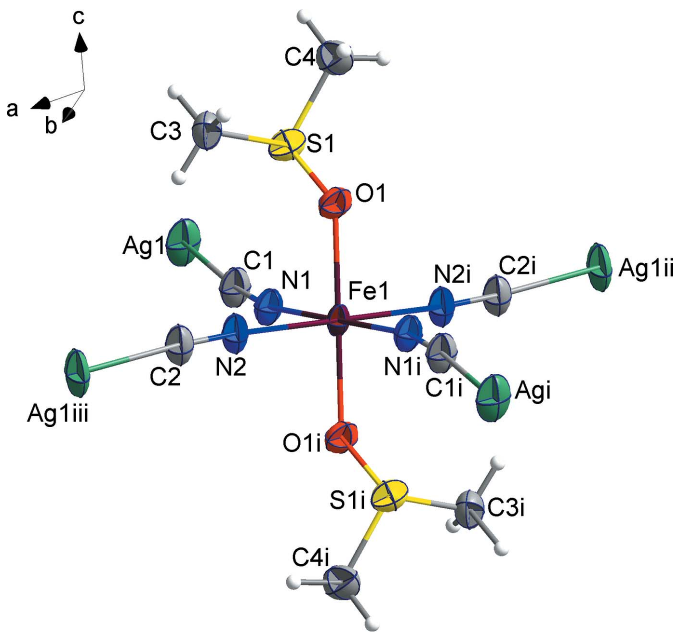

Figure 1
coordination environments of the Fe^{II} and Ag^{I} atoms in the structure of the title compound, showing the atom-labelling scheme, with displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

Hofmann clathrate analogues represent a huge group of MOFs. The first prototype clathrate of this family was $[Ni(NH_3)_2\{Ni(CN)_4\}]$ reported by Hofmann & Küspert (1897), however its structure was only obtained by Powell & Rayner (1949). The structure analysis showed that the coordination framework of this complex is supported by bridging square-planar tetracyanidonickelate ligands, and the octahedral coordination sphere of Ni^{II} is completed by two NH_3 molecules. The layers in this clathrate are separated by ~8 Å, which leads to the formation of guest-accessible cavities. This has allowed a series of clathrates to obtained with different aromatic guests such as benzene, phenol, aniline, pyridine, thiophene and pyrrole. Later, the group of Hofmann clathrate analogues was expanded to $[M(L)_2\{M'(CN)_4\}]$ where M = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Mn^{2+}, M' = Ni^{2+}, Pd^{2+}, Pt^{2+} and L is either a unidentate or bridging ligand to form two- or three-dimensional coordination frameworks, respectively.

More importantly, due to the rational choice of ligand, Kitazawa *et al.* (1996) succeeded in obtaining the first Hofmann-type complex $[Fe(py)_2\{Ni(CN)_4\}]$ that exhibited spin-crossover behavior. This phenomenon is a spectacular ability of some 3*d* metals to exist in two different spin states. This discovery has led to multiple attempts to modify this compound in order to obtain other spin-crossover materials. The main synthetic approaches are: (*a*) the change of the pyridine ligand to other unidentate or bridging ligands; (*b*) the induction of various guest molecules that influence spin-crossover characteristics; (*c*) use of different square-planar $\{[M(CN)_4]^{2-}$, M = Ni^{2+}, Pt^{2+}, Pd^{2+}; Kucheriv *et al.*, 2016}, dodecahedral $\{[Nb(CN)_8]^{4-}$; Ohkoshi *et al.*, 2013} or linear $\{[M(CN)_2]^{-}$, M = Ag^{+}, Au^{+}; Gural'skiy *et al.*, 2016*b*} linkers. Here we offer a new Hofmann-like coordination compound with general formula $[Fe(dmso)_2\{Ag(CN)_2\}_2]$ in which the Fe^{II} atoms are stabilized in a high-spin state.

