

STUDIES ON SCHIFF BASE COMPLEXES

IV. SYNTHESIS AND CRYSTAL STRUCTURE OF Fe (SALDPT) SAL *

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制备了 Fe (saldpt) sal 单晶并作了晶体结构分析。晶体数据: 单斜, 空间群 $P2_1 / C(\#14)$, $a = 12.486(5)$, $b = 18.502(8)$, $c = 10.870(5) \text{ \AA}$, $\beta = 104.23(3)^\circ$, $V = 2434(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.40 \text{ g/cm}^3$.

关键词: 铁(III)Schiff 碱配合物 晶体结构

Introduction

There has only been a relatively small number of studies dealing with Fe complexes with pentadentate ligands. The linear, dianionic Schiff base type ligands with the general formula, $[o\text{-OC}_6\text{H}_4\text{CH}=\text{N}(\text{CH}_2)_x\text{NH}_2]^{2-}$, where $x = 3$ (saldpt) or 2 (saldien) have served to show the structural relationship involved in pentadentate complexes. With its potential to use the three N and two O ligating atoms to form four six-membered chelate rings, saldpt usually binds to five of the octahedral positions about a single metal ion^[1-3]. More work has been done with those of Fe (II), which form Mn (saldien)-like dimers^[4], than those of Fe (III). Fe (III) complexes require an additional potential ligand in order to balance the charge and this arises the question as to whether this monodentate ligand will be bound to the Fe ion or not. Fe(saldien)Cl and Fe(saldpt)Cl were prepared by Patton and Taylor^[5]. Niswander and Martell^[6] prepared $[\text{Fe}(5\text{-NO}_2\text{saldpt})_2]\text{O}$ by the oxidation of the Fe (II) complex. Two Fe (saldien)⁺ units were found able to be bridged with a hydroquinone by Tuchagues and Hendrickson^[4]. In this study, the first mononuclear octahedral complex of an Fe (III) with a H₂saldpt-type ligand has been characterized by an X-ray crystal structure.

Experimental

Preparation

A solution containing 150ml of ethanol, 2.02g (20mmol) of triethylamine and 5ml of triethyl orthoformate was prepared and warmed. 2.44g (20mmol) of salicylaldehyde was added in one portion with stirring under nitrogen flow. 1.32g (10mmol) of 3,3'-iminobispropylamine (dpt) dissolved in 15ml of ethanol was added dropwise to the solution. The reaction mixture was

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Abbreviations: saldpt, α, α -[iminobis(trimethylenenitrilo)] di-*o*-cresolato(-2); sal, salicylaldehyde anion.

stirred for 20min. The addition funnel was washed with ethanol and 4.04g (10ml) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 50ml of ethanol was added dropwise. The reaction mixture immediately changed from yellow to a purple mixture. After refluxing for 3hr, the mixture was cooled overnight and filtered. The black solid product (3.62g) of $\text{Fe}(\text{saldpt})\text{NO}_3$ was dried at 78° in vacuum for 24hr. 2.06g (4.5mmol) of $\text{Fe}(\text{saldpt})\text{NO}_3$ was added to 200ml of dichloromethane. To this magnetically-stirred slurry was added 200ml of $0.05\text{mol} \cdot \text{l}^{-1}$ KOH aqueous solution. After stirring for 2hr, the aqueous phase was removed and organic layer filtered. The solution was evaporated using the rotary evaporator resulting in a brown solid which was recrystallized in $\text{EtOH}-\text{H}_2\text{O}(60/40, \text{V/V})$. Black crystals (0.72g) were obtained. One of these crystals was used for the X-ray examination. Anal. Calcd. for $\text{Fe}(\text{saldpt})\text{sal}$: C, 63.05; H, 5.49; N, 8.17; Fe, 10.86; Found: C, 61.05; H, 5.29; N, 8.08; Fe, 11.06.

Data Collection

A black parallelepiped crystal of $\text{C}_{27}\text{H}_{28}\text{FeN}_3\text{O}_4$, having approximate dimensions of $0.50 \times 0.50 \times 0.40\text{mm}$, was mounted on the end of a glass fiber. All measurements were made on a Nicolet R3/V diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073\text{\AA}$)

Stationary crystal, stationary counter background counts were measured at each end of the scan for one-half of the total scan time. Of the 3533 reflections collected, 3205 were unique ($R_{\text{int}} = 0.019$). The intensities of three representative reflections, measured after every 100 reflections remained constant throughout data collection (37.10 hours of X-ray exposure), indicating crystal and electronic stability. The linear absorption coefficient for MoK_α radiation is 6.54cm^{-1} . An empirical absorption correction based on azimuthal scans of several intense reflections resulted in transmission factors ranging from 0.77 to 1.00. Data collection parameters are given in Table 1 along with crystal data. The data were corrected for Lorentz and polarization factors.

