



Synthesis and Structure of Iron(III) Complex with N,N,O-Donor Aroylhydrazones: The Chloride Anion as Hydrogen Bond Acceptor Forming Infinite Chains

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A new iron(III) complex, $[\text{FeL}_2](\text{Cl})\cdot(\text{CH}_3\text{OH})_{0.5}$ with acyclic tridentate 5-bromo-salicylaldehyde-6-chloro-2-pyridyl hydrazone (HL) has been synthesized and structurally characterized. The crystal structure consists of chains of alternating $[\text{FeL}_2]^+$ cations and Cl^- anions, linked together by $\text{N-H}\cdots\text{Cl}\cdots\text{H-N}$ hydrogen bonds. Two tridentate monoanionic meridionally spanning ligands form a distorted octahedral N_4O_2 coordination sphere around the metal ion.

Key Words: Synthesis, Structure, Iron(III), Complex, Aroylhydrazones.

INTRODUCTION

Considerable effort is currently devoted to the investigation of the coordination chemistry of aroylhydrazones due to their chelating capability and potential pharmacological application¹⁻³. Aroylhydrazones are potential ligands due to presence of several coordination sites. They can act as a neutral or monoanionic bidentate or tridentate ligand depending on the substituents and the reaction conditions^{4,5}. Furthermore, abilities to coordinate to metals either in keto(I) or enol(I) tautomeric form make them attractive as ligand⁵⁻¹⁵.

In this work, we described the synthesis and characterization of an iron(III) complex with 5-bromo-salicylaldehyde-6-chloro-2-pyridyl hydrazone ligand (HL) which in the deprotonated state (L^-) can coordinate a metal ion *via* the pyridine-N, the imine-N and the phenolate-O atoms. The crystal structure features infinite $\cdots\text{cation-anion-cation}\cdots$ chains formed by intermolecular $\text{N-H}\cdots\text{Cl}$ hydrogen bonds. Each chloride anion is involved in two hydrogen bonds. In addition, the spectroscopic properties of complex have also been studied.

EXPERIMENTAL

C, N and H elemental analyses were carried out with a Varian EL elemental analyzer. IR spectra were recorded on a Bruker Tensor27 FT-IR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Shimadzu 2500PC spectrophotometer. The hydrazone ligand (HL) was prepared by condensation reaction of 2-hydrazinopyridine with 5-bromo-salicylaldehyde in methanol. All other chemicals and solvents used were of analytical grade available commercially and were used without further purification.

Synthesis of complex: To a solution of methanol (15 mL) of HL (0.07 g, 0.2 mmol), a methanol solution (5 mL) of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.03 g, 0.1 mmol) was added gradually with stirring. The resulting deep brown solution was further stirred for 2 h and filtered. The deep brown crystals separated after *ca.* 4 days and were collected. Yield: 60 %. Anal. calcd. for $\text{C}_{24.5}\text{H}_{18}\text{N}_6\text{O}_{2.5}\text{Br}_2\text{Cl}_3\text{Fe}$ (%): C, 38.79; N, 11.08; H, 2.40; Found: C, 38.65; N, 10.92; H, 2.45.

Crystal structure determination: X-ray diffraction data were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. All the hydrogen atoms were located geometrically and refined isotropically. O_3 atom of methanol molecule was disordered over two positions, with site occupation factor of 0.644/0.356. The data collection and refinement details are summarized in Table-1.

RESULTS AND DISCUSSION

The structure of $[\text{FeL}_2](\text{Cl})\cdot(\text{CH}_3\text{OH})_{0.5}$ is illustrated in Fig. 1 with the atom numbering scheme. The asymmetric unit contains $[\text{FeL}_2]^+$ cation with chloride counterion and half methanol molecule.

In complex, the tridentate ligands bind the metal ion meridionally with pairs of pyridyl-N, phenolato-O and imine-N atoms and form a N_4O_2 coordination sphere. The bond parameters associated with the metal ion (Table-2) indicate a distorted octahedral coordination geometry. The average chelate bite angles in the five-membered rings formed by the

TABLE-1
CRYSTAL DATA AND REFINEMENT DETAILS
FOR $[\text{FeL}_2](\text{Cl})\cdot(\text{CH}_3\text{OH})_{0.5}$

Empirical formula	$\text{C}_{24.5}\text{H}_{18}\text{N}_6\text{O}_{2.5}\text{Br}_2\text{Cl}_3\text{Fe}$
Formula weight	758.47
Crystal size (mm)	$0.27 \times 0.26 \times 0.12$
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	8.4986(7)
b (Å)	20.974(2)
c (Å)	16.5351(14)
α (°)	90
β (°)	95.8540(10)
γ (°)	90
Cell volume (Å ³)	2932.1(5)
Z	4
D_{calc} (g cm ⁻³)	1.718
F(000)	1496
μ (mm ⁻¹)	3.082
Theta range for data collection (°)	1.57 to 25.02
Total reflections	14484
Independent reflections	5146 (Rint = 0.0877)
Observed reflections	3406 [$I > 2\sigma(I)$]
Goodness-of-fit on F^2	1.073
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0615$, $wR_2 = 0.1193$
R indices (all data)	$R_1 = 0.1503$, $wR_2 = 0.1335$

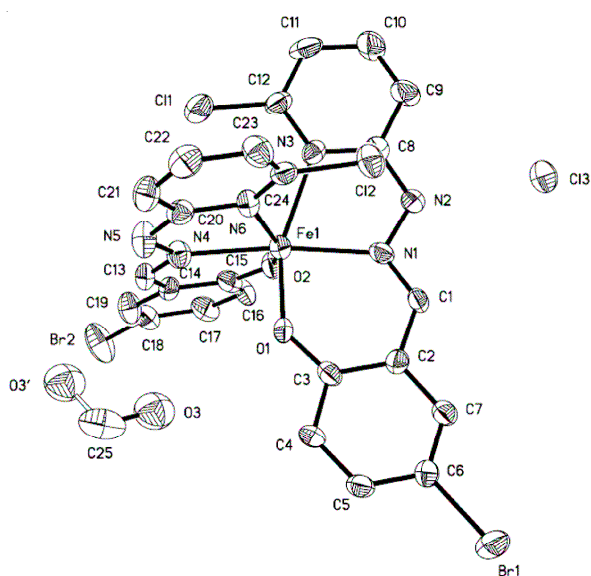


Fig. 1. Structure of $[\text{FeL}_2](\text{Cl})\cdot(\text{CH}_3\text{OH})_{0.5}$ with the atom labeling scheme

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°)
FOR $[\text{FeL}_2](\text{Cl})\cdot(\text{CH}_3\text{OH})_{0.5}$

Fe(1)-N(1)	2.114(7)	Fe(1)-O(1)	1.882(5)
Fe(1)-N(3)	2.201(7)	Fe(1)-O(2)	1.897(6)
Fe(1)-N(4)	2.115(7)	N(1)-N(2)	1.377(8)
Fe(1)-N(6)	2.204(7)	N(4)-N(5)	1.396(8)
N(1)-Fe(1)-N(4)	172.8(3)	O(1)-Fe(1)-N(4)	88.4(2)
N(1)-Fe(1)-N(3)	74.5(3)	O(1)-Fe(1)-N(6)	88.0(2)
N(1)-Fe(1)-N(6)	107.4(2)	O(2)-Fe(1)-N(1)	95.2(2)
N(3)-Fe(1)-N(6)	86.7(2)	O(2)-Fe(1)-N(4)	83.8(2)
N(4)-Fe(1)-N(3)	112.5(3)	O(2)-Fe(1)-N(3)	88.7(2)
N(4)-Fe(1)-N(6)	75.2(3)	O(2)-Fe(1)-N(6)	154.8(2)
O(1)-Fe(1)-N(1)	85.0(2)	O(2)-Fe(1)-O(1)	105.4(2)
O(1)-Fe(1)-N(3)	156.2(2)	-	-

pyridine-N and the imine-N and in the six-membered rings formed by the imine-N and the phenolate-O are 107.8° and 119.8°, respectively. The five-membered rings formed by the pyridine-N and the imine-N are essentially planar. The r.m.s. deviations of the five fitted atoms are 0.0405 for ring [Fe1, N1, N2, C8, N3] and 0.0561 for ring [Fe1, N4, N5, C20, N6]. The six-membered rings formed by the imine-N and the phenolate-O are also essentially planar, with the r.m.s. deviations of the six fitted atoms being 0.0245 for ring [Fe1, O1, C3, C2, C1, N1] and 0.0508 for ring [Fe1, O2, C15, C14, C13, N4]. The Fe-N(pyridine), Fe-N(imine) and Fe-O(phenolate) distances observed in the complex are within the range reported for iron(II) complexes having the same coordinating atoms¹⁶⁻¹⁸.

Interestingly, the $[\text{FeL}_2]^+$ cations and the chloride anions form an alternating, infinite \cdots cation-anion-cation \cdots chain along the b direction, as shown in Fig. 2. The chloride anion is a strong hydrogen bond acceptor^{19,20} and behaves, as a multiple acceptor to the N-H groups of hydrazine fragments of the two adjacent ligands ($\text{N}2\cdots\text{Cl}3$, 3.062 Å, $\text{N}2\text{-H}2\cdots\text{Cl}3$, 122.44 °; $\text{N}5\cdots\text{Cl}3$, 3.090 Å, $\text{N}5\text{-H}5\cdots\text{Cl}3$, 171.27°). Methanol molecule has no role in the formation of the chain, which is only connected to the bromine atom in $[\text{FeL}_2]^+$ cations through O-H \cdots Br interactions ($\text{O}3\cdots\text{Br}2$, 3.082 Å, $\text{O}3\text{-H}3\cdots\text{Br}2$, 165.87°).

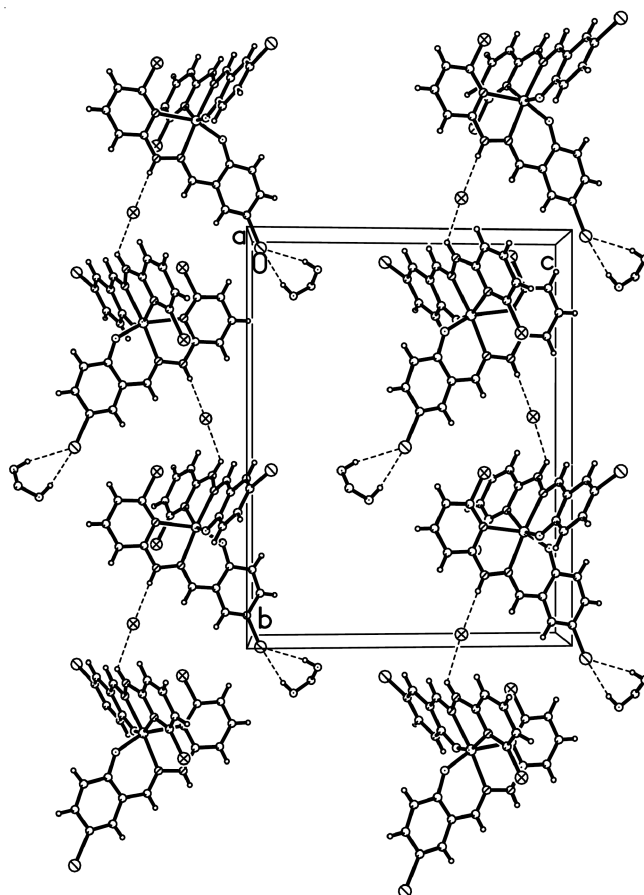


Fig. 2. Cation and anion disposition in the chain in the $[\text{FeL}_2](\text{Cl})\cdot(\text{CH}_3\text{OH})_{0.5}$

IR spectra display a broad band centred at 3200 cm^{-1} . This band is possibly due to the N-H stretch of the hydrazine fragment of the ligand^{12,14}. The strong and sharp band observed at

1613 cm^{-1} is most likely due to the azomethine C=N stretching. The medium to strong bands in the range 1583-1458 cm^{-1} are possibly due to the vibrations associated with the aromatic C=C fragments of the ligands¹³⁻¹⁵. The coordination through the oxygen atom is inferred from a sharp band^{14,15} of $\nu(\text{ph-O})$ at 1177 cm^{-1} .

The electronic spectrum of acetonitrile solutions exhibits several absorptions at 216, 244, 317, 341 and 427 nm. The highest energy absorptions observed in the range 216-341 nm are most likely due to ligand centred transition and the absorption at 427 nm is possibly correspond to the ligand-to-metal charge transfer transition^{3,13}.

Conclusion

A new iron(III) complex, $[\text{FeL}_2](\text{Cl})\cdot(\text{CH}_3\text{OH})_{0.5}$ with acyclic tridentate 5-bromo-salicylaldehyde-6-chloro-2-pyridyl hydrazone ligand (HL) has been synthesized and characterized. The X-ray structural analysis reveals that the two tridentate ligands bind the metal ion meridionally with pairs of pyridyl-N, phenolato-O and imine-N atoms and form a N_4O_2 coordination sphere. The complex features infinite \cdots -cation-anion-cation- \cdots chain formed by intermolecular N-H \cdots Cl hydrogen bonds.

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