ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 7, pp. 526–533. © Pleiades Publishing, Ltd., 2009.

Synthesis and Spectroscopic Characterization of New Iron(III) Complexes of S-Alkyl/Aryl Dithiocarbazates of 5-Methyl–3-Formylpyrazole and 5-Methyl–3-Formylpyrazolyl-Thiosemicarbazones[1]

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Received August 05, 2008

Abstract—New iron(III) complexes of S-methyl-β-N-(5-methylpyrazole-3-yl)methylenedithiocarbazate, S-benzyl-β-N-(5-methylpyrazole-3-yl)methylenedithiocarbazate, 5-methyl-3-formylpyrazole-3-pyrrolidinylthiosemicarbazone, and 5-methyl-3-formylpyrazole-^{4}N-benzylthiosemicarbazone have been synthesized and physicochemically characterized by elemental analyses, magnetic moment measurements (polycrystalline state), electronic, IR, and EPR spectra, as well as conductance measurements, are used to confirm the coordination geometry. The spectral studies reveal the low-spin distorted octahedral structure of the iron(III) complexes containing two uninegative tridentate ligands with NNS donor sites, where the EPR data confirm the presence of a spin-paired iron(III) with d_{xz}^2 d_{yz}^2 d_{xy}^1 configuration in the ground state.

DOI: 10.1134/S1070328409070100

INTRODUCTION

N-Heterocyclic thiosemicarbazones, as well as S-alkyl/aryl dithiocarbazates and their metal complexes, are important due to their biological activities [1, 2]. Thiosemicarbazones and dithiocarbazates derivatives have attracted considerable interest in chemistry and biology due to their antitumor [3], antiviral [4], antibacterial [5], antimalarial [6, 7], antineoplastic [8], and antiamoebic [9] activities. The iron and copper complexes show antitumor activity by inhibiting ribonucleotide diphosphate reductase, an obligatory enzyme in the pathway of synthesis of precursors of DNA [10, 11]. The non-heme iron subunit has been shown to be inhibited/inactivated by thiosemicarbazones [12]; the ability to provide this inhibitory action is thought to be due to coordination of iron via their NNS tridentate ligating system, either by a preformed iron complex binding to the enzyme, or by the free ligand complexing with iron-charged enzyme [13, 14]. Iron(III) complexes have been shown to be more active in cell destruction, as well as in the inhibition of DNA synthesis than the uncomplexed thiosemicarbazones [15]. The success in therapeutic applications of several heterocyclic thiosemicarbazones [14, 16, 17] for removing excess iron from iron-loaded mice through chelation therapy is also remarkable. These observations have accelerated further research in this specific area. In continuation of our earlier report on the iron(III) complexes [18–20] and related publications on the metal ion complexes of pyrazolyl thiosemicarbazones and dithiocarbazates [21–23], the present communication reports the synthesis and spectroscopic characterization of a series of new iron(III) complexes of S-methyl-β-N-(5-methylpyrazole–3-yl)methylenedithiocarbazate (**HMPzSM**), S-benzyl-β-N-(5-methylpyrazole–3-yl)methylenedithiocarbazate (**HMPzSB**), 5-methyl–3-formylpyrazole–3-pyrrolidinylthiosemicarbazone (**HMPzPy**), and 5-methyl–3-formylpyrazole-^{4}N-benzylthiosemicarbazone (**HMPzNB**). Ligand in thione-thiol forms are shown below:

