

## NOTE

### Synthesis and Structure of Fe(III) Complex Derived from An Octadentate Schiff Base Ligand

GUANG-QI JIANG\* and YONG-ZHONG LU

College of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550 025, P.R. China

\*Corresponding author: Tel: +86 851 8292313; E-mail: [gqjiang@163.com](mailto:gqjiang@163.com)

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A new Fe(III) complex,  $[\text{Fe}(\text{C}_{26}\text{H}_{26}\text{O}_3\text{N}_4)]\text{NO}_3 \cdot \text{H}_2\text{O}$ , was obtained by the reaction of Schiff base ligand  $\text{H}_4\text{L}$  ( $\text{H}_4\text{L} = 1,1,1,1$ -tetrakis[(salicylaldimino)methyl]methane) with  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  at 1:2 mol ratio and was structurally determined by elemental analyses, IR, EI-MS and single crystal X-ray diffraction analysis. The complex crystallized in the monoclinic system, space group P 21/n with unit cell parameters:  $a = 12.486(5) \text{ \AA}$ ,  $b = 15.769(5) \text{ \AA}$ ,  $c = 12.989(5) \text{ \AA}$ ,  $\beta = 95.764(5)^\circ$ ,  $V = 2544.5(16) \text{ \AA}^3$ ,  $Z = 4$ ,  $M_r = 578.38$ ,  $D_c = 1.510 \text{ g/cm}^3$ ,  $\mu = 0.650 \text{ mm}^{-1}$ ,  $F(000) = 1204$ ,  $R = 0.0400$ ,  $wR = 0.1109$  for 3701 reflections with  $I > 2\sigma(I)$ . It is of interest to note that one of the pendant arms of  $\text{H}_4\text{L}$  ligand was hydrolyzed when  $\text{H}_4\text{L}$  coordinated with Fe(III) ions, simultaneously, the resulting amino group was protonated to maintain the charge balance of the system.

**Key Words:** Schiff base, Complex, Crystal structure.

Increasing attentions have been focused on the Fe(III) containing Schiff base complexes being their similarities to the active centers of some metalloenzymes<sup>1</sup>, fascinating magnetic properties in single molecule magnets<sup>2,3</sup> and their potential utilities as new catalysts<sup>4-6</sup>. However, to the best of our knowledge, the preparation of these complexes mainly depends on the use of multiple ligands rather than single multifunctional ligand in order to modulate the nuclearities and dimensionalities of the complexes. As an extension of our work, an octadentate Schiff base ligand  $\text{H}_4\text{L}$  ( $\text{H}_4\text{L} = 1,1,1,1$ -tetrakis[(salicylaldimino)methyl]methane) was synthesized according to our reported procedures<sup>7,8</sup>. Here, we presented the crystal structure of a new Fe(III) complex of this multifunctional ligand.

All other reagents and solvents except  $\text{H}_4\text{L}$  ligand were used as commercial sources without further purification. Elemental analyses for C, H, N were performed on a Vario ELIII analyzer. The IR spectra were recorded on a Bio-Rad spectrophotometer using KBr discs in the 4000-400  $\text{cm}^{-1}$  region. Crystal structure was determined on a Bruker Apex 2 diffractometer.

**Synthesis of the Fe(III) complex:** To a solution of the ligand  $\text{H}_4\text{L}$  (0.55 g, 1 mmol) in 10 mL ethanol, ethanolic  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.80 g, 2 mmol) solution was added dropwise. The mixture was stirred for 1.5 h at room temperature, then filtered, the filtrate afforded purple black crystals after several days in 45.4 % yield. Anal. calcd. (%) for  $\text{C}_{26}\text{H}_{28}\text{N}_5\text{O}_7\text{Fe}$  (%):

C, 53.99; H, 4.88; N, 12.11. Found (%): C, 54.40; H, 4.75; N, 12.21. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3131(w), 2924(w), 2855(w), 1617(vs), 1550(w), 1446(m), 1385(vs), 1315(m), 1247(m), 1223(m), 973(w), 860(w), 742(m). EI-MS:  $m/z$  (%) = 497 ( $M^+$ , 38), 347 (100), 243 (20), 176 (28), 91 (14), 30 (18).

**Crystal structure determination:** The X-ray data were collected on a Bruker Apex-II CCD diffractometer using graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 (2)K with crystal size 0.16 mm  $\times$  0.12 mm  $\times$  0.11 mm. A total of 4566 ( $R_{\text{int}} = 0.0412$ ) independent reflections were collected by  $\phi$  and  $\omega$  scans technique in the range of  $0.998 \leq \theta \leq 25.20^\circ$  from which 3701 [ $I > 2\sigma(I)$ ] reflection were corrected for Lorentz and polarization factors. The structure was solved by direct method using SHELXS-97 and refined using a full-matrix least-squares procedure on  $F^2$  in SHELXS-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model.