Structure Solution and Refinement

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by standard difference Fourier techniques, and were included in the structure factor calculation either at the difference map position, if bonded to nitrogen, or at idealized positions ($d_{\text{C-H}} = 0.95\text{\AA}$), if bonded to carbon. All hydrogen atoms were allowed to ride on the atom to which they were bonded; an isotropic group thermal parameter ($U_{\text{iso}} = 0.10(1)$) was refined for all of the hydrogens. The final cycle of full-matrix least-squares refinement was based on 2107 observed reflections ($I > 3\sigma(I)$) and 317 variable parameters and converged (largest parameter shift was 0.01 times its esd) with final residual values of $R = 0.0473$, $R_w = 0.0681$ and $S = 0.90$. The weighting scheme was based on counting statistics and included a factor ($p = 0.004$) to downweight the intense reflections. An analysis of the variance of reflections based on $\sin\theta/\lambda$, magnitude of F and parity class showed no unusual trends. The maximum and minimum peaks on the final difference map corresponded to 0.35 and $-0.38\text{e}^-/\text{\AA}^3$, respectively.

Table 1 Crystal Data for Fe (saldpt) sal

formula	$C_{27}H_{28}N_3O_4Fe$
formula weight	514.43
space group	$P21/c(\#14)$
systematic absences	$h0l, l \neq 2n; 0k0, k \neq 2n$
$a(\text{\AA})$	12.486(5)
$b(\text{\AA})$	18.502(8)
$c(\text{\AA})$	10.870(5)
$\beta(^{\circ})$	104.23(3)
$V(\text{\AA}^3)$	2434(2)
Z	4
$D_{\text{calc}}(\text{g}/\text{cm}^3)$	1.40
crystal size (mm)	$0.50 \times 0.50 \times 0.40$
$\mu(\text{MoK}\alpha, \text{cm}^{-1})$; correction	6.54; 0.77–1.00
factor range	
data collection instrument	Nicolet R3/V
radiation (monochromated in incident beam)	$\text{MoK}\alpha = 0.71073 \text{\AA}$
orientation reflections, number, range (2θ)	35, 26.4–30.0 $^{\circ}$
temperature ($^{\circ}\text{C}$)	21
scan method	$\omega/2\theta$ or $\omega-2\theta$
data collection range, $2\theta(^{\circ})$	2–45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3205, 2107
No. parameters refined	317
R^a	0.047
R_w^b	0.068
quality-of-fit indicator, S^c	0.90
largest shift / e.s.d., final cycle	0.01
largest peak ($\text{e}/\text{\AA}^3$)	0.35

$$a \ R = \Sigma | | F_{\text{obs}} | - | F_{\text{calc}} | | / \Sigma | F_{\text{obs}} |$$

$$b \ R_w = \sqrt{[(\Sigma_w (| F_{\text{obs}} | - | F_{\text{calc}} |)^2 / \Sigma_w F_{\text{obs}}^2)]}$$

$$c \ S = \sqrt{[\Sigma (| F_{\text{obs}} | - | F_{\text{calc}} |)^2 / (N_o - N_v)]}, \text{ where } N_o = \text{number of observations and } N_v = \text{number of variables.}$$

Results and Discussion

Table 2 lists the atomic coordinates and equivalent isotropic thermal parameters. Some selected bond lengths and bond angles are given in Table 3. The structural representation of Fe(saldpt)sal and the packing view are shown in Fig.1 and Fig.2, respectively.

Some base hydrolysis of the saldpt ligand must occur in order to produce sal, used to form Fe(saldpt)sal. Acid hydrolysis of the Schiff bases is well-known^[7], but base hydrolysis was unexpected. The mechanism should be studied further.

The sample crystallizes in the monoclinic space group $P2_1/c(\#14)$, with one molecule per asymmetric unit. Although the possibility of hydrogen bonding between the central nitrogen atom of the 'saldpt' ligand and the carbonyl oxygen atom of the salicylaldehyde ligand exists, no unusually short intermolecular contacts were observed.