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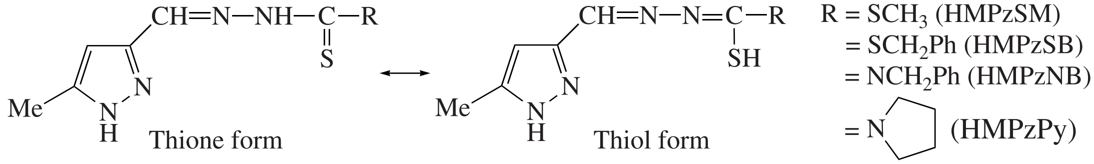
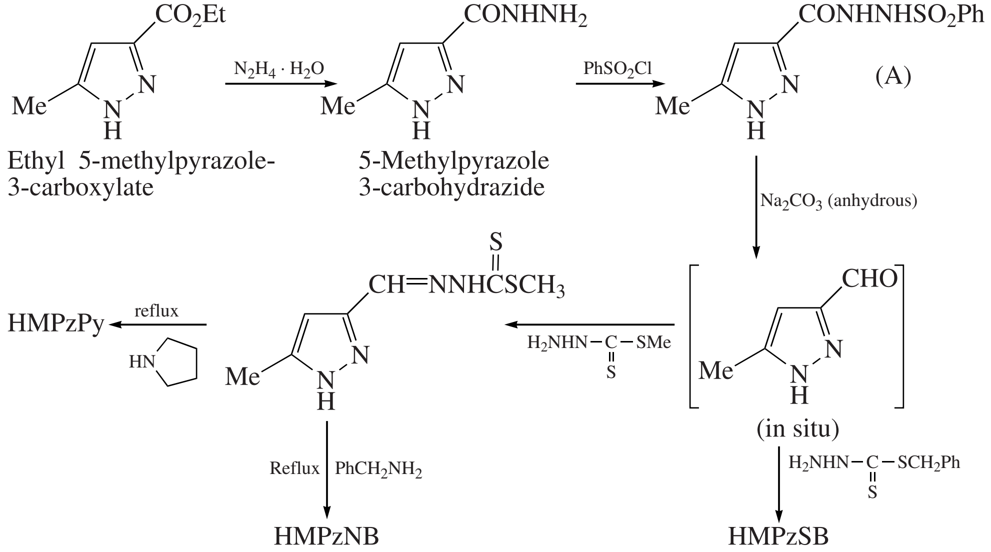
† Deceased.



EXPERIMENTAL

Reagents. All the materials used at different stages for the preparation of the ligands and the reported iron(III) complexes were GR/AR quality and used without further purification. Solvents were reagent grade chemicals and distilled before use.

Synthesis of ligands. The ligands were synthesized and characterized by us earlier [22, 23]. The reaction detail of ligands synthesis was given below for ready reference:



Briefly, the ligands HMPzSM and HMPzSB were prepared by dissolving 5.0 g (17 mmol) of the benzenesulfonyl derivative of 5-methylpyrazole–3-carbohydrazide (**A**) in 20 ml of ethylene glycol at 120–130°C, and the resulting solution was heated to ~160°C followed by the addition of 3.0 g of anhydrous Na_2CO_3 causing brisk effervescences. When the effervescences ceased, the solution was filtered. To the filtrate 2.44 g (20 mmol) of S-methyl dithiocarbazate (for HMPzSM) or 3.96 g (20 mmol) of S-benzyl dithiocarbazate (for HMPzSB) was added with stirring. To this solution hot water (36 ml) was added with constant stirring. A light yellow solid in each case was separated out by filtration, and washed with water (20 ml). The ligands HMPzPy and HMPzNB were synthesized from HMPzSMe by the transamination-like reaction. The recrystallized HMPzSM (1 mmol, 0.214 g) in 30 ml of ethanol when refluxed with freshly distilled pyrrolidine (1 mmol, 0.071 g) (for HMPzPy) or with benzylamine (1 mmol, 1.07 g) (for HMPzNB) for 12 h at water bath temperature afforded expected ligands. S-Methyl dithiocarbazate and S-benzyl dithiocarbazate are prepared according to the literature method [24].

Synthesis of complexes was carried out for the molar ratio 2 : 1 ligand to metal salt maintained in all the preparations.

Synthesis of $[Fe(MPzSMe)_2]Cl$ and $[Fe(MPzSB)_2]Cl$. Hydrated iron(III) chloride (2 mmol, 0.54 g) was dissolved in a minimum quantity of aqueous ethanol (15 ml) containing 0.5 ml of dilute HCl to have a clear solution. This was then mixed with a dry ethanolic solution (30 ml) of the ligand (4 mmol). The resulting solution was then stirred at water bath temperature for 30 min and concentrated at room temperature to have deep brown crystals of the desired complexes. This was then in each case filtered off, washed with cold ethanol, and dried in a desiccator over fused $CaCl_2$. The yields were 0.642 g (62.04%) and 0.891 g (66.99%) for $[Fe(MPzSMe)_2]Cl$ and $[Fe(MPzSB)_2]Cl$, respectively. The compounds are soluble in common polar solvents like methanol, ethanol, DMF, and DMSO and partially soluble in ether, benzene, and chloroform.

