

两个线型三核铁(II)配合物 $[\text{Fe}_3\text{L}_2(\text{CH}_3\text{COO})_2]$ 的合成和晶体结构

王天维

(南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)

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Synthesis and Crystal Structure of Two New Linear Trinuclear Iron Complex $[\text{Fe}_3\text{L}_2(\text{CH}_3\text{COO})_2]$

WANG Tian-Wei

(State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093)

Abstract: The title linear trinuclear complexes, $[\text{Fe}_3\text{L}_2(\text{CH}_3\text{COO})_2]$ (L=bis-(salicylidene)-1,3-diaminopropane (salpd) (**1**) and L=bis-(salicylidene)-1,4-diaminobutane (salbd) (**2**)) were synthesized simply using solvothermal method in methanol and were characterized by X-ray single crystal diffraction. $[\text{Fe}_3\text{L}_2(\text{CH}_3\text{COO})_2]$ (**1**) was obtained using salicylaldehyde, 1,3-diaminopropane and $\text{Fe}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ via the above method with monoclinic crystal system and space group of $P2_1/c$, and lattice parameters of $a=0.945\ 0(8)$ nm, $b=1.037\ 0(8)$ nm, $c=1.830\ 5(14)$ nm, $\beta=94.357(16)^\circ$. The $[\text{Fe}_3\text{L}_2(\text{CH}_3\text{COO})_2]$ (**2**) was obtained using 1,4-diaminobutane instead of 1,3-diaminopropane while keeping the other conditions the same as that for synthesis of $[\text{Fe}_3\text{L}_2(\text{CH}_3\text{COO})_2]$ (**1**). The $[\text{Fe}_3\text{L}_2(\text{CH}_3\text{COO})_2]$ (**2**) was in monoclinic crystal system and space group of $P2_1/c$, and lattice parameters of $a=0.919\ 0(5)$ nm, $b=1.675\ 6(9)$ nm, $c=1.270\ 0(7)$ nm, $\beta=95.126(11)^\circ$. CCDC: 754930, **1**; 754931, **2**.

Key words: synthesis; crystal structure; linear trinuclear complex

0 Introduction

The prime strategy for designing the coordination molecules is to use a suitable bridging ligand that determines the nature of the magnetic interactions^[1]. The Schiff base was used extensively in the Synthesis of these complexes. The structure and magnetic properties of the trinuclear complex $[\text{Zn}\{\text{Cu}(\text{CH}_3\text{COO})(\text{Salpd})\}_2]$ {(Salpd) =bis-(salicylidene)-1,3-diaminopropane} has been reported previously^[2]. After that, similar examples of tri- homo- and hetero-nuclear metal (including Mn

Co Ni Cu Zn Gd) complexes derived from the Schiff bases ligand Salpd and bis-(salicylidene)-1,4-diaminobutane (salbd) have also been reported^[3~7]. The Iron complexes of these ligands are reported in this paper with the crystal system, space group and the corresponding lattice parameters.

1 Experimental section

1.1 Syntheses

$[\text{Fe}_3(\text{salpd})_2(\text{CH}_3\text{COO})_2]$ (**1**): salicylaldehyde (4 mmol, 49 mg), 1,3-diaminopropane (2 mmol, 15 mg)

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E-mail: wangtw@nju.edu.cn

作者: 王天维, 男, 34 岁, 博士生; 研究方向: 配位化学、磁化学。

was dissolved in methal (7 mL), The mixture was stirred for 1 h to give a clear yellow solution of salpd. Then the methal solution (4 mL) of $\text{Fe}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (4 mmol, 98 mg) were added with stirring for 10 min. The resulting solution was aged in a teflonlined Parr bomb at 140 °C for 48 h, and cooled down to room temperature naturally. The black micro crystals were filtered, washed with water and dried at room temperature.

$[\text{Fe}_3(\text{salbd})_2(\text{CH}_3\text{COO})_2]$ (**2**): Sample **2** was obtained with a similar procedure for synthesis of sample (**1**) but using 1,4-diaminobutane (2 mmol, 18 mg) instead of 1,3-diaminopropane (2 mmol, 15 mg).

1.2 X-ray crystallography

The crystal data were collected in Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at room temperature (291 K). The measurement uses φ

and ω scans method and absorption correction type is multi-scan. Cell parameters and orientation matrix for data collection were obtained from least-squares refinement. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares on F^2 method. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C-H distances of 0.093~0.097 nm, and with $U_{\text{iso}}(\text{H})=1.2$ or $1.5U_{\text{eq}}(\text{C})$. The agreement indices are $R_1=0.037\ 5$, $wR_2=0.101\ 9$, $w=1/[\sigma^2(F_o^2)+(0.056\ 3P)^2+0.166\ 1P]$ for Sample **1** and $R_1=0.477$, $wR_2=0.100\ 3$, $w=1/[\sigma^2(F_o^2)+(0.03P)^2]$ for Sample **2**, where $P=(F_o^2+2F_c^2)/3$. All calculations were carried out by using SADABS; Bruker, 2000 Package. The detail parameters of crystal data collection and refinement are listed in Table 1, and the selected bond lengths and angles are listed in Table 2.

