Chinese Journal of Chemistry, **2004**, *22*, 533—536 **Article**

A Three-dimensional Heteronuclear Polymer of $[Ag_2Fe(SCN)_5(DMF)]_n$ Containing Channels and One-dimensional Ag_2S_2-S-Ag_2S_2 Chains with Ag···Ag Interaction

LI, Xiu-Ling*,[a](李秀玲) ZHAO, Chang-Chun[a](赵长春) CHEN, Jiu-Tong[b](陈久桐)
DU, Wen-Xin[b](杜文新)

[a]*Department of Chemistry, Xuzhou Normal University, Xuzhou, Jiangsu 221116, China*
[b]*Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

The Ag_2S_2 rings connect $[Fe(NCS)_5(DMF)]^{2-}$ (DMF = *N*,*N*-dimethylformamide) octahedrons by bridging thiocyanates leading to a 3-D $[Ag_2Fe(SCN)_5(DMF)]_n$ framework. The Fe(III) atoms are in the octahedral geometry and Ag(I) atoms are in the distorted tetrahedral geometry. One-dimensional Ag_2S_2-S-Ag_2S_2 wave-like strand chains along the *b*-axis and channels constructed from ten-membered $Ag_2Fe(SCN)_2S$ rings along the *c*-axis feature the three-dimensional framework. The Ag···Ag distance of 0.3103(1) nm in Ag_2S_2 rings indicates weak Ag···Ag interaction. Such an Ag_2S_2-S-Ag_2S_2 chain in silver(I) complexes is unprecedented. Crystal data: M_r = 635.09, orthorhombic, *Pnma*, a = 1.64214(13) nm, b = 1.40075(11) nm, c = 0.84445(7) nm, V = 1.9424(3) nm^3, Z = 4, μ(Mo Kα) = 3.278 mm^{-1}, D_{calcd} = 2.172 g·cm^{-3}, $F(000)$ = 1220, R_1 = 0.0443, wR_2 = 0.1138.

Keywords silver(I)-iron(III) heteronuclear polymer, crystal structure, thiocyanate bridge, one-dimensional chain, Ag···Ag interaction

Introduction

So far, considerable attention has been paid to magnetic interaction between two different metal ions.[1-3] As a potential bridging ligand, thiocyanate can coordinate to a harder metal center with N atom and softer ones with S atom at the same time, resulting in the formation of small ferromagnetic coupling.[2] On the other hand, the Fe(III) atom is a good candidate as a hard acid and Ag(I) is a good candidate as a soft acid, so that the Fe(III) centers could be expected to connect the Ag(I) centers by thiocyanates to form multi-dimensional heteronuclear coordination polymers. We have reported two coordination polymers $\{[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$ and $\{[Ag_2Fe(SCN)_6](C_5H_6N)(H_2O)\}_\infty$.[4,5] But no 3-D coordination polymer has been reported for the Fe(III)-Ag(I)-SCN^- system. Therefore, the development of proper rational synthetic strategies is very important. As a continuing work of our systematic research on Fe(III)-Ag(I)-SCN^- system, here we report the synthesis and characterization of a three-dimensional framework of heteronuclear coordination polymer $[Ag_2Fe(SCN)_5(DMF)]_n$.

Experimental

Instrumentation

The C, H, N and S elemental analyses were carried out with a Perkin-Elmer 2400 elemental analyzer. The infrared absorption spectra were recorded on a Tensor 27 (Bruker) spectrophotometer with KBr discs in the range of 4000—400 cm^{-1}.

Synthesis

$FeCl_3 \cdot 6H_2O$ (0.81 g, 3.0 mmol) and $AgNO_3$ (1.02 g, 6.0 mmol) were added to a stirred aquatic solution (20 mL) of NH_4SCN (1.37 g, 18 mmol) consecutively. The mixed solution was further stirred in air overnight. After filtration, the resulting dark-sanguine solution was allowed to stand in air at room temperature for two weeks, yielding dark-brown crystals (0.15 g, yield 7.87% based on $AgNO_3$). IR (KBr) ν: 3014 (vw), 2968 (vw), 2938 (vw), 2910 (vw), 2899 (vw), 2148 (s), 2114 (s), 2094 (vs), 2077 (s), 1650 (s), 1559 (vw), 1541 (vw), 1522 (vw), 1506 (vw), 1488 (w), 1456 (vw), 1429 (m), 1385 (vw), 1357 (m), 1253 (w), 1122 (w), 1061 (w), 952 (w), 928 (w), 869 (vw), 814 (vw), 800 (vw), 705 (m), 463 (m), 421 (m) cm^{-1}. Anal. calcd for $C_8H_7Ag_2FeN_6OS_5$: C 15.13, H 1.11, N 13.23, S 25.24; found C 15.14, H 0.97, N 13.26, S 25.10.

