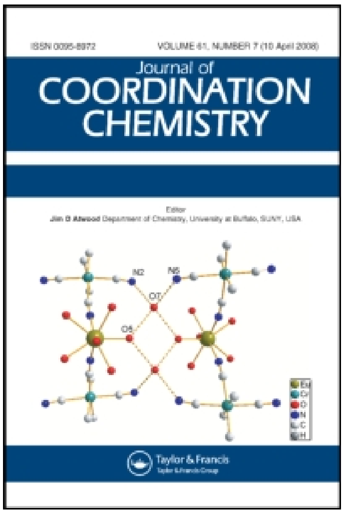


**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Synthesis, structural characterization, and DFT studies of new mixed-ligand iron(III) Schiff-base complexes

Chira R. Bhattacharjee[a]; Pankaj Goswami[b]; Paritosh Mondal[a]
[a] Department of Chemistry, Assam University, Silchar 788011, Assam, India [b] Department of Chemistry, Silchar Polytechnic, Silchar 788015, Assam, India

**To cite this Article** Bhattacharjee, Chira R. , Goswami, Pankaj and Mondal, Paritosh(2010) 'Synthesis, structural characterization, and DFT studies of new mixed-ligand iron(III) Schiff-base complexes', Journal of Coordination Chemistry, 63: 11, 2002 — 2011, First published on: 25 June 2010 (iFirst)

**To link to this Article: DOI:** 10.1080/00958972.2010.495405

**URL:** http://dx.doi.org/10.1080/00958972.2010.495405

*Journal of Coordination Chemistry*
Vol. 63, No. 11, 10 June 2010, 2002–2011

Taylor & Francis
Taylor & Francis Group

# Synthesis, structural characterization, and DFT studies of new mixed-ligand iron(III) Schiff-base complexes

CHIRA R. BHATTACHARJEE*†, PANKAJ GOSWAMI‡ and
PARITOSH MONDAL†

†Department of Chemistry, Assam University, Silchar 788011, Assam, India
‡Department of Chemistry, Silchar Polytechnic, Silchar 788015, Assam, India

(*Received 16 September 2009; in final form 16 March 2010*)

Cationic iron(III) Schiff-base aquo complex of the type $[FeL(H_2O)_2]NO_3$ ($L = C_{12}H_{18}N_2O_2$) was accessed from the interaction of $Fe(NO_3)_3 \cdot 9H_2O$ with the $[N_2O_2]$ donor Schiff base. Reaction of the aquated complex with bifluoride ($HF_2^-$), thiocyanate ($SCN^-$), or azide ($N_3^-$) in 1 : 2 molar ratio in methanolic medium led to the synthesis of anionic mixed-ligand complexes, $[FeLX_2]^{n-}$ ($L = C_{12}H_{18}N_2O_2$, X = F, NCS, $N_3$). The tetradentate Schiff-base ligand was prepared from the condensation of acetylacetone and ethylenediamine following literature method and characterized by spectroscopic and single crystal X-ray diffraction technique. The complexes were characterized using elemental analysis, FT-IR, UV-Vis, mass spectroscopy, and solution electrical conductivity studies. The magnetic susceptibility measurements suggested high-spin Fe(III). The electronic structures of the compounds were analyzed by DFT method using B3LYP/6-31G(d,p) functional and overall, very good agreement between theoretical expectations and experimental data was achieved. The electrochemical behavior of the complexes was examined by cyclic voltammetric method.

*Keywords*: Schiff base; Mixed-ligand iron(III) complex; DFT; Acetylacetone; Ethylenediamine

## 1. Introduction

Metal–Schiff base complexes have synthetic proclivity, structural diversity, and potential applications in pharmacology and catalysis. The design, synthesis, and characterization of iron complexes with Schiff-base ligands play a role in the coordination chemistry of iron due to their importance as synthetic models for iron-containing enzymes [1, 2], oxidation catalysts [3–5], and bistable molecular materials based on temperature, pressure, or light-induced spin crossover behavior [6–9]. Attention has been devoted in recent years to the mixed-ligand complexes of transition metals containing nitrogen donors [10–12], with potential applications as separation materials, catalysis precursors, potential models of the catalyse enzymes [13–16] and interesting structures [17–19]. Mixed-ligand complexes containing N, O, and/or S donors are important owing to their antifungal, antibacterial, and anticancer activities [20]. Use of iron–Schiff-base complexes in different catalytic reactions have

