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X-ray structures of iron(III) and cobalt(III) complexes containing 2-*S*-methyl-6-methyl-4-formylpyrimidine-*N*(4)-ethylthiosemicarbazone

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Abstract Iron(III) and cobalt(III) complexes of types $[Fe(LEt)_2]ClO_4 \cdot 3/2C_6H_6$ (**1**) and $[Co(LEt)_2]ClO_4 \cdot 2CH_2Cl_2$ (**2**) with a new pyrimidine-derived thiosemicarbazone ligand, 2-*S*-methyl-6-methyl-4-formylpyrimidine-*N*(4)-ethylthiosemicarbazone (HLEt), having *N*, *N*, *S* donor centers have been synthesized and characterized by X-ray crystallography. The structural study shows distorted octahedral geometry for both **1** and **2** with MN_4S_2 chromophores. The space group of **1** is $C2/c$ (monoclinic) and that of **2** is $P2_12_12_1$ (orthorhombic). The electrochemical electron transfer study in MeCN solutions shows a one-electron reductive response presumably due to a metal(III)–metal(II) couple.

Keywords Pyrimidine thiosemicarbazone · Iron(III)/cobalt(III) complex · Crystal structures · Redox behavior

Introduction

Transition metal complexes of ligands containing sulphur and nitrogen donors are found to constitute the active centers of several oxidoreductases such as hydrogenase, xanthine-oxidase and nitrogenase [1, 2]. Synthesis, characterization and structure and reactivity studies of such complexes with *N*, *S* and *N*, *N*, *S* donor sets lead to valuable information toward understanding the functions of different enzymes at the molecular level [1]. Most of such studies have largely been concentrated on various pyridine-derived ligands [3–8] and other heterocyclic thiosemicarbazones [9–16]. This work stems from our interest in exploring the chemistry of pyrimidine-based thiosemicarbazones with different transition metal ions. Nucleic acids, vitamins and coenzymes contain the pyrimidine ring system and provide potential binding sites for metal ions. The higher π-acidity [3, 4] and presence of more than one hetero atom in pyrimidine play an important role in their coordination chemistry compared to that of pyridine bases and serve as better models in biological systems [17–20]. We have successfully synthesized a new pyrimidine-derived thiosemicarbazone ligand, 2-*S*-methyl-6-methyl-4-formylpyrimidine-*N*(4)-ethylthiosemicarbazone (HLEt) and investigated its complexation behavior toward two 3d metal ions, iron(III) and cobalt(III). The present work describes the details of the synthesis, characterization, structure and properties of two complexes of the types $[Fe(LEt)_2]ClO_4 \cdot 3/2C_6H_6$ (**1**) and $[Co(LEt)_2]ClO_4 \cdot 2CH_2Cl_2$ (**2**).

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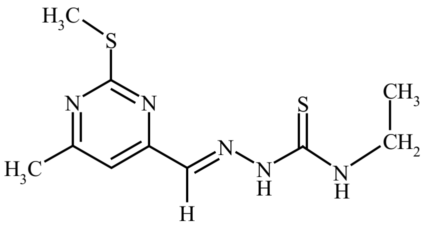


HLEt

Experimental

Materials

Ethyldiethoxyacetate and *N*(4)-ethyl-3-thiosemicarbazide, $CDCl_3$, d_6-DMSO were purchased from Aldrich and used as received. All other reagents and solvents were purchased from commercial sources and purified and dried by standard procedures [21]. 2-*S*-Methyl-6-methyl-4-formylpyrimidine was synthesized following a reported method [22]. $[Fe(DMSO)_6](ClO_4)_3$, used as a starting material in the synthesis of iron(III) complexes, was obtained by a literature procedure [23].

Physical measurements

Elemental analyses (C, H and N), solution electrical conductivity measurements (MeOH), IR spectra (KBr discs, 4000–200 cm^{-1}), ^1H NMR spectra (d_6-DMSO) and UV-Vis spectra (MeCN), as well as diffuse reflectance spectra, were done with a Perkin-Elmer Model 240 C CHN analyzer, a Systronics model 304 digital conductivity meter, a Jasco FTIR model 420 spectrophotometer, a Bruker AM300L (300 MHz) superconducting FT NMR and a Hitachi U-3501 spectrophotometer, respectively. Room temperature magnetic susceptibilities were measured with a PAR 155 vibrating sample magnetometer. Cyclic voltammetry (CV) experiments were carried out using Sycopel Model AEW2 1820F/S instrument. The measurements were performed at 300 K in a MeCN solution containing 0.2 M TEAP and 10^{-3}–10^{-4} M iron(III)/cobalt(III) complex, deoxygenated by bubbling with nitrogen. A platinum wire, a platinum coil and a SCE were used as a working, a counter and a reference electrodes, respectively.

