Synthesis and Crystal Structure of a Two-dimensional Silver(I)-Iron(III) Heteronuclear Coordination Polymer: {[Ag$_4$Fe$_2$(SCN)$_{12}$(H$_2$O)$_2$] [(inaH)$_2$(H$_2$O)$_2$]}$_n$

LI, Xiu-Ling*^{,a}(李秀玲)   TONG, Ming-Liang^b(童明良)   NIU, De-Zhong^a(牛德仲)
CHEN, Jiu-Tong^c(陈久桐)

^{a} *Department of Chemistry, Xuzhou Normal University, Xuzhou, Jiangsu 221116, China*

^{b} *School of Chemistry & Chemical Engineering, Zhongshan University, Guangzhou, Gongdong 510275, China*

^{c} *Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

The 2-D heteronuclear coordination polymer {[Ag$_4$Fe$_2$(SCN)$_{12}$(H$_2$O)$_2$] [(inaH)$_2$(H$_2$O)$_2$]}$_n$ (**1**) (inaH is the abbreviation of protonated isonicotinic acid) with chemical formula C$_{24}$H$_{20}$Ag$_4$Fe$_2$N$_{14}$O$_8$S$_{12}$ has been synthesized and characterized by single crystal X-ray diffraction, elemental analysis and IR spectroscopy. The Ag$_2$S$_2$ rings connect two kinds of octahedral geometries of Fe(III) ions, [Fe(NCS)$_6$]$^{3-}$ and [Fe(H$_2$O)$_2$(NCS)$_4$]$^-$ units with bridging thiocyanate ions leading to 2-D [Ag$_4$Fe$_2$(SCN)$_{12}$(H$_2$O)$_2$]$^{2-}$ anion framework. Four kinds of rings including the unprecedented thirty-two membered Ag$_4$Fe$_4$(SCN)$_8$ rings share corners or edges in the 2-D anion layer structure. All thiocyanates coordinate to the metal ions according to the HSAB principle with N atoms binding to the Fe(III) ions and with S atoms binding to Ag(I) ions. Pronoated ina cations stabilize the layer structure as counter ions and hydrogen bonds were formed within the pronoated ina cations dimer and between the dimers and the lattice waters. Crystal data: M_r=1560.44, triclinic, $P\bar{1}$, a=0.76082(1) nm, b=0.9234 nm, c=1.85611(4) nm, α=103.0170(10)°, β=93.7780(10)°, γ=97.4080(10)°, V=1.25385(3) nm^3, Z=1, μ(Mo Kα)=2.650 mm^{-1}, D_c=2.067 g • cm^{-3}, F(000)=758, R_1=0.0412, wR_2=0.1003.

Keywords   silver(I)−iron(III) heteronuclear polymer, crystal structure, thiocyanate bridge, protonated isonicotinic acid

Introduction

Molecules containing different kinds of metal ions play an important role in molecular magnetism.[1-3] So considerable attention has been paid to synthesizing heteronuclear complexes.[1-4] As a potential bridging ligand, thiocyanate can coordinate to a harder metal center and softer ones with N and S atoms respectively. The complexes of thiocyanate and representative hard acid—Fe(III) ions usually have a six-coordinate octahedral structure such as [Fe(SCN)$_n$]$^{3-n}$ and (Bu$_4$N)$_4$[Ag$_2$Fe$_2$(SCN)$_{12}$] • 2CH$_3$NO$_2$.[5,6] While a large number of coordination polymers containing thiocyanate and representative soft acid—silver(I) ions have exhibited interesting structural diversities including basic tetrahedral coordination geometry.[6-8] One of the synthetic methods used to construct the functional compounds is that octahedral metal centers connect tetrahedral metal centers by bridging ligands such as thiocyanate to form multi-dimensional coordination polymers.[6,8,9] So it could be expected to get Fe(III)-Ag(I)-SCN$^-$ multi-dimensional frameworks through designing proper routes. However, to our knowlwdge, only a heteronu-

clear Fe(III)-Ag(I) compound with SCN$^-$, a tetranuclear anion—[Ag$_2$Fe$_2$(SCN)$_{12}$]$^{4-}$ has been reported.[6] Therefore, development of proper synthetic strategies leading to the desired species is much important. Here we report the synthesis and characterization of the two-dimensional heteronuclear coordination polymer of {[Ag$_4$Fe$_2$(SCN)$_{12}$(H$_2$O)$_2$] [(inaH)$_2$(H$_2$O)$_2$]}$_n$ (**1**).