Synthesis of $[Fe(MPzSMe)_2]ClO_4$ and $[Fe(MPzSB)_2]ClO_4$. $Fe(ClO_4)_3 \cdot 6H_2O$ (2 mmol, 0.92 g) dissolved in a minimum quantity of dry ethanol (10 ml) was added at a time to a dry ethanolic solution (30 ml) of S-alkyl/aryl dithiocarbazate (4 mmol). The resulting brown solution was then stirred for 1 h at water bath temperature, and the solid thus obtained was filtered off, washed with cold ethanol, and dried over anhydrous $CaSO_4$ in vacuo. The yields were 0.754 g (65%) and 0.963 g (65.95%) for $[Fe(MPzSMe)_2]ClO_4$ and $[Fe(MPzSB)_2]ClO_4$, respectively. The compounds are soluble in common polar solvents like methanol, ethanol, DMF, and DMSO and partially soluble in ether, benzene, and chloroform.

Synthesis of $[Fe(MPzSMe)_2]SCN$ and $[Fe(MPzSB)_2]SCN$. To a solution of $FeCl_3 \cdot 6H_2O$ (2 mmol, 0.54 g) in aqueous ethanol (10 ml) containing 0.5 ml of dilute HCl was added a solution of the ligand (0.004 mol) in dry ethanol (40 ml). The resulting mixture was stirred for 1 h at water bath temperature, a solution of 1M KSCN (5 ml) was then added to the mentioned mixture, and stirring was continued for 1 h. Slow evaporation of the solution at room temperature furnished reddish brown crystals, which were filtered off, washed with cold ethanol, and dried over fused $CaCl_2$. The yields were 0.538 g (54.48%) and 0.686 g (49.7%) for $[Fe(MPzSMe)_2]SCN$ and $[Fe(MPzSB)_2]SCN$, respectively. The compounds are soluble in common polar solvents like methanol, ethanol, DMF, and DMSO and also soluble in ether, benzene, and chloroform.

Synthesis of $[Fe(MPzPy)_2]Cl$ and $[Fe(MPzNB)_2]Cl$. Hydrated iron(III) chloride (2 mmol, 0.54 g) was dissolved in a minimum quantity of water containing a little amount of dilute hydrochloric acid to have a clear solution. This was then mixed with ethanolic solution (40 ml) of the ligand (4 mmol). The resulting mixture was stirred for ~4 h and then left at room temperature for slow evaporation finally to have brown crystals of the desired complexes. The product, in each case, was washed with cold ethanol and dried in a desiccator over anhydrous $CaCl_2$. The yields were 0.6944 g (62%) and 0.736 g (57.95%) for $[Fe(MPzPy)_2]Cl$ and $[Fe(MPzNB)_2]Cl$, respectively. The compounds are soluble in common polar solvents like methanol, ethanol, DMF, and DMSO and partially soluble in ether, benzene, and chloroform.

Synthesis of $[Fe(MPzPy)_2]ClO_4$ and $[Fe(MPzNB)_2]ClO_4$. Hexahydrated iron(III) perchlorate (2 mmol, 0.92 g) dissolved in a minimum quantity of dry ethanol (10 ml) was added to a hot ethanolic solution (40 ml) of thiosemicarbazone (4 mmol). The resulting solution, in each case, was refluxed for 10 h, and the solid thus obtained was filtered, washed with cold ethanol, and dried over anhydrous $CaSO_4$ in vacuo. The yields were 0.820 g (65.6%) and 0.8787 g (63.21%) for $[Fe(MPzPy)_2]ClO_4$ and $[Fe(MPzNB)_2]ClO_4$, respectively. The compounds are soluble in common polar solvents like methanol, ethanol, DMF, and DMSO and partially soluble in ether, benzene, and chloroform.

Synthesis of $[Fe(MPzPy)_2]SCN$ and $[Fe(MPzNB)_2]SCN$. To a solution of hydrated iron(III) chloride (2 mmol, 0.54 g) in aqueous ethanol (20 ml) containing a minimum quantity of dilute HCl was added a solution of the ligand (4 mmol) in dry ethanol (50 ml). The resulting mixture was stirred for 1 h at water bath temperature, a solution of 1 M KSCN (25 ml) was added to the said mixture, and stirring was continued for 1 h. This was finally left at room temperature for slow evaporation, while a dark brown precipitate appeared, the desired compounds, in each case, were controlled as above. The yields were 0.544 g (46.49%) and 0.645 g (49.23%) for $[Fe(MPzPy)_2]SCN$ and $[Fe(MPzNB)_2]SCN$, respectively. The compounds are soluble in common polar solvents like methanol, ethanol, DMF, and DMSO and also soluble in solvent like ether, benzene, and chloroform.