The coordination about the iron atom is approximately octahedral. The saldpt ligand bonds in a pentadentate fashion similar to that observed for a binuclear μ -peroxo-cobalt(III) complex^[3] and a peroxy-*p*-quinolatoscobalt(III) complex^[11], with the two phenolic oxygen atoms in a *cis*-arrangement and the three nitrogen atoms in a *mer*-configuration. The sixth coordination site is occupied by the phenolic oxygen atom of a salicylaldehyde ligand.

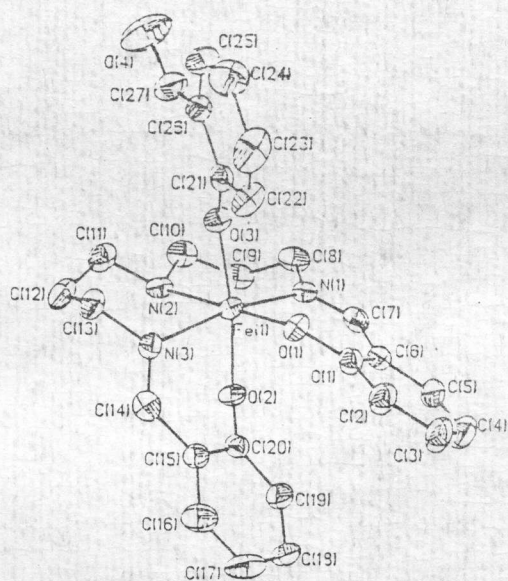


Fig.1 Structural representation of Fe(saldpt)sal with hydrogen atoms omitted (35% probability thermal ellipsoids)

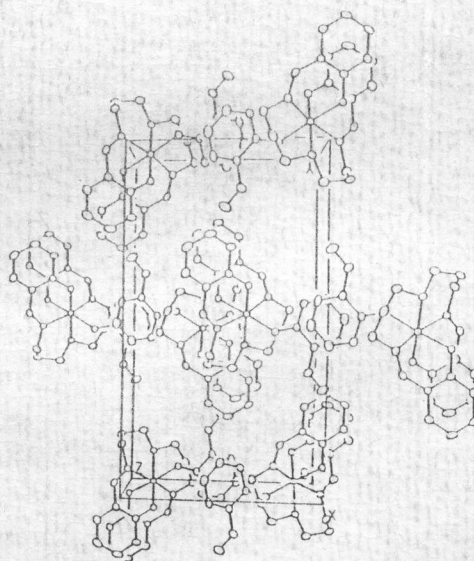


Fig.2 Packing view

Table 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$).

Fe(1)	2832(1)	223(1)	1131(1)	36(1)
O(1)	1868(3)	1030(2)	1218(3)	43(1)
O(2)	3337(3)	672(2)	-300(3)	42(1)
O(3)	2525(3)	-297(2)	2564(3)	48(1)
O(4)	2637(7)	-1947(3)	4998(6)	120(3)
N(1)	1530(4)	-220(2)	-326(4)	41(2)
N(2)	3968(4)	-700(2)	1061(4)	43(2)
N(3)	4282(3)	731(3)	2253(4)	42(2)
C(1)	-1196(4)	1353(3)	235(5)	44(2)
C(2)	918(5)	2086(3)	320(7)	59(2)
C(3)	233(5)	2427(4)	-700(8)	78(3)
C(4)	-218(6)	2063(4)	-1829	80(3)
C(5)	-1(5)	1352(4)	-1891(6)	60(2)
C(6)	690(4)	971(3)	880(5)	47(2)
C(7)	821(5)	201(3)	-1033(5)	47(2)
C(8)	1497(6)	-992(3)	-683(6)	59(3)
C(9)	2611(6)	-1269(3)	-783(6)	58(3)
C(10)	3425(6)	-1368(3)	476(6)	59(3)
C(11)	4707(5)	-888(3)	2301(6)	59(2)
C(12)	5497(6)	-300(4)	2925(6)	63(3)
C(13)	4948(5)	358(3)	3361(5)	53(2)
C(14)	4632(5)	1351(3)	1956(5)	46(2)
C(15)	4155(4)	1737(3)	792(5)	39(2)
C(16)	4376(6)	2475(4)	738(6)	59(3)
C(17)	3951(6)	2867(4)	-322(7)	72(3)
C(18)	3302(5)	2534(3)	-1395(6)	56(2)
C(19)	3107(5)	1800(3)	-1377(5)	49(2)
C(20)	3516(4)	1381(3)	-293(5)	40(2)
C(21)	2215(4)	-161(3)	3619(5)	41(2)
C(22)	1908(5)	532(4)	3941(6)	58(2)
C(23)	1609(6)	642(5)	5048(7)	78(3)
C(24)	1578(7)	88(5)	5891(7)	78(3)
C(25)	1884(6)	-584(5)	5608(6)	65(3)
C(26)	2202(5)	-723(3)	4493(5)	48(2)
C(27)	2541(6)	-1457(4)	4244(7)	65(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected Bond Lengths (Å) and Bond Angles(°)

