

## КРАТКИЕ СООБЩЕНИЯ

UDC 541.66:547.13:546.72

CRYSTAL STRUCTURE AND THERMAL STABILITY OF A  $\mu_{1,1}$ -(OMe)-BRIDGED DIMERIC SCHIFF BASE IRON(III) COMPLEXS.-S. Qian<sup>1</sup>, X. Wang<sup>2</sup>, Z.-L. You<sup>2</sup>, H.-L. Zhu<sup>1</sup><sup>1</sup>School of Life Sciences, Shandong University of Technology, Zibo, P. R. China

E-mail: hailiang\_zhu@163.com

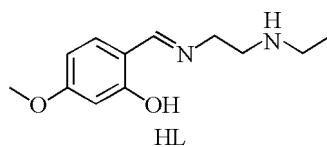
<sup>2</sup>Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China

Received February, 24, 2012

A new  $\mu_{1,1}$ -OMe-bridged dimeric iron(III) complex,  $[\text{Fe}_2\text{L}_2(\mu_{1,1}\text{-OMe})_2(\text{NCS})_2]$ , where L is the deprotonated form of 2-[(2-ethylaminoethylimino)methyl]-5-methoxyphenol, has been prepared and structural characterized by elemental analysis, IR spectrum, and single crystal X-ray crystallography. The complex crystallizes in the monoclinic space group  $P2_1/c$ , with unit cell dimensions  $a = 10.156(1) \text{ \AA}$ ,  $b = 11.972(1) \text{ \AA}$ ,  $c = 14.256(2) \text{ \AA}$ ,  $\beta = 102.643(3)^\circ$ ,  $V = 1691.3(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $R_1 = 0.0394$ , and  $wR_2 = 0.0922$ . Each Fe atom in the complex is in an octahedral coordination. The  $\text{Fe}\cdots\text{Fe}$  distance is  $3.102(1) \text{ \AA}$ . The thermal stability of the complex was studied.

**Key words:** Schiff base, iron complex, dimeric complex, crystal structure, thermal stability.

Dimeric structures of complexes with bridging groups are currently attracting much attention for their interesting structures and wide applications [1–3]. The Schiff bases derived from salicylaldehyde and its derivatives are a kind of versatile ligands in coordination chemistry. The rational design and construction of dimeric structures of complexes with Schiff bases are of particular interest in coordination and structural chemistry. The preferred way to construct polynuclear complexes is the use of suitable bridging groups, such as  $\text{N}_3^-$ ,  $\text{NCS}^-$ ,  $\text{N}(\text{CN})_2^-$ , dicarboxylate, 4,4'-bipy, and so on [4–7]. Methanol is a common solvent for the preparation of complexes with Schiff bases. In addition, methanol can also act as a co-ligand in the self-assembly of complexes [8–10], however,  $\mu_{1,1}$ -(OMe)-bridged iron complexes are very rare. In this paper, a new  $\mu_{1,1}$ -OMe-bridged dimeric iron(III) complex  $[\text{Fe}_2\text{L}_2(\mu_{1,1}\text{-OMe})_2(\text{NCS})_2]$ , where L is the deprotonated form of 2-[(2-ethylaminoethylimino)methyl]-5-methoxyphenol (HL), was prepared and structurally characterized. The thermal stability of the complex was also studied.



**Experimental. General methods and materials.** Starting materials, reagents and solvents of analytical grade were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the range  $4000\text{--}200 \text{ cm}^{-1}$ . Single crystal X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

**Synthesis of the Schiff base HL.** The yellow gummy product of the Schiff base was prepared by the reaction of equimolar quantities (1.0 mmol each) of 4-methoxysalicylaldehyde with *N*-ethylethane-1,2-diamine in methanol and by subsequent evaporation of the solvent. *Anal.* Calc. for  $C_{12}H_{18}N_2O_2$ : C 64.8, H 8.2, N 12.6 %. Found: C 64.7, H 8.2, N 12.7 %. Characteristic IR data (KBr,  $cm^{-1}$ ): 1617 (C=N).

