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ORIGINAL PAPER

The Structure and Characterization of [1,11-Bis(2-Hydroxybenzyl)-1,4,8,11-Tetraazaundecane] Iron(III) Perchlorate

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Abstract The structure of an Fe(III) complex of reduced Schiff base is reported. The title compound, $C_{21}H_{30}ClFeN_4O_6$ (I), crystallizes in the monoclinic space group $P2_1/n$ with cell constants: $a = 9.988(2)$ Å, $b = 20.430(5)$ Å, $c = 11.415(3)$ Å, $\beta = 105.480(4)°$. It contains a six-coordinate FeN_4O_2 cation where the ligand is a reduced Schiff base resulting from the $NaBH_4$ reduction of the condensation product between salicylaldehyde and 1,4,8,11-tetraazaundecane. Due to the increased flexibility of the saturated backbone of the ligand compared to the Schiff base from which it was synthesized, the complex adopts a *trans*-FeN_4O_2 conformation. There is extensive hydrogen bonding between the amine H atoms and the anion O atoms.

Keywords Linear hexadentate ligands · Reduced Schiff base ligands · Six-coordinate iron (III)

Introduction

Metal complexes of linear hexadentate ligands have fascinated inorganic chemists since their first report in 1947 [1]. The first such report of a Fe complex of a linear FeN_4O_2 ligand derived from the Schiff base condensation of salicylaldehyde and triethylenetetraamine (Sal222, see Fig. 1) was in 1955 [2]. However, this interest lapsed for several years until the discovery that such complexes exhibited spin-crossover magnetic behavior [3]. Hexadentate linear FeN_4O_2 ligands derived from the Schiff base condensation of salicylaldehyde and linear tetramines can be characterized by the number of linking carbon atoms in the tetramine backbone (see Fig. 1). The structures of Fe complexes of Sal222 [3–12], Sal232 [4], Sal323 [4, 13], and Sal333 [13] have been reported.

When chelating to Fe, as the number of carbon atoms in the tetramine backbone increases from 6 to 9, the conformation adopted by the ligand changes from a *cis*-FeN_4O_2 to a *trans*-FeN_4O_2 arrangement for the phenolic O donors. All structurally characterized Fe complexes with Sal222 have adopted the *cis*-FeN_4O_2 conformation while all those with either Sal323 or Sal333 have adopted the *trans*-FeN_4O_2 conformation. For Sal232 both conformations have been observed [4]. Further, it has been observed that the angles subtended at the Fe center reflect the magnetic properties of the compound [4, 8] with low-spin compounds having such angles closer to 90° and 180°.

Despite the interest outlined above shown in salicyclaldimine complexes with Fe(III) due their interesting structural and magnetic properties, there have been very few structures reported on related complexes where the $C=N$ imine groups have been reduced to C–N–H amine groups. A search of the Cambridge Structural Database [14] gives only one example [15] involving an Fe(III) complex of a reduced Sal323 ligand. As expected, due to increased flexibility of the saturated amine, compared to the more rigid Schiff base, and also the length of the carbon backbone, this compound has adopted a *trans*-FeN_4O_2 conformation. To further characterize such compounds and determine the conformation adopted the structure of an Fe(III) complex of reduced Sal232 is reported.