CCDC: 754930, **1**; 754931, **2**.

Table 1 Crystal data collection and refinement retails for complex **1** and **2**

	$[\text{Fe}_3(\text{salpd})_2(\text{CH}_3\text{COO})_2]$ (1)	$[\text{Fe}_3(\text{salbd})_2(\text{CH}_3\text{COO})_2]$ (2)
Formula	$\text{C}_{38}\text{H}_{38}\text{Fe}_3\text{N}_4\text{O}_8$	$\text{C}_{40}\text{H}_{42}\text{Fe}_3\text{N}_4\text{O}_8$
Formula weight	846.27	874.33
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	0.945 0(8)	0.919 0(5)
b / nm	1.037 0(8)	1.675 6(9)
c / nm	1.830 5(14)	1.270 0(7)
$\beta / (^\circ)$	94.357(16)	95.126(11)
V / nm^3	1.789(2)	1.947 8(19)
Z	2	2
$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.571	1.491
$\theta / (^\circ)$	2.12~23.52	2.11~22.35
μ / mm^{-1}	1.260	1.160
T / K	291(2)	291(2)
Size / mm	0.30×0.30×0.25	0.26×0.20×0.13
T_{min} and T_{max}	0.688, 0.729	0.752 5, 0.863 9
Measured reflections	7 230	10 096
Independent reflections	3 145	3 432
Reflections with $I>2\sigma(I)$	2 436	2 059
R_{int}	0.023 8	0.053 4
$\theta_{\text{max}} / (^\circ)$	25.02	25.02
h	−9~11	−10~10
k	−11~12	−17~19
l	−19~21	−9~15
$R [F^2>2\sigma(F^2)]$	0.037 5	0.047 7

Continued Table 1

$wR (F^2)$	0.101 9	0.100 3
S	1.03	1.05
Reflections / parameters	3 145 / 242	3 432 / 250
$(\Delta/\sigma)_{\max}$	<0.001	<0.001
$\Delta\rho_{\max} / (\text{e} \cdot \text{nm}^{-3})$	730	410
$\Delta\rho_{\min} / (\text{e} \cdot \text{nm}^{-3})$	-210	-430

Table 2 Selected bond lengths (nm) and bond angles (°) of [Fe₃L₂(CH₃COO)₂]

[Fe ₃ (salpd) ₂ (CH ₃ COO) ₂] (1)					
Fe1-O1	0.204 4(2)	Fe1-N1	0.202 9(3)	Fe2-O2	0.214 2(2)
Fe1-O2	0.199 3(3)	Fe1-N2	0.206 1(3)	Fe2-O4	0.208 9(3)
Fe1-O3	0.199 6(3)	Fe2-O1	0.206 5(3)		
O1-Fe1-O2	80.97(9)	O2-Fe1-N2	89.15(11)	O1 ⁱ -Fe2-O2	102.98(9)
O2-Fe1-O3	102.46(10)	O3-Fe1-N2	96.16(12)	O2-Fe2-O4	89.89(10)
O3-Fe1-O1	99.77(11)	N1-Fe1-N2	94.88(11)	O2 ⁱ -Fe2-O4	90.11(10)
O1-Fe1-N1	88.68(10)	O1-Fe2-O1 ⁱ	180	O4-Fe2-O1	87.51(9)
O2-Fe1-N1	155.84(11)	O2-Fe2-O2 ⁱ	180	O4 ⁱ -Fe2-O1	92.49(9)
O3-Fe1-N1	100.77(10)	O4-Fe2-O4 ⁱ	180		
O1-Fe1-N2	162.74(11)	O1-Fe2-O2	77.02(9)		
[Fe ₃ (salbd) ₂ (CH ₃ COO) ₂] (2)					
Fe1-O1	0.210 3(3)	Fe1-N1	0.216 1(4)	Fe2-O2	0.221 7(3)
Fe1-O2	0.208 1(3)	Fe1-N2	0.217 7(4)	Fe2-O4	0.219 6(3)
Fe1-O3	0.208 5(3)	Fe2-O1	0.216 5(3)		
O1-Fe1-O2	81.25(11)	O2-Fe1-N2	85.30(13)	O1 ⁱ -Fe2-O2	103.14(10)
O2-Fe1-O3	108.72(12)	O3-Fe1-N2	102.38(13)	O2-Fe2-O4	87.38(10)
O3-Fe1-O1	94.08(12)	N1-Fe1-N2	93.71(14)	O2 ⁱ -Fe2-O4	92.62(10)
O1-Fe1-N1	86.47(12)	O1-Fe2-O1 ⁱ	180	O4-Fe2-O1	87.78(11)
O2-Fe1-N1	133.73(12)	O2-Fe2-O2 ⁱ	180	O4 ⁱ -Fe2-O1	92.22(11)
O3-Fe1-N1	116.56(13)	O4-Fe2-O4 ⁱ	180		
O1-Fe1-N2	161.42(12)	O1-Fe2-O2	76.86(10)		