**Synthesis of the complex.** To the methanolic solution (10 ml) of HL (0.022 g, 0.1 mmol) a methanolic solution (10 ml) of  $FeCl_3$  (0.016 g, 0.1 mmol) and an aqueous solution of ammonium thiocyanate (0.008 g, 0.1 mmol) were added with stirring. The mixture was stirred for 30 min at room temperature to give a brown solution. After keeping the solution in air for a few days, brown block-shaped crystals of the complex, suitable for the X-ray crystal structural determination, were formed on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in air. Yield 45 %. Characteristic IR data (KBr,  $cm^{-1}$ ): 3165 (m), 2048 (N—H), 1600 (NCS), 1602 (C=N). *Anal.* Calc. for  $C_{28}H_{40}Fe_2N_6O_6S_2$ : C 45.9, H 5.5, N 11.5 %. Found: C 45.7, H 5.6, N 11.5 %.

**X-ray crystallography.** Diffraction intensities for the complex were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector diffractometer with  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The collected data were reduced with the SAINT program [11], and multi-scan absorption correction was performed using the SADABS program [12]. The structure was solved by the direct method and refined against  $F^2$  by the full-matrix least-squares technique using the SHELXTL package [13]. All of the non-hydrogen atoms were refined anisotropically. The amino hydrogen atom was located from a difference Fourier map and refined isotropically with the N—H distance restrained to 0.90(1)  $\text{\AA}$ . The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent

Table 1

Crystallographic data and refinement parameters for the complex

Formula	$C_{28}H_{40}Fe_2N_6O_6S_2$
$M_r$	732.5
$T$ , K	298(2)
Crystal shape / color	Block / brown
Crystal size, mm	0.25×0.20×0.20
Crystal system	Monoclinic
Space group	$P2_1/c$
$a, b, c$	10.156(1), 11.972(1), 14.256(2)
$\beta$ , deg.	102.643(3)
$V$ , $\text{\AA}^3$	1691.3(3)
$Z$	2
$D_c$ , $g \cdot cm^{-3}$	1.438
$\mu(MoK_{\alpha})$ , $mm^{-1}$	1.029
$F(000)$	764
Indepen. / Observ. reflections ( $I \geq 2\sigma(I)$ )	3639 / 2418
Min. and max. transmission	0.783 and 0.821
Parameters	205
Restraints	1
Goodness-of-fit on $F^2$	1.057
$R_1, wR_2 [I \geq 2\sigma(I)]^a$	0.0394, 0.0922
$R_1, wR_2$ (all data) <sup>a</sup>	0.0694, 0.1030

$$^a R_1 = F_0 - F_c / F_0, \quad wR_2 = [\sum w(F_0^2 - F_c^2) / \sum w(F_0^2)]^{1/2}.$$

Table 2

Selected bond distances (Å) and angles (deg.) for the complex

Fe1—O1	1.9126(18)	O1—Fe1—O3	97.77(7)	O1—Fe1—O3A	94.23(8)
Fe1—O3A	2.0075(16)	O3—Fe1—O3A	77.06(7)	O1—Fe1—N3	92.66(9)
Fe1—N1	2.104(2)	O3—Fe1—N3	96.13(8)	O3A—Fe1—N3	170.90(8)
Fe1—O3	1.9581(15)	O1—Fe1—N1	87.10(8)	O3—Fe1—N1	171.40(8)
Fe1—N3	2.083(2)	O3A—Fe1—N1	95.57(8)	N3—Fe1—N1	90.70(9)
Fe1—N2	2.207(2)	O1—Fe1—N2	165.66(8)	O3—Fe1—N2	96.53(7)
		O3A—Fe1—N2	88.01(7)	N3—Fe1—N2	86.78(9)
		N1—Fe1—N2	78.58(9)		

atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

**Results and discussion. Chemistry.** The complex was prepared by the reaction of equimolar quantities of HL with FeCl<sub>3</sub> and NH<sub>4</sub>NCS in methanol. The choice of the solvent used for the preparation of the complex is important. The crystals were obtained from the methanol solution containing the complex. However, it is difficult to obtain single crystals from other solvents such as ethanol, acetonitrile, and chloroform. Previously, a mononuclear copper complex with the same Schiff base and the thiocyanate co-ligand has been reported [14], in which there are no thiocyanate co-ligands.

