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# A novel binuclear iron(III)-salicylaldazine complex; synthesis, X-ray structure and catalytic activity in sulfide oxidation

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ABSTRACT

A novel binuclear iron(III)-salicylaldazine complex has been synthesized and characterized by various techniques such as IR and UV-Vis spectroscopy and X-ray crystallography. The catalytic oxidation of sulfides in the presence of the aforementioned complex was explored at room temperature using urea hydrogen peroxide (UHP) as an oxidant. Effects of different reaction conditions consisting catalyst and oxidant amount, solvent effect and reaction time on the catalytic activity and selectivity in the reaction of methylphenylsulfide oxidation has been surveyed. Perfect selectivity toward sulfoxide was achieved after 15 min in CH<sub>3</sub>CN by choice of a properly optimized reaction condition.

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# 1. Introduction

With regard to the presence of diiron centers in a variety of biological systems, such as  $(\mu$ -oxo) bis $(\mu$ -carboxylato) diiron(III) core in methemerythrin and a  $(\mu-oxo)(\mu-carboxylato)diiron(III)$  core in E. coli ribonucleotide reductase, synthesis and characterization of novel binuclear iron complexes have been paid attention considerably in the field of inorganic chemistry. These complexes could be considered as a synthetic model mimicking the actual biological systems closely as possible [1-5]. Transition metal complexes consisting of various ligands such as phthalocyanines, porphyrins, and azines have been widely studied in this case. Azines are potential ligands capable of forming metal chelates with transition metal ions. Salicylaldazine, as a member of azine compounds, has also the tendency to form a chelate with different transition metals. Although there have been a lot of studies investigating the crystal structure of the salicylaldazine, there has been fewer surveys reporting the structure of its metal complexes so far [6].

The selective oxidation of sulfides to sulfoxides is one of the chemical transformations in chemistry [7–11]. Variety of catalytic systems constructed from iron complexes have been successfully

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employed in the sulfoxidation process due to their availability, low cost and environmental benignity [12–15].

In this paper, the synthesis and x-ray crystallography of a novel binuclear iron(III) complex using N<sub>2</sub>O<sub>2</sub>-donor Schiff base salicylaldazine (H<sub>2</sub>salcyn) as a ligand is reported. Moreover, the catalytic activity of the mentioned complex in the presence of urea hydrogen peroxide (UHP) as an oxidant during selective oxidation of sulfides to corresponding sulfoxides under mild reaction condition is explored (Scheme 1).

# 2. Experimental section

All chemicals and solvents were purchased from Fluka and Merck companies. Salicylaldazine (H<sub>2</sub>salcyn) was synthesized according to a published procedure [16].

# 2.1. Synthesis of the complex $[Fe_2(salcyn)_3] \cdot C_2 H_5 OH$

The complex was synthesized through the addition of an ethanolic solution (15 ml) containing ligand H<sub>2</sub>salcyn (3 mmol) to an ethanol solution (10 ml) of FeCl<sub>3</sub>·6H<sub>2</sub>O (2 mmol). The mixture was refluxed for 24 h. After cooling the reaction solution, the dark brownish microcrystalline particles were filtered, washed with cool ethanol and then dried in the air at room temperature.





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**Scheme 1.** Oxidation of sulfides in the presence of a binuclear iron(III)-salicylaldazine complex.

# 2.2. X-ray structure analysis for complex

A black prism-like specimen of C43H32Fe2N6O6.50, approximate dimensions 0.100 mm  $\times$  0.100 mm  $\times$  0.260 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 2.35 h. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 13,420 reflections to a maximum  $\theta$  angle of 26.37° (0.80 Å resolution), of which 7555 were independent (average redundancy 1.776, completeness = 97.4%, R<sub>int</sub> = 1.88%) and 6436 (85.19%) were greater than  $2\sigma(F^2)$ . The final cell constants of a = 11.6354(10) Å, b = 12.2637(10) Å, c = 15.4676(13) Å,  $\alpha$  = 67.0810(12)°,  $\beta$  = 87.0400(13)°,  $\gamma$  = 69.5260(13)°, volume = 1895.3(3) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 5635 reflections above 20  $\sigma$ (I) with 4.315° < 2 $\theta$  < 57.42°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to the maximum apparent transmission was 0.892. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8140 and 0.9220.