Physical measurements. Elemental analyses were done with a Perkin Elmer CHNS/O analyzer 2400. The iron content of each of the complexes was estimated by the conventional method of volumetry using a standard potassium dichromate solution after decomposing the metal complex with a mixture of 1 : 1 perchloric acid and nitric acid. The molar conductance values of the complexes were measured in a methanolic solution with a systronic Model 304 digital conductivity meter. Magnetic measurements were made in the polycrystalline state on a PAR 155 vibrating magnetometer at 5500 G. The electronic spectra of the complexes in a DMF solution (~30°C) were recorded on a Hitachi model UV2000 spectrophotometer. The IR spectra (4000–200 cm^{-1}) were recorded on a Perkin Elmer model 833 infrared spectrometer using KBr pellets. The EPR spectra were recorded on a Varian model E–112 spectrophotometer (X-band) in the polycrystalline state at room temperature using DPPH ($g = 2.0036$) as a standard.

RESULTS AND DISCUSSION

Solid-state isolation and satisfactory results of elemental analysis, magnetic moment, conductance values, and spectral studies (Table 1) revealed that the complexes were of good purity. The molar conductivity values of $\sim 10^{-3}$ M solution in DMF/MeOH are quite close to those expected for 1 : 1 electrolytes. Various attempts to obtain single crystals have so far been unsuccessful.

A careful comparison of the IR spectral data of the iron(III) complexes (Table 2) with those of the ligands furnished considerable information regarding the bonding sites of the ligand molecule(s). The presence of a strong band at 1620 cm^{-1} for HMPzSM or at 1580 cm^{-1} for HMPzSB, or at 1570 cm^{-1} for HMPzPy, or at 1550 cm^{-1} for HMPzNB due to the presence of azome-

Table 1. Elemental analysis, conductance, magnetic moment and spectral data for the complexes