2. Structural commentary

The crystal structure of the title compound was determined from 243 K data. The Fe^{II} cation is located at an inversion centre and coordinated by four CN^{-} anions and two dimethylsulfoxide molecules in a slightly compressed N_4O_2 octahedral environment (Fig. 1). The Ag^{I} cation is C-coordinated by two CN^{-} anions in a nearly linear mode [C1—Ag—C2 = 173.0 (3)°]. The CN^{-} anions bridge the Fe^{II} and Ag^{I} cations to form a two-dimensional polymeric structure. In the structure, the equatorial Fe—N bonds [2.166 (4) and 2.176 (4) Å] have the typical value for Fe^{II} in a high-spin state. The axial positions of the Fe^{II} cation are occupied by two dimethylsulfoxide molecules with an Fe—O bond length of 2.096 (4) Å. The S=O bond length of 1.532 (4) Å is increased

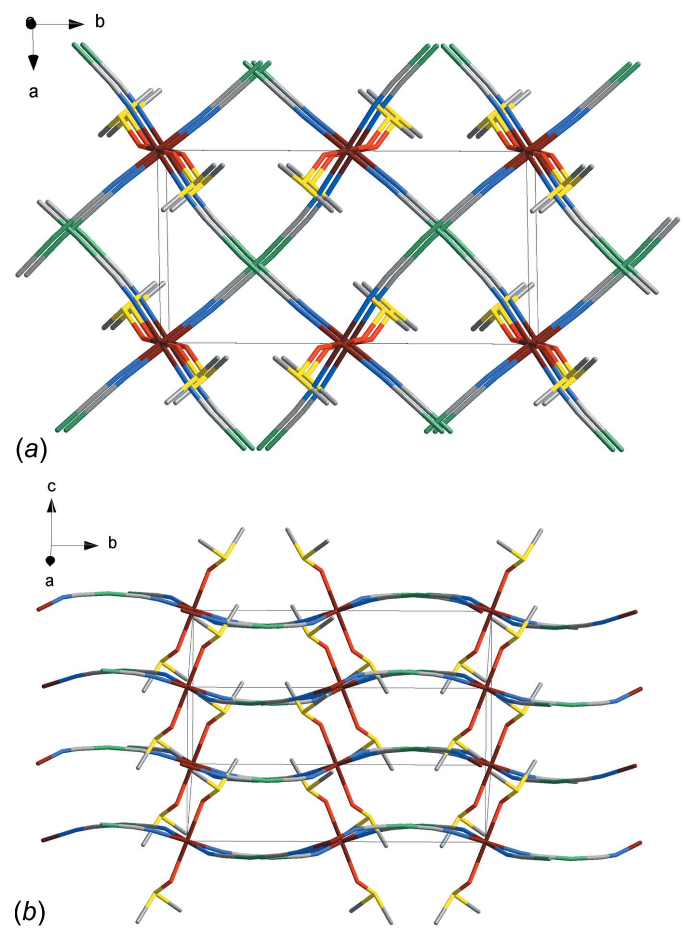

Figure 2
(a) View of the crystal structure of the title compound in the *ab* plane. H atoms have been omitted for clarity. (b) View of the crystal structure showing the two-dimensional layers. Colour key: brown Fe, green Ag, yellow S, blue N, grey C and red O.

by 0.03 Å with respect to non-coordinating dmso; the average S—C bond of 1.774 (6) Å is shorter than in those in non-coordinating dimethylsulfoxide. This is a typical value for O-bonded dimethylsulfoxide complexes (Calligaris, 2004). The torsion angles around the Fe—O bond are Fe1—O1—S1—C3 = 96.3 (3)° and Fe1—O1—S1—C4 = −159.2 (3)°. The polyhedral distortion which is described by the deviation from an octahedral geometry is ΣFe\|90 − Θ\| = 9.86 (16)° where Θ is the N—Fe—N or O—Fe—N angle in the coordination environment of the metal; however, this value is slightly lower than expected for a high-spin Fe^{II} complex.

3. Supramolecular features

The coordination framework is connected by bridging dicyanidoargentate moieties into a two-dimensional grid that propagates along the (102) plane (Fig. 2*a*). The short interlayer Ag···Ag distance of 3.8122 (12) Å indicates argentophilic interactions that propagate along the *c*-axis direction. A similar type of intermolecular bonding between seemingly closed-shell metal atoms has previously been reported for many Ag- and Au-containing Hofmann-type structures, *e.g.* Au···Au distances of 3.3792 (3) Å were found between the $[Fe\{Au(CN)_2\}^-]$ planes (Gural'skiy *et al.*, 2016*a*). In addition, in the title compound the Fe—N—C and Ag—C—N linkages show a slight deviation from linearity (9.5 and 6° on average, respectively) that leads to a slight corrugation of $[Fe\{Ag(CN)_2\}^-]$ layers (Fig. 2*b*).