The final anisotropic full-matrix least-squares refinement on  $F^2$  with 532 variables converged at R1 = 3.21%, for the observed data and wR2 = 8.64% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 0.890 e-/Å<sup>3</sup> and the largest hole was -0.300 e-/Å<sup>3</sup> with an RMS deviation of 0.055 e-/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.487 g/cm<sup>3</sup> and *F*(0 0 0), 872 e<sup>-</sup>.

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Crystal data and structure refinement for the complex [Fe2(salcyn)3]•C2H5OH.

	$[Fe_2(salcyn)_3] \cdot C_2 H_5 OH$
Empirical formula Formula weight Temperature	C <sub>43</sub> H <sub>32</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>6.50</sub> 848.44 g/mol 173(2) K
Wavelength Crustel system	U./IU/3 A
Crystal system	
Unit cell dimensions	$ \begin{array}{l} a = 11.6354(10) \ \text{\AA}, \ \alpha = 67.0810(12)^{\circ} \\ b = 12.2637(10) \ \text{\AA}, \ \beta = 87.0400(13)^{\circ} \\ c = 15.4676(13) \ \text{\AA}, \ \gamma = 69.5260(13)^{\circ} \end{array} $
Volume	1895.3(3) Å <sup>3</sup>
Z	2
Density (calculated)	1.487 Mg/m <sup>3</sup>
Absorption coefficient	$0.826 \text{ mm}^{-1}$
$F(0 \ 0 \ 0)$	872
Crystal size	$0.100 \times 0.100 \times 0.260 \mbox{ mm}$
Theta range for data collection	1.44–26.37
Index ranges	$-14 \le h \le 11,  -15 \le k \le 15,  -19 \le l \le 19$
Reflections collected	13,420
Independent reflections	7555 [R(int) = 0.0188]
Completeness to theta = $25.00^{\circ}$	97.4%
Absorption correction	Multi-scan
Max. and min. transmission	0.9220 and 0.8140
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	7555/0/532
Goodness-of-fit on F <sup>2</sup>	1.025
Final R indices [I > 2sigma(I)]	<i>R</i> 1 = 0.0321, <i>wR</i> 2 = 0.0814
R indices (all data)	R1 = 0.0400, wR2 = 0.0864
Largest diff. peak and hole	0.890 and $-0.300 \text{ e.A}^{-3}$

#### 2.3. Catalytic sulfoxidation

0.2 mmol UHP as an oxidant was added slowly to a stirring solution of 1 ml of CH<sub>3</sub>CN containing the complex  $[Fe_2(salcyn)_3]$ , a substrate (0.2 mmol) and chlorobenzene (0.2 mmol) as an internal standard. Stirring was continued for 15 min at room temperature in a closed system. The reaction progress was monitored by



 $\label{eq:constraint} \begin{array}{l} \mbox{Table 2} \\ \mbox{Significant Bond lengths [Å] and angles [°] for the complex [Fe_2(salcyn)_3]. \end{array}$ 

Bond lengths	(Å)	Bond angles (°)	
Fe1-01	1.9090(14)	03-Fe1-01	95.08(6)
Fe1-03	1.8942(14)	03-Fe1-04	101.10(6)
Fe1-04	1.9401(14)	03-Fe1-N4	90.90(6)
Fe1-N1	2.1857(16)	01-Fe1-N1	85.19(6)
Fe1-N3	2.1742(17)	N4-Fe1-N1	88.10(6)
Fe1-N4	2.1590(16)	N3-Fe1-N1	85.47(6)

GC. Assignments of the products were made by comparison with authentic samples.

# 3. Results and discussion

# 3.1. Complex characterization

The complex  $[Fe_2(salcyn)_3]$  has been synthesized by the reaction of three equivalent of H<sub>2</sub>salcyn with two equivalents of FeCl<sub>3</sub>- $\cdot$ 5H<sub>2</sub>O in the presence of triethylamine in ethanol. The complex is stable under air and moisture and is fully soluble in polar solvents such as ethanol, methanol, dichloromethane, and acetonitrile. The complex is characterized by spectroscopic methods like FT-IR and UV–Vis spectroscopy and X-ray crystallography.