**Structure description of the complex.** The molecular structure of the complex is shown in Fig. 1. X-ray crystallography reveals that the complex is a  $\mu_{1,1}$ -OMe-bridged centrosymmetric and dimeric iron(III) compound. The inversion center is located at the midpoint of the two metal atoms. The Fe...Fe distance is 3.102(1) Å. The Schiff base serves as a tridentate ligand to form five- and six-membered chelate rings with the Fe atom in the complex. The coordination geometry around the metal center can be best described as a slightly distorted octahedron, with three donor atoms of the Schiff base ligand and one methoxy O atom defining the equatorial plane, and with the symmetry-related

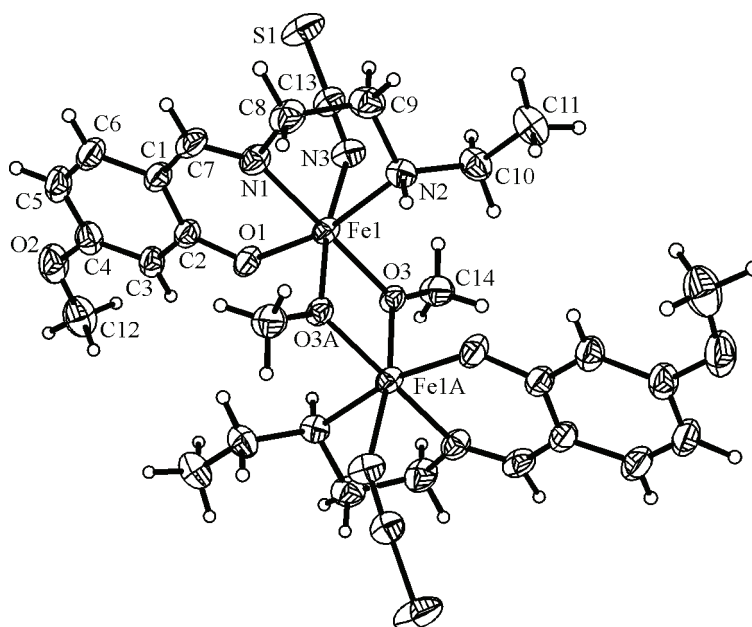


Fig. 1. A perspective view of the molecular structure of the complex with the atom labeling scheme. The thermal ellipsoids are drawn at the 30 % probability level. Atoms labeled with the suffix A or unlabeled are at the symmetry position  $2-x, 1-y, -z$

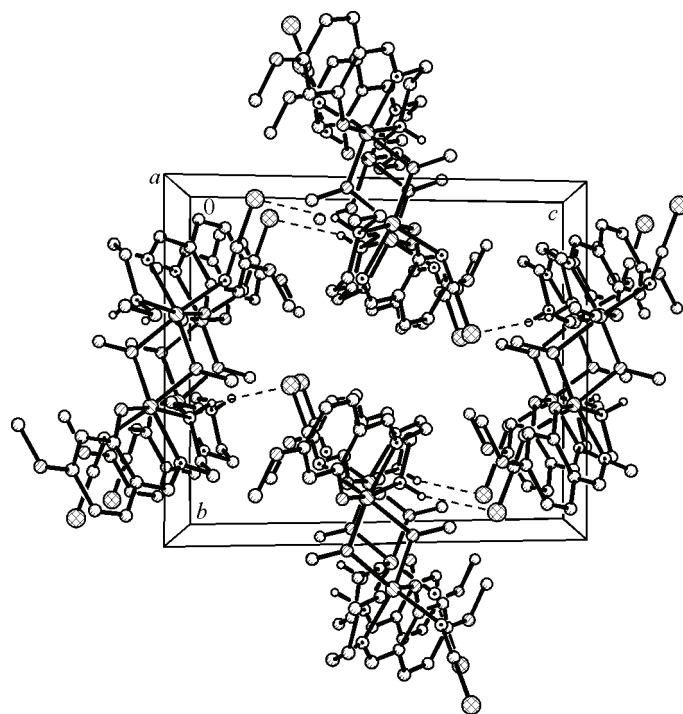


Fig. 2. Molecular packing of the complex viewed along the *a* axis.  
Hydrogen bonds are shown as thin dashed lines

methoxy O atom and one thiocyanate N atom occupying two axial positions. The Fe atom in the complex lies at 0.064(2) Å from the least-squares plane of the equatorial donor atoms in the direction of the axial thiocyanate ligand. The bond distances and bond angles of the complex are typical, and are comparable to those observed in other similar iron(III) complexes with Schiff bases [15–17].

In the crystal structure of the complex, the dimeric iron(III) complex molecules are linked through intermolecular N2—H2···S1 hydrogen bonds to form layers parallel to the *bc* plane. The layers are further stacked *via* weak  $\pi\cdots\pi$  interactions along the *a* axis, as shown in Fig. 2.