Synthesis

2-S-Methyl-6-methyl-4-formylpyrimidine-N(4)-ethylthiosemicarbazone (HLEt)

This was prepared by refluxing a mixture of 2-*S*-methyl-6-methyl-4-formylpyrimidine (0.84 g, 5 mmol) and *N*(4)-ethyl-3-thiosemicarbazide (0.595 g, 5 mmol) in ethanol (75 cm^3) for 4 h. The resulting yellow solution was filtered and reduced to one-third of its original volume followed by cooling in refrigerator, yielding a light yellow powder of HLEt. The organic ligand was collected by filtration, washed with cold ethanol and dried over fused $CaCl_2$. Yield: 1.0 g (75%). The melting point of the recrystallized product was noted at 186–190°C. Anal. Calcd. for $C_{10}H_{15}N_5S_2$ (%): C, 44.6; H, 5.57; N, 26.02. Found (%): C, 44.9; H, 5.35; N, 26.73. ^1H NMR (d_6-DMSO, 300 MHz, 298 K): δ: 1.36 (s, 3H, CH_3-terminal), 2.51 (m, 3H, S–CH_3), 2.57 (m, 3H, Pym–CH_3), 3.8 (s, 2H, N–CH_2), 7.27 (s, 1H, Pym–C–*H*), 7.73 (s, 1H, –N=C–*H*), 9.9 (s, 1H, –NH). IR (ν, cm^{-1}): 3265–2979 (ν_{NH}), 1608 ($\nu_{CH=N}$), 1326, 1225 ($\nu_{C=S}$); 1049 (ν_{N-Npz}), 800 ($\nu_{C=S}$).

*Preparation of **1***

A solution of $[Fe(DMSO)_6](ClO_4)_3$ (0.82 g, 1 mmol) in hot ethanol (40 cm^3) was added dropwise to a stirred hot solution of HLEt (0.538 g, 2 mmol) in the same solvent (40 cm^3). The mixture was refluxed for 4 h resulting in a dark-red solution, which was filtered and kept for slow evaporation. The dark-brown product that precipitated out was filtered and washed with cold ethanol followed by drying over fused $CaCl_2$ and resulted pure **1**. Dark-red single crystals $[Fe(LEt)_2]ClO_4\cdot 3/2C_6H_6$ of **1** were obtained by slow diffusion of benzene into a MeCN solution of the complex. The crystals are unstable outside the mother liquor. Yield: 0.48 g (70%). Anal. Calcd. for $C_{20}H_{32}N_{10}O_4ClS_4Fe$ (**1**) (%): C, 34.71; H, 4.05; N, 20.25. Found (%): C, 34.63; H, 3.96; N, 20.08. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeOH): 80. μ_{eff} (at 298 K): 2.21 BM. Diffuse reflectance spectrum (DRS; λ_{max}, nm): 876, 616, 402. UV-Vis [MeCN, λ_{max}, nm (ε, M^{-1} cm^{-1})]: 827 (454), 608 (860), 393 (27, 112). IR (cm^{-1}): 3263, 2930, 1571, 1521, 1423, 1338, 1272, 1089(br), 879, 749, 682, 620, 569.

*Preparation of **2***

A solution of HLEt (0.538 g, 2 mmol) in hot ethanol (40 cm^3) was treated with a hot solution (20 cm^3) of $Co(ClO_4)_2\cdot 6H_2O$ (0.366 g, 1 mmol) in the same solvent and the resulting mixture was refluxed on steam-bath for 10 h. The deep red-brown solution thus formed was kept for slow evaporation for 3–4 days. A dark-brown compound separated out, was filtered off and washed with cold chloroform and dried over fused $CaCl_2$. X-ray quality single crystals of $[Co(LEt)_2]ClO_4\cdot 2CH_2Cl_2$ (**2**) were grown by the slow diffusion of *n*-hexane into a dichloromethane solution of the complex. The crystals are unstable outside the mother liquor.