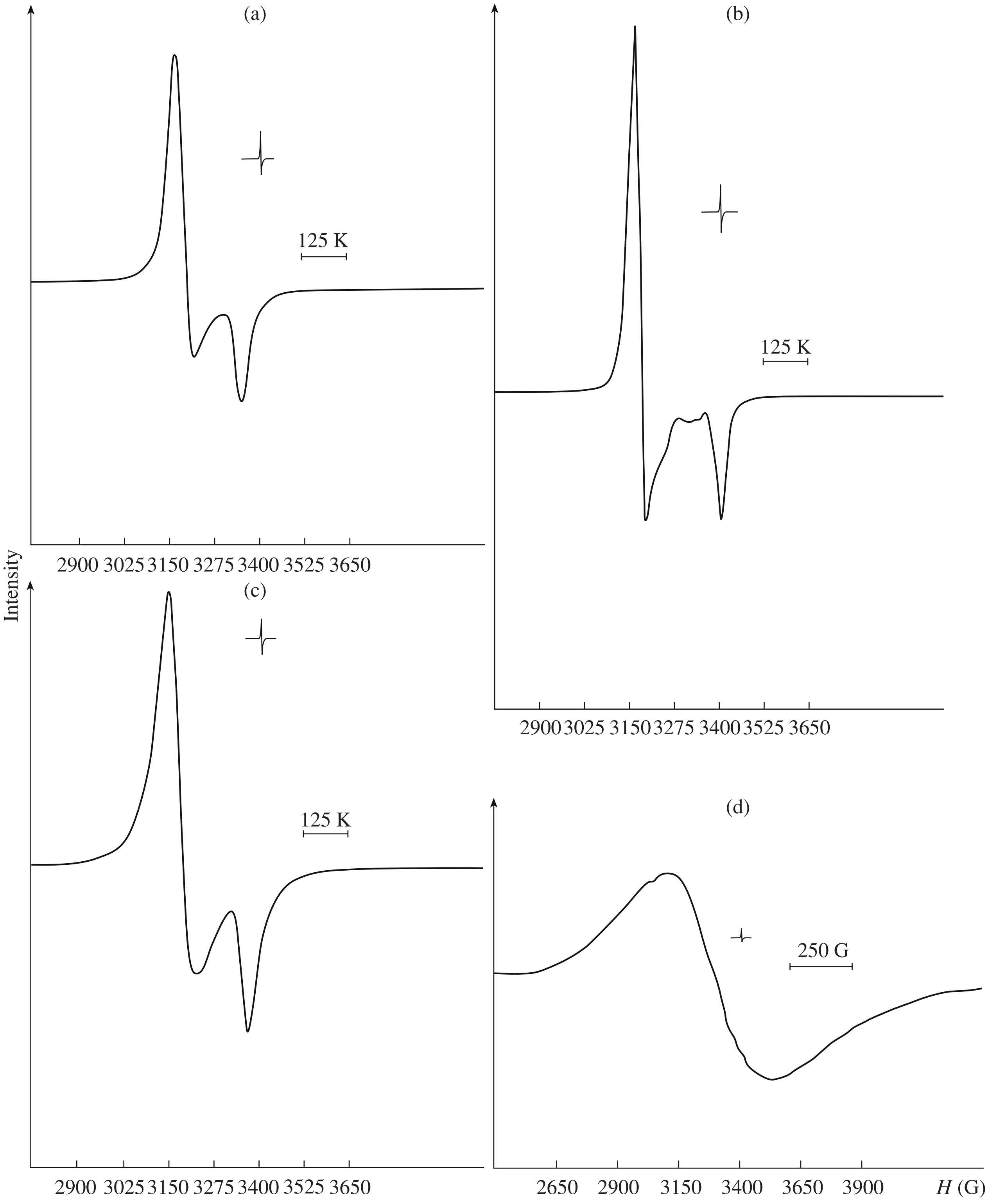
Complex (color)	Contents (found/calcd), %				μ_{eff}	Λ, $Ohm^{-1} cm^2 mol^{-1}$ in DMF (MeOH)	Spectral data		
	C	H	N	Fe			state of spectral study	wave numbers, cm^{-1} ($\log \varepsilon$) intraligand and charge transfer	$d \longrightarrow d$
$[Fe(MPzSM)_2]Cl$ (deep brown)	33.0/32.5	3.4/3.5	22.1/21.6	11.2/10.8	1.85	68.1 (87.7)	Solid Solution	22935(0.91), 19645(0.91) 31500(4.47), 23.720(2.71), 18.630(2.62)	11300(0.92) 11610(0.4)
$[Fe(MPzSM)_2]ClO_4$ (brown)	29.2/28.9	2.9/3.0	20.5/19.3	10.1/9.6	1.69	72.5 (91.1)	Solid Solution	24450(0.88), 20408(0.55), 16155(0.76) 30580(4.52), 23750(2.80), 19230(2.47)	10990(0.79) 11580(0.3)
$[Fe(MPzSM)_2]SCN$ (reddish brown)	33.0/33.3	3.4/3.3	21.0/20.8	10.6/10.3	1.84	78.2 (96.2)	Solid Solution	26500(0.90), 22520(0.80), 18400(0.60) 32360(4.52), 24095(4.06), 18348(3.31)	11560(0.6) 11570(0.64)
$[Fe(MPzSB)_2]Cl$ (deep brown)	46.79/46.6	3.9/3.9	17.7/16.7	8.7/8.3	1.78	82.1 (97.7)	Solid Solution	22935(0.99), 20000(0.99), 19645(0.99) 32470(5.21), 24095(4.70)	11390(0.99) 11587(0.99)
$[Fe(MPzSB)_2]ClO_4$ (dark brown)	42.7/42.5	3.4/3.5	16.5/15.3	7.9/7.6	1.81	80.2 (98.1)	Solid Solution	22780(0.8), 19250(0.7) 34480(3.82), 23530(3.33)	11680(0.8) 11630(0.95)
$[Fe(MPzSB)_2]SCN$ (reddish brown)	46.5/46.8	3.7/3.7	17.9/18.2	8.3/8.0	1.80	78.3 (86.6)	Solid Solution	22960(0.99), 19730(0.82) 34130(5.38), 23750(5.11)	11580(0.7) 11630(0.9)
$[Fe(MPzPy)_2]Cl$ (brown)	42.7/42.6	4.9/5.0	25.1/24.9	10.1/9.9	1.85	75 (85)	Solid Solution	19800(1.1), 16250(0.9) 31950(4.71), 20450(2.86),	10990(0.79) 11530(0.27)
$[Fe(MPzPy)_2]ClO_4$ (deep brown)	37.9/38.2	4.4/4.4	22.5/22.3	9.2/8.9	1.73	77 (89)	Solid Solution	19762(1.0), 16130(0.91) 31800(4.36), 20400(3.25), 16800(2.85)	11820(0.85) 11980(0.3)
$[Fe(MPzPy)_2]SCN$ (reddish brown)	42.8/43.0	4.9/4.8	26.6/26.3	9.9/9.5	1.85	73 (91)	Solid Solution	20720(1.1), 18560(0.9) 31780(4.89), 22600(2.76), 20.340(2.55)	11570(0.3) 11660(0.3)
$[Fe(MPzNB)_2]Cl$ (brown)	49.3/49.3	4.0/4.1	22.5/22.1	9.1/8.8	1.89	72 (88)	Solid Solution	20200(1.1), 16780(0.8) 31900(4.28), 20660(2.71), 17200(2.61)	11740(0.3) 11760(0.3)
$[Fe(MPzNB)_2]ClO_4$ (deep brown)	44.9/44.7	3.9/3.7	20.4/20.0	8.3/8.0	1.75	78 (90)	Solid Solution	20600(0.92), 18250(0.7) 32470(4.37), 20450(2.82), 18691(2.78)	11630(0.2) 11535(0.5)
$[Fe(MPzNB)_2]SCN$ (brown)	49.2/49.4	4.0/3.9	23.8/23.5	8.4/8.5	1.81	78 (91)	Solid Solution	21320(1.1), 18100(0.9) 31690(4.31), 21730(2.77), 17690(2.68)	11710(0.3) 11560(0.5)

