Li Ya*, Fang Xiangqing, Liu Junyi, Dong Chi and Yang Ligu

Crystal structure of (μ_2 -oxido)-bis(*N,N'*-*o*-phenylenebis(salicylideneiminato))diiron(III) – *N,N'*-dimethylformamide, $C_{47}H_{43}Fe_2N_4O_9$

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.10 × 0.08 × 0.06 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.74 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	95920, 7442, 0.061
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5491
$N(\text{param})_{\text{refined}}$:	583
Programs:	Bruker [1], SHELX [2, 3]

<https://doi.org/10.1515/ncrs-2019-0256>

Received April 8, 2019; accepted June 5, 2019; available online July 9, 2019

Abstract

$C_{47}H_{43}Fe_2N_4O_9$, orthorhombic, *Pbca* (no. 61), $a = 24.6961(8)$ Å, $b = 14.0952(5)$ Å, $c = 24.696(3)$ Å, $V = 8596.6(4)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0374$, $wR_{\text{ref}}(F^2) = 0.1209$, $T = 296(2)$ K [1–3].

CCDC no.: 1921096

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Schiff base ligand was purchased from Acros Ltd. Company and used without further purification, the other reagents were commercially available and used as purchased. The title compound was synthesized by the reaction

***Corresponding author:** Li Ya, Department of Energy and Architecture, Xi'an Aeronautical University, Xi'an 710077, Shanxi, P.R. China, e-mail: 40929637@qq.com

Fang Xiangqing, Liu Junyi and Dong Chi: Department of Energy and Architecture, Xi'an Aeronautical University, Xi'an 710077, Shanxi, P.R. China