---

*Corresponding author. Email: crbhattacharjee@rediffmail.com

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.495405

been reported [21–24]. Although a large number of metal–[$N_2O_2$] compounds exist [25–28], reports on corresponding Fe(III) complexes are scarce. Mostly divalent metal ions have been used for the complexation with Schiff bases having [$N_2O_2$] core [29–31]. Recent study showed iron(III) tridentate Schiff-base complexes as efficient catalysts for the oxidation of sulfides to sulfoxides by urea hydrogen peroxide [32]. Similarly, [$N_2O_2$] donor Schiff-base complexes of palladium(II) have been used as catalysts for the reduction of organic substrates under mild conditions [33]; oxovanadium(IV)–[$N_2O_2$] Schiff-base complexes exhibit insulin-mimetic activity [34]. [$N_2O_2$] planar tetradentate ligands render two axial sites open to ancillary ligands. For instance, iron(III) complexes of [$N_2O_2$] donor tetradentate Schiff-base ligands, $[FeL(Im)_2] \cdot BPh_4$ (L = salen, acacen), possess interesting magnetic behavior [35, 36]. The coordination of varying donor ligands at the axial site allow tunability to physical properties. The complexes of VO(II), Ni(II), Co(II), and Cu(II) with unsymmetrical [$N_2O_2$] donor Schiff base derived from 2,4-pentanedione/1-phenyl-1,3-butanedione and ethylenediamine have recently been reported [37].

We report herein the synthesis and structural characterization of mixed-ligand iron(III) complexes with the $N_2O_2$ donor Schiff base derived from the condensation of acetylacetone with ethylenediamine incorporating aquo, fluoro, thiocyanato, or azido groups. Density functional theory (DFT) methods have been used to model the geometry of the complexes. Electrochemical behavior of the complexes is also studied.

## 2. Experimental

### 2.1. *Materials*

Reagent grade and HPLC grade solvents and chemicals were used. Acetylacetone, ethanol, methanol, and other solvents were distilled prior to use. Ethylenediamine, ammonium bifluoride, ammonium thiocyanate, sodium azide, and ferric nitrate were obtained from E. Merck. India Ltd. and used as received.

### 2.2. *Measurements*

Microanalytical (C, H, and N) data were obtained with a Perkin-Elmer Model 240C elemental analyzer. Infrared (IR) spectra were obtained using KBr pellets on a Spectrum BX series FT-IR spectrophotometer from 400 to 4000 $cm^{-1}$. Electronic spectra were recorded in $CH_2Cl_2$ on a Shimadzu 1600-PC UV-Vis spectrophotometer from 200 to 800 nm. Nuclear magnetic resonance spectra ($^1H$ and $^{13}C$) were acquired from a Bruker Advance 300 MHz FT NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a Jeol SX-102 spectrometer with fast atom bombardment. Magnetic susceptibilities of the complexes were measured at room temperature on a Sherwood scientific susceptibility balance using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of complexes were determined in DMSO (*ca* $10^{-3}$ M) at room temperature using a Toa CM 405 conductivity meter. Electrochemical behavior of the complexes was investigated by cyclic voltammetric method in a CHI 660C Electrochemical Workstation in dicholoromethane *versus* saturated calomel electrode (SCE) electrode at room temperature in the potential range −1.0 to 1.0 V.

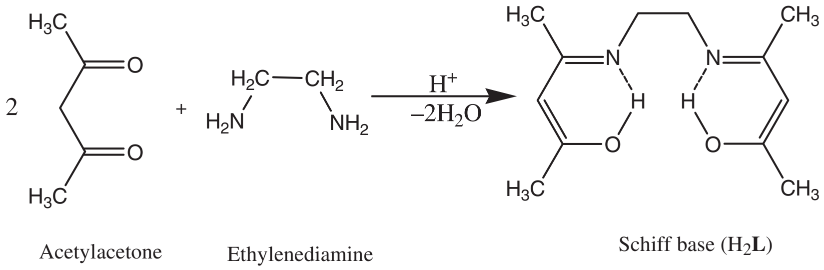
### 2.3. *Synthesis*

**2.3.1. Synthesis of Schiff-base ligand, $C_{12}H_{20}N_2O_2$ ($H_2L$).** The ligand was prepared from the condensation of acetylacetone and ethylenediamine in 2 : 1 molar ratio according to the reported method [38]. Acetylacetone (0.02 mol, 2.0 g) and ethylenediamine (0.01 mol, 0.06 g) in 60 $cm^3$ dry ethanol were refluxed for 2 h in the presence of few drops of acetic acid and cooled in a refrigerator. The resulting compound was precipitated, filtered, and recrystallized from methanol. Yield 66%. Elemental Anal. Calcd (%): C (64.29), H (8.93), and N (12.50). Found (%): C (64.22), H (8.84), and N (12.45). FT-IR [KBr pellets, $\nu$ ($cm^{-1}$)] 1143 (C–O), 1617 (C=N), 3447 (O–H). UV-Vis [$CH_2Cl_2$, $\lambda_{max}$ (nm), $\varepsilon$ ((mol $L^{-1})^{-1}$ $cm^{-1}$)] 231 (2233), 317 (20749). $^1H$ NMR [300 MHz, $\delta$ (ppm), from TMS in $CDCl_3$] 10.89 (s, 2H, OH), 5.00 (s, 2H, –CH=C), 3.42 (t, 4H, –$CH_2$–), 2.17 (s, 6H, $CH_3$), 1.91 (s, 6H, $CH_3$). $^{13}C$ NMR [300 MHz, $\delta$ (ppm), from TMS in $CDCl_3$] 195.5, 162.9, 96.1, 43.4, 28.8, 18.6. MS(FAB, *m*/*z*) 225$[M+H]^+$.