Table 2. Some characteristic IR bands (cm^{-1}) of the ligands and their iron(III) complexes

Compound	ν(CH=N(Pz))	ν(CH=N(azom)	ν(N–N(Pz))	ν(C=S)	ν(Fe–N(azom))	ν(Fe–N(Pz))	ν(Fe–S)
HMPzSM	1410	1620	1030	830			
$[Fe(MPzSM)_2]Cl$	1430	1575	1060	810	475	270	360
$[Fe(MPzSM)_2]ClO_4$	1440	1580	1060	810	480	280	375
$[Fe(MPzSM)_2]SCN$	1430	1580	1060	800	490	275	370
HMPzSB	1618	1580	1015	850			
$[Fe(MPzSB)_2]Cl$	1670	1560	1060	825	470	265	345
$[Fe(MPzSB)_2]ClO_4$	1665	1575	1065	820	470	275	360
$[Fe(MPzSB)_2]SCN$	1660	1575	1060	810	480	280	350
HMPzPy	1440	1570	1010	860			
$[Fe(MPzPy)_2]Cl$	1490	1560	1050	800	490	330	390
$[Fe(MPzPy)_2]ClO_4$	1480	1560	1040	800	480	350	400
$[Fe(MPzPy)_2]SCN$	1460	1540	1040	820	495	320	400
HMPzNB	1508	1550	1010	800			
$[Fe(MPzNB)_2]Cl$	1580	1540	1040	760	480	290	370
$[Fe(MPzNB)_2]ClO_4$	1580	1530	1040	750	490	280	360
$[Fe(MPzNB)_2]SCN$	1570	1540	1040	760	490	290	380

thine linkage (CH=N) shifted to lower frequency by 10–40 cm^{-1} in their respective iron(III) complexes. These data indicate that the nitrogen atom of azomethine function in the respective ligand molecule was involved in bonding to Fe(III). An intense band at 830 cm^{-1} for HMPzSM or at 850 cm^{-1} for HMPzSB, or at 860 cm^{-1} for HMPzPy, or at 800 cm^{-1} for HMPzNB was due to ν(C=S), which was shifted to lower frequency by 20–60 cm^{-1}; pointing to the formation of a C–S–Fe(III) via the deprotonated thiol group (SH) from the thiol form of the ligand(s) during complexation [25]. The positive shifts of the ν(N–N(Pz)) frequencies (1030 cm^{-1} for HMPzSM or 1015 cm^{-1} for HMPzSB, or 1010 cm^{-1} for HMPzPy/HMPzNB) to ~1060 cm^{-1} on complexation with Fe(III) indicated involvement of pyrazolyl (tertiary) nitrogen in bonding [18–20]. The free ligand band in the range 1410 cm^{-1} in HMPzSM or 1620 cm^{-1} in HMPzSB, or 1440 cm^{-1} in HMPzPy, or 1508 cm^{-1} in HMPzNB assignable to ν(C=N) (pyrazole ring) was shifted to higher wave number ($\Delta\nu = 20–70$ cm^{-1}) in all the complexes. These data indirectly suggested that the tertiary nitrogen atom of the pyrazole ring as a possible bonding sites [26]. This proposition was further substantiated by strong IR bands in the range 270–350 cm^{-1} (absent in the free ligand spectrum) assignable to the ν(Fe–N(Pz)). The other low frequency bands appearing in the 470–495 and 345–400 cm^{-1} regions in all the complexes could be attributed to ν(Fe–N(azom)) and ν(Fe–S), respectively.