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) spectrometer with KBr discs in the 4000—400 cm^{-1} region.

Synthesis

All the reagents for the preparation were of analytical grade quality and used without further purification. AgNO$_3$ (1.02 g, 6.0 mmol), FeCl$_3$ • 6H$_2$O (0.81 g, 3.0 mmol) and ina (2.21 g, 18 mmol) were added to a solu-

Heteronuclear polymer

Chin. J. Chem., 2004, Vol. 22, No. 1   **65**

tion of NH_4SCN (1.37 g, 18 mmol) in 20 mL mixed solvent ($V_{acetonitrile}$: V_{water} = 1 : 1) with stirring in a short time consecutively. Dark sanguine solution and the red-brown powders (1.29 g, yield 55% based on $AgNO_3$) were obtained after filtration and then the filtrate was left to evaporate slowly at room temperature avoiding illumination for about three weeks, finally dark brown crystals suitable for single crystal X-ray determination were obtained. Characteristic IR absorption bands: 3596 (m), 3504 (w), 3329 (w), 3270 (w), 3211 (vw), 3153 (vw), 3111 (w), 3069 (w), 3036 (w), 3003 (w), 2886 (w), 2769 (w), 2677 (w), 2535 (w), 2094 (s), 2075 (vs), 1724 (s) cm^{-1}. Anal. calcd for $C_{24}H_{20}Ag_4Fe_2N_{14}O_8S_{12}$: C 18.47, H 1.29, N 12.57, S 24.66; found C 18.51, H 1.24, N 12.55, S 24.44.

X-ray crystallography

A dark brown crystal of **1** with approximate 0.82 mm $\times$ 0.40 mm $\times$ 0.36 mm was mounted on a glass fiber capillary which was put on a Siemens Smart CCD diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.071073 nm). A total of 6531 (4366 independent, R(int) = 0.0208) 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.

Table 1   Crystal data for the title coordination polymer

Formula	$C_{24}H_{20}Ag_4Fe_2N_{14}O_8S_{12}$
Formula weight	1560.44
Temperature/K	293(2)
Wavelength/nm	0.071073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a/nm	0.76082(1)
b/nm	0.9234
c/nm	1.85611(4)
α/(°)	103.0170(10)
β/(°)	93.7780(10)
γ/(°)	97.4080(10)
V/nm^3	1.25385(3)
Z	1
Calculated density/(g • cm^{-3})	2.067
Absorption coefficient/mm^{-1}	2.650
F(000)	758
Reflections collected	6531
Independent reflections	4366

continued

Reflections with $I>2\sigma(I)$	3966
Data/restraint/parameter	4366/0/330
Goodness-of-fit on F^2	1.095
R_1 [$I>2\sigma(I)$]	0.0412
wR_2 (all data)	0.1003
Largest diff. Peak/(e • nm^{-3})	823
Largest diff. Hole/(e • nm^{-3})	$-$1031