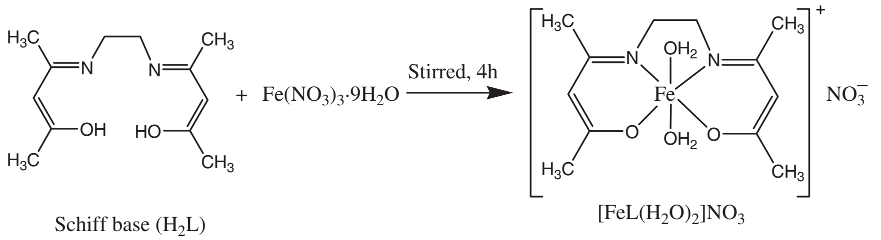
**2.3.2. Synthesis of $[FeL(H_2O)_2]NO_3$.** The ligand, $H_2L$ (0.005 mol, 1.12 g) was dissolved in methanol (20 $cm^3$) and added to a methanol solution (20 $cm^3$) of $[Fe(NO_3)_3]\cdot 9H_2O$ (0.005 mol, 2.02 g) and the mixture was stirred for 4 h. On cooling to room temperature dark brown microcrystalline solid was obtained, which was washed with cold absolute ethanol and then dried in air. Yield 68%. Elemental Anal. Calcd (%): C (38.30), H (5.85), and N (11.17). Found (%): C (38.23), H (5.88), and N (11.25). FT-IR [KBr pellets, $\nu$ ($cm^{-1}$)] 435 (Fe–O), 453 (Fe–N), 654 ($\rho_{wagg}H_2O$), 930 ($\rho_{rock}H_2O$), 1274 (C–O), 1385 (N–O), 1573 (C=N), 3419 (O–H). UV-Vis [$CH_2Cl_2$, $\lambda_{max}$ (nm), $\varepsilon$ ($M^{-1}$ $cm^{-1}$)] 278 (9169), 323 (21,986), 410 (549), 482 (330). MS (FAB, *m*/*z*) 376$[M]^+$.

**2.3.3. Synthesis of $NH_4[FeLF_2]$.** $[FeL(H_2O)_2]NO_3$ (0.001 mol, 0.376 g) was dissolved in 10 $cm^3$ of methanol and to this a methanol solution (10 $cm^3$) of $NH_4F\cdot HF$ (0.002 mol, 0.112 g) was added with continuous stirring and the mixture was further stirred for 1 h. On standing overnight the compound precipitated was collected, washed with ethanol, and then dried in open air. Yield 63%. Elemental Anal. Calcd (%): C (43.11), H (6.59), and N(12.66). Found (%): C (43.18), H (6.52), and N (12.66). FT-IR [KBr pellets, $\nu$ ($cm^{-1}$)] 442 (Fe–O), 466 (Fe–N), 652 (Fe–F), 1508 (C–O), 1607 (C=N). UV-Vis [$CH_2Cl_2$, $\lambda_{max}$ (nm), $\varepsilon$ ($M^{-1}$ $cm^{-1}$)] 365 (53.29), 323 (22400). MS (FAB, *m*/*z*) 334$[M]^+$.

**2.3.4. Synthesis of $NH_4[FeL(NCS)_2]$.** The complex was prepared by a procedure similar to that of $NH_4[FeLF_2]$ with $NH_4SCN$ added instead of $NH_4F\cdot HF$. Yield 70%. Elemental Anal. Calcd (%): C (40.78), H (5.34), and N (19.99). Found (%): C (40.85), H (5.39), and N (20.02). FT-IR [KBr pellets, $\nu$ ($cm^{-1}$)] 414 (Fe–NCS), 435 (Fe–O), 483 (Fe–N), 771 (C–S), 1420 (C–O), 1569 (C=N), 2073 (C–N sym), 2049 (C–N asym). UV-Vis [$CH_2Cl_2$, $\lambda_{max}$ (nm), $\varepsilon$ ($M^{-1}$ $cm^{-1}$)] 251 (19,864), 303 (22,189), 361 (4000), 483 (8889). MS (FAB, *m*/*z*) 412$[M]^+$.



Scheme 1. Synthesis of the ligand $H_2L$.



Scheme 2. Synthesis of Fe(III) complex with Schiff base $H_2L$.