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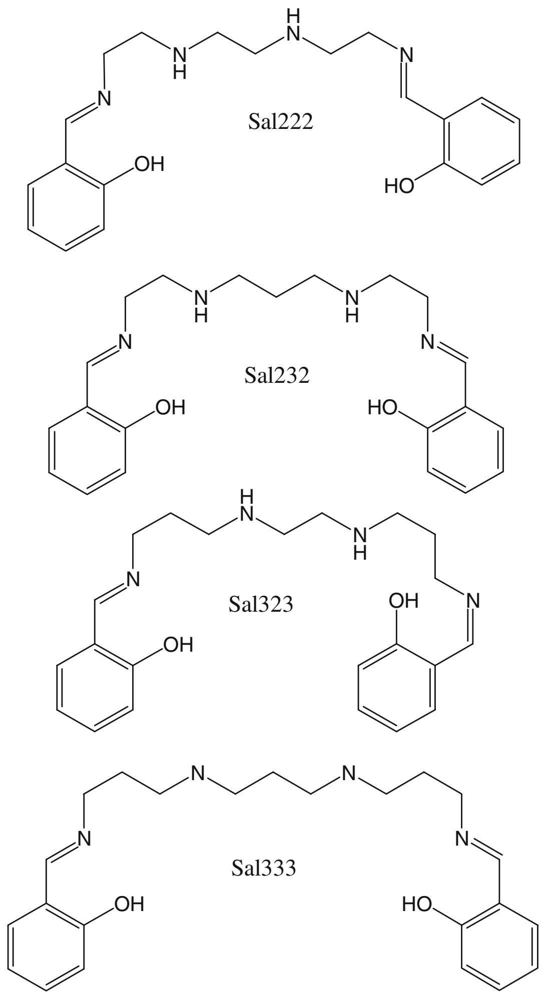


Fig. 1 Schiff bases derived from linear tetramine

Experimental

Synthesis

Synthesis of 1,11-Bis(2-Hydroxybenzyl)-1,4,8,11-Tetraazaundecane (H_2L)

To 4.0 g (25 mmol) of 1,4,8,11-tetraazaundecane in 15 ml of ethanol was added 6.1 g (50 mmol) of salicylaldehyde in 10 ml of ethanol drop-wise. The deep yellow solution was left to stir for half an hour. To this yellow solution was added a $NaBH_4$ solution (3.0 g $NaBH_4$, 0.4 g NaOH, 40 ml H_2O) resulting in a colorless solution. The volume of the solution was reduced to 20 ml and extracted with chloroform (3 × 40 ml). The extracts were combined and dried with Na_2SO_4. The Na_2SO_4 was filtered and the filtrate concentrated to colorless thick oil (8.1 g, 87%).

Complex Synthesis and Characterization

Synthesis of [Fe(III)(L)](ClO_4) To 0.85 g of H_2L dissolved in 10.0 ml of methanol was added 0.58 g of $Fe(ClO_4)_2 \times H_2O$. The solution became violet and a red-purple solid precipitated. This was stirred overnight, the solid filtered, washed with methanol and dried to give 1.65 g of red powder. Crystallization was effected by slow evaporation of a DMF solution of the complex. Elemental analysis: found: C, 47.91; H, 5.89; N, 10.64. Calc. (for $C_{21}H_{30}ClFeN_4O_6$) C, 47.93; H, 5.75; N, 10.65. IR (mineral oil) 3250, 3289, 3200, 1600, 1565, 1495, 1421, 1371, 1312, 1083, 1048, 1028, 974, 894, 874, 785, 750, 616 cm^{-1}.

Cyclic Voltammetry and Differential Pulse Voltammetry

Measurements were done on a solution 2.4×10^{-3} M solution of the complex in acetonitrile containing 0.1 M $[N(Bu_4)][PF_6]$ with Ag/AgCl as reference electrode, glassy carbon as working electrode and platinum wire as counter electrode were used.

Room Temperature Magnetic Study

Fine crystals of the complex (0.0729 g) were packed in to a magnetic susceptibility tube (1.9 cm) and susceptibility readings measured using a Johnson–Matthey susceptibility balance with and without the sample. These readings were converted to BM units after diamagnetic correction for the ligand.

UV/vis Spectroscopy

UV/vis spectrum was taken for 1.14×10^{-4} M of the complex in acetonitrile on a Hewlett-Packard 8453 A diode array spectrometer in a 1-cm quartz cuvet.

