

Available online at www.sciencedirect.com



Journal of Molecular Structure 737 (2005) 61-67

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

# Structural and spectral studies of an iron(III) complex $[Fe(Pranthas)_2][FeCl_4]$ derived from 2-acetylpyridine-N(4), N(4)-(butane-1, 4-diyl) thiosemicarbazone (HPranthas)

A. Sreekanth<sup>a</sup>, Hoong-Kun Fun<sup>b</sup>, M.R. Prathapachandra Kurup<sup>a,\*</sup>

<sup>a</sup>Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala 682 022, India <sup>b</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Received 5 July 2004; revised 8 October 2004; accepted 21 October 2004

#### Abstract

A novel iron(III) complex of 2-acetylpyridine N(4), N(4)-(butyl-1, 4-diyl) thiosemicarbazone (HPranthas), [Fe(Pranthas)<sub>2</sub>]FeCl<sub>4</sub> was synthesized and physico-chemically characterized by means of partial elemental analysis, magnetic measurements (polycrystalline state), UV–Vis and IR spectroscopies. The presence of spin-paired iron(III) cation with  $d_{xz}^2 d_{yz}^2 d_{xy}^1$  ground state is revealed by the EPR and Mössbauer spectral data. Structure of the free ligand HPranthas and the complex [Fe(Pranthas)<sub>2</sub>]FeCl<sub>4</sub> were solved by single crystal X-ray diffraction. The framework of iron(III) complex consists of a discrete monomeric cationic entity containing low spin iron(III) in a slightly distorted octahedral environment. The metal ion is bonded to one sulfur and two nitrogens of each thiosemicarbazone molecule. The tetrachloroferrate(III) ion acts as counterion.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Iron(III) complex; Thiosemicarbazone; Single crystal X-ray diffraction; Mössbauer spectrum; EPR spectrum; IR spectrum

# 1. Introduction

Thiosemicarbazones and their metal complexes have been subject of interest in numerous studies because of their chemical and biological properties [1,2]. Thiosemicarbazones generally exist in the thione form in the solid state but exist as an equilibrium mixture of thione and thioenol forms in solution (A and B) which is essential for their versatile chelating behavior.



The well documented biological activities of several heterocyclic thiosemicarbazones have been often attributed to a chelation phenomenon with transition metal ions [3].

The success in therapeutic applications of N-heterocyclic thiosemicarbazones for removing excess iron from ironloaded mice through chelation therapy is quite remarkable [4]. 2-Acetylpyridine thiosemicarbazones were the first thiosemicarbazones in which antimalarial activity was detected, and the highest activity is reported when the N(4) position is either disubstituted or part of a ring system [5]. There are some reports on the iron(III) complexes of biologically active 2-acetylpyridine thiosemicarbazones [6,7]. Recently we have reported the copper(II) [8] and iron(III) [9] complexes synthesized from 2-benzoylpyridine N(4), N(4)-(butane-1, 4-divl)thiosemicarbazone. This paper stems from our interests in the investigation of some biologically active 2-acetylpyridine thiosemicarbazones and their metal complexes. In continuation of our investigations on the thiosemicarbazones and semicarbazones and their metal complexes [10-12], we have synthesized 2-acetylpyridine N(4), N(4)-(butane-1, 4diyl)thiosemicarbazone (HPranthas), and its iron(III) complex using ferric chloride.

<sup>\*</sup> Corresponding author. Tel.: +91 484 2575804; fax: +91 484 2577595. *E-mail address:* mrp@cusat.ac.in (M.R. Prathapachandra Kurup).

# 2. Experimental

## 2.1. General

2-Acetylpyridine (Aldrich), pyrrolidine (SRL), *N*methylaniline (Merck), thiosemicarbazide (SRL), carbon disulfide (Merck), hydrazine hydrate (99%, SRL) and ferric chloride (Merck) were used as received. All solvents were distilled before use. 2-Acetylpyridine N(4), N(4)-(butane-1, 4-diyl)thiosemicarbazone (HPranthas) was synthesized (Scheme 1) by the following adoption of a reported procedure [13].