Results and discussion

Single crystal X-ray structural analysis shows that the title compound formulated as **1**. The crystal structure consists of two-dimensional $[Ag_4Fe_2(SCN)_{12}(H_2O)_2]^{2-}$ anion framework, lattice water and inaH ions. The latter two are connected by hydrogen bonds. The coordination geometries of the iron(III) and silver(I) ions and the two-dimensional layer structure of the framework together with the numbering scheme, are shown in Figure 1. Selected bond lengths and bond angles with standard deviations in parenthesis are shown in Table 2. All thiocyanates coordinate to the metal ions according to the HSAB principle[10,11] with N atoms binding to the Fe(III) ions and with S atoms binding to Ag(I) ions. There are two kinds of centrosymmetric octahedral geometries for Fe(III) ions—$[Fe(NCS)_6]^{3-}$ and $[Fe(H_2O)_2(NCS)_4]^-$ units. In the $[Fe(NCS)_6]^{3-}$ unit, Fe(III) is coordinated by six N atoms from six bridging SCN^- ions of which four in 1,3-μ_2-mode, one in 1,1,3-μ_3-mode and one in 1,1-μ_2-mode. The ratio of the two kinds of metal ions and thiocyanates in the $[Ag_2Fe(NCS)_6]^{3-}$ unit is similar to those of the $[Cd(NCS)_6Ag_2]^{2-}$ ion and $[Ag_2Fe(NCS)_6]^{2-}$ ion found in $[CdL][Cd(NCS)_6Ag_2]$[8] and $(Et_4N)_2[Ag_2Fe(NCS)_6]$[6] respectively, but the linking modes between metal centers are different from one another. In the $[Fe(H_2O)_2(NCS)_4]^-$
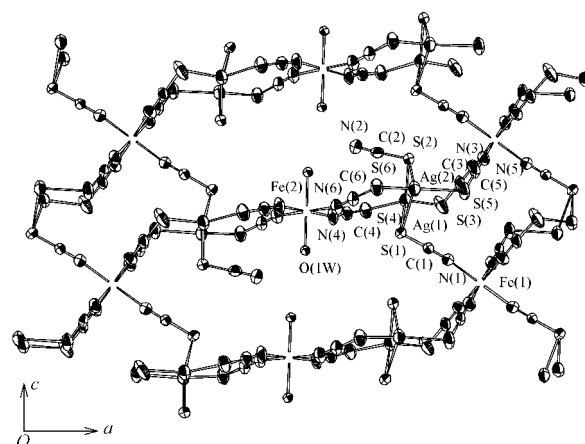

Figure 1   The coordination geometries of the iron(III) and silver(I) ions and the two-dimensional layer structure.

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

Ag(1)—S(3)	0.25115(17)	Fe)—N(6)	0.2030(5)
Ag(1)—S(4)	0.25480(15)	S(1)—C(1)	0.1637(5)
Ag(1)—S(2)	0.25987(14)	S(2)—C(2)	0.1663(6)
Ag(1)—S(1)	0.26968(14)	S(3)—C(3)	0.1625(5)
Ag(2)—S(6)	0.25216(15)	S(4)—C(4)	0.1620(6)
Ag(2)—S(5)	0.25247(14)	S(5)—C(5)	0.1630(5)
Ag(2)—S(2)	0.26469(14)	S(6)—C(6)	0.1632(5)
Ag(2)—S(1)	0.27963 (13)	C(1)—N(1)	0.1157(6)
Fe(1)—N(1)	0.2054(4)	C(2)—N(2)	0.1151(7)
Fe(1)—N(3a)	0.2057(4)	C(3)—N(3)	0.1157(7)
Fe(1)—N(5a)	0.2059(4)	C(4)—N(4)	0.1153(7)
Fe(2)—N(4)	0.2023(5)	C(5)—N(5)	0.1151(7)
Fe(2)—O(1W)	0.2028(4)	C(6)—N(6)	0.1154(7)
S(3)-Ag(1)-S(4)	105.08(6)	Ag(1)-S(1)-Ag(2)	83.46(4)
S(3)-Ag(1)-S(2)	113.22(5)	C(2)-S(2)-Ag(1)	99.59(18)
S(4)-Ag(1)-S(2)	121.14(5)	C(2)-S(2)-Ag(2)	98.22(19)
S(3)-Ag(1)-S(1)	120.94(8)	Ag(1)-S(2)-Ag(2)	88.39(4)
S(4)-Ag(1)-S(1)	102.06(5)	C(3)-S(3)-Ag(1)	99.39(19)
S(2)-Ag(1)-S(1)	94.77(4)	C(4)-S(4)-Ag(1)	95.74(19)
S(6)-Ag(2)-S(5)	128.64(5)	C(5)-S(5)-Ag(2)	102.25(18)
S(6)-Ag(2)-S(2)	115.96(5)	C(6)-S(6)-Ag(2)	98.87(19)
S(5)-Ag(2)-S(2)	105.95(4)	N(1)-C(1)-S(1)	178.0(5)
S(6)-Ag(2)-S(1)	100.54(4)	N(2)-C(2)-S(2)	177.9(5)
S(5)-Ag(2)-S(1)	106.94(5)	N(3)-C(3)-S(3)	177.4(6)
S(2)-Ag(2)-S(1)	91.42(4)	N(4)-C(4)-S(4)	177.7(5)
N(1)-Fe(1)-N(3a)	90.44(19)	N(5)-C(5)-S(5)	178.1(5)
N(1)-Fe(1)-N(5b)	89.81(19)	N(6)-C(6)-S(6)	179.3(5)
N(3a) -Fe(1)-N(5b)	91.1(2)	C(1)-N(1)-Fe(1)	174.9(4)
N(4)-Fe(2)-O(1W)	90.5(2)	C(3)-N(3)-Fe(1c)	164.0(5)
N(4)-Fe(2)-N(6)	88.8(2)	C(4)-N(4)-Fe(2)	164.8(5)
OW1-Fe(2)-N(6)	92.1(2)	C(5)-N(5)-Fe(1c)	167.4(5)
C(1)-S(1)-Ag(1)	100.10(17)	C(6)-N(6)-Fe(2)	165.9(5)
C(1)-S(1)-Ag(2)	102.60(17)		