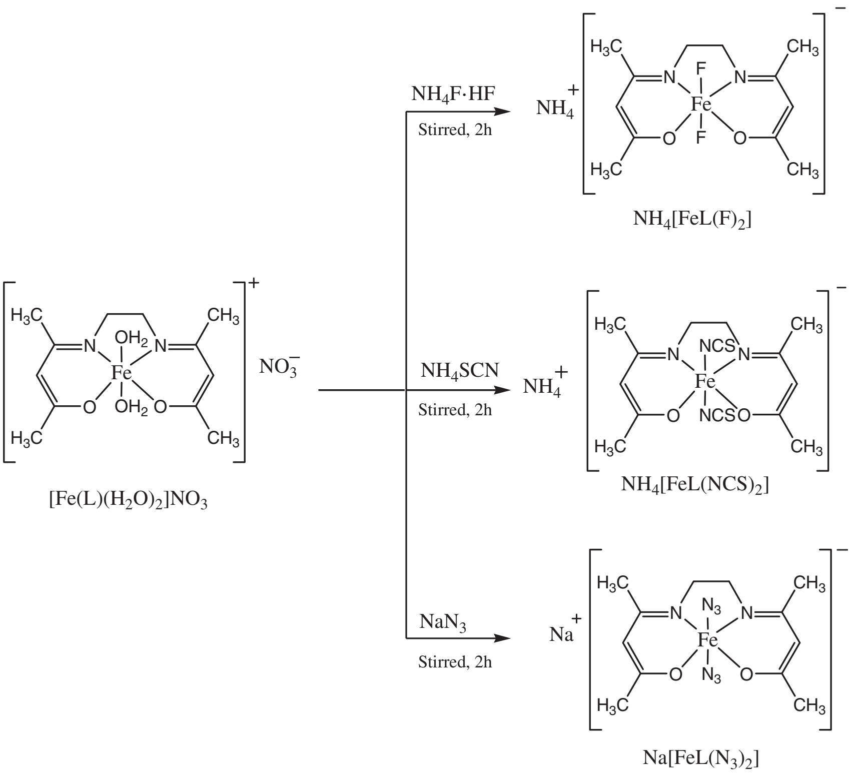
**2.3.5. Synthesis of Na[FeL($N_3$)$_2$].** The complex was prepared by a procedure similar to that of $NH_4[FeLF_2]$ with $NaN_3$ instead of $NH_4F \cdot HF$. Yield 64%. Elemental Anal. Calcd (%): C (37.40), H (4.68), and N (29.09). Found (%): C (37.36), H (4.62), and N (29.15). FT-IR [KBr pellets, $\nu$ ($cm^{-1}$)] 425 (Fe–$N_3$), 438 (Fe–O), 472 (Fe–N), 1508 (C–O), 1590 (C=N), 2044 (N–N–N), 2066 (N–N–N). UV-Vis [$CH_2Cl_2$, $\lambda_{max}$ (nm), $\varepsilon$ ($M^{-1}cm^{-1}$)] 276 (16,742), 320 (13,451), 429 (1244), 699 (13.82). MS (FAB, $m/z$) $385[M]^+$.

## 3. Results and discussion

### 3.1. *Chemistry*

Condensation between acetylacetone and ethylenediamine in 1 : 2 molar ratio yields a pale yellow Schiff base, bis(acetylacetonato)ethylenediamine in weakly acidic medium (scheme 1). The formation of Schiff base was confirmed by FT-IR, UV-Vis, $^1H$ NMR, $^{13}C$ NMR, mass spectroscopy, and single crystal X-ray diffraction (XRD) study. The compound is soluble in polar solvents like methanol, ethanol, chloroform, dichloromethane, but insoluble in nonpolar solvents.

Iron(III) complexes were prepared in good yield by the reaction of iron(III)nitrate and the ligand in 1 : 1 molar ratio (scheme 2). Two molecules of water coordinate to the metal center as supported by microanalysis and spectral data. The complex reacts with ammonium bifluoride, ammonium thiocyanate, or sodium azide in 1 : 2 molar ratio



Scheme 3. Reactivity of the complex $[FeL(H_2O)_2]NO_3$.

to give mixed-ligand complexes $NH_4[FeLF_2]$, $NH_4[FeL(NCS)_2]$, and $NH_4[FeL(N_3)_2]$, respectively. The two axial aquo groups were replaced by fluoro, thiocyanato, or azido (scheme 3). Isothiocyanato (NCS) in the coordination sphere of iron has been earlier exploited as probe for surface-enhanced Raman spectroscopy (SERS) and for the functionalization of metal nano particle [39, 40].