The electronic spectral data in Table 1 ($\log\varepsilon$ values for solution spectra and absorbance values for solid state spectra are given in parentheses) were characterized by the appearance of three main bands around 23000, 20000, and 11500 cm^{-1} regions for the iron(III) complexes of HMPzSM/HMPzSB and 21320–19800, 18560–16130, and 11820–11430 cm^{-1} for the iron(III) complexes of HMPzPy/HMPzNB. The absorption bands could be assigned to the $^2T_2$ ground state for iron(III). In the solid state spectra, the highest intense bands above 20000 cm^{-1} were assigned to intraligand $\pi \longrightarrow \pi^*$ or $n \longrightarrow \pi^*$ transitions of the pyrazolyl ring, whereas the second highest regions at ~17000 cm^{-1} might be assigned to CT transitions arising from the $d \longrightarrow \pi^*$ transition as well as $S \longrightarrow Fe$ transitions. The *d–d* transition bands are located at ~11500 cm^{-1} that might correspond to the $^2T_2 \longrightarrow {}^2T_1$ transitions [27, 28]. There was no significant difference between the spectra obtained in solution and in solid state, indicating similar stereochemical environments in both the states. In the solution spectra, the intraligand bands ($\pi \longrightarrow \pi^*$) ~31000 cm^{-1} or above with high extinction coefficient values ($\log\varepsilon \approx 3.82–5.38$) dominated the solution spectra of the iron(III) complexes. Bands, which were found in the range 16000 to 24000 cm^{-1} in the solution spectra, were likely due to $d \longrightarrow \pi^*$ metal to ligand as well as sulfur to Fe(III). The *d–d* transition of these complexes appeared at *ca.* 11000 cm^{-1} in the solution spectra that correspond to $^2T_2 \longrightarrow {}^2T_1$ transitions of a spin paired d^5 iron. The similar electronic spectra were observed in several published papers [18–20]. The magnetic moment data ($\mu_{eff} = 2.83\sqrt{\chi_M \times 10^6 T}$ at 25°C) of the complexes (Table 1) were also indicative of low-spin character of iron. From the spectroscopic and magnetic moment data, the structure of the iron(III) com-



Solid state X-band EPR spectra of the iron(III) complexes: $[Fe(MPzSM)_2]Cl$ (a), $[Fe(MPzSB)_2]ClO_4$ (b), $[Fe(MPzPy)_2]ClO_4$ (c), and $[Fe(MPzNB)_2]Cl$ (d).

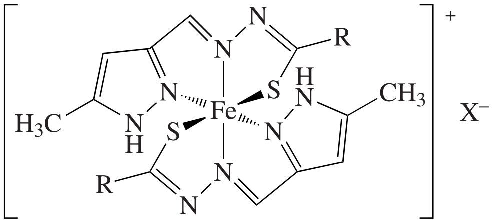
Table 3. EPR spectral parameters of the iron(III) complexes

Complexes	g values		Complexes	g values	
$[Fe(MPzSM)_2]Cl$	$g_\perp = 2.13$	$g_\parallel = 2.03$	$[Fe(MPzPy)_2]Cl$	$g_\perp = 2.18$	$g_\parallel = 2.01$
$[Fe(MPzSM)_2]ClO_4$	$g_1 = 2.19$, $g_2 = 2.13$	$g_3 = 2.03$	$[Fe(MPzPy)_2]ClO_4$	$g_1 = 2.06$, $g_2 = 2.14$	$g_3 = 2.02$
$[Fe(MPzSM)_2]SCN$	$g_\perp = 2.14$	$g_\parallel = 2.04$	$[Fe(MPzPy)_2]SCN$	$g_\perp = 2.12$	$g_\parallel = 1.98$
$[Fe(MPzSB)_2]Cl$	$g_\perp = 2.16$	$g_\parallel = 2.02$	$[Fe(MPzNB)_2]Cl$	$g_\perp = 2.13$	$g_\parallel = 1.87$
$[Fe(MPzSB)_2]ClO_4$	$g_1 = 2.15$, $g_2 = 2.13$	$g_3 = 2.00$	$[Fe(MPzNB)_2]ClO_4$	$g_\perp = 2.14$	$g_\parallel = 1.99$
$[Fe(MPzSB)_2]SCN$	$g_\perp = 2.13$	$g_\parallel = 2.04$	$[Fe(MPzNB)_2]SCN$	$g_\perp = 2.16$	$g_\parallel = 2.07$