X-ray crystallography

A dark-brown crystal with approximate dimensions 0.34 mm × 0.26 mm × 0.18 mm was mounted on a glass fiber capillary which was put on a Siemens Smart CCD

* E-mail: lxllyt@sohu.com
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diffractometer equipped with graphite monochromated Mo Kα radiation (λ=0.071073 nm). A total of 5776 (1791 independent, R(int)=0.0326) reflections were collected at temperature 293(2) K. The structure was solved by direct methods (SHELXL-97) and refined by the full-matrix least-squares method on F^2. Anisotropic temperature factors were applied to all nonhydrogen atoms. The crystal data for the title coordination polymer are shown in Table 1. Selected bond lengths and bond angles with standard deviations in parenthesis are shown in Table 2. The perspective views of the coordination geometries of the Fe(III) and Ag(I), and the one-dimensional Ag_2S_2-S-Ag_2S_2 chain along the *b*-axis are shown in Figure 1. The three-dimensional network viewed along the *c*-axis in the title compound is shown in Figure 2.

Table 1 Crystal data for the title coordination polymer

Formula	$C_8H_7Ag_2FeN_6OS_5$
Formula weight	635.09
Temperature/K	293(2)
Wavelength/nm	0.071073
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	
a/nm	1.64214(13)
b/nm	1.40075(11)
c/nm	0.84445(7)
V/nm^3	1.9424(3)
Z	4
Calculated density/(g • cm^{-3})	2.172
Absorption coefficient/mm^{-1}	3.278
F(000)	1220
Reflections collected	5776
Independent reflections	1791
Reflections with $I>2\sigma(I)$	1318
Data/restraints/parameters	1791/0/118
Goodness-of-fit on F^2	1.071
R_1 [$I>2\sigma(I)$]	0.0443
wR_2 (all data)	0.1138
Largest diff. peak/(e • nm^{-3})	788
Largest diff. hole/(e • nm^{-3})	−806

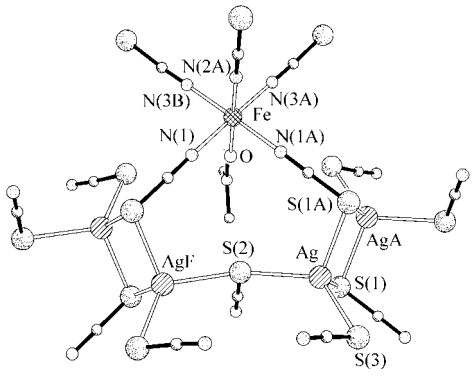

Figure 1 rspective view of the coordination geometries of the Fe(III) and Ag(I), and the one-dimensional Ag_2S_2-S-Ag_2S_2 chain along the *b*-axis in the title compound.

Table 2 Selected bond lengths (nm) and angles (°)

Ag—S(3)	0.2523(2)	Fe—N(2e)	0.2058(8)
Ag—S(2)	0.26052(11)	S(1)—C(1)	0.1645(7)
Ag—S(1)	0.2692(2)	S(2)—C(2)	0.1635(11)
Ag—S(1a)	0.2635(2)	S(3)—C(3)	0.1646(8)
Ag—Ag(a)	0.31031(12)	C(1)—N(1)	0.1149(8)
Fe—O	0.2001(7)	C(2)—N(2)	0.1154(12)
Fe—N(3b)	0.2035(6)	C(3)—N(3)	0.1121(8)
Fe—N(1)	0.2050(6)	O—C(4)	0.1182(14)
S(3)-Ag-S(2)	121.68(11)	C(1)-S(1)-Ag	93.2(2)
S(3)-Ag-S(1a)	109.11(9)	Ag(a)-S(1)-Ag	71.24(5)
S(2)-Ag-S(1a)	107.81(8)	C(2)-S(2)-Ag	97.06(9)
S(3)-Ag-S(1)	106.42(7)	Ag(f)-S(2)-Ag	154.22(17)
S(2)-Ag-S(1)	102.35(8)	C(3)-S(3)-Ag	95.9(2)
S(1a)-Ag-S(1)	108.76(5)	C(4)-O-Fe	136.3(9)
O-Fe-N(3b)	91.5(2)	C(1)-N(1)-Fe	177.9(6)
N(3b)-Fe-N(3c)	90.2(3)	C(2)-N(2)-Fe(e)	178.3(8)
O-Fe-N(1)	87.1(2)	C(3)-N(3)-Fe(g)	178.9(6)
N(3b)-Fe-N(1)	90.1(2)	C(4)-N(4)-C(5)	120.1(12)
N(3c)-Fe-N(1)	178.5(2)	C(4)-N(4)-C(6)	120.5(13)
N(1d)-Fe-N(1)	89.5(3)	C(5)-N(4)-C(6)	119.4(13)
O-Fe-N(2e)	175.8(3)	N(1)-C(1)-S(1)	178.6(6)
N(3b)-Fe-N(2e)	91.5(2)	N(2)-C(2)-S(2)	178.4(9)
N(1)-Fe-N(2e)	90.0(2)	N(3)-C(3)-S(3)	176.7(7)
C(1)-S(1)-Ag(a)	100.9(2)	O-C(4)-N(4)	127.5(12)