Symmetry transformations used to generate equivalent atoms: a: $-x+1$, $-y$, $-z$; b: $x-1$, y, z; c: $x+1$, y, z.

unit, Fe(III) is coordinated by four N atoms from four 1,3-μ_2-bridging SCN^- ions and two O atoms from two water molecules. The Fe(III)—N bond lengths are in the range of 0.2023(5)—0.2059(4) nm which are much shorter than the corresponding average value 0.2107 nm in $(Bu_4N)_4[Ag_2Fe_2(SCN)_{12}] \cdot 2CH_3NO_2$[6] and close to 0.2048 nm and 0.206 nm in the terminal N coordination complexes $(Me_4N)_3[Fe(NCS)_6]$[12] and $[(C_{10}H_{12})Fe(C_5-H_5)]_3[Fe(NCS)_6]$[13] respectively. The Fe-N-C angles range from 164.0(5)° to 174.9(4)° and the deviations from 180° are much smaller than those of Fe-N-C angles 144.6°—175.8° found in $(Bu_4N)_4[Ag_2Fe_2(SCN)_{12}] \cdot 2CH_3NO_2$ and 145.2°—148.0° in $(Et_4N)_2[Ag_2Fe(NCS)_6]$.[6]

The NCS is almost linear with N-C-S angle 177.4(6)° —179.3(5)°. The Fe(III)—O bond length is 0.2028(4) nm which is similar to that 0.2033(2) nm reported in the complex of Fe(III) ion with acetylamino pyridine N-oxide.[14] There are two incoordinate distorted tetrahedral geometries for Ag(I) ions. Each Ag(I) ion is coordinated by four sulfur atoms from four SCN^- ions of which two are in 1,3-μ_2-mode with Ag—S bond lengths from 0.25115(17) nm to 0.25480(15) nm which are close to those 0.2532—0.2556(1) nm in $(Bu_4N)_4$-$[Ag_2Fe_2(SCN)_{12}] \cdot 2CH_3NO_2$,[6] one in 1,1,3-$\mu_3$-mode with Ag—S(1) bond length 0.26968(14) or 0.27963(13) nm which is near those of 0.2672—0.2706(1) nm re-

Heteronuclear polymer

Chin. J. Chem., 2004, Vol. 22, No. 1   **67**

ported in (Bu$_4$N)$_4$[Ag$_2$Fe$_2$(SCN)$_{12}$] •2CH$_3$NO$_2$,[6] and one in 1,1-μ$_2$-mode with Ag—S(2) bond length 0.25987(14) or 0.26469(14) nm. The Ag(1)-S-C angles are from 95.74(19)° to 100.10(17)° and Ag(2)-S-C angles are from 83.46(4)° to 102.25(18)° with different bond lengths resulting in two kinds of highly distorted tetrahedral coordination geometry. Each pair of Ag(1) and Ag(2) atoms are bridged by a pair of S(1) and S(2) atoms completing the four-membered Ag$_2$S$_2$ rings [Ag(1)-S(1)-Ag(2), 83.46(4)°, Ag(1)-S(2)-Ag(2), 88.39(4)°] which is similar to those reported previously.[7] In the Ag$_2$S$_2$ rings, the Ag···Ag distance of 0.3657 nm is larger than the summation of van der Waals radii of two silver atoms (0.344 nm),[15] indicating no Ag···Ag interaction.