Fig. 1 shows the molecular structure of the Fe(III) complex. It crystallized in the monoclinic system with P 21/n space group. The selected bond lengths and bond angles are listed in Table-1. The hydrogen bondings parameters are given in Table-2. As shown in Fig. 1, Fe(III) ion is coordinated by imine nitrogen atoms [N(1), N(2), N(3)] and phenolic oxygen atoms [O(1), O(2), O(3)] from three pendant arms of  $\text{H}_4\text{L}$  ligand. The distances of Fe-N, Fe-O bonds varied from 2.126 to 2.161, 1.922 to 1.978  $\text{ \AA}$ , respectively. Fe(III) ion located at

TABLE-2  
 HYDROGEN BOND DISTANCES (Å) AND ANGLES (°)

Type (D-H...A)	d (D-H)	d (H...A)	∠(DHA)	d (D...A)	Symmetry codes
O1W-H1WA...N6	0.8500	2.1500	129.00	2.7719	-1/2+x,1/2-y,-1/2+z
O1W-H1WB...O1	0.8500	2.4100	130.00	3.0216	-1+x,y,z
O1W-H1WB...O2	0.8500	2.4800	151.00	3.2518	-1+x,y,z
N6-H6A...O4	0.8600	2.2100	173.00	3.0660	1/2+x,1/2-y,1/2+z
N6-H6B...O3	0.8600	2.2500	130.00	2.8747	-1/2+x,1/2-y,1/2+z
N6-H6C...O5	0.8900	2.3300	162.00	3.1913	1/2+x,1/2-y,1/2+z
C5-H5...O2	0.9300	2.5800	138.00	3.3343	-1/2+x,1/2-y,-1/2+z
C10-H10A...O5	0.9700	2.3900	157.00	3.3079	1/2+x,1/2-y,1/2+z
C11-H11...O5	0.9300	2.5400	136.00	3.2788	1/2+x,1/2-y,1/2+z
C22-H22...O4	0.9300	2.3700	167.00	3.2803	3/2-x,-1/2+y,1/2-z

the center of octahedral coordination geometry. It is worth noting that one of the salicylaldehyde moieties of H<sub>4</sub>L hydrolyzed to the amine ending group and kept protonated when it coordinated with Fe(III) ions. Furthermore, we also found a nitrate anion and a crystal water molecular were involved in the crystallographic lattice, they played important roles in the formation of hydrogen bondings and maintained the charge balance of the system.

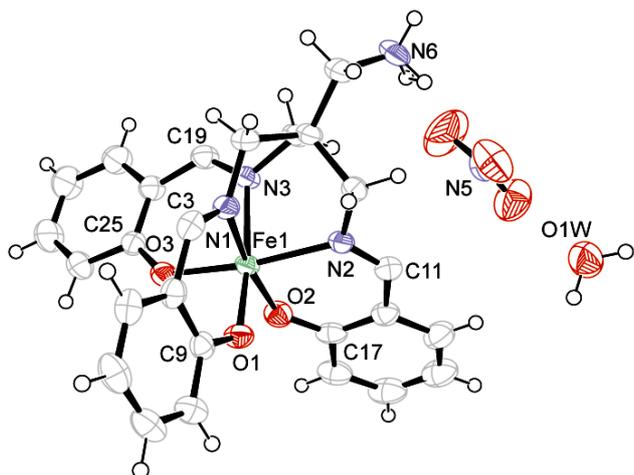

 Fig. 1. Molecular structure of [Fe(C<sub>26</sub>H<sub>26</sub>O<sub>3</sub>N<sub>4</sub>)]NO<sub>3</sub>.H<sub>2</sub>O

 TABLE-1  
 SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Fe1-N1	2.153(2)	C3-N1	1.285(4)	O1-Fe1-O2	92.24(8)
Fe1-N2	2.126(2)	C9-O1	1.321(3)	O1-Fe1-O3	93.07(8)
Fe1-N3	2.161(2)	C11-N2	1.284(3)	O1-Fe1-N1	85.77(8)
Fe1-O1	1.943(19)	C17-O2	1.321(3)	O1-Fe1-N2	98.47(8)
Fe1-O2	1.922(19)	C19-N3	1.286(3)	O1-Fe1-N3	165.33(8)
Fe1-O3	1.9775(19)	C25-O3	1.324(3)	O2-Fe1-O3	90.81(8)

## Conclusion

A new Fe(III) complex, [Fe(C<sub>26</sub>H<sub>26</sub>O<sub>3</sub>N<sub>4</sub>)]NO<sub>3</sub>.H<sub>2</sub>O has been synthesized and characterized by elemental analyses, IR, EI-MS and single crystal X-ray diffraction analysis. X-ray crystal structure reveals Fe(III) ion coordinated with imine nitrogen atoms and phenolic oxygen atoms from three pendant arms of H<sub>4</sub>L ligand. The other arm of H<sub>4</sub>L ligand hydrolyzed to the amine ending group and kept protonated. Hydrogen bondings also have been found exist extensively in the structure.

**Supplementary material:** Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 860018.

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## REFERENCES

- Z.D. Liu, R. Kayyali, R.C. Hider, J.B. Porter and A.E. Theobald, *J. Med. Chem.*, **45**, 631 (2002).
- L.H. Li, J.M. Becker, L.E.N. Allan, G.J. Clarkson, S.S. Turner and P. Scott, *Inorg. Chem.*, **50**, 5925 (2011).
- M. Ferbinteanu, T. Kajiwara, K.Y. Choi, H. Nojiri, A. Nakamoto, N. Kojima, F. Cimpoesu, Y. Fujimura, S. Takaishi and M. Yamashita, *J. Am. Chem. Soc.*, **128**, 9008 (2006).
- M.C. Cheng, M.C.W. Chan, S.M. Peng, K.K. Cheung and C.M. Che, *J. Chem. Soc. Dalton Trans.*, 3479 (1997).
- K.K. Bania, D. Bharali, B. Viswanathan and R.C. Deka, *Inorg. Chem.*, **51**, 1675 (2012).
- B.L. Small, R. Rios, E.R. Fernandez and M.J. Carney, *Organometallics*, **26**, 1744 (2007).
- G.Q. Jiang, J. Cai, Y.Q. Zhang and Q.J. Zhang, *Chinese J. Appl. Chem.*, **26**, 329 (2009).
- G.Q. Jiang, J. Cai, Y.Q. Zhang and Q.J. Zhang, *Acta Cryst.*, **E64**, o1455 (2008).