### 3.2. *IR spectra*

The free ligand showed stretching modes attributed to C=N, C–O, and O–H at 1617, 1143, and 3447 cm$^{-1}$, respectively. On complexation, the C=N band shifts to lower wavenumber, indicating coordination through the azomethine nitrogen [41]. Bands due to the $\nu$(O–H) were absent in the complexes, indicating coordination through deprotonated ligand. The participation of enolate oxygen and azomethine nitrogen in the complexes is further supported by prominent IR peaks for $\nu$(Fe–O) and $\nu$(Fe–N) at 435–442 cm$^{-1}$ and 454–483 cm$^{-1}$, respectively [42]. Coordinated water in $[FeL(H_2O)_2]NO_3$ was confirmed by a broad band at *ca* 3420 cm$^{-1}$ for $\nu$(O–H) with weak bands at 650 and 930 cm$^{-1}$ attributable to wagging and rocking modes of coordinated water, respectively [43]. A sharp band at 1385 cm$^{-1}$ assignable to $\nu NO_{(asy)}$ is typical of uncoordinated nitrate. A strong doublet at 2049 and 2073 cm$^{-1}$ along with a medium intensity band at 770 cm$^{-1}$ in $NH_4[FeL(NCS)_2]$ attributed, respectively, to ν(C–N) and ν(N–C–S), suggest the presence of nitrogen bonded terminal $NCS^-$ [44]. Peaks at 2044 and 2066 $cm^{-1}$ in $Na[FeL(N_3)_2]$ are attributable to azido.

### 3.3. *Electronic spectra*

UV-Vis spectra of complexes in dichloromethane solution show a very weak d–d band at 480 nm except for the azido complex at *ca* 700 nm. An absorption band at *ca* 320 nm *in aquo*, fluoro or azido complexes is attributed to a ligand $(p_\pi) \rightarrow$ iron(III) $(d_\sigma{}^*)$ charge transfer transition [45, 46]. The higher energy bands in the region 250–280 nm have been attributed to intraligand $\pi \rightarrow \pi^*$ transitions [47].

### 3.4. *NMR spectra*

The $^1H$ NMR spectrum of the ligand revealed a singlet at 10.89 ppm for the enolic proton. Signals for methylene protons $(–N–CH_2–CH_2–N–)$, olefinic proton $(–CH{=}C<)$, and methyl protons $(–CH_3)$ were at 3.42, 2.17, and 1.91 ppm, respectively [48].

The $^{13}C$ NMR spectra showed resonances at six different positions concordant with six different types of carbon. Peaks at 18.69 and 28.66 ppm are due to the carbon of magnetically nonequivalent methyl groups, while azomethine carbon showed at 62.91 ppm. Peaks at 43.49, 96.15, and 195.53 are attributable to carbon atom of $–CH_2$, $–CH{=}$, and $=C–OH$ groups, respectively.

### 3.5. *Mass spectra*

Mass spectra of the compounds were recorded in $FAB^+$ ionization mode. The molecular ion peak of the ligand appeared at *m/z* 225$[M+H]^+$. Molecular formulas $C_{12}H_{22}N_3O_7Fe$, $C_{12}H_{22}N_3O_2F_2Fe$, $C_{14}H_{22}N_5O_2S_2Fe$, and $C_{12}H_{18}N_8O_2FeNa$ were confirmed by their mass spectra with peaks at *m/z* 378 (*ca* 376), 334 (*ca* 334), 413 (*ca* 412), and 386 (*ca* 385), respectively. Peaks at *m/z* 360 and 340 observed for $[FeL(H_2O)_2]NO_3$ are attributed to $[M–H_2O]^+$ and $[M–2H_2O]^+$ from loss of coordinated water. $Na[FeL(N_3)_2]$ and $NH_4[FeL(NCS)_2]$ showed peaks corresponding to the complex anionic species at *m/z* 364 (*ca* 362) and 393 (*ca* 394), respectively.

### 3.6. *Magnetic susceptibility*

The magnetic moment values of the complexes $[FeL(H_2O)_2]NO_3$, $NH_4[FeLF_2]$, $NH_4[FeL(NCS)_2]$, and $NH_4[FeL(N_3)_2]$ at room temperature were 5.97, 6.54, 6.00, and 6.45 B.M., respectively, supporting high spin ($d^5$, $S = 6$) octahedral geometry for the complexes. A rather high value of magnetic moment is presumably due to the orbital contributions [49].

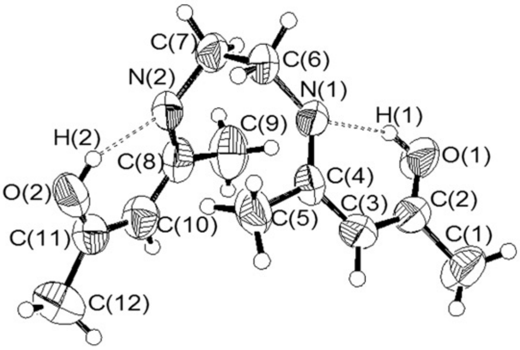


Figure 1. XRD structure of the ligand $H_2L$.