The IR spectrum of the complex (Fig. S1) shows strong absorptions in the 1686 cm<sup>-1</sup> corresponding to the v(C=N) stretching frequency of the H<sub>2</sub>salcyn ligands [17]. Because coordinated H<sub>2</sub>salcyn ligands are dianionic, thus the bands due to phenolic OH stretch of ligands are absent.

The UV–Vis spectra of the complex [Fe<sub>2</sub>(salcyn)<sub>3</sub>] shows intense bands in the 220, 295 and 362 nm regions, which are respectively attributed to intraligand  $\pi \rightarrow \pi^*$ , phenolate ( $p_{\pi}$ )  $\rightarrow$  iron(III) ( $d_{\sigma^*}$ ) and a charge transfer (CT) transitions (Fig. S1) [18–20]. The molecular structure of the complex  $[Fe_2(salcyn)_3]$ - $C_2H_5OH$ is shown in Fig. 1. Crystal data, selected bond lengths, and angles (Å, °) are listed in Tables 1 and 2. As shown in Fig. 1, each of the three H<sub>2</sub>salcyn ligands loses one hydrogen atom and coordinates to two iron ions by the two phenolate-O and the two imine-N atoms to form a facial O<sub>3</sub>N<sub>3</sub> coordination sphere which is connected via three diaza (=N-N=) bridges. Complex  $[Fe_2(salcyn)_3]$ · $C_2H_5OH$  crystallizes in the space group P-1 with one full complex molecule in the asymmetric unit. One cluster and a half of disordered by two positions EtOH solvent were found in the asymmetric unit of the triclinic cell. The Fe<sup>...</sup>Fe distance of the complex is 3.901(4) Å.

The iron-oxygen and iron-nitrogen bond distances of the  $H_2$ salcyn groups are in the 1.894–1.940(14) and 1.159–1.186(16) Å ranges, respectively.

In the crystal lattice of the complex  $[Fe_2(salcyn)_3] \cdot C_2H_5OH$ , the intermolecular hydrogen bonds  $C-H \cdots O$  (2.715 Å) between a benzene ring C-H group and phenolate-O belonging to the two neighboring complexes, form an infinite 1-D polymeric array along the axis (Fig. 2). Also, a  $\pi$ - $\pi$  interaction with the benzene ring of the adjacent chain is observed with interplanar distance about 3.345 Å.

In order to optimize the reaction conditions in the sulfide oxidation, oxidation of methylphenylsulfide (MPS) in the presence of the complex [Fe<sub>2</sub>(salcyn)<sub>3</sub>] using UHP as an oxidant was carried out initially (Table 3). Note that the reaction in the absence of catalyst resulted in only a trace amount of sulfoxide (entry 1). The solvent effect on the oxidation reaction of MPS has been surveyed using various solvents viz CH<sub>3</sub>CN, CH<sub>3</sub>OH, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub> (entries 2–5). The lower conversion was observed in (1:1) mixture of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH as a solvent (entry 4). A trace amount of product was achieved in the case of CH<sub>2</sub>Cl<sub>2</sub> (entry 5). Excellent conversions were observed considering CH<sub>3</sub>CN and CH<sub>3</sub>OH as reaction media (entries 2, 3). Overall CH<sub>3</sub>CN was considered as the optimized solvent with regard to the high selectivity of the current reaction achieved. Reducing the amount of complex from 0.0048 mmol to



Fig. 2. Crystal packing diagram of the complex [Fe<sub>2</sub>(salcyn)<sub>3</sub>]·C<sub>2</sub>H<sub>5</sub>OH along a axis.

Entry	Solvent	Catalyst loading (mmol)	Amount of UHP (mmol)	Reaction time (h)	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>
1	CH <sub>3</sub> CN	_	0.4	30	trace	-
2	CH <sub>3</sub> CN	0.0048	0.4	30	>99	99
3	CH <sub>3</sub> OH	0.0048	0.4	30	>99	87
4	CH <sub>2</sub> Cl <sub>2</sub> :CH <sub>3</sub> OH	0.0048	0.4	30	81	89
5	CH <sub>2</sub> Cl <sub>2</sub>	0.0048	0.4	30	trace	-
6	CH <sub>3</sub> CN	0.0012	0.4	15	>99	99
7	CH <sub>3</sub> CN	0.0024	0.5	15	>99	100
8	CH <sub>3</sub> CN	0.0024	0.1	15	73	100
9	CH <sub>3</sub> CN	0.0024	0.2	15	>99 (51) <sup>d</sup>	100 (83) <sup>d</sup>
10	CH₂CN	0.0024	0.3	15	>99	99

 Table 3

 Oxidation of methylphenylsulfide in different conditions.<sup>a</sup>

<sup>a</sup> Reaction conditions: 1 ml of solvent; 0.2 mmol of methylphenylsulfide.