Bond Lengths (Å)			
Fe(1)—O(1)	1.936(4)	Fe(1)—O(2)	1.998(3)
Fe(1)—O(3)	1.947(4)	Fe(1)—N(1)	2.134(4)
Fe(1)—N(2)	2.233(4)	Fe(1)—N(3)	2.136(4)
O(1)—C(1)	1.328(6)	O(2)—C(20)	1.330(6)
O(3)—C(21)	1.322(6)	O(4)—C(27)	1.207(8)
N(1)—C(7)	1.283(7)	N(1)—C(8)	1.478(7)
N(1)—C(10)	1.477(8)	N(2)—C(11)	1.476(7)
N(3)—C(13)	1.458(7)	N(3)—C(14)	1.296(7)
C(6)—C(7)	1.448(8)	C(8)—C(9)	1.511(9)
C(9)—C(10)	1.502(9)	C(11)—C(12)	1.514(9)
C(12)—C(13)	1.528(8)	C(14)—C(15)	1.448(8)
C(26)—C(27)	1.467(9)		
Bond Angles (°)			
O(2)—Fe(1)—O(1)	92.1(2)	O(3)—Fe(1)—O(1)	95.4(2)
O(3)—Fe(1)—O(2)	172.0(2)	N(1)—Fe(1)—O(1)	87.9(2)
N(1)—Fe(1)—O(2)	84.9(2)	N(1)—Fe(1)—O(3)	98.1(2)
N(2)—Fe(1)—O(1)	178.9(2)	N(2)—Fe(1)—O(2)	88.1(2)
N(2)—Fe(1)—O(3)	84.3(2)	N(2)—Fe(1)—N(1)	93.2(2)
N(3)—Fe(1)—O(1)	94.7(2)	N(3)—Fe(1)—O(2)	82.9(2)
N(3)—Fe(1)—O(3)	93.8(2)	N(3)—Fe(1)—N(1)	167.6(2)
N(3)—Fe(1)—N(2)	84.2(2)	C(1)—O(1)—Fe(1)	125.8(3)
C(20)—O(2)—Fe(1)	119.3(3)	C(21)—O(3)—Fe(1)	139.3(4)
C(7)—N(1)—Fe(1)	119.9(4)	C(8)—N(1)—Fe(1)	122.2(4)
C(8)—N(1)—C(7)	117.3(5)	C(10)—N(2)—Fe(1)	115.3(4)
C(11)—N(2)—Fe(1)	114.2(3)	C(11)—N(2)—C(10)	108.2(4)
C(13)—N(3)—Fe(1)	119.7(4)	C(14)—N(3)—Fe(1)	122.5(4)
C(14)—N(3)—C(13)	117.7(5)	C(2)—C(1)—O(1)	119.8(5)
C(6)—C(1)—O(1)	121.8(5)	C(7)—C(6)—C(1)	123.5(5)
C(7)—C(6)—C(5)	117.9(5)	C(6)—C(7)—N(1)	127.5(5)
C(9)—C(8)—N(1)	112.3(5)	C(10)—C(9)—C(8)	113.9(5)
C(9)—C(10)—N(2)	115.2(5)	C(12)—C(11)—N(2)	115.6(5)
C(13)—C(12)—C(11)	114.6(5)	C(12)—C(13)—N(3)	109.2(5)

C(15)–(14)–C(3)	124.2(5)	C(16)–C(15)–C(14)	118.4(5)
C(20)–C(15)–C(14)	121.8(5)	C(15)–C(20)–O(2)	121.6(5)
C(19)–C(20)–O(2)	121.1(5)	C(27)–C(26)–C(21)	120.5(6)
C(26)–C(21)–O(3)	119.9(5)	C(22)–C(21)–O(3)	123.0(5)
C(27)–C(26)–C(25)	119.3(6)	C(26)–C(27)–O(4)	123.7(7)