plexes could be tentatively assigned as low-spin capped octahedron [16, 29].

The electronic spin-resonance spectra of the iron(III) complexes were recorded in the polycrystalline state at room temperature (~25°C) and showed the low-spin character of the iron(III) ions. The representative EPR spectra of complexes are given in figure. The complexes usually provided axial spectra with small difference between $g_\parallel$ and $g_\perp$ (Table 3), while the most of the perchlorate complexes, e.g., $[Fe(MPzSB)_2]ClO_4$, $[Fe(MPzPy)_2]ClO_4$, and $[Fe(MPzNB)_2]ClO_4$, showed slightly distortion in the axial spectrum compared to the other anions. This distortion might be due to lattice effects; in conjugation with the solid state effect due to involvement of perchlorate ion and where the symmetry of the spectra were lifted. According to the literature [30, 31], there are two quite distinct limiting ground states for the low-spin iron(III) porphyrin complexes that gave rise to three different types of EPR spectra: (a) the generally observed $(d_{xy})^2 (d_{xz}, d_{yz})^3$ state for which $g_{zz} > g_{yy} > g_{xx}$ and for which the EPR spectra may be either rhombic or "large $g_{\max}$" in appearance, depending on the relative orientation of planar axial ligands, but in each case, with g_{zz} along or near the normal to the ligand plane, and (b) the novel $(d_{xz}, d_{yz})^4 (d_{xy})^1$ state, for which $g_{xx} \approx g_{yy} > g_{zz}$, where the d_{xz}, d_{yz} pairs are degenerate or nearly so, and below the d_{xy} orbital in energy. The deviation of the anisotropic "g" values from 2.00 and nearly the same values of g_{xx} and g_{yy} suggested that the electronic structure of the ground state is $d_{xz}^2\ d_{yz}^2\ d_{xy}^1$ for the present iron(III) complexes. A definite explanation for this uncommon electronic state cannot be given for non-macrocyclic iron(III) complexes, but the reason might be included due to stabilization of d_{xz} and d_{yz} orbitals compared to d_{xy} by the π-acceptor orbitals (imine π* and sulfur $d\pi^*$) of the ligand molecules. Similar observations also reported for the iron(III) complexes of N-heterocyclic thiosemicarbazones [18–20, 25, 26, 32].

On the basis of the available physicochemical parameters and the discussion made therein, it could be reasonably concluded that the ligands coordinate with iron(III) as monodeprotonated NNS tridentate through the tertiary pyrazolyl ring nitrogen, azomethine nitrogen, and thiolato sulfur atom in all the reported bis-complexes. It was tentatively concluded that the structures of these low-spin iron(III) complexes are distorted octahedra in accordance with the proposition as shown below, where each ligand occupied mutually perpendicular meridional plane, because that allowed large delocalizsation to occur over the entire ligand framework.



This proposition was further supported by the published X-ray crystallography studies of similar bis-iron(III) complexes derived from pyrazolylthiosemicarbazones [19, 20], where the pyrazolyl ring nitrogen atoms and thiolato sulfur atoms are in *cis* position and two azomethine nitrogen atoms are *trans* to each other and the coordinating tridentate ligands are nearly planar but orthogonal to each other.

ACKNOWLEDGMENTS

Authors are thankful to the financial support by a grant from the Fundamental R and D Program for Core Technology of Materials funded by the Ministry of Commerce, Industry and Energy (Republic of Korea). This work is also supported by the Korea Foundation for International Cooperation of Science and Technology through the Global Research Laboratory (GRL) Program. The authors are also grateful to Professor S.K. Chattopadhyay (Department of Chemistry, Bengal Engineering and Science University formerly known as Bengal Engineering College, Shibpur, West Bengal, India) for useful discussion on EPR.

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