Symmetry transformations used to generate equivalent atoms: a: $-x+1$, $-y+1$, $-z$; b: $-x+1/2$, $-y+1$, $z+1/2$; c: $-x+1/2$, $y+1/2$, $z+1/2$; d: x, $-y+3/2$, z; e: $-x+1$, $-y+1$, $-z+1$; f: x, $-y+1/2$, z; g: $-x+1/2$, $-y+1$, $z-1/2$.

Results and discussion

Single crystal X-ray structural analysis shows that the title compound consists of a three-dimensional network formulated as $[Ag_2Fe(SCN)_5(DMF)]_n$, which is unexpected. Where the DMF arose from is obscure. Maybe it came from the air in the laboratory, since there is an open DMF solution nearby. When the DMF (0.22 g, 3 mmol) was added to the primary synthesis system of the title compound, nigger-brown powders (1.92 g, yield 98% based on $AgNO_3$) were obtained. The results of IR and EA of the nigger-brown powders are the same

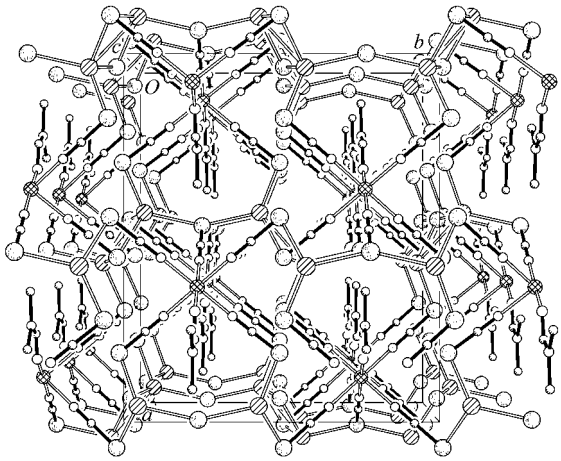

Figure 2 Three-dimensional network viewed along the *c*-axis in the title compound.

as the experimental result and the calculated result of the tilte compound. The existence of DMF in the title compound can be confirmed from the above results and the latter IR discussion.

As shown in Figure 1, each thiocyanate is coordinated to the metal atoms according to HSAB principle with N atom binding to the Fe(III) atom and with S atom binding to Ag(I) atom. The Fe(III) atom is in the octahedral geometry, and coordinated by one oxygen atom from DMF and five nitrogen atoms from different bridging SCN^- ions, among which three are in 1,1,3-μ_3-mode [-S(1)-C(1)-N(1)-, -S(1A)-C(1A)-N(1A)- and -S(2)-C(2)-N(2)-] and two are in 1,3-μ_2-mode [-S(3A)-C(3A)-N(3A)- and -S(3B)-C(3B)-N(3B)]. The Fe—N bond lengths of 0.2035(6) nm (for the 1,3-μ_2-bridging SCN) and 0.2050(6)—0.2058(8) nm (for the 1,1,3-μ_3-bridging SCN) are similar to those corresponding values of 0.2054(4)—0.2059(4) and 0.2054(4) nm in $\{[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$,[4] and 0.2037(14)—0.2038(13) nm and 0.2057(11) nm in $\{[Ag_2Fe(SCN)_6](C_5H_6N)(H_2O)\}_\infty$.[5] The Fe-N-C angles are from 177.9(6)° to 178.9(6)°, indicating that these atoms are almost collinear and the deviation from 180° is much smaller than the others reported, such as $(Bu_4N)_4[Ag_2Fe_2(SCN)_{12}] \cdot 2CH_3NO_2$ (144.6°—175.8°),[6] $\{[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$ (164.0(5)°—174.9(4)°) and $\{[Ag_2Fe(SCN)_6](C_5H_6N)(H_2O)\}_\infty$ (168.3(14)°—170.7(11)°).[4,5] The NCS^- is almost linear with N-C-S angle of 176.7(7)°—178.6(6)° which is similar to those 177.4(6)°—179.3(5)° in $\{[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$ and 177.0(16)°—178.2(15)° in $\{[Ag_2Fe(SCN)_6](C_5H_6N)(H_2O)\}_\infty$.[4,5] Each Ag(I) atom is coordinated to three sulfur atoms of 1,1,3-μ_3-bridging SCN^- ions (Ag—S(2) 0.2605(1), Ag—S(1a) 0.2635(2) and Ag—S(1) 0.2692(2) nm, which are in the range of 0.25987(14)—0.26968(14) nm reported in $\{[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$[4]) and one sulfur atom of 1,3-μ_2-SCN^- ion (Ag—S(3) 0.2523(2) nm, which is close to 0.25115(17)—0.25480(15) nm found in $\{[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$[4]), resulting in a distorted tetrahedral coordination geometry with bond angles in the range of 102.35(8)°—121.68(11)°. Each pair of silver(I) atoms are bridged by two S(1) atoms completing a four-membered Ag_2S_2 ring [Ag(a)-S(1)-Ag 71.24(5)°] with the Ag···Ag(a) distance of 0.3103(1) nm, which is similar to that reported in $^2_\infty[(AgSCN)_2(C_3H_{10}N_2)]$ and is well below the summed van der Waals radii of two silver atoms (0.344 nm),[7,8] indicating some weak Ag···Ag interaction.