Table 1 Crystal data and structure refinement for $[Fe(LEt)_2](ClO_4)\cdot 3/2C_6H_6$ (**1**) and $[Co(LEt)_2]\ ClO_4\cdot 2CH_2Cl_2$ (**2**)

	Compound **1**	Compound **2**
Empirical formula	$2(C_{20}H_{32}FeN_{10}S_4)$, $3(C_6H_6)$, $2(ClO_4)$	$C_{20}H_{32}CoN_{10}S_4$, $2(CH_2Cl_2)$, ClO_4
Formula weight	1626.60	869.07
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c* (No. 15)	$P2_12_12_1$ (No. 19)
Unit cell dimensions		
a (Å)	19.9982(9)	10.8439(1)
b (Å)	22.5597(10)	17.0762(2)
c (Å)	18.2249(8)	19.4498(3)
α (°)	90	90
β (°)	111.8195(10)	90
γ (°)	90	90
Volume (Å^3)	7633.2(6)	3601.57(8)
Z	4	4
D(calc) (g cm^{-3})	1.415	1.603
F (0 0 0)	3392	1784
μ(Mo Kα) (mm^{-1})	0.7	1.1
Crystal size (mm)	0.30 × 0.30 × 0.35	0.30 × 0.38 × 0.50
Temperature (K)	295	150
Radiation (Å)	Mo K$_\alpha$ 0.71073	Mo K$_\alpha$ 0.71073
Theta min–max (°)	1.4, 27.5	1.6, 27.5
Data set	−25:25; −29:28; −23:23	−14: 14; −17: 22; −25: 25
Tot. uniq. data, *R*(int)	37913, 8776, 0.054	31893, 8196, 0.043
Observed data [$I > 2\sigma(I)$]	5704	6858
N_{ref}, N_{par}	8776, 474	8196, 434
R, *wR*, *S*	0.0561, 0.1644, 1.02	0.0597, 0.1745, 1.02
Maximum and average shift/error	0.00, 0.00	0.00, 0.00
Minimum and maximum residual density (e A^{-3})	−0.53, 0.75	−0.66, 1.14

Note. $w = 1/[\sigma^2 F_o^2) + (0.0868P)^2 + 5.6030P]$ for **1**,$w = 1/[\sigma^2(F_o^2) + (0.1105P)^2 + 3.9769P]$ for **2** [where $P = (F_o^2 + 2F_c^2)/3$]

Yield: 0.52 g (60%). Anal. Calcd. for $C_{22}H_{36}N_{10}O_4Cl_5S_4Co$ (**2**) (%): C, 34.56; H, 4.03; N, 20.16. Found (%): C, 34.60; H, 4.17; N, 20.01. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeOH): 88. μ_{eff} (at 298 K): 0.00 BM. DRS ($\lambda_{\max}$, nm): 680, 480, 415. UV-Vis [MeOH, $\lambda_{\max}$, nm (ε, M^{-1} cm^{-1})]: 413 (27,653). IR (cm^{-1}): 3289, 3216, 2972, 1582, 1534, 1422(br), 1323, 1269, 1082(br), 874, 746, 620, 569.

Crystallographic data collection and refinement

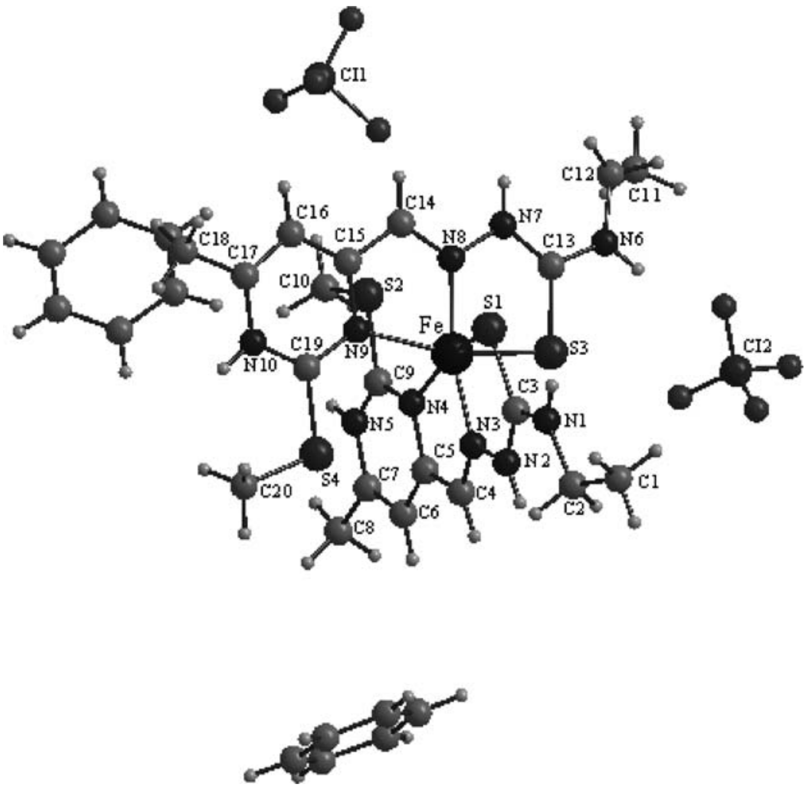
Relevant crystallographic data are listed in Table 1. Intensity data for **1** were measured on a Bruker SMART APEX CCD diffractometer and the same for **2** were measured on a NONIUS Kappa-CCD diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω–2θ scan mode. These were corrected for Lorentz-polarization effects. The structures were solved by using SHELXS-97 package of programme and refined by full-matrix least-squares technique based on F^2 (SHELXL-97). Hydrogen atoms were added in the calculated positions.