X-ray Experimental

A suitable crystal was chosen and attached to a glass rod on a goniometer head with epoxy cement. This was transferred to a Siemens P4S diffractometer. All measurements were made by standard methods [16]. The crystal data is summarized in Table 1. All H atoms were initially located in a difference Fourier map. The position of the amine H atoms were refined freely with $U_{iso}(H) = 1.2U_{eq}(N)$. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ [17]. Table 2 contains the fractional coordinates and equivalent isotropic thermal parameters for all refined atoms.

Table 1 Crystal data and structure refinement for I

Empirical formula	$C_{21}H_{30}ClFeN_4O_6$	
Formula weight	525.79	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 9.988(2)$ Å	$\alpha = 90°$
	$b = 20.430(5)$ Å	$\beta = 105.480(4)°$
	$c = 11.415(3)$ Å	$\gamma = 90°$
Volume	2244.8(9) $Å^3$	
Z	4	
Density (calculated)	1.556 Mg/m^3	
Absorption coefficient	0.838 mm^{-1}	
F(000)	1100	
Crystal size	0.1 × 0.2 × 0.34 mm^3	
Theta range for data collection	1.99°–28.37°	
Index ranges	$-13 \le h \le 13, -27 \le k \le 26, -15 \le l \le 15$	
Reflections collected	25,158	
Independent reflections	5517 [R(int) = 0.1053]	
Completeness to theta = 28.37°	98.1%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6763 and 0.2092	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5517/0/299	
Goodness-of-fit on F^2	1.003	
Final R indices [I > 2sigma(I)]	$R_1 = 0.0559$, $wR_2 = 0.1352$	
R indices (all data)	$R_1 = 0.0895$, $wR_2 = 0.1534$	
Largest diff. peak and hole	0.945 and −0.991 e $Å^{-3}$	

Table 2 Comparison of selected metrical parameters for Fe(III) complexes of reduced and unreduced Sal232 ligand (Å,°)

Parameter	R-Sal232[a]	U-Sal232[b]	Parameter	R-Sal232	U-Sal232
Fe–O1	1.8746(19)	1.886(5)	O2–Fe–N1	88.53(9)	90.9(3)
Fe–O2	1.8760(18)	1.895(5)	O2–Fe–N2	88.10(8)	90.9(3)
Fe–N1	2.004(2)	1.922(6)	O2–Fe–N3	98.23(9)	95.7(3)
Fe–N2	2.004(2)	2.017(6)	O2–Fe–N4	92.78(9)	87.3(3)
Fe–N3	2.022(2)	2.008(6)	N1–Fe–N2	84.59(10)	84.0(3)
Fe–N4	2.017(2)	1.916(6)	N1–Fe–N3	172.49(9)	172.1(3)
O1–Fe–O2	177.43(8)	176.8(3)	N1–Fe–N4	98.06(10)	100.2(3)
O1–Fe–N1	89.63(9)	87.8(3)	N2–Fe–N3	92.33(10)	91.5(3)
O1–Fe–N2	89.95(9)	91.8(3)	N2–Fe–N4	177.22(10)	175.5(3)
O1–Fe–N3	83.51(9)	85.9(3)	N3–Fe–N4	84.94(10)	84.6(3)
O1–Fe–N4	89.24(9)	90.1(3)			

[a] Title compound (R-Sal232 is the Fe(III) complex of the reduced Schiff base formed between salicylaldehyde and 1,4,8,11-tetrazaundecane)

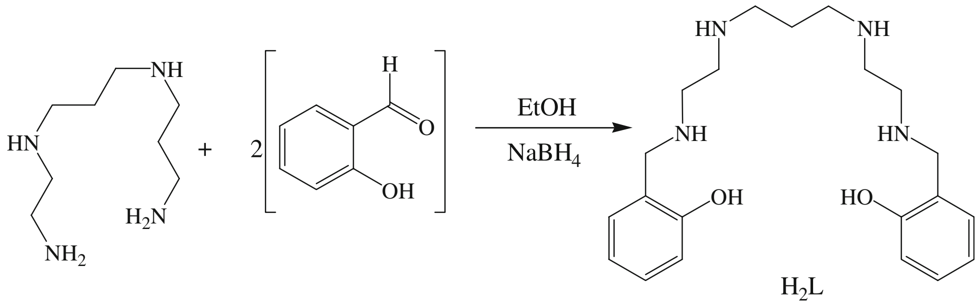
[b] U-Sal232 is the Fe(III) complex of the Schiff base formed between 2-hydroxybenzophenone and 1,4,8,11-tetrazaundecane (Hayami et al. [4])