### 3.7. *Molar conductance*

The molar conductances of $[FeL(H_2O)_2]NO_3$, $NH_4[FeLF_2]$, $NH_4[FeL(NCS)_2]$, and $NH_4[FeL(N_3)_2]$ in DMSO solution (*ca* $10^{-3}$ M) were 53.8, 47.2, 50.8, and 51.4 $\Omega^{-1}\,cm^2\,mol^{-1}$, suggesting 1 : 1 electrolytic nature of the complexes [50].

### 3.8. *Single crystal XRD*

Single crystal X-ray diffraction study of the ligand showed the existence of intramolecular O–H $\cdots$ N hydrogen bonds between the pair of atoms $H_1$–$N_2$ and $H_2$–$N_1$ (figure 1). Crystal/refinement data: empirical formula $C_{12}H_{20}N_2O_2$, M = 224.30. Triclinic, P-1 (No. 2), $a = 7.1158(5)$, $b = 10.4490(8)$, $c = 10.4810(8)$ Å, $\alpha = 62.589(5)$, $\beta = 78.531(6)$, $\gamma = 75.900(6)^\circ$, $V = 667.55(9)$ Å$^3$. $D_{\text{Calcd}}$ $(Z = 2) = 1.116\,g\,cm^{-3}$. $\mu_{\text{Mo}} = 0.076\,mm^{-1}$; specimen: $0.06\,mm \times 0.60\,mm \times 0.80\,mm$; "$\theta$" Min–Max = 2.2–27.5°; $N_{(\text{total})} = 9466$, $N_{(\text{unique})} = 3057$ $(R_{\text{int}} = 0.091)$, $N_o$ $(I > 2\sigma(I)) = 1079$; $R_1 = 0.0842$, $wR2 = 0.2622$. S = 0.94.

### 3.9. *DFT study*

As efforts to obtain single crystal of the complexes failed, quantum chemical DFT calculations were performed using B3LYP/6-31G(d,p) functional implemented in commercially available Gaussian 03 program suite [51], without imposing symmetry constraints. The optimized structures of the complexes and significant structural data are provided in the "Supplementary material". The geometry around the metal is slightly distorted octahedral with aquo, fluoro, thiocyanato, or azido groups along the axial direction. Intramolecular hydrogen bonding between O1–H19 and O2–H21 are seen in the optimized structure of $[Fe(L)(H_2O)_2]NO_3$. The Fe–N (azomethine) bond length is nearly the same in all complexes while Fe–O bond length differs significantly. The largest Fe–O bond distance was when axial positions were occupied by fluoride and the smallest when the axial positions were occupied by water. On comparing the bond angles of different complexes, it was found that (N1–Fe1–N2) angle differs negligibly while large variation in (O1–Fe1–O2), (N1–Fe1–O1), and (N2–Fe1–O2) bond angles are calculated. The harmonic vibrational frequencies of the complexes were also computed theoretically by DFT methods (Supplementary material) using 0.9664

Table 1. Electrochemical data of the complexes.

| Compound | $E_p^a$ (V) | $E_p^c$ (V) | $\Delta E$ (V) | $E_{1/2}$ (V) |
|---|---|---|---|---|
| $[Fe(L)(H_2O)_2]NO_3$ | −0.448 | −0.854 | 0.406 | −0.651 |
| $NH_4[Fe(L)F_2]$ | −0.253 | −0.648 | 0.395 | −0.450 |
| $NH_4[Fe(L)(NCS)_2]$ | −0.152 | −0.553 | 0.399 | −0.351 |
| $Na[Fe(L)(N_3)_2]$ | −0.433 | −0.570 | 0.137 | −0.501 |

as scaling factor [52] and the empirically scaled harmonic vibrational frequencies are in fairly good agreement with the experimental ones. Little deviations are due to the negligence of anharmonicity in B3LYP method [53, 54]; average error for frequencies calculated with B3LYP functional was reported to be of the order of 40–50 $cm^{-1}$ [55].

### 3.10. *Electrochemical behavior*

Electrochemical behaviors of the compounds were studied by cyclic voltammetry in dichloromethane ($10^{-3}$ M), containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte from −1.0 to 1.0 V *versus* SCE at 100 $mV\,s^{-1}$. The redox potentials of the compounds are given in table 1 and a representative voltammogram is presented in "Supplementary material". The complexes displayed quasireversible one-electron wave with $\Delta E > 100$ mV, assignable to Fe(III)/Fe(II) redox couple. The half wave potentials $E_{1/2}$ are negative and small, indicating ready redox susceptibility, rendering the complexes as valuable catalysts for redox reactions [56]. The free ligand did not show any response in the potential range of −1.0 to 1.0 V under similar experimental condition, implying redox innocence.