Discussion of results

Description of crystal structures

The structure of **1** and **2** with the atom numbering scheme are represented in Figs. 1 and 2, respectively. The positional parameters are listed in Table 1. The bond lengths and angles are given in Table 2. The structure, in each case, contains an $[M(LEt)_2]^+$ cation and a $ClO_4{}^-$ anion. The metal ion is octahedrally coordinated by the two tridentate NNS ligands. Two ligands have undergone chelation in which thiolato sulphur atoms are positioned *cis* to each other. The pyrimidine nitrogen atoms also lie in mutually *cis* positions. The coordination sphere around the metal is completed by azomethine nitrogen atoms occupying the other two sites (*trans* to each other). The mutual disposition of the donor sets is *meridional*. The coordination is via the pyrimidyl nitrogen atoms [N(4), N(9) for **1** and N(1), N(6) for **2**], the azomethine nitrogen atoms [N(3), N(8) for both] and the thiolato sulphur atoms [S(1), S(3) for **1** and S(2), S(4) for **2**]. The pyrimidyl nitrogen [N(9)], the thiolato sulphur [S(3)] and two azomethine nitrogen atoms [N(3), N(8)] in **1** are nearly planar, whereas pyrimidyl

Fig. 1 Molecular structure of **1**



nitrogen [N(6)], the thiolato sulphur [S(4)] and two azomethine nitrogen atoms [N(3), N(8)] in **2** are planar. The N–M–N, N–M–S and S–M–S angular distributions indicate that the coordination polyhedron is distorted. This distortion in metal ion coordinated polyhedron results from steric interactions. The maximum distortions from the ideal octahedral geometry occur for N(3)–Fe–N(4) [80.21(1)°], N(3)–Fe–N(9) [109.24(1)°] and S(1)–Fe–N(4) [162.83(8)°] in **1** and for N(3)–Co–N(1) [81.19(1)°], N(3)–Co–N(6) [107.93(1)°] and N(1)–Co–S(2) [165.27(1)°] in **2**. Similar distortions have been reported in [24]. Four five-membered chelate rings are formed because of encapsulation of the metal atom by the coordination of six donor atoms from two ligand molecules. In each ligand molecule, the chelate rings and the pyrimidine ring lie nearly in the same plane. The pyrimidine ring, thus, makes an extended coplanar system with the two chelate rings. This extended coplanar ring system of the two ligands approach each other orthogonally, as is evident from the analysis of the dihedral angles [84.63(7)° for **1** and 88.11(7)° for **2**]. Deprotonation of the ligand accompanied by tautomerisation generates the iminothiolate form and the negative charge so formed is delocalized in the C–N–N–C system, as is reflected by their intermediate bond distances (Table 2). These values compare well with those of other six-coordinate Co(III) complexes of related NNS donor ligands [25]. The C–S bond distances [ca. 1.750(4) Å for **1** and ca. 1.749(5) Å for **2**] appear to be longer than those reported for free thiosemicarbazones 1.678(2) Å in 4-formylpyridinethiosemicarbazone [26]; 1.684(4) Å in 2-keto-3-ethoxybutyraldehyde-bis(thiosemicarbazone) [27]). The lengthening of the C–S bonds is attributed to the enethiolization process that occurs prior to coordination of the ligand.