Yang Ligu: College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.52550(2)	0.71504(3)	0.63533(2)	0.03486(13)
N1	0.79736(13)	0.0119(2)	0.73154(15)	0.0792(9)
O1	0.58499(8)	0.38875(14)	0.63622(8)	0.0514(5)
C1	0.53504(17)	0.4742(3)	0.92416(16)	0.0771(11)
H1A	0.5340	0.4081	0.9150	0.116*
H1B	0.5396	0.4810	0.9626	0.116*
H1C	0.5648	0.5040	0.9058	0.116*
Fe2	0.52293(2)	0.47247(3)	0.64541(2)	0.03739(13)
N2	0.49206(9)	0.41138(15)	0.57417(10)	0.0410(6)
O2	0.52168(8)	0.45185(14)	0.72238(8)	0.0475(5)
C2	0.47301(14)	0.5166(2)	0.85461(13)	0.0558(9)
O3	0.70929(10)	0.15478(16)	0.57262(10)	0.0695(7)
N3	0.43797(9)	0.49383(16)	0.65052(10)	0.0415(6)
C3	0.42165(15)	0.5531(2)	0.84272(15)	0.0642(9)
H3	0.3998	0.5774	0.8701	0.077*
C4	0.40438(14)	0.5527(2)	0.79114(15)	0.0585(9)
H4	0.3699	0.5756	0.7837	0.070*
O4	0.48615(11)	0.51777(18)	0.90816(10)	0.0739(7)
N4	0.50100(9)	0.74156(15)	0.71605(9)	0.0379(5)
C5	0.43618(12)	0.51898(19)	0.74768(13)	0.0453(7)
O5	0.25958(9)	0.7883(2)	0.61751(11)	0.0802(8)
N5	0.59207(9)	0.78663(15)	0.67104(9)	0.0379(5)
O6	0.64832(11)	0.8924(2)	0.42401(9)	0.0795(8)
C6	0.48881(12)	0.48484(19)	0.75972(12)	0.0435(7)
O7	0.54892(8)	0.76792(14)	0.56725(8)	0.0482(5)
C7	0.50578(13)	0.4821(2)	0.81398(13)	0.0479(7)
H7	0.5395	0.4569	0.8226	0.057*
C8	0.41333(12)	0.5175(2)	0.69504(14)	0.0487(8)
H8	0.3772	0.5352	0.6921	0.058*
O8	0.45020(8)	0.73485(14)	0.61633(8)	0.0461(5)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
O9	0.74998(15)	−0.0952(3)	0.68331(15)	0.1446(16)
C9	0.41154(11)	0.4919(2)	0.60013(13)	0.0457(7)
C10	0.36052(13)	0.5292(2)	0.58843(15)	0.0624(9)
H10	0.3399	0.5568	0.6157	0.075*
O10	0.54291(8)	0.59225(12)	0.63298(8)	0.0441(5)
C11	0.34081(15)	0.5248(3)	0.53633(17)	0.0766(11)
H11	0.3067	0.5495	0.5288	0.092*
C12	0.37063(15)	0.4847(3)	0.49538(17)	0.0715(10)
H12	0.3569	0.4834	0.4603	0.086*
C15	0.51341(11)	0.3430(2)	0.54649(12)	0.0450(7)
H15	0.4941	0.3216	0.5166	0.054*
C14	0.44105(11)	0.4492(2)	0.55852(13)	0.0456(7)
C13	0.42053(13)	0.4464(2)	0.50598(14)	0.0562(8)
H13	0.4406	0.4186	0.4783	0.067*
C16	0.56339(12)	0.29780(19)	0.55735(12)	0.0429(7)
C17	0.59797(11)	0.32341(19)	0.60063(12)	0.0411(7)
C18	0.64806(12)	0.2758(2)	0.60565(13)	0.0475(7)
H18	0.6720	0.2930	0.6330	0.057*
C19	0.66184(13)	0.2040(2)	0.57022(13)	0.0505(8)
C20	0.62657(14)	0.1755(2)	0.52940(13)	0.0568(8)
H20	0.6355	0.1251	0.5068	0.068*
C21	0.57875(13)	0.2225(2)	0.52302(13)	0.0534(8)
H21	0.5556	0.2044	0.4952	0.064*
C22	0.74769(18)	0.1793(3)	0.6129(2)	0.1029(16)
H22A	0.7563	0.2456	0.6100	0.154*
H22B	0.7800	0.1425	0.6079	0.154*
H22C	0.7328	0.1666	0.6481	0.154*
C23	0.6877(2)	0.9532(4)	0.40174(17)	0.1119(18)
H23A	0.6846	1.0149	0.4179	0.168*
H23B	0.6823	0.9581	0.3633	0.168*
H23C	0.7231	0.9280	0.4088	0.168*
C24	0.64485(12)	0.8825(2)	0.47888(13)	0.0519(8)
C25	0.68134(12)	0.9213(2)	0.51472(14)	0.0554(8)
H25	0.7102	0.9578	0.5025	0.066*
C26	0.67402(12)	0.9048(2)	0.56866(14)	0.0565(8)
H26	0.6986	0.9307	0.5930	0.068*
C27	0.63106(11)	0.8507(2)	0.58882(12)	0.0418(7)
C28	0.59245(11)	0.81400(19)	0.55163(12)	0.0400(7)
C29	0.60103(12)	0.8308(2)	0.49690(12)	0.0529(8)
H29	0.5766	0.8067	0.4718	0.064*
C30	0.62794(11)	0.8370(2)	0.64560(12)	0.0452(7)
H30	0.6541	0.8669	0.6666	0.054*
C31	0.59404(11)	0.77841(19)	0.72797(12)	0.0405(7)
C32	0.63990(13)	0.7940(2)	0.75999(13)	0.0530(8)
H32	0.6723	0.8129	0.7441	0.064*
C33	0.63676(15)	0.7814(2)	0.81518(14)	0.0615(9)
H33	0.6671	0.7922	0.8366	0.074*
C34	0.58849(15)	0.7524(2)	0.83900(14)	0.0597(9)
H34	0.5869	0.7433	0.8763	0.072*
C35	0.54300(14)	0.7371(2)	0.80775(13)	0.0511(8)
H35	0.5109	0.7174	0.8238	0.061*
C36	0.54543(12)	0.75119(19)	0.75225(12)	0.0414(7)
C37	0.45241(12)	0.75649(19)	0.73349(12)	0.0426(7)
H37	0.4481	0.7670	0.7704	0.051*
C38	0.40505(11)	0.75817(19)	0.70095(12)	0.0417(7)
C39	0.40598(11)	0.7498(2)	0.64355(12)	0.0408(7)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C40	0.35661(11)	0.7607(2)	0.61482(13)	0.0490(8)
H40	0.3566	0.7567	0.5772	0.059*
C41	0.30874(12)	0.7773(2)	0.64180(14)	0.0566(9)
C42	0.30764(13)	0.7833(3)	0.69814(15)	0.0664(10)
H42	0.2751	0.7929	0.7162	0.080*
C43	0.35528(13)	0.7749(2)	0.72670(14)	0.0582(9)
H43	0.3545	0.7805	0.7642	0.070*
C44	0.25620(15)	0.7867(3)	0.56023(16)	0.0826(12)
H44A	0.2775	0.8375	0.5455	0.124*
H44B	0.2191	0.7943	0.5494	0.124*
H44C	0.2697	0.7271	0.5470	0.124*
C45	0.7528(2)	0.0294(5)	0.7667(2)	0.146(3)
H45A	0.7196	0.0146	0.7484	0.220*
H45B	0.7527	0.0951	0.7771	0.220*
H45C	0.7561	−0.0095	0.7984	0.220*
C46	0.8515(2)	0.0449(5)	0.7431(3)	0.191(4)
H46A	0.8769	0.0117	0.7206	0.287*
H46B	0.8598	0.0333	0.7805	0.287*
H46C	0.8537	0.1117	0.7359	0.287*
C47	0.79054(18)	−0.0497(3)	0.69243(19)	0.0873(13)
H47	0.8198	−0.0594	0.6694	0.105*