## 4. Conclusion

Aquated iron(III)-Schiff base complex, $[FeL(H_2O)_2]NO_3$, prepared by the reaction of $H_2L$ and $Fe(NO_3)_3 \cdot 9H_2O$ in 1 : 1 molar ratio, reacts with ammonium bifluoride, ammonium thiocyanate, or sodium azide in 1 : 2 molar ratio affording $A^+[FeL(X)_2]^-$ ($A = NH_4$; X = F, NCS and A = Na; $X = N_3$). The crystal structure of the ligand indicated intramolecular hydrogen bonding in its enolic form. The distorted octahedral structures of the complexes were consistent with analytical and spectral data. B3LYP/6-31G(d,p) DFT study also showed geometry around iron(III) to be octahedral with axial aquo, fluoro, thiocyanato, or azido. The harmonic vibrational frequencies of the complexes, computed by DFT, matches well with the experimental. All the complexes showed quasireversible redox behavior with small and negative $E_{1/2}$ values, suggesting potential as catalysts in redox reactions. The complexes may be used as stabilizing agents for the synthesis of metal nano particles.

## Supplementary materials

Crystallographic data for the structural analysis of the ligand have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 262373. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

## Acknowledgments

The authors express sincere thanks to SAIF, NEHU, Shillong and SAIF, CDRI, Lucknow, India for providing analytical and spectral results.

## References

[1] V.K. Sivasubramanian, M. Ganesan, S. Rajagopal, R. Ramaraj. *J. Org. Chem.*, **67**, 1506 (2002).
[2] H. Fuijii, T. Kurahashi, M. Sugimoto, K. Oda, T. Ogura. *J. Inorg. Biochem.*, **96**, 133 (2003).
[3] R.B. Bedford, D.W. Bruce, R.M. Frost, J.W. Goodby, M. Hird. *Chem. Commun.*, 2822 (2004).
[4] K.P. Bryliakov, E.P. Talsi. *Angew. Chem. Int. Ed.*, 43, 5288 (2004).
[5] T. Katsuki. *Chem. Soc. Rev.*, **33**, 437 (2004).
[6] M.M. Bhadbhade, D. Srinivas. *Polyhedron*, **17**, 2669 (1998).
[7] S. Hayami, K. Inoue, Y. Maeda. *Mol. Cryst. Liq. Cryst.*, **334**, 1285 (1999).
[8] W. Chiang, D. Vanengen, M.E. Thompson. *Polyhedron*, **15**, 2369 (1996).
[9] C.T. Brewer, G. Brewer, G.B. Jameson, P. Kamaras, L. May, M. Rapta. *J. Chem. Soc., Dalton Trans.*, 37 (1995).
[10] H. Olmez, F. Arslan, H. Icbudak. *J. Therm. Anal. Calorim.*, **76**, 793 (2004).
[11] D. Czakis-Sulikowska, J. Radwanska-Doczekalska, A. Czylkowska, J. Gouchowska. *J. Therm. Anal. Calorim.*, **78**, 501 (2004).
[12] R. Carballo, A. Castineiras, S. Balboa, B. Covelo, J. Niclós. *Polyhedron*, **21**, 2811 (2002).
[13] J.B. Vincent, H.L. Tsai, A.G. Blackman, S. Wang, P.D.W. Boyd, K. Folting, J.C. Huffman, E.B. Lobkovsky, D.N. Hendrickson, G. Christou. *J. Am. Chem. Soc.*, **115**, 12353 (1993).
[14] C. Kaes, A. Katz, M.W. Hosseini. *Chem. Rev.*, **100**, 3553 (2000).
[15] G. Psomas, C. Dendrinou-Samara, P. Philippakopoulos, V. Tangoulis, C.P. Raptopoulou, E. Samaras, D.P. Kessissoglou. *Inorg. Chim. Acta*, **272**, 24 (1998).
[16] P. Losier, M.J. Zaworotka. *Angew. Chem. Int. Ed. Engl.*, **35**, 2779 (1996).
[17] R. Kruszynski, B. Kuznik, T.J. Bartczak, D. Czakis-Sulikowska. *J. Coord. Chem.*, **58**, 165 (2005).
[18] J.-M. Li, Y.-G. Zhang, J.-H. Chen, L. Rui, Q-M. Wang, X.-T. Wu. *Polyhedron*, **19**, 1117 (2000).
[19] J.H. Liao, S.H. Cheng, C.T. Su. *Inorg. Chem. Commun.*, **5**, 761 (2002).
[20] A. Saxena, J.K. Koacher, J.P. Tandon. *Inorg. Nucl. Chem. Lett.*, **17**, 229 (1981).
[21] P.G. Cozzi. *Chem. Soc. Rev.*, **33**, 410 (2004).
[22] S.K. Edulji, S.T. Nguyen. *Organometallics*, **22**, 3374 (2009).
[23] J.A. Miller, W. Jin, S.T. Nguyen. *Angew. Chem. Int. Ed.*, **41**, 2953 (2002).
[24] C. Celic, M. Tumer, S. Serin. *Synth. React. Inorg. Met-Org. Chem.*, **32**, 1839 (2002).
[25] M.T. Kaczmarck, I. Pospieszna-Markiewick, W. Radecka-Paryzek. *J. Inclustion Phenom. Macrocyclic Chem.*, **49**, 115 (2004).
[26] S. Ilhan, H. Temel, A. Kilic, E. Tas. *J. Coord. Chem.*, **61**, 1443 (2008).
[27] S. Chandra, R. Kumar. *Synth. React. Inorg. Met-Org. Chem.*, **35**, 161 (2005).
[28] S. Ilhan, H. Temel, I. Yilmaz, A. Kilic. *Transition Met. Chem.*, **32**, 344 (2007).
[29] S.K. Gupta, P.B. Hitchcock, Y.S. Kushwah. *J. Coord. Chem.*, **55**, 1401 (2002).
[30] C. Che, J. Huang. *Coord. Chem. Rev.*, **247**, 97 (2003).
[31] F. Marchetti, C. Pettinary, R. Pettinary, A. Cingolari, D. Leonesi, A. Lorenzotti. *Polyhedron*, **18**, 3041 (1999).
[32] M. Bagherzadeh, M. Amini. *Inorg. Chem. Commun.*, **12**, 21 (2009).
[33] K. Shanker, P.M. Reddy, R. Rohini, Y. Ho, V. Ravinder. *J. Coord. Chem.*, **62**, 2388 (2009).
[34] A.A. Nejo, G.A. Kolawole, A.R. Opoku, C. Muller, J. Wolowska. *J. Coord. Chem.*, **62**, 3411 (2009).
[35] Y. Nishida, S. Oshio, S. Kida. *Chem. Lett.*, 79 (1975).
[36] Y. Nishida, S. Oshio, S. Kida. *Bull. Chem. Soc. Jpn.*, **50**, 119 (1975).
[37] G.A. Kolawole, A.A. Osowok. *J. Coord. Chem.*, **62**, 1437 (2009).
[38] K.C. Gupta, H.K. Abdulkadir, S. Chad. *J. Appl. Polym. Sci.*, **90**, 1398 (2003).