Electronic spectra

Spectral (diffuse reflectance and solution) data are dominated by various $\pi \rightarrow \pi^*$ transitions of the ligand. There is no significant difference between the spectral results obtained in solid and in solution phases, reflecting similar gross geometric and electronic structures in solid state as well as in

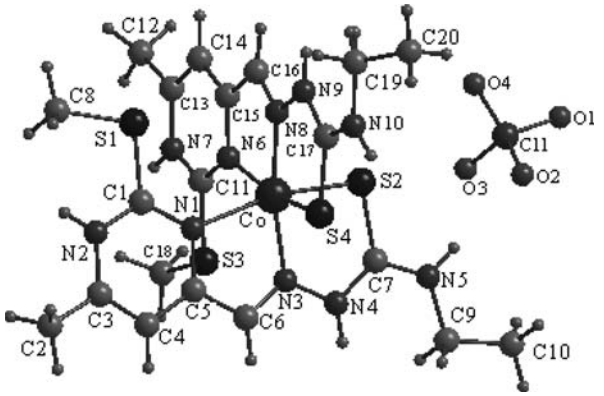


Fig. 2 Molecular structures of **2**

Table 2 Bond lengths (Å) and bond angles (°) of **1** and **2**

Compound **1**		Compound **2**	
Fe–S(1)	2.2078(10)	Co–N(8)	1.903(4)
Fe–S(3)	2.1928(11)	Co–N(6)	2.025(4)
Fe–N(3)	1.928(3)	Co–S(4)	2.2135(13)
Fe–N(4)	2.051(3)	Co–N(3)	1.916(4)
Fe–N(8)	1.921(3)	Co–N(1)	2.045(4)
Fe–N(9)	2.059(2)	Co–S(2)	2.2186(13)
C(3)–S(1)	1.750(4)	N(3)–N(4)	1.354 (6)
C(13)–S(3)	1.751(4)	N(8)–N(9)	1.363 (8)
C(3)–N(2)	1.312(4)	C(6)–N(3)	1.281 (6)
N(2)–N(3)	1.356(4)	C(16)–N(8)	1.306 (7)
N(3)– C(4)	1.298(4)	N(4)–C(7)	1.312 (7)
C(4)–C(5)	1.437(5)	N(9)–C(17)	1.316 (8)
C(13)–N(7)	1.300(5)	C(7)–S(2)	1.746(5)
N(7)–N(8)	1.358(4)	C(17)–S(4)	1.753(6)
N(8)– C(14)	1.295(5)	N(8)–Co–N(3)	168.34(17)
C(14)–C(15)	1.435(5)	N(3)–Co–N(6)	107.93(16)
S(1)–Fe–S(3)	96.99(4)	N(3)–Co–N(1)	81.19(17)
S(1)–Fe–N(3)	84.43(9)	N(8)–Co–S(4)	84.59(14)
S(1)–Fe–N(4)	162.83(8)	N(6)–Co–S(4)	166.15(12)
S(1)–Fe–N(8)	88.25(9)	N(8)–Co–S(2)	88.88(13)
S(1)–Fe–N(9)	88.48(8)	N(6)–Co–S(2)	89.41(12)
S(3)–Fe–N(3)	86.32(9)	S(4)–Co–S(2)	92.70(5)
S(3)–Fe–N(4)	89.69(9)	N(8)–Co–N(6)	81.76(18)
S(3)–Fe–N(8)	84.89(9)	N(8)–Co–N(1)	105.66(17)
S(3)–Fe–N(9)	164.00(8)	N(6)–Co–N(1)	90.45(16)
N(3)–Fe–N(4)	80.21(11)	N(3)–Co–S(4)	85.90(12)
N(3)–Fe–N(8)	167.79(12)	N(1)–Co–S(4)	90.95(12)
N(3)–Fe–N(9)	109.24(12)	N(3)–Co–S(2)	84.85(13)
N(4)–Fe–N(8)	108.16(12)	N(1)–Co–S(2)	165.27(12)
N(4)–Fe–N(9)	89.37(11)		
N(8)–Fe–N(9)	80.25(12)		

solution. Bands at ca. 610 and ca. 400 nm in **1** are due to metal-to-ligand (d→π^*) bands as well as S→Fe(III) transitions, respectively. The bands at ca. 876 and ca. 827 nm are assigned to d–d transitions of the spin-paired d^5 iron(III) ions [28, 29].