of FeCl₃ (64.88 mg, 0.4 mmol) and 6,6'-((1,2-phenylenebis (azanylylidene))bis(methanylylidene))bis(3-methoxyphenol) (49.64 mg, 0.4 mmol) in DMF (10 mL). The mixture was stirred for 6 h, then a colourless solution formed. The resulting solution was filtered. The filtrate was allowed to stand for a few days at room temperature until light-pink crystals were obtained. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a DMF solution. (25%, m.p. 320–325 K).

Experimental details

Hydrogen atoms were added with geometric restraints.

Comment

Organic molecules containing imine groups, commonly known as Schiff bases, are of interest to inorganic chemists as these are widely used in designing molecular ferromagnets, in catalysis, in biological modeling applications and in preparing liquid crystals [4–8]. Schiff bases also play a key role as chelating ligands in main group and transition metal coordination chemistry, due to their ease of synthesis, stability under a variety of oxidative and reductive conditions, and their structural versatility, which is associated with their applications [9–11]. Undoubtedly, salen type ligands are receiving the most attention among all the Schiff bases. Ligands categorized under this class consist of two imine nitrogen and two phenolic oxygen donors that usually coordinate in the basal plane of the metal ion, salen-type ligands are significant because of the ability of the phenoxo oxygen atoms

to form 2-bridges, thus affording high-nuclearity compounds, which could act as promising candidates to offer valuable insight into various natural electron-transfer events [12]. Now, we synthesized the new dinuclear Fe compounds with N,N' -bis(salicylidene)phenyldiamine ligands. Some similar compounds have been reported [13–15].

As shown in the figure, the title compound contains a dinuclear Fe(III) complex. The compound shows a distorted octahedral geometry involving N_2O_2 donors as the basal plane. Both the Fe centers have a five coordinated square-pyramidal geometry, in which N_2O_2 donors from the ligand and the axial position is occupied by a bridging oxygen atom.

Acknowledgements: The authors gratefully acknowledge the financial support by Young Talent fund of University Association for Science and Technology in Shaanxi, China, Educational Commission of Shaanxi Province of China (16 J K1393) and Science Foundation of Shaanxi Province of China (2016JQ2001).