2 Results and discussion

2.1 Structure discription

[Fe₃(salpd)₂(CH₃COO)₂] (**1**) is a liner trinuclear iron (II) compound (Fig.1). The neutral compound consists of two Fe (Salbd) units connected to each other by a completely encapsulated third metal ion Fe2, which is located on the symmetry center of the molecule. The coordination of Fe1 is distorted square pyramid, whose basal planes are formed by two bridging O atoms and two N atoms of the Schiff base ligand, but the two benzene cycles in a Shift base molecule are not in the same plane anymore. The coordination of Fe2 is a

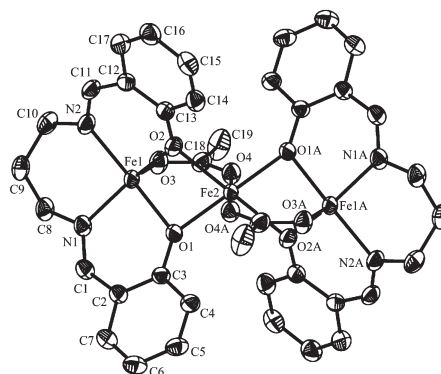


Fig.1 Structure of sample **1**, showing the atom-numbering scheme, Displacement ellipsoids are drawn at the 30% probability level, Unlabeled atoms are related by the symmetry

distorted octahedron. The Fe2 is connected with Fe1 by two phenolic hydroxy oxygen bridges, O1 and O2, of the Schiff base, and a methanol bridge. All these bond lengths and angles are comparable to those in $[\text{Co}_3(\text{salpd})_2(\text{CH}_3\text{COO})_2]$ ^[3].

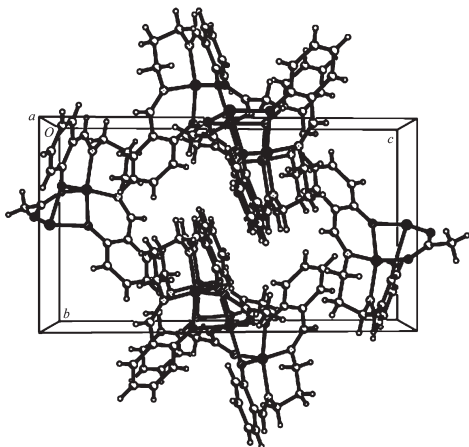


Fig.2 Crystal packing of compound **1**, viewed along the *a* axis

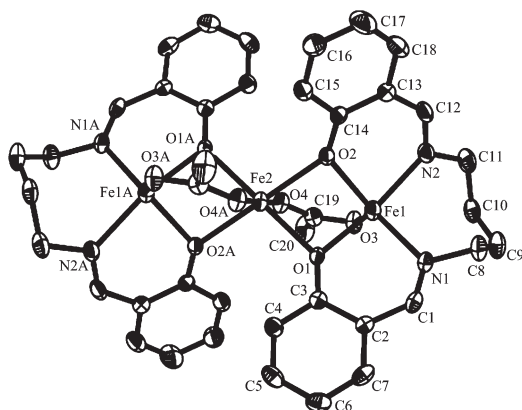


Fig.3 Structure of sample **2**, showing the atom-numbering scheme, Displacement ellipsoids are drawn at the 30% probability level, Unlabeled atoms are related by the symmetry

$[\text{Fe}_3(\text{salbd})_2(\text{CH}_3\text{COO})_2]$ (**2**) is a trinuclear cobalt(II) compound (Fig.3), which has the similar structure as Sample **1**, where the propane is replaced by butane. All the bond lengths and angles are listed in Table 1, which are comparable to those in $[\text{Co}_3(\text{salbd})_2(\text{CH}_3\text{COO})_2]$ ^[4].

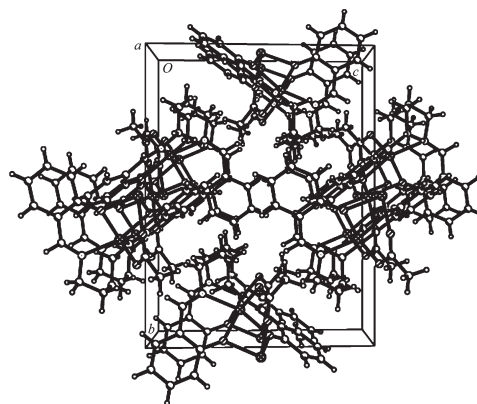


Fig.4 Crystal packing of compound **2**, viewed along the *a* axis

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