DRS of **2** exhibits a broad band at ca. 415 nm with two distinct shoulders at the low-energy side (at ca. 480 and ca. 680 nm). The broad band is due to the S→Co(III) charge transfer transition, as is also evident from the solution spectral study. The other two bands may be assigned as $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ transitions, respectively [25]. In methanolic solution, it displays S→Co(III) charge transfer transition (LMCT) at 413 nm (ε, 27,653 L mol^{-1} cm^{-1}) without any d–d bands. The absence of the latter may presumably be due to the intrusion of trails of intense CT bands into the visible portion of the spectrum, which obscures the weaker d–d bands [25, 29].

Redox behavior

The electro activity of the complexes was examined in MeCN solutions using CV at platinum electrode. The complexes show (Table 3) a nearly reversible reductive response (Fig. 3a and b), owing probably to a metal(III)–metal(II) couple [30]. In variable scan cyclic voltammograms, i_{pc}/i_{pa} ratio is nearly equal to unity, reflecting gross similar solution structure of the electroreduced product and the original compound.

Table 3 cyclic voltammogram data of Fe(III) and Co(III) complexes in acetonitrile solution containing tetraethyl ammonium perchlorate at RT

Complex	E_{pc}(V)	E_{pa}(V)	ΔEp(V)	$E_{1/2}$(V)
$[Fe(LEt)_2](ClO_4)\cdot 3/2C_6H_6$	−0.0791	0.0115	0.0906	−0.0338
$[Co(LEt)_2]ClO_4\cdot 2CH_2Cl_2$	−0.3987	−0.2938	0.1049	−0.3463

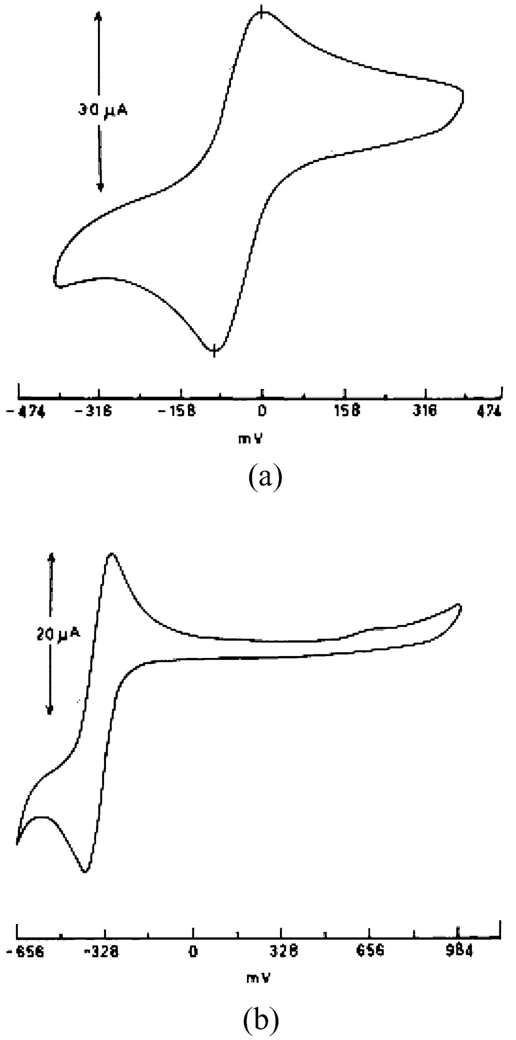


Fig. 3 **a** Cyclic voltammogram of **1**. **b** Cyclic voltammogram of **2**. This was recorded with a scan rate 100 mV s^{-1}. All potentials are given vs SCE. All measurements have been carried out in TEAP/CH_3CN at 293 K

Conclusion

HLEt with hard (N) and soft (S) donor sites acts as a monoanionic *N,N,S* tridentate ligand through deprotonation of one proton and forms bis-chelates with hard metal ions like iron(III) and cobalt(III) having gross octahedral geometry. The deprotonation accompanied with tautomerisation produces a delocalised ring system with overall intermediate interatomic bond distances on the ligand network. A nearly reversible one-electron reductive response in both complexes is in line with similar gross solution structure of the electroreduced products.

Supplementary data

Crystallographic data for the structural analyses have been deposited with CCDC Nos. 262069 for **1** and 262070 for **2**. These can be obtained free of charge at CCDC Home Page: http://www.ccdc.cam.ac.uk or from Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK; Tel. +44-1223 336031, fax +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk.

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