The conformation assumed by the *saldpt* ligand appears to be largely influenced by the bulkiness of the ligand bonded to the sixth coordination site. As was observed for the quinolato complex, the N–H group projects toward the phenolic oxygen atom *trans* to the sixth coordination site; the salicylaldehyde groups are roughly parallel to each other (the dihedral angle between the planes of the two salicylaldehyde groups of the ligand is 24.8° , as opposed to 28.4° for the quinolato complex), and are oriented away from the sixth coordination site as well (the dihedral angle between the planes of the salicylaldehyde groups and the equatorial plane, defined by the three nitrogen atoms and the phenolic oxygen atom *trans* to the central nitrogen atom, are -35.4 and -55.4° for the present compound and -35.5 and 64.2° for the quinolato complex). By contrast, the conformation of the μ -peroxo complex has the N–H group projected toward the sixth coordination site, the salicylaldehyde groups are nearly perpendicular (dihedral angle = 97.3°) and lie on opposite sides of the equatorial plane (dihedral angles = -65.4 and 32.0°).

The conformation adopted by the two six-membered chelate rings composed of the metal atom, an imine nitrogen atom, the central nitrogen atom and three propyl carbon atoms in the present compound is also more similar to that observed in the quinolato complex. Ring one (Fe1–N1–C8–C9–C10–N2) has a flattened chair conformation and ring two (Fe1–N2–C11–C12–C13–N3) has a more idealized chair conformation, as compared to chair and half-chair conformations observed for the quinolato complex and chair and boat conformation observed for the μ -peroxo complex.

As observed for both the quinolato and μ -peroxo cobalt(III) complexes, the metal–nitrogen distances for the *trans*-imine groups are essentially identical (Fe1–N1 = $2.134(4)\text{\AA}$: Fe1–N3 = $2.136(4)\text{\AA}$), while the bond to the central nitrogen atom is significantly longer (Fe1–N2 = $2.233(4)\text{\AA}$). The bond to the phenolic oxygen atom of the *saldpt* ligand which is *trans* to the salicylaldehyde ligand is longer than the other iron–phenolic oxygen distance (Fe1–O2 = $1.998(3)\text{\AA}$ vs Fe1–O1 = $1.936(4)\text{\AA}$). This lengthening of the metal–oxygen bond *trans* to the sixth coordination site was also observed in the quinolato complex.

Although there are no unusually close intermolecular contacts, packing interactions play a significant role in the bonding of the salicylaldehyde ligand. The salicylaldehyde groups of molecules related by an inversion center at ($x=0.0, y=0.0, z=0.5$), lie in an overlapping fashion

with their planes parallel, with an average distance between the planes of 3.94 Å. This intermolecular packing arrangement forces the salicylaldehyde group to be oriented nearly along the Fe1–O1 bond (torsion angle (O1–Fe1–O3–C21) = -26.9°), resulting in a great deal of intramolecular steric repulsion as is evidenced by the bond angles: O1–Fe1–O3 ($95.4(2)^\circ$), N2–Fe1–O3 ($84.3(2)^\circ$) Fe1–O3–C21 ($139.3(4)^\circ$) and O3–C21–C22 ($123.0(5)^\circ$).

Supplementary Material

Full tables of bond distances and angles and calculated factors for Fe(saldpt)sal may be obtained from the author W.T.P.

Crystals of Fe (saldpt) sal have been prepared and characterized by an X-ray crystal structure. Crystal data: monoclinic, space group $P2_1/c$ (# 14), $a = 12.486(5)$, $b = 18.502(8)$, $c = 10.870(5)$ Å, $\beta = 104.23(3)^\circ$, $V = 2434(2)$ Å³, $Z = 4$, $D_c = 1.40$ g/cm³.

Keywords: schiff base Fe(III) complex crystal structure

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References

- [1] Nishinaga, A., Tamita, H., Nishizawa, K., Matsuura, T., *J. Chem. Soc. Dalton Trans.*, 1504(1981).
- [2] Kistenmacher, T.J., Marzilli, L.G., Marzilli, P.A., *Inorg. Chem.*, 13, 2089(1974).
- [3] Lindholm, L.A., Schaefer, W.P., Marsh, R.E., *Acta Cryst.*, B27, 1461(1971).
- [4] Tuchagues, J-P.M., Hendrickson, D.P., *Inorg. Chem.*, 22, 2545(1983).
- [5] Patton, R.D., Taylor, L.T., *Inorg. Chim. Acta.*, 8, 191(1974).
- [6] Nishwander, R.H., Martell, A.E., *Inorg. Chem.*, 17, 1511(1978).
- [7] Lloret, F., Moratell, J., Faus, J., *J. Chem. Soc. Dalton Tran.*, 1743(1983).