References

1. Bruker. SMART and SAINT for Windows NT Software Reference Manuals, Version 5.0. Bruker Analytical X-Ray Systems, Madison, WI (1997).
2. Sheldrick, G. M.: SADABS, a software for empirical absorption correction. University of Göttingen, Göttingen, Germany (1997).
3. SHELXL. Reference Manual, version 5.1; Bruker Analytical X-Ray Systems, Madison, WI (1997).
4. de Barbarin, C. O. R.; Bailey, N. A.; Fenton, D. E.; He, Q. Y.: Zinc (II) complexes derived from potentially hexadentate (N_4O_2) acyclic ligands containing pyridinyl and phenolic groups. *J. Chem. Soc. Dalton Trans.* **2** (1997) 161–166.
5. Larson, E. J.; Pecoraro, V. L.: The peroxide-dependent μ_2 -O bond formation of manganese complex $[Mn(IV)SALPN(O)_2]$. *J. Am. Chem. Soc.* **113** (1991) 3810–3818.
6. Khan, M. M. T.; Srinivas, D.; Kureshy, R. I.; Khan, N. H.: Synthesis, characterization, and EPR studies of stable ruthenium (III) Schiff base chloro and carbonyl complexes. *Inorg. Chem.* **29** (1990) 2320–2326.
7. Miyasaka, H.; Ieda, H.; Mastumoto, N.; Crescenzi, R.; Floriani, C.: Assembling bi-, tri- and pentanuclear complexes into extended structures using a desolvation reaction: synthesis, structure, and magnetic properties of manganese(III) Schiff-Base hexacyanoferrate polymeric compounds and their derived extended structures. *Inorg. Chem.* **37** (1998) 255–263.
8. Ramade, I.; Kahn, O.; Jeannin, Y.; Robert, F.: Design and magnetic properties of a magnetically isolated GdIII/CuII pair. crystal structures of $[Gd(hfa)_3Cu(salen)]$, $[Y(hfa)_3Cu(salen)]$, $[Gd(hfa)_3Cu(salen)(Meim)]$, and $[La(hfa)_3(H_2O)Cu(salen)]$ [hfa = Hexafluoroacetylacetonato, $salen$ = N,N' -ethylenebis(salicylideneaminato), $Meim$ = 1-Methylimidazole]. *Inorg. Chem.* **36** (1997) 930–936.
9. Ziessel, R.: Schiff-based bipyridine ligands. unusual coordination features and mesomorphic behaviour. *Coord. Chem. Rev.* **216** (2001) 195–223.
10. Cozzi, P. G.: Metal-salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.* **64** (2004) 410–421.
11. Gupta, K. C.; Sutar, A. K.: Catalytic activities of Schiff base transition metal complexes. *Coord. Chem. Rev.* **252** (2008) 1420–1450.
12. Katsuki, T.: Catalytic asymmetric oxidations using optically active (salen)manganese(III) complexes as catalysts. *Coord. Chem. Rev.* **140** (1995) 189–214.
13. Jana, S.; Chatterjee, S.; Chattopadhyay, S.: Syntheses, characterization and X-ray crystal structures of hexa-coordinated monomeric and oxo-bridged dimeric Fe(III) compounds with salen-type Schiff bases. *Polyhedron* **48** (2012) 189–198.
14. Meng, Q.; Clegg, J. K.; Brock, A. J.; Jolliffe, K. A.; Lindoy, L. F.; Wei, G.: Mono- and dinuclear Ni(II), Cu(II), Zn(II) and Fe(III) complexes of symmetric and unsymmetric Schiff bases incorporating salicylimine functions—synthetic and structural studies. *Polyhedron* **74** (2014) 113–121.
15. Oyaizu, K.; Dewi, E. L.; Tsuchida, E. A.: μ -Oxo diiron(III) complex with a short Fe-Fe distance: crystal structure of (μ -oxo) bis[N,N' -*o*-phenylenebis(salicylideneiminato)iron(III)]. *Inorg. Chim. Acta* **321** (2001) 205–208.