# 2.3. Synthesis of 4-methyl-4-phenyl-3-thiosemicarbazide (1a)

A solution of carboxymethyl *N*-methyl *N*-phenyldithiocarbamate in 20 ml 99% hydrazine hydrate and 10 ml of water was heated on the rings of a steam bath. After 3 min crystals begin to separate. Heating was continued for 22 min. The crystals were collected by filtration, washed well with water and dried under a heat lamp. The crude product was recrystallized from a mixture of 50 ml ethanol and 25 ml of water. This gave 10.8 g of stout colorless rods of 4-methyl-4-phenyl-3-thiosemicarbazide (**1a**). Mp 124– 125 °C.



# 2.2. Synthesis of carboxymethyl N-methyl N-phenyldithiocarbamate

A mixture consisting of 12.0 ml (15.2 g, 0.2 mol) of CS<sub>2</sub> and 21.6 ml *N*-methylaniline was treated with a solution of 8.4 g (0.21 mol) of NaOH in 250 ml water. After stirring at room temperature for 4 h, the organic layer had disappeared. At this point, the straw colored solution was treated with 23.2 g (0.20 mol) of sodium chloroacetate and allowed to stand overnight for 17 h. The solution was acidified with 25 ml of conc. HCl and the solid which separated was collected and dried. This afforded 39.7 g of pale buff colored carboxymethyl *N*-methyl *N*-phenyldithiocarbamate. Mp 197–198 °C.



# 2.4. Pyrrolidine-1-thiocarboxylic acid hydrazide (1b)

A solution of 1.0 g of **1a** in 5 ml of acetonitrile was treated with 395 mg of pyrrolidine and the solution was heated under reflux for 15 min. The solution was chilled and the microporous off white crystals separated were collected and washed with acetonitrile. This afforded 570 mg of **1b**. Mp 174–175 °C.



#### 2.5. Synthesis of HPranthas

A solution 1 g (2 mmol) of 4-methyl-4-phenyl-3thiosemicarbazide in 5 ml of acetonitrile was treated with 2 mmol of pyrrolidine-1-thiocarboxylic acid



Scheme 1.

hydrazide (1b). The solution was heated at reflux for 2 h. The solution was chilled and the crystals that separated were collected and washed well with acetonitrile. This afforded stout yellow rods of HPranthas in 65% yield. The compound was recrystallized from methanol, mp 148 °C. X-ray quality single crystals of the compound were grown from a mixture of methanol and chloroform. Anal. Calcd (Found) %: C, 58.21 (58.03); H, 6.57 (6.49); N, 22.39 (22.56). UV–Vis,  $cm^{-1}(\log \varepsilon, 1 mol^{-1} cm^{-1})$ : 34,480 (4.11), 30,120 (3.96), 32,250 (4.08). IR  $(cm^{-1})$ : 1604 s, 1118 m, 1380 s, 843 sh. <sup>1</sup>H NMR (CDCl<sub>3</sub>-TMS)  $\delta$  (ppm): N(2)H, 8.63 s; C(11)H, 8.12 d; C(10)H, 7.61 dd; C(9)H, 7.79 dd; C(8)H, 7.58 d; C(12)H<sub>3</sub>, 2.2 s; C(1-4)H, 3.48-3.62 m.  ${}^{13}C{}^{1}H$  NMR  $\delta$  (ppm): C(5), 185.32; C(6), 151.13; C(7), 147.92; C(11), 137.19; C(8), 124.10; C(9), 119.77; C(10); 119.13, C(12), 13.66; C2 and C3, 52.11; C1 and C4, 65.79.