The Ag$_2$S$_2$ rings connect two kinds of Fe(III) octahedral geometries with four 1,3-μ$_2$-bridging SCN$^-$ ions to form one-dimensional step-shaped chain structure extending in the ac plane. There are three kinds of non-planar rings in the 1-D chain as follows: four-membered Ag$_2$S$_2$ rings (∑Ag = 358.04°), ten-membered Ag$_2$Fe(SCN)$_2$S rings and sixteen-membered Ag$_2$Fe$_2$(SCN)$_4$ rings. The 1-D chains are connected with each other by the 1,1,3-μ$_3$-bridging SCN$^-$ ions into 2-D [Ag$_4$Fe$_2$(SCN)$_{12}$(H$_2$O)$_2$]$^{2-}$ anion layer structure in ac plane leading to the formation of another thirty-two membered Ag$_4$Fe$_4$(SCN)$_8$ rings, which is unprecedented in thiocyanate complexes.

In IR spectra, the two strong vibrations 2094 and 2076 cm^{-1} should be attributed to ν_{CN} of the 1,1,3-μ$_3$-bridging SCN$^-$ ions and 1,3-μ$_2$-mode respectively, since the former always has higher values. However, 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.[16] The ν_{CS} vibration is obscured by the inaH IR bands and can not be assigned definitely.

Organic amine ligands are always used to coordinate to the metal centers constructing the framework together with thiocyanate,[7,16,17] while the carboxylic acid is rarely found especially in pronoated form in heteronuclear thiocynate complexes. But the anion frameworks are always formed in heteronuclear SCN$^-$ complexes,[6,8] so the counter ions of suitable size are needed to stabilize the framework. Here, as a kind of special carboxylic acid containing carboxyl and nitrogen atoms at the same time, isonicotinic acid molecules bind the 2-D framework with electrostatic interaction in its pronoated form stabilizing the framework. On the other

hand, they form strong intermolecular hydrogen bonds between carboxyl groups in dimer and between pronoated nitrogen and lattice waters (see Figure 2 and Table 3). Thus ina molecules take an important role in this host-guest compound.
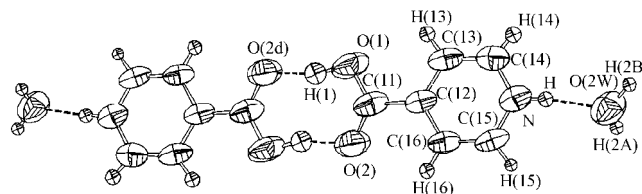

Figure 2   The hydrogen bonds in the inaH dimers and between the inaH dimers and lattice waters.

In the course of preparing (Et$_4$N)$_2$[Ag$_2$Fe(NCS)$_6$] compound, it was found that the oxidation state of the iron is changed from the starting Fe(III) into Fe(II) oxidation state.[6] Here, the average Fe(III)—N bond distance 0.2045 nm in the title compound is significantly shorter than the corresponding average Fe(II)—N bond distances 0.2125 nm, 0.2137 nm, 0.2149 nm and 0.2167 nm found in FeHg(NCS)$_4$(dmtp)$_2$(H$_2$O)$_{1.5}$,[17] FeHg(NCS)$_4$(dmtp)$_2$(H$_2$O),[17] FeHg(NCS)$_4$(dmtp)(H$_2$O)$_2$ • (Me$_2$CO)[17] and (Et$_4$N)$_2$ [Ag$_2$Fe(NCS)$_6$][6] respectively and the Fe(III)—O bond length 0.2028(4) nm is also much shorter than the corresponding average Fe(II)—O bond distances 0.2161 nm, 0.2130 nm and 0.2130 nm in the three Fe(II)-Hg-SCN$^-$ complexes[17] mentioned above. The larger difference of the above bond distances shows that there is no change for the oxidation state of iron. This result may be attributable to the rapid mixing of the materials and the rapid formation of the title compound. On the other hand, the suitable acidity of the solution kept by the ina molecules and NH$_4^+$ ions keeps the metals from hydrolyzing.