Results and Discussion

The ligand was synthesized according to the reaction: Fig. 2.

The title compound, [1,11-bis(2-hydroxybenzyl)-1,4,8,11-tetraazaundecane]iron(III) perchlorate, $C_{21}H_{30}ClFeN_4O_6$ (**I**), contains a six-coordinate FeN_4O_2 cation where the ligand (H_2L) is the $NaBH_4$ reduction product of the

Fig. 2 Synthesis of H_2L



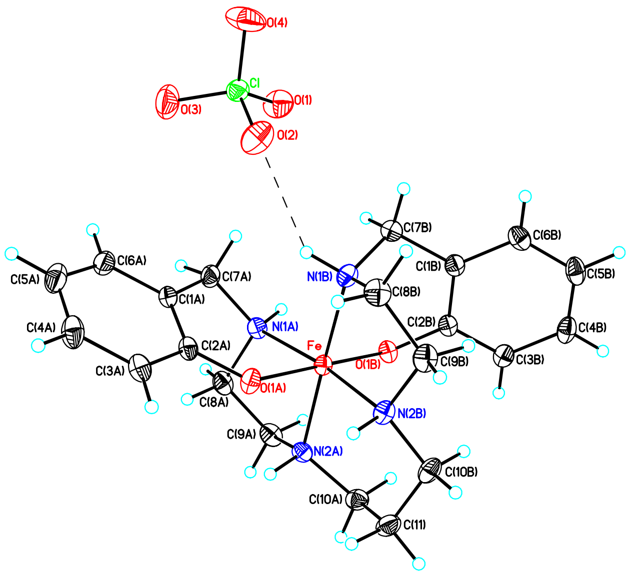


Fig. 3 View of the molecule of I showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size

Schiff base resulting from the condensation of salicylaldehyde and 1,4,8,11-tetraazaundecane.

Figure 3 shows the ORTEP representation of the structure of the cation. As indicated above, Fe(III) complexes of Schiff bases derived from salicyclaldehyde derivatives and 1,4,8,11-tetraazaundecane (Sal232) can be either *cis* or *trans* but there is only one example of the latter conformation, (*N*,*N*′-bis(2-(1-(2-phenoxy)benzylideneamino)-ethyl)propane-1,2-diamine)iron(III) perchlorate, **II** [4]. In the present instance, **I** has adopted a *trans*-FeN_4O_2 conformation. It is of interest to compare the metrical parameters of the Fe(III) complexes of the two types of *trans*-FeN_4O_2 complex with both reduced Schiff base, **I**, and Schiff base, **II** (see Table 3); [4]. The major differences are in the Fe–N bonds to the related imine and amine N's (N1A and N1B in **I** and N1 and N4 in **II**) which are 2.004(2) and 2.017(2) Å in **I** and 1.922(6) and 1.916(6) Å in **II**. The majority of the bond angles subtended at the Fe are close to either 90° or 180° with the major deviations being due to the smaller bite size of the 5-membered N1A–Fe–N2A and N1B–Fe–N2B chelate rings (84.59(10)° and 94.94(1)°, respectively.