The Ag_2S_2 rings link with each other through S(2) atoms [Ag-S(2)-Ag(f) 154.2(2)°] forming one-dimensional Ag_2S_2-S-Ag_2S_2 chains along the *b*-axis as shown in Figure 1. Each $[Fe(NCS)_5(DMF)]^{2-}$ octahedron links with two pairs of Ag(I) atoms in four Ag_2S_2 rings, which are bridged by S(2) atoms through two 1,3-μ_2-SCN^- ions and two 1,1,3-μ_3-SCN^- ions, respectively, resulting in double ten-membered $Ag_2Fe(SCN)_2S$ rings which share the corner Fe(III) atoms. The ten-membered $Ag_2Fe(SCN)_2S$ rings featuring the boat conformation are similar to the ten-membered $Cu_3(SCN)_2S$ rings (in chair conformation), $Ag_3(SCN)_2S$ rings (in boat conformation) and $Ag_2Cu(SCN)_2S$ rings reported in homonuclear coordination polymers of [Cu(SCN)(py)], [Ag(SCN)(py)] and heteromuclear coordination polymer of $[AgCu(SCN)_2(py)_3]$.[9] The double ten-membered $Ag_2Fe(SCN)_2S$ rings share Ag—S(2) edges leading to the wave-like strands along the *a*-axis.

As shown in Figure 2, the one-dimensional Ag_2S_2-S-Ag_2S_2 chains are linked with each other through $[Fe(NCS)_5(DMF)]^{2-}$ octahedron completing a three-dimensional framework. The ten-membered $Ag_2Fe(SCN)_2S$ rings parallel to each other forming channels along the *c*-axis. It should be noted that the Ag_2S_2-S-Ag_2S_2 chain is unprecedented, since it is bridged by only a sulfur atom between two Ag_2S_2 rings, and quite different from those in literature, which were connected by the full bridging SCN^- ions[4,5] and by other ligands such as di-amines[7] or by another metal center.[6,10]

In its IR spectrum, the strong vibrations (2148, 2114 cm^{-1}, and 2094, 2077 cm^{-1}) may be identified with the ν_{CN} of 1,1,3-μ_3-bridging SCN^- ions and 1,3-μ_2-mode, respectively, since the former always has higher values than 2100 cm^{-1} and this fact is in agreement with infrared data reported previously.[2,6,9] In fact, the 2094 and 2077 cm^{-1} is almost the same with those in $\{[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$[4] (2094 and 2076 cm^{-1}) and this further shows that the values for the vibrational modes of the above two kinds of bridging SCN^- ions do not differ significantly from each other. So it is not always possible to deduce the bridging mode definitely from vibrational data. Three weak absorptions 814, 800 and 738 cm^{-1} should be assigned to ν_{CS} of thiocyanate groups. The 463 and 421 cm^{-1} should be assigned to δ_{NCS} of N-bonded and S-bonded respectively. The 1651 cm^{-1} strong absorption is the characteristic band of C=O group.

In conclusion, the adding of DMF in the Ag(I)-Fe(III)-CN^- system leads to the formation of the 3-D $[Ag_2Fe(SCN)_5(DMF)]_n$ framework which contains the

unprecedented Ag_2S_2-S-Ag_2S_2 chain. Compared with the synthetic system of $(inaH)_2[Fe(SCN)_5(H_2O)]\cdot(ina)_2$,[4] **{**$[Ag_4Fe_2(SCN)_{12}(H_2O)_2][(inaH)_2(H_2O)_2]\}_n$,[4] and $\{[Ag_2Fe(SCN)_6](C_5H_6N)(H_2O)\}_\infty$,[5] it can be concluded that the proportion of the materials, the varieties of the ligands and the solvents, and the pH value of the solutions all play important roles in determining the species of the products for the Fe(III)-Ag(I)-SCN^- system.

Supplementary materials

Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center in cif format with CCDC reference number 205095.

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