**IR spectra.** In the IR spectrum of the complex, the middle band centered at 3166  $\text{cm}^{-1}$  is assigned to the vibration of N—H group. The strong absorption band at 1602  $\text{cm}^{-1}$  is assigned to the C=N group. The intense band indicative of the thiocyanate ligand is located at 2048  $\text{cm}^{-1}$ . The weak bands in the region 300–600  $\text{cm}^{-1}$  for the complex may be assigned to Fe—O and Fe—N vibrations.

**Thermal stability.** Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complex. The first step started at about 214 °C and was completed at about 328 °C, corresponding to the loss of the thiocyanate ligands. The observed weight loss of 15.5 % is very close to the calculated value (15.8 %). The second step, from 328 °C to 411 °C, corresponds to the loss of the methoxy ligands. The observed weight loss of 8.5 % is equal to the calculated value. The third step, from 411 °C to 455 °C, corresponds to the loss of the Schiff base ligands. The observed weight loss of 55.9 % is close to the calculated value (54.0 %), and the formation of the final product ( $\text{Fe}_2\text{O}_3$ ). The total weight loss of 80.6 % is close to the calculated value (78.2 %).

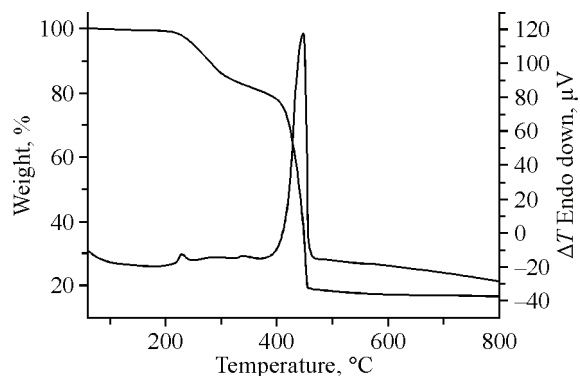


Fig. 3. DT-TGA curve of the complex

**Conclusions.** In summary, the present paper reports the synthesis, structure, and thermal stability of an iron(III) complex with a tridentate Schiff base ligand. The methoxy groups act as interesting bridging ligands in the complex.

**Supplementary information.** CCDC-855109 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

#### REFERENCES

1. Lou S.-F., Zheng X., Chen Y. *et al.* // *J. Struct. Chem.* – 2011. – **52**, N 6. – P. 1091/1097.
2. Mamoor G.M., Sahin O., Khan I.U. *et al.* // *J. Struct. Chem.* – 2011. – **52**, N 6. – P. 1115/1119.
3. You Z.-L., Lu Y., Zhang N. *et al.* // *Polyhedron.* – 2011. – **30**, N 13. – P. 2186/2194.
4. Mautner F.A., Albering J.H., Mikuriya M. *et al.* // *Inorg. Chem.* – 2010. – **13**, N 6. – P. 796/799.
5. Andreev G., Budantseva N., Fedoseev A. *et al.* // *Inorg. Chem.* – 2011. – **22**, N 22. – P. 11481/11486.
6. Banu K.S., Mondal S., Guha A. *et al.* // *Polyhedron.* – 2011. – **30**, N 1. – P. 163/168.
7. Das A., Demeshko S., Dechert S. *et al.* // *Eur. J. Inorg. Chem.* – 2011. – N 8. – P. 1240/1248.
8. Godbole M.D., Roubeau O., Clerac R. *et al.* // *Chem. Commun.* – 2005. – N 29. – P. 3715/3717.
9. Sayre H., Milos K., Goldcamp M.J. *et al.* // *Inorg. Chem.* – 2010. – **49**, N 10. – P. 4433/4439.
10. Hoshino N., Ako A.M., Powell A.K. *et al.* // *Inorg. Chem.* – 2009. – **48**, N 8. – P. 3396/3407.
11. Bruker, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, 2002.
12. Sheldrick G.M. SADABS. Program for Empirical Absorption Correction of Area Detector, University of Göttingen, Germany, 1996.
13. Sheldrick G.M. SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA, 1997.
14. Zhu Y. // *Acta Crystallogr.* – 2010. – **E66**, N 4. – P. m419.
15. Tissot A., Bertoni R., Collet E. *et al.* // *J. Mater. Chem.* – 2011. – **21**, N 45. – P. 18347/18353.
16. Banse F., Balland V., Philouze C. *et al.* // *Inorg. Chim. Acta.* – 2003. – **353**. – P. 223/230.
17. Negoro S., Asada H., Fujiwara M. *et al.* // *Inorg. Chem. Commun.* – 2003. – **6**, N 4. – P. 357/360.