Table 3 Hydrogen bonds for I [Å and °]

D–H…A	d(D–H)	d(H…A)	d(D…A)	<(DHA)
N(2A)–H(2AA)…O(4)#1	0.91	2.16	3.055(4)	168.4
N(1B)–H(1BA)…O(2)	0.91	2.37	3.150(4)	143.4
N(2B)–H(2BA)…O(3)#2	0.91	2.22	3.049(4)	151.1

Symmetry transformations used to generate equivalent atoms

#1 x + 1, y, z

#2 x + 1/2, −y + 1/2, z − 1/2

As discussed above these values indicate a low spin Fe(III) complex. This is confirmed by the room temperature magnetic moment which was found to be 2.07 BM. It is of interest to compare this value with that obtained for other Fe complexes containing the unreduced Sal232 ligand [4]. Four examples have been reported of which three are high spin (room temperature magnetic moments ranging from 5.86 to 5.96 BM) and have the O donors in a *cis* conformation, while one (**II**) is low spin (room temperature magnetic moment of 1.91 BM) with the O donors in a *trans* conformation and with similar bond lengths and angles to **I**.

As might be expected there is extensive hydrogen bonding between the amine H atoms and the perchlorate anions (see Fig. 4).

UV–Visible Spectroscopy

UV–visible spectrum was taken for 1.14×10^{-4} M of the complex in acetonitrile shows absorption peaks in the UV–vis region at λ_{max}(nm), (ε M^{-1} cm^{-1}): 236 (2.0×10^4), 286 (8.7×10^3), 322 (6.4×10^3) and 496 (4.7×10^3).

Cyclic Voltammetry

Cyclic voltammetry (and differential pulse voltammetry) show two reversible redox waves due at $E_{1/2}$ (versus Ag/AgCl) of −0.54 and 0.89 V due to Fe(III)/Fe(II) and Fe(III)/Fe(IV) reversible redox processes.