When the filtrate was further left in air for longer time, crystals of another kind of simple compound (inaH)$_2$[Fe(SCN)$_5$(H$_2$O)] • (ina)$_2$ (**2**) with chemical formula C$_{29}$H$_{24}$FeN$_9$O$_9$S$_5$ together with **1** were obtained, which have been confirmed by single-crystal X-ray diffraction and element analysis. When the filtrate was further laid in air, only crystals of compound **2** was obtained. That's to say, along with the volatilization and decreasing of the acetonitrile, the product changed from **1** into **2**. On the other hand, when the solvent was changed into simple water, the crystals of compound **2** in the filtrate were obtained exclusively.

Table 3   Hydrogen bonds in the inaH dimers and between the inaH dimers and lattice waters

D—H/nm	H···A/nm	D···A/nm	∠(DHA)/(°)	D—H···A
0.104(13)	0.171(14)	0.2658(9)	150(11)	O(1)—H(1)···O(2d)
0.085(8)	0.184(8)	0.2670(10)	166(8)	N—H···O(2W)

Symmetry transformations used to generate equivalent atoms: d: −x, 2−y, 1−z.

In a word, ina molecules play an important role in the host-guest chemistry of the title compound. On the other hand, solvent is also very important to decide the varieties of the products.

Supplementary materials

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center in .cif format with CCDC reference number 209547.

Acknowledgements

References

1   Kovbasyuk, L. A.; Vassilyeva, O. Y.; Kokozay, V. N.; Linert, W.; Reedijk, J.; Skelton, B. W.; Oliver, A. G. *J. Chem. Soc., Dalton Trans.* **1998**, 2735.

2   Ribas, J.; Diaz, C.; Costa, R.; Tercero, J.; Solans, X.; Font-Bardía, M.; Stoeckli-Evans, H. *Inorg. Chem.* **1998**, *37,* 233.

3   Zhang, K. L.; Chen, W.; Xu, Y.; Wang, Z.; Zhong, Z. J.; You, X. Z. *Polyhedron* **2001**, *20,* 2033.

4   Zhou, B. C.; Kou, H. Z.; He, Y.; Wang, R. J.; Li, Y. D.; Wang, H. G. *Chin. J. Chem.* **2003**, *21,* 352.

5   Ozutsumi, K.; Kurihara, M.; Kawashima, T. *Talanta* **1993**, *5,* 599.

6   Krautschied, H.; Gerber, S. *Z. Anorg. Allg. Chem.* **1999**, *625,* 2041.

7   Ren, C. X.; Zhu, H. L.; Yang, G.; Chen, X. M. *J. Chem. Soc., Dalton Trans.* **2001**, 85.

8   Matthews, R. W.; Mcpartlin, M. M.; Scowen, I. J. *Chem. Commun.* **1996**, 309.

9   Cingi, M. B.; Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1985**, *101,* 49.

10   Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85,* 3533.

11   Kroeger, M. K.; Drago, R. S. *J. Am. Chem. Soc.* **1981**, *103,* 3250.

12   Müller, U. *Acta Crystallogr.* **1977**, *B33,* 2197.

13   Coleman, A. W.; Baskar, A. J.; Bott, S. G.; Atwood, J. L. *J. Coord. Chem.* **1988**, *17,* 339.

14   Li, X. L.; Niu, D. Z.; Lu, Z. S.; Shi, D. Q. *Chin. J. Struct. Chem.* **2003**, *22,* 47 (in Chinese).

15   Bondi, A. *J. Phys. Chem.* **1964**, *68,* 411.

16   Krautschied, H.; Emig, N.; Klaassen, N.; Seringer, P. *J. Chem. Soc., Dalton Trans.* **1998**, 3071.

17   Cingi, M. B.; Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1985**, *101,* 49.

(E0305121   ZHAO, X. J.)