[39] C.R. Mayer, G. Cucchiaro, J. Jullien, F. Dumur, J. Marrot, E. Dumas, F. Secheresse. *Eur. J. Inorg. Chem.*, 3614 (2008).

[40] G. Hu, Z. Feng, J. Li, G. Jia, D. Han, Z. Liu, C. Li. *J. Phys. Chem.*, **111**, 11267 (2007).

[41] B. Chiswell, J.P. Crawford, E.J. O'Reilly. *Inorg. Chim. Acta*, **40**, 223 (1980).

[42] N. Nawar, N.M. Hosny. *Transition Met. Chem.*, **25**, 1 (2000).

[43] N. Raman, S. Ravichandran, C. Thangaraja. *J. Chem. Sci.*, **116**, 215 (2004).

[44] M.X. Li, G.Y. Xie, Y.D. Gu, J. Chen, P.J. Zheng. *Polyhedron*, **14**, 1235 (1995).

[45] M.S. Shongwe, B.A. Al-Rashdi, H. Adams, M.J. Morris, M. Mikuriya, G.R. Hearne. *Inorg. Chem.*, **46**, 9558 (2007).

[46] M.I. Davis, A.M. Orville, F. Neese, J.M. Zaleski, J.D. Lipscomb, E.I.J. Solomon. *J. Am. Chem. Soc.*, **124**, 602 (2002).

[47] S.N. Rao, K.N. Munshi, N.N. Rao, M.M. Bhadbhade, E. Suresh. *Polyhedron*, **18**, 2491 (1999).

[48] G. Prabusankar, G. Ashok, N. Sengottuvelan, D. Saravanakumar, V. Narayanan, M. Kandaswamy. *Indian J. Chem. Tech.*, **9**, 9 (2002).

[49] A. Bajpai, S. Rai. *J. Appl. Polym. Sci.*, **69**, 751 (1998).

[50] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).

[51] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *Gaussian 03, Revision D.01*, Gaussian, Wallingford, CT (2004).

[52] C.J. Cramer. *Essentials of Computational Chemistry*, John Wiley and Sons, West Sussex, England (2004).

[53] N. Sundaraganesan, B.W. Joshua, C. Meghanathan, S. Sebastian. *Ind. J. Chem.*, **47**, 821 (2008).

[54] D. Kalita, R.C. Deka, N.S. Islam. *Inorg. Chem. Commun.*, **10**, 45 (2007).

[55] I. Bytheway, M.W. Wong. *Chem. Phys. Lett.*, **282**, 219 (1998).

[56] F.R. Perez, L. Basaez, J. Belmar, P. Vanysek. *J. Chil. Chem. Soc.*, **50**, 575 (2005).