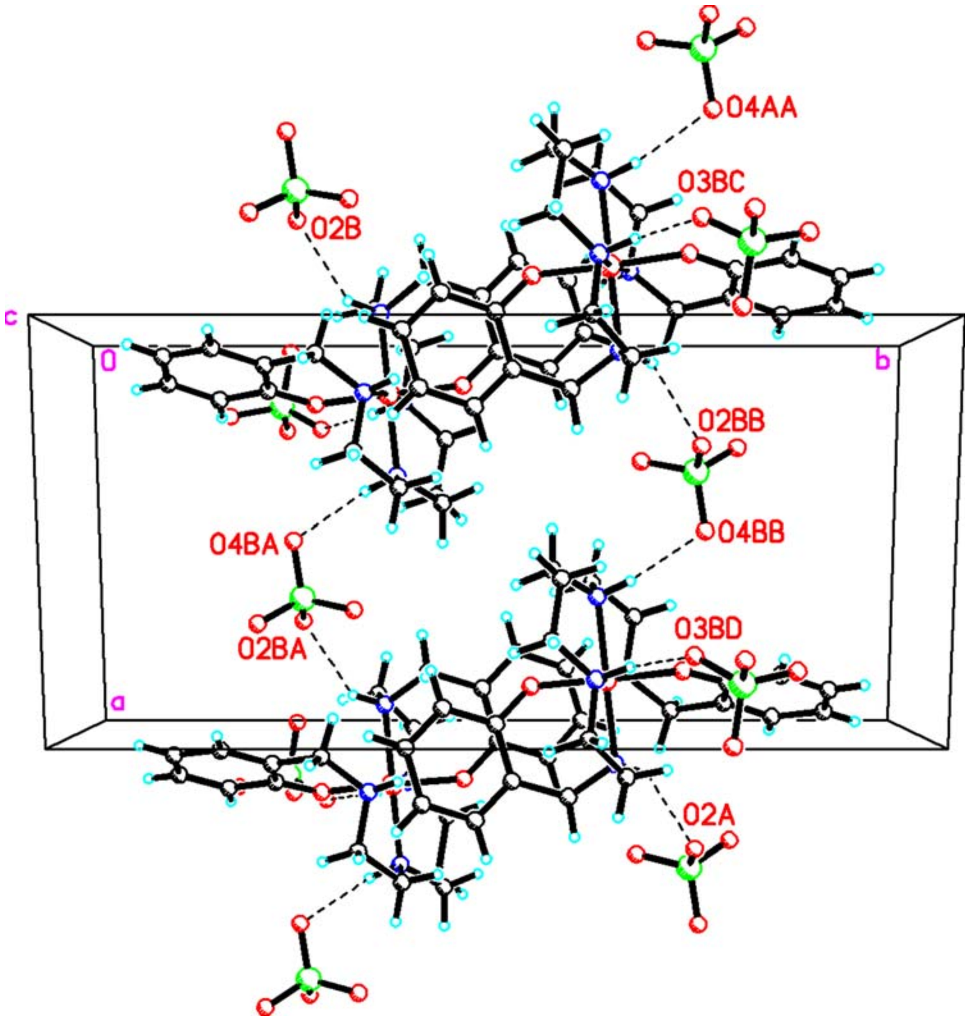


Fig. 4 The molecular packing of I viewed along the b-axis

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References

1. Dwyer FPJ, Lions F (1947) J Am Chem Soc 69:2917. doi:10.1021/ja01203a514
2. Das Sarma B, Bailar JC Jr (1955) J Am Chem Soc 77:5476–5480. doi:10.1021/ja01626a007
3. Sinn E, Sim G, Dose EV, Tweedle MF, Wilson LJ (1978) J Am Chem Soc 100:3375–3390. doi:10.1021/ja00479a021
4. Hayami S, Matoba T, Nomiyama S, Kojima T, Osaki S, Maeda Y (1997) Bull Chem Soc Jpn 70:3001–3009. doi:10.1246/bcsj.70.3001
5. Floquet S, Munoz MC, Riviere E, Clement R, Audiere J-P, Boillot M-L (2004) New J Chem (Nouv J Chim) 28:535–541. doi:10.1039/b311371j
6. Dorbes S, Valade L, Real JA, Faulmann C (2005) Chem Commun (Camb) 69–71. doi:10.1039/b412182a
7. Bera M, Mukhopadhyay U, Ray D (2005) Inorg Chim Acta 358:437–443. doi:10.1016/j.ica.2004.07.034
8. Nishida Y, Kino K, Kida S (1987) J Chem Soc Dalton Trans 1957–1961. doi:10.1039/dt9870001957
9. Salmon L, Donnadieu B, Bousseksou A, Tuchagues J-P (1999) C R Acad Sci Ser IIc Chim 2:305–309. doi:10.1016/S1387-1609(00)88540-0
10. McPartlin M, Tasker PA, Bailey NA, McKenzie ED, Worthington JM (1978) Crystallogr Struct Commun 7:115–120
11. Maeda Y, Oshio H, Tanigawa Y, Oniki T, Takashima Y (1991) Bull Chem Soc Jpn 64:1522–1527. doi:10.1246/bcsj.64.1522
12. Boinnard D, Bousseksou A, Dworkin A, Savariault J-M, Varret F, Tuchagues J-P (1994) Inorg Chem 33:271–281. doi:10.1021/ic00080a015
13. Ito T, Sugimoto M, Ito H, Toriumi K, Nakayama H, Mori W, Sekizaki M (1983) Chem Lett 12:121–124. doi:10.1246/cl.1983.121
14. Allen FH (2002) Acta Crystallogr B 58:380–388. doi:10.1107/S0108768102003890
15. Harpstrite SE, Beatty AA, Collins D, Oksman A, Goldberg DE, Sharma V (2003) Inorg Chem 42:2294–2300. doi:10.1021/ic034036e
16. Gultneh Y, Tesema YT, Yisgedu TB, Butcher RJ, Wang G, Yee GT (2006) Inorg Chem 45:3023–3033. doi:10.1021/ic060039q
17. CCDC 605584 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif