Synthesis and Crystal Structures of a New μ-Bis(tetradentate) Schiff Base Ligand and its Mononuclear Iron(III) Complex: Iron(III) Induced Imidazolidine Ring Hydrolysis of Binucleating Schiff Base Ligand

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The μ-bis(tetradentate) ligand, $[C_{27}H_{26}Cl_3N_4O_4]$, H_3L', 1,3-bis[N-(5-chloro-2-hydroxybenzylidene)-2-aminoethyl]-2-(5-chloro-2-hydroxyphenyl)imidazolidine and its mononuclear iron(III) complex, $[Fe(L)](ClO_4)$, $L = N$, N'-bis(5-chloro-2-hydroxybenzylidene)-triethylenetetramine have been synthesized and their crystal structures determined. Minimum energy conformations of the ligand were calculated (MOPAC, AM1) as a function of two torsion angles and the results compared with optimized crystal structure. The ligand (H_3L') reacts with $Fe(ClO_4)_2 \cdot 6H_2O$ in aqueous methanol to form the mononuclear $[Fe(L)](ClO_4)$ complex with the imidazolidine ring cleaved by hydrolysis. The complex has an N_4O_2 donor atom set forming a distorted octahedral coordination geometry around the metal atom as established from a crystal structure determination. The terminal oxygen donor atoms occupy *cis* positions, and the remaining four nitrogen atoms (two *cis* amine and two *trans* imine) complete the coordination sphere.

Key words: Schiff Base, Iron Complex, Imidazolidine Ring, Crystal Structure, Conformational Analyses

Introduction

Schiff bases have been used extensively as ligands in the field of coordination chemistry. Some of the reasons are that intramolecular hydrogen bonds between the O and the N atoms play an important role in the formation of metal complexes [1, 2]. Iron(III) complexes of Schiff base ligands have received considerable attention as potential models for biologically important enzymes [3, 4] and oxidation catalysts [5].

Among various products of the condensation of aromatic aldehydes, an α, ω-tetramine containing both primary and secondary amino groups is a binucleating Schiff base with an in-built imidazolidine ring spacer, which can take up two equal or two different metal ions [6 – 8]. Others [9] have also found that phenol containing binucleating polydentate ligands are useful to stabilize both homo and heterodimetallic complexes of distorted coordination geometry. The use of such binucleating ligands for the synthesis of a new family of dinuclear 3d-metal complexes has received consider-

able attention in recent years. There has always been a great interest in coordination chemistry of mononuclear iron complexes owing to the relevant role that this transition metal ion plays in biology, particularly as the active metal center embedded in a large number of proteins involved in oxygen activation chemistry [10, 11].

Recently, we studied the structures of four-, five- and six-coordinate tetradentate Schiff base complexes with substituted of [N,N'-bis(salicylidene)-1,3-diaminopropane] [12 – 15]. We reported also the structures and conformations of N-(2,5-methylphenyl)salicylaldimine [16], N-(2-methyl-5-chlorophenyl)salicylaldimine [17] and [N-(5-chlorosalicylidene)-2-hydroxy-5-chloroaniline [18]. Herein, we report the syntheses and structural characterization of the ClO_4^- salt of a mononuclear ferric complex as the end product of the reaction of hitherto unknown ligand H_3L' and ferrous(II) perchlorate hexahydrate in air. Also, a conformational analysis of the ligand H_3L' and has been carried out.
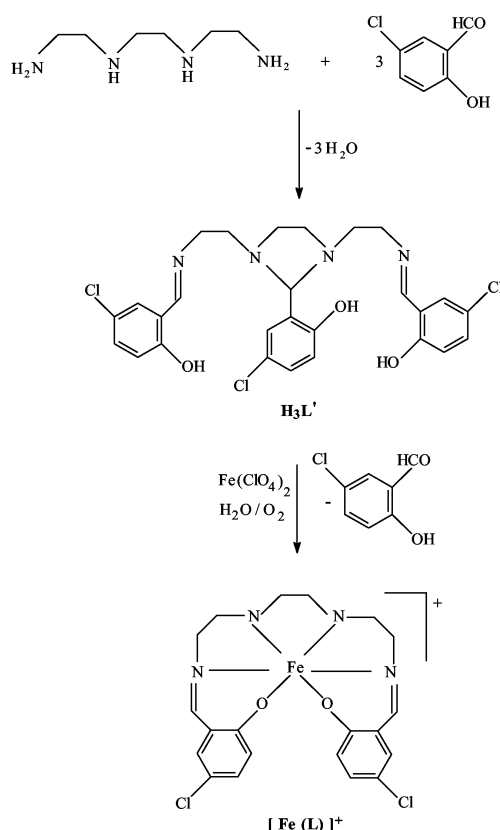
Table 1. Crystallographic data and structure refinement.

	H$_3$L'	[Fe(L)](ClO$_4$)
Formula	C$_{27}$H$_{26}$Cl$_3$N$_4$O$_4$	C$_{20}$H$_{22}$N$_4$O$_6$Cl$_3$Fe
Color / shape	yellow / long prism	dark violet / prism
f$_w$ (g·mol^{-1})	576.88	576.62
Crystal system	orthorhombic	triclinic
Space group	*Pnma*	*P*$\bar{1}$
a (Å)	10.8250(10)	11.395(17)
b (Å)	11.2910(10)	11.91(2)
c (Å)	21.321(3)	9.771(18)
α (°)	90	93.205(17)
β (°)	90	99.093(15)
γ (°)	90	113.52(11)
Vol (Å^3)	2606.0(5)	1190(4)
Z	4	2
D_{calc} (g·cm^{-3})	1.473	1.609
μ (cm^{-1})	3.94	10.15
F(000)	1200	590
θ Range for data collection	2.61° < θ < 30.15°	2.10° < θ < 25.87°
Index ranges	0 ≤ h ≤ 14	−0 ≤ h ≤ 13
	0 ≤ k ≤ 15	−14 ≤ k ≤ 13
	0 ≤ l ≤ 29	−11 ≤ l ≤ 10
Reflections collected	3715	4854
Independent reflections	3705	4605
Data / parameters	3705 / 185	4605/307
Goodness-of-fit on F^2	1.066	1.014
Final *R* indices	R = 0.0624	R = 0.0483
[I > 2σ(I)]	wR = 0.1469	wR = 0.1204
Largest diff. peak and hole [e Å^{-3}]	0.364 and −0.528	0.482 and −0.662

Fig. 1. Formation and cleavage of the ligand H$_3$L' to give the complex [Fe(L)](ClO$_4$).

Experimental Section

Synthesis of the ligand, H$_3$L'

A solution of triethylenetetramine (2.2 g, 15 mmol) in methanol (20 ml) was added dropwise to a methanolic solution (40 ml) of 5-chlorosalicylaldehyde (7.8 g, 45 mmol) with stirring at room temperature. Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at room temperature. The formula of the molecule is shown in Fig. 1. Yield 4.2 g (56.8%). C$_{27}$H$_{26}$Cl$_3$N$_4$O$_4$ (576.88): calcd. C 56.22, H 4.54, N 9.71; found C 56.81, H 4.10, N 10.01. Infrared spectrum (cm^{-1}, KBr disk, in the 4000–400 cm^{-1} range): ν(phenolic OH) 3446(w); ν(C,N) 1640(s); ν(phenolic C–O) 1376(s); ν(CH$_2$) 853(m); ν(aromatic CH) 759(m).

Synthesis of [Fe(L)](ClO$_4$)

The Schiff base ligand H$_3$L' (1.15 g, 2 mmol) was dissolved in hot methanol (70 ml) and a solution of Fe(ClO$_4$)$_2$·6H$_2$O (1.45 g, 4 mmol) in 50 ml of methanol was added with stirring within 10 min. The dark violet solution was al-

lowed to evaporate at room temperature for five days to give prismatic dark violet crystals, which were collected, washed with cold ethanol and finally dried in air (Fig. 1). Yield 1.82 g (69.7%). C$_{20}$H$_{22}$N$_4$O$_6$Cl$_3$Fe (576.62): calcd. C 41.66, H 3.84, N 9.72, Fe 9.69; found C 41.97, H 3.10, N 10.16, Fe 10.81. Infrared spectrum (cm^{-1}, KBr disk, in the 4000 – 400 cm^{-1} range): ν 3438(b), 1627(vs), 1538(s), 1451(s),1398(s), 1302(s), 1206(s), 1085(s), 897(s), 765(s), 618(s).

Caution: Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities with due care.

X-ray structure determination

Crystals of H$_3$L' and [Fe(L)](ClO$_4$) were mounted on an Enraf-Nonius CAD-4 diffractometer (graphite monochromatized Mo-K$_\alpha$ radiation, λ = 0.71073 Å [19] (Table 1). The structures were solved by SHELXS-97 and refined with SHELXL-97 [20, 21]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å) and refined using a riding model. H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. Fractional atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table 2 for H$_3$L'

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $\mathbf{H_3L}'$.

Atom	x	y	z	U(eq)[a]
Cl1	0.20701(3)	0.40627(2)	0.408013(11)	0.06692(15)
Cl2	−0.64574(4)	1.10661(3)	1/4	0.06457(16)
O1	−0.17114(5)	0.76910(4)	0.45125(2)	0.03828(16)
O2	−0.27226(5)	0.73964(4)	0.28449(2)	0.03852(16)
N1	−0.33659(5)	0.61028(5)	0.42480(3)	0.03694(16)
N2	−0.47158(5)	0.59129(5)	0.30266(2)	0.03541(16)
C1	−0.08420(5)	0.68688(5)	0.43935(3)	0.03313(16)
C3	0.12821(5)	0.62692(6)	0.43852(3)	0.03718(17)
C2	0.04117(5)	0.71221(6)	0.44874(3)	0.03728(17)
C4	0.09372(5)	0.51317(6)	0.42044(3)	0.03729(17)
C5	−0.02900(5)	0.48678(6)	0.41163(3)	0.03714(17)
C6	−0.11973(6)	0.56921(6)	0.42213(3)	0.03737(17)
C7	−0.25080(6)	0.53640(6)	0.41417(3)	0.03706(17)
C8	−0.46425(7)	0.56671(8)	0.41899(4)	0.0485(2)
C9	−0.52592(7)	0.62772(7)	0.36263(4)	0.04802(19)
C10	−0.49735(8)	0.46725(6)	0.28512(3)	0.04639(19)
C11	−0.51843(7)	0.65993(8)	1/4	0.0371(2)
C12	−0.48208(8)	0.78843(7)	1/4	0.0364(2)
C13	−0.56797(8)	0.87366(8)	1/4	0.03657(19)
C14	−0.53592(8)	0.99329(8)	1/4	0.0364(2)
C15	−0.41054(10)	1.02951(8)	1/4	0.0441(2)
C16	−0.32644(9)	0.94116(8)	1/4	0.0374(2)
C17	−0.36037(7)	0.82261(7)	1/4	0.03299(19)

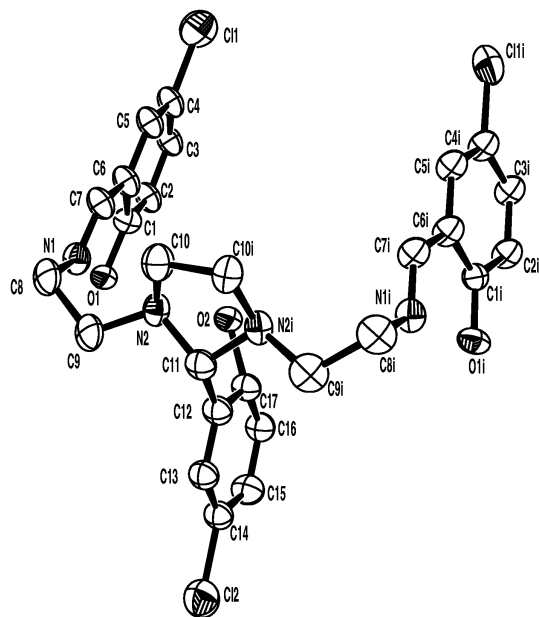[a] Equivalent isotropic U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fig. 2. ORTEP drawing of $\mathbf{H_3L}'$ (numbering of atoms corresponds to Table 5). Displacement ellipsoids are plotted at the 50% probability level. The hydrogen atoms are omitted for clarity.

and in Table 3 for [Fe(L)](ClO$_4$). Selected bond distances and bond angles are listed in Tables 4 and 5. ORTEP views

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $[\mathbf{Fe(L)}](\mathbf{ClO_4})$.

Atom	x	y	z	U(eq)[a]
Fe1	0.73014(6)	0.77198(6)	0.26699(7)	0.0333(2)
Cl1	1.21457(13)	0.75077(14)	−0.11408(15)	0.0541(4)
Cl2	0.79951(15)	0.29879(14)	0.65292(17)	0.0664(4)
O1	0.7549(3)	0.6697(3)	0.1335(3)	0.0393(8)
O2	0.8441(3)	0.7529(3)	0.4155(3)	0.0398(8)
N1	0.8760(4)	0.9177(3)	0.2391(4)	0.0344(9)
N2	0.6990(4)	0.8897(4)	0.3950(4)	0.0414(10)
N3	0.5984(4)	0.7941(4)	0.1213(4)	0.0412(10)
N4	0.5825(4)	0.6252(4)	0.2910(4)	0.0382(9)
C1	0.8610(4)	0.6943(4)	0.0811(5)	0.0360(11)
C2	0.8705(4)	0.5978(4)	0.0044(5)	0.0393(11)
C3	0.9764(5)	0.6151(5)	−0.0564(5)	0.0409(12)
C4	1.0789(4)	0.7322(5)	−0.0386(5)	0.0396(11)
C5	1.0747(4)	0.8289(4)	0.0373(5)	0.0375(11)
C6	0.9663(4)	0.8135(4)	0.0985(5)	0.0334(10)
C7	0.9658(4)	0.9196(4)	0.1739(5)	0.0362(11)
C8	0.8867(5)	1.0356(4)	0.3083(5)	0.0475(13)
C9	0.8229(5)	1.0035(5)	0.4351(5)	0.0484(13)
C10	0.5826(6)	0.9107(6)	0.3302(6)	0.0623(16)
C11	0.5656(6)	0.8953(5)	0.1720(6)	0.0561(15)
C12	0.4848(5)	0.6709(5)	0.0788(5)	0.0520(14)
C13	0.4559(5)	0.6082(5)	0.2089(6)	0.0516(14)
C14	0.5906(4)	0.5374(5)	0.3553(5)	0.0393(11)
C15	0.7085(4)	0.5409(4)	0.4374(5)	0.0383(11)
C16	0.7028(5)	0.4336(5)	0.4957(5)	0.0440(12)
C17	0.8096(5)	0.4319(5)	0.5782(5)	0.0430(12)
C18	0.9277(5)	0.5354(5)	0.6038(5)	0.0405(12)
C19	0.9362(5)	0.6396(5)	0.5479(5)	0.0390(11)
C20	0.8277(4)	0.6474(4)	0.4637(5)	0.0360(11)
Cl3	0.62304(14)	0.85731(14)	0.75281(14)	0.0598(4)
O3	0.6608(6)	0.9750(5)	0.7016(5)	0.1030(17)
O4	0.6193(5)	0.7712(4)	0.6439(5)	0.0913(16)
O5	0.7172(4)	0.8671(5)	0.8729(4)	0.0828(14)
O6	0.4992(5)	0.8184(7)	0.7899(6)	0.130(2)

[a] Equivalent isotropic U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected bond distances (Å) and bond angles (°) with e. s. d. in parentheses for $\mathbf{H_3L}'$.

Cl1–C4	1.741(1)	C7–N1–C8	116.9(1)
Cl2–C14	1.747(1)	C11–N2–C9	112.6(1)
O1–C1	1.346(1)	C11–N2–C10	104.1(1)
N1–C7	1.269(1)	C9–N2–C10	114.3(1)
N1–C8	1.472(1)	O1–C1–C2	120.6(1)
N2–C11	1.455(1)	C3–C2–C1	120.1(1)
N2–C9	1.466(1)	C5–C4–Cl1	120.7(1)
N2–C10	1.476(1)	N1–C7–C6	121.2(1)
C1–C2	1.401(1)	N1–C8–C9	108.9(1)
C3–C2	1.365(1)	N2–C9–C8	112.4(1)
		N2–C11–C12	115.0(1)
		C13–C14–Cl2	122.7(1)
		C15–C14–Cl2	116.1(1)

of the molecular structures are given in Figs 2 and 3 [22, 23]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre

Table 5. Bond distances (Å) and bond angles (°) with e.s.d. in parentheses for [**Fe(L)**](**ClO₄**).

Fe1–O1	1.864(4)	O1–Fe1–O2	95.1(2)
Fe1–O2	1.877(4)	O1–Fe1–N1	93.4(2)
Fe1–N1	1.935(5)	O2–Fe1–N1	87.7(2)
Fe1–N4	1.940(5)	O1–Fe1–N4	85.9(2)
Fe1–N2	1.999(5)	O2–Fe1–N4	93.3(2)
Fe1–N3	2.008(4)	N1–Fe1–N4	178.9(2)
Cl1–C4	1.757(5)	O1–Fe1–N2	174.5(2)
Cl2–C17	1.752(6)	O2–Fe1–N2	89.9(2)
O1–C1	1.319(5)	N1–Fe1–N2	84.4(2)
O2–C20	1.319(6)	N4–Fe1–N2	96.2(2)
N1–C7	1.282(6)	O1–Fe1–N3	89.6(2)
N1–C8	1.474(6)	O2–Fe1–N3	174.6(2)
N2–C9	1.490(7)	N1–Fe1–N3	94.9(2)
N2–C10	1.497(7)	N4–Fe1–N3	84.2(2)
N3–C11	1.479(7)	N2–Fe1–N3	85.6(2)
N3–C12	1.500(7)	C1–O1–Fe1	126.6(3)
N4–C14	1.277(6)	C7–N1–Fe1	126.2(3)
N4–C13	1.466(6)	C8–N1–Fe1	115.4(3)
C1–C2	1.387(7)	C9–N2–Fe1	107.8(3)
C1–C6	1.426(7)	C10–N2–Fe1	110.9(3)
		C11–N3–Fe1	110.9(3)
		C14–N4–Fe1	125.0(3)
		C13–N4–Fe1	115.3(3)
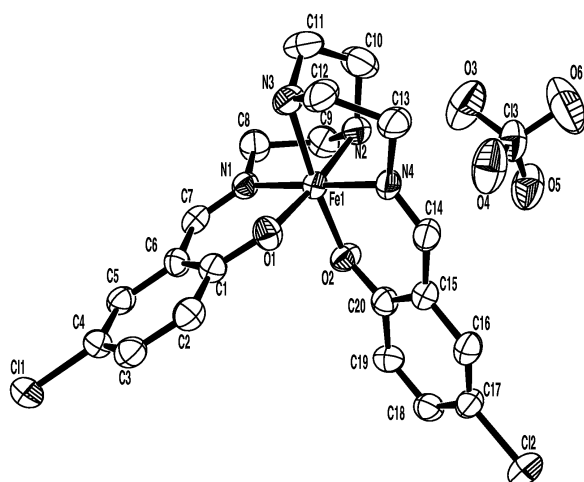
Fig. 3. ORTEP drawing of [Fe(L)](ClO₄) (numbering of atoms corresponds to Table 5). Displacement ellipsoids are plotted at the 50% probability level. The hydrogen atoms are omitted for clarity.

as supplementary publication no. CCDC 254592 for H₃L′ and CCDC 254593 for [Fe(L)](ClO₄) [24].

Conformational analysis for the H₃L′ ligand

Theoretical calculations were carried out with the standard parameters using a locally modified version of the MOPAC 6.0 program package [25] which includes the AM1 Hamiltonian [26] running on a Pentium IV 1.6 Ghz PC. Ge-

ometry optimization of the structure of the title compound was carried out using the Fletcher-Powell-Davidson algorithm [27, 28] implemented in the package and the PRECISE option to improve the convergence criteria. To determine the conformational energy profiles full geometrical optimizations were performed and values of the AM1 total energy were calculated as a function of torsion angles $\theta 1$ (C6-C7- N1-C8) and $\theta 2$ (N2-C9-C8-N1), varied every 10° from −180° to 180°.

Results and Discussion

Synthesis and iron(III) promoted hydrolysis of the imidazolidine ring

The reactivity pattern of the present binucleating ligand is different towards iron compared to vanadium, manganese, copper and zinc, where binuclear metal complexes are readily obtained both in solution and in solid state. The dark violet complex was prepared by reacting the ligand with ferrous(II) perchlorate hexahydrate in 1:2 mole ratio in aqueous methanol in air. During reaction the imidazolidine ring is cleaved regenerating the diamine. Air oxidation of the metal under and complexation by the ligand afford the product. Recently, a trisphenolate ligand was reported to be formed from borohydride reduction of imidazolidino-based Salen ligand [29]. The mononuclear complex having a $Fe^{III}N_4O_2$ coordination sphere has been structurally characterized [30 – 33] to establish the role of pendant 2-(2'-hydroxyphenyl) group on the imidazolidine ring in stabilizing the diiron complex [34 – 38].

In the complexation reaction, the expulsion of one 5-chloro-2-hydroxybenzaldehyde molecule takes place, which is different from the selective imidazolidine ring opening reaction as observed earlier in a different ligand system with no loss of any aldehyde molecule [39]. This type of imidazolidine ring-cleavage reaction with removal of one aldehyde molecule was not observed earlier for reactions of similar ligands with vanadium, iron, copper and zinc [40 – 43]. The presence of iron in the +3 oxidation state, generated by air oxidation of the starting +2 state, is responsible for the imidazolidine ring hydrolysis and therefore the transformation is dependent on the metal ion and its coordinated and acidified water molecules [44].

Conformational analysis of the H₃L′ Schiff base

In order to define the conformational flexibility of the Schiff base molecule H₃L′, semi-empirical calcu-
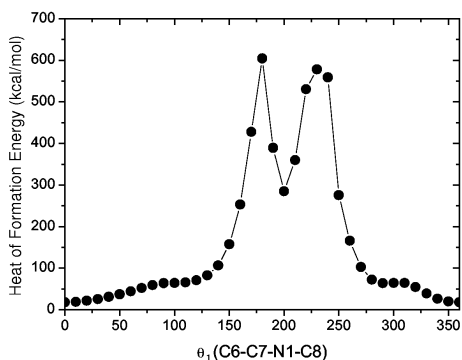
Fig. 4. AM1 calculated conformation energies of the *enol* form as a function of the torsion angle θ_1 (C6-C7-N1-C8).
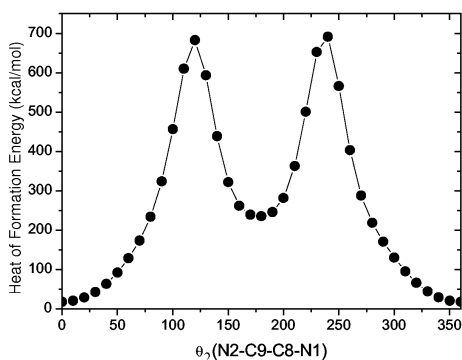

Fig. 5. AM1 calculated conformation energies of the *enol* form as a function of the torsion angle θ_2 (N1-C8-C9-N2).

lations using the AM1 molecular orbital method were carried out. The optimized geometry and conformations are in agreement with those observed crystallographically.

In order to determine the conformational energy profiles, the optimized geometry of H_3L' was kept fixed, and values of the AM1 total energy were calculated as a function of two torsion angles, θ_1 (C6-C7-N1-C8) and θ_2 (N1-C8-C9-N2) from 0 to $360°$, varied every $10°$. For each θ, the second θ value was kept constant. Results are illustrated in Figs 4 and 5. From the X-ray structure determination θ_1 (C6-C7-N1-C8) and θ_2 (N1-C8-C9-N2) values are found to be $-176.6(2)°$ and $67.8(2)°$, respectively. The optimized zero values of the θ_1 (C6-C7-N1-C8) and θ_2 (N1-C8-C9-N2) torsion angles relative to the *cis* conformation are $178.2(2)°$ and $58.7(2)°$, respectively. The energy profile as a function of θ_1 (C6-C7-N1-C8) shows two maxima near $180°$ and $230°$. These energy barriers arise from the steric interaction between H(O1) and H(C8) at $180°$ and H(O1) and H(C10) at $230°$.

The energy profile as a function of θ_2 (N1-C8-C9-N2) also shows two maxima near $120°$ and $238°$ due to the steric interaction between N2 and H(C9) (at $120°$) and the H atoms at C9 and C10 (at $238°$).

It appears that the AM1 optimized geometry of H_3L' is the most stable conformation in all calculations considered, primarily determined by non-bonded hydrogen-hydrogen repulsions.

X-ray crystal structures

In the H_3L' ligand, two parts of the molecule are related by a mirror plane represented by the central aromatic ring and its substituents. The N1–C7 distance of $1.269(1)$ Å corresponds to a typical N=C double bond. The O1–C1 and O2–C17 bond lengths are $1.346(2)$ and $1.526(1)$ Å. The maximum deviation from the imidazolidine ring plane defined by atoms C11, N2, C10, $N2^i$ and $C10^i$ [symmetry code: (i) x, y, $-z+1/2$] is $0.331(1)$ Å for the N2 atom. The N–C–C–N torsion angle (θ_2) is $58.7(2)°$. A strong intramolecular hydrogen bond occurs between the O and N_{imine} atoms, the hydrogen atoms being essentially bonded to the O atoms: $O1–HO1\cdots N1$ and $O1^i–HO1^i\cdots N1^i$ [$2.596(1)$].

The crystal structure of the complex salt contains $[Fe^{III}L]^+$ cations and perchlorate anions. The coordination geometry of the metal atom is a distorted octahedron, with two terminal phenolic oxygen and amine nitrogen atoms in *cis* positions, and imine nitrogen atoms in *trans* positions. The bonds to the oxygen atoms are the shortest [average $1.870(4)$ Å] followed by those to the imine [average $1.938(5)$ Å] and the amine [average $2.004(4)$ Å] nitrogen atoms. The angles O1–Fe1–N2, N1–Fe1–N4 and N3–Fe1–O2 are all close to $180°$ [$174.5(1)$, $178.9(1)$, and $174.6(2)$, respectively]. The twelve angles subtended at the iron atom by adjacent donor atoms are approximate right angles, ranging from $84.1(2)°$ to $95.1(2)°$. For the N1 = C7 double bond a lengthening is observed [$1.286(6)$, in contrast to $1.269(1)$ Å in the free ligand]. The metal–ligand bond distances are consistent with those of other reported low-spin iron(III) complexes [45, 46]. The iron(III)-imine nitrogen bond distance is characteristic of the spin states in different Schiff base complexes: For high-spin complexes it is in the range of $2.00-2.10$, and $1.93-1.96$ Å for low spin complexes [46]. The coordinated imine groups in $[Fe(L)](ClO_4)$ are planar within experimental error, and the Fe–N(imine) bond lengths at $1.935(5)$ and $1.941(5)$ Å are significantly shorter than the Fe–N(amine) bond lengths at

1.999(4) and 2.008(4) Å. The overall geometry is as expected for an octahedral low-spin d^5 iron(III) ion with hexadentate chelation.

Spectroscopic properties

The IR spectra of the free H_3L' ligand show a broad band at $\sim 3250 - 3446$ cm^{-1}, which is likely to be a superposition of bands from alcoholic and phenolic groups. The ν(phenolic OH) band is absent in the IR spectra of the complex. This indicates that these protons are lost upon complexation. A strong bond at ~ 1640 cm^{-1} of the ligand is assigned to the ν(C=N) stretching frequency. This band is slightly shifted to lower frequencies (~ 1627 cm^{-1}) upon complexation, suggesting that the imine nitrogen atoms are coordinated to the iron ion as confirmed by the structural work (above). The strong unsplit band at 1086 cm^{-1} ($\nu_{ClO_4^-}$) suggests non-coordinated perchlorate ions [47].

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