<sup>b</sup> Determined by GC on the crude reaction mixture.

<sup>c</sup> Selectivity to sulfoxide = (sulfoxide%/(sulfoxide% + sulfone%)) × 100.

<sup>d</sup> In the presence of FeCl<sub>3</sub>·6H<sub>2</sub>O as a catalyst.

0.0012 mmol, gave rise to the high conversion of MPS and product selectivity. Therefore optimized amount (0.0024 mmol) of the complex  $[Fe_2(salcyn)_3]$  was used for the other oxidation reactions. Moreover, it is worth mentioning that MPS is totally converted to the corresponding sulfoxide with selectivity (100%) after 15 min using a low amount of oxidant (0.2 mmol) (entry 8).

The complex  $[Fe_2(salcyn)_3]$  behaved as a good sulfoxidation catalyst. The catalytic efficiency of the complex  $[Fe_2(salcyn)_3]$  in the presence of various sulfide substrates is recorded in Table 4. A comparative catalytic study has been performed taking methylphenylsulfide, dibenzylsulfide, benzyl phenyl sulfide, divinyl sulfide, diethyl sulfide, and dioctyl sulfide as substrates using UHP as an oxidant. Good to excellent conversions (75–99%) and selectivities (95–99%) were obtained depending on the nature of the sulfide substrates for all the cases mentioned above. No over oxidation was observed for the substrates containing C=C bonds and benzylic C–H bonds, (entries 2–4). Oxidation of dioctyl sulfide as an aliphatic substrate showed the lowest conversion (75%) as compared to other substrates (entry 6).

According to the previous reports [21,22], in the presence of UHP oxidant ( $H_2O_2 \cdots H_2NCONH_2$ ), interaction of  $H_2O_2$  with one Fe center results in the formation of an intermediate with Fe=O

Table 4

Oxidation of sulfides with UHP catalyzed by the complex [Fe<sub>2</sub>(salcyn)<sub>3</sub>].<sup>a</sup>



<sup>a</sup> Reaction conditions: 1 ml of CH<sub>3</sub>CN; 0.2 mmol of substrate; 0.2 mmol UHP; 0.0024 mmol the complex [ $Fe_2(salcyn)_3$ ].

<sup>c</sup> Selectivity to sulfoxide = (sulfoxide%/(sulfoxide% + sulfone%)) × 100.



**Scheme 2.** Proposed reaction mechanism in the presence of the complex [Fe<sub>2</sub>(salcyn)<sub>3</sub>].

bond following by the reaction of organic sulfide with the mentioned Fe=O bond, and giving rise to the production of sulfoxides (Scheme 2).

In conclusion, the complex  $[Fe_2(salcyn)_3]$  was synthesized by the reaction of H<sub>2</sub>salcyn and FeCl<sub>3</sub>·5H<sub>2</sub>O in 2:3 mol ratio. The asprepared complex was used as an efficient catalyst for the oxidation of sulfides. In the presence of complex  $[Fe_2(salcyn)_3]$ , all of the substrates show satisfactory reactivity and corresponding sulfoxides could be furnished in relatively high yields. To the best of our knowledge, this work is the first study of a binuclear iron(III) complex catalyzed oxidation of sulfides.

### **CRediT authorship contribution statement**

**Elnaz Mesbahi:** Conceptualization, Methodology. **Mojtaba Bagherzadeh:** Supervision. **Mojtaba Amini:** Supervision. **Ali Akbari:** Writing - original draft. **Arkady Ellern:** Software. **L. Keith Woo:** Software.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

<sup>&</sup>lt;sup>b</sup> Determined by GC on the crude reaction mixture.

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# Appendix A. Supplementary data

The CIF file of crystal structure [Fe<sub>2</sub>(salcyn)<sub>3</sub>]•C<sub>2</sub>H<sub>5</sub>OH has been deposited with the CCDC, No. 1860847. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020. 114531.

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