4. Database survey

The title compound has never been obtained before. A database survey reveals numerous Fe–Ag CN-bridged frameworks supported by various co-ligands axially bound to the iron atoms.

5. Synthesis and crystallization

Crystals of the title compound were obtained by the slow-diffusion method within three layers in 10 ml tubes: the first layer was a solution of $Fe(ClO_4)_2$ (0.1 mmol, 26 mg) in dimethylsulfoxide (2 ml); second one was a dimethylsulfoxide–ethanol mixture (1:1, 5 ml); the third was a solution of $K[Ag(CN)_2]$ (0.1 mmol, 20 mg) in an ethanol–water mixture (9:1 ratio *v*/*v*, 2 ml). After two weeks, orange crystals grew in the second layer; they were collected and kept under the mother solution prior to the measurements.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms of methyl groups were placed geometrically at their expected calculated positions with C—H = 0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The idealized CH_3 group was fixed using an AFIX 137 command that allowed the H atoms to ride on C atom and rotate around S—C bond. Twining of two components was considered with the transformation matrix ($\bar{1}$ 0 $\bar{1}$ 0 $\bar{1}$ 0 0 0 1) and a twin contribution of BASF = 0.2108 (12).

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Ag_2Fe(CN)_4(C_2H_6OS)_2]$
M_r	531.93
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	243
a, *b*, *c* (Å)	8.4125 (16), 14.492 (3), 7.4679 (14)
β (°)	116.053 (4)
V (Å^3)	817.9 (3)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	3.50
Crystal size (mm)	0.15 × 0.1 × 0.05
Data collection	
Diffractometer	Bruker SMART
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.625, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16468, 1970, 1726
R_{int}	0.045
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.031, 0.071, 1.16
No. of reflections	1970
No. of parameters	91
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.42, −1.05

Computer programs: *SMART* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg *et al.*, 1999) and *publCIF* (Westrip, 2010).

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Computing details

Data collection: *SMART* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg *et al.*, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[tetra-μ_2-cyanido-1:2κ^8*N*:*C*-bis(dimethyl sulfoxide-1κ*O*)diargentate(I)iron(II)]

Crystal data

$[Ag_2Fe(CN)_4(C_2H_6OS)_2]$
M_r = 531.93
Monoclinic, $P2_1/c$
a = 8.4125 (16) Å
b = 14.492 (3) Å
c = 7.4679 (14) Å
β = 116.053 (4)°
V = 817.9 (3) Å^3
Z = 2
$F(000)$ = 512
D_x = 2.160 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4840 reflections
θ = 2.7–26.2°
μ = 3.50 mm^{-1}
T = 243 K
Plate, orange
0.15 × 0.1 × 0.05 mm

Data collection

Bruker SMART diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.625, T_{max} = 0.746
16468 measured reflections
1970 independent reflections
1726 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 28.0°, θ_{min} = 1.4°
$h = -11 \rightarrow 11$
$k = -19 \rightarrow 19$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.071
S = 1.16
1970 reflections
91 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0068P)^2 + 2.779P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.42 e Å^{-3} $\Delta\rho_{min}$ = −1.05 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ag1	0.45426 (6)	0.72349 (3)	0.33300 (9)	0.05178 (15)
Fe1	1.0000	0.5000	0.5000	0.0255 (2)
S1	1.17380 (18)	0.39095 (9)	0.9253 (2)	0.0377 (3)
C3	1.3090 (7)	0.4721 (4)	1.1049 (9)	0.0494 (16)
H3A	1.3567	0.5158	1.0427	0.074*
H3B	1.4054	0.4402	1.2119	0.074*
H3C	1.2389	0.5049	1.1586	0.074*
C4	1.0778 (8)	0.3340 (4)	1.0651 (9)	0.0478 (15)
H4A	1.0194	0.3789	1.1121	0.072*
H4B	1.1697	0.3029	1.1782	0.072*
H4C	0.9920	0.2890	0.9811	0.072*
O1	1.0225 (5)	0.4471 (3)	0.7713 (5)	0.0376 (8)
N1	0.7675 (5)	0.5774 (3)	0.4638 (7)	0.0349 (10)
C1	0.6498 (6)	0.6262 (4)	0.4204 (9)	0.0404 (12)
N2	0.1741 (5)	0.8859 (3)	0.1555 (7)	0.0391 (11)
C2	0.2720 (7)	0.8283 (4)	0.2252 (10)	0.0419 (13)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.03045 (19)	0.0337 (2)	0.0765 (3)	0.01486 (16)	0.0099 (2)	0.0063 (2)
Fe1	0.0182 (4)	0.0186 (4)	0.0328 (5)	0.0011 (3)	0.0048 (4)	0.0001 (4)
S1	0.0387 (7)	0.0344 (6)	0.0375 (7)	0.0129 (5)	0.0146 (6)	0.0053 (5)
C3	0.029 (3)	0.057 (4)	0.053 (4)	−0.006 (2)	0.010 (3)	0.008 (3)
C4	0.057 (4)	0.035 (3)	0.045 (3)	−0.007 (3)	0.017 (3)	0.002 (3)
O1	0.0322 (18)	0.041 (2)	0.034 (2)	0.0086 (16)	0.0097 (16)	0.0076 (17)
N1	0.0260 (19)	0.033 (2)	0.039 (3)	0.0043 (16)	0.0084 (18)	−0.0005 (19)
C1	0.028 (2)	0.035 (3)	0.051 (3)	0.006 (2)	0.011 (2)	0.001 (3)
N2	0.025 (2)	0.027 (2)	0.054 (3)	0.0036 (17)	0.007 (2)	0.001 (2)
C2	0.028 (2)	0.031 (3)	0.057 (4)	0.003 (2)	0.009 (3)	0.000 (3)

Geometric parameters (Å, º)

Ag1—C1	2.044 (5)	S1—O1	1.523 (4)
Ag1—C2	2.054 (5)	C3—H3A	0.9700
Fe1—O1^{i}	2.096 (4)	C3—H3B	0.9700
Fe1—O1	2.096 (4)	C3—H3C	0.9700
Fe1—N1	2.166 (4)	C4—H4A	0.9700

Fe1—N1^{i}	2.166 (4)	C4—H4B	0.9700
Fe1—N2^{ii}	2.176 (4)	C4—H4C	0.9700
Fe1—N2^{iii}	2.176 (4)	N1—C1	1.142 (6)
S1—C3	1.771 (6)	N2—Fe1^{iv}	2.176 (4)
S1—C4	1.778 (6)	N2—C2	1.127 (6)
C1—Ag1—C2	173.0 (3)	O1—S1—C4	104.3 (3)
O1^{i}—Fe1—O1	180.0	S1—C3—H3A	109.5
O1—Fe1—N1^{i}	89.82 (16)	S1—C3—H3B	109.5
O1—Fe1—N1	90.18 (16)	S1—C3—H3C	109.5
O1^{i}—Fe1—N1	89.82 (16)	H3A—C3—H3B	109.5
O1^{i}—Fe1—N1^{i}	90.18 (16)	H3A—C3—H3C	109.5
O1^{i}—Fe1—N2^{ii}	89.54 (17)	H3B—C3—H3C	109.5
O1—Fe1—N2^{iii}	89.54 (17)	S1—C4—H4A	109.5
O1^{i}—Fe1—N2^{iii}	90.46 (17)	S1—C4—H4B	109.5
O1—Fe1—N2^{ii}	90.46 (17)	S1—C4—H4C	109.5
N1—Fe1—N1^{i}	180.0	H4A—C4—H4B	109.5
N1^{i}—Fe1—N2^{iii}	91.82 (16)	H4A—C4—H4C	109.5
N1^{i}—Fe1—N2^{ii}	88.18 (16)	H4B—C4—H4C	109.5
N1—Fe1—N2^{ii}	91.83 (16)	S1—O1—Fe1	128.0 (2)
N1—Fe1—N2^{iii}	88.17 (16)	C1—N1—Fe1	168.3 (5)
N2^{ii}—Fe1—N2^{iii}	180.0	N1—C1—Ag1	173.7 (5)
C3—S1—C4	99.8 (3)	C2—N2—Fe1^{iv}	173.6 (5)
O1—S1—C3	105.2 (3)	N2—C2—Ag1	175.5 (6)
C3—S1—O1—Fe1	96.3 (3)	C4—S1—O1—Fe1	−159.2 (3)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) *x*+1, −*y*+3/2, *z*+1/2; (iii) −*x*+1, *y*−1/2, −*z*+1/2; (iv) −*x*+1, *y*+1/2, −*z*+1/2.