# 2.6. Synthesis of [Fe(Pranthas)<sub>2</sub>]FeCl<sub>4</sub>

To a methanolic solution of ferric chloride (1 mmol) was added a solution of HPranthas (1 mmol) in chloroform and refluxed for 30 min. The resulting deep green colored solution was evaporated to half its volume. On cooling dark brown shining crystals of the compound which separated out (yield, 70%) were washed with ether and dried over  $P_4O_{10}$  in vacuo. X-ray quality single crystals of the compound were grown by slow evaporation of a methanolic solution of the complex in 7 days. Anal. Calcd (Found) %: C, 38.54 (38.53); H, 4.00 (4.04); N, 14.91 (14.98).

Table 1

Crystal data and	structure refinement	parameters
------------------	----------------------	------------

# 2.7. Physical methods

Microanalyses were carried out using a Heraeus Elemental Analyzer at CDRI, Lucknow, India. Infrared spectra were recorded on a Shimadzu DR 8001 series FT-IR instrument as KBr pellets in the range  $400-4000 \text{ cm}^{-1}$ and far IR spectra were recorded in the range 50-500 cm<sup>-1</sup> on a NICOLET MAGNA 550 FT-IR spectrometer using polyethylene pellets at RSIC, IIT, Bombay, India. Electronic spectra were recorded in the 900-250 nm range in a diffused reflectance mode in MgO matrix in Ocean Optics SD 200 fiber optic Spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in a Brucker DRX 500 instrument using CDCl<sub>3</sub> as the solvent and TMS as the internal reference. Magnetic measurements were made in the polycrystalline state on a home built simple Gouy balance using Hg[Co(SCN)<sub>4</sub>] as calibrant. EPR spectrum was recorded in a Bruker ESP300, X-band CW spectrometer operating at 9.52 GHz equipped with a liquid nitrogen cryostat. The spectrum was recorded with a modulation amplitude of 0.05 (0.1) mT and 100 kHz modulation frequency, and the field was calibrated by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) with a gvalue of 2.0036. Mössbauer spectrum was recorded on a constant-acceleration spectrometer with multi channel analyzer using a <sup>57</sup>Co source in a rhodium matrix at Inter University Consortium, Indore, India.

# 2.8. X-ray crystallography

A pale yellow monoclinic crystal of HPranthas and a dark brown triclinic crystal of Fe(Pranthas)<sub>2</sub>FeCl<sub>4</sub> having

	HPranthas	Fe(Pranthas) <sub>2</sub> FeCl <sub>4</sub>
Empirical formula	$C_{12}H_{16}N_4S$	$C_{24}H_{30}Cl_4Fe_2N_8S_2$
Formula weight (M)	248.35	748.18
Temperature $(T)$ , K	293	293(2)
Wave length (Mo Kα), Å	0.71073	0.71073
Crystal system/Space group	Monoclinic, $P2_1/c$	Triclinic, P-1
Unit cell dimensions	$a = 15.627$ Å, $\alpha = 90.000^{\circ}$ ; $b = 22.115$ Å,	$a = 8.7431(7)$ Å, $\alpha = 82.619(2)^\circ$ ; $b = 13.4881(11)$ Å,
	$\beta = 94.362^\circ$ ; $c = 7.444$ Å, $\gamma = 90.000^\circ$	$\beta = 87.482(2)^\circ$ ; $c = 14.4522(12)$ Å, $\gamma = 75.535(2)^\circ$
Volume (V), $Å^3$	2565.1	1636.5(2)
Z, Calculated density ( $\rho$ ), mg m <sup>-3</sup>	8, 1.286	2, 1.518
Absorption coefficient ( $\mu$ ), mm <sup>-1</sup>	0.237	1.370
F(000)	1056	764
Crystal size	$0.52 \times 0.40 \times 0.20 \text{ mm}^3$	$0.44 \times 0.26 \times 0.26 \text{ mm}^3$
$\theta$ Range for data collection (°)	2.61-25.00	2.24-25.00
Limiting indices	$-17 \le h \le 8, -24 \le k \le 22, -8 \le l \le 8$	$-8 \le h \le 10, -15 \le k \le 16, -17 \le l \le 15 \ 1.095$
Completeness to $2\theta$	25.00, 92.8%	25.00, 97.7%
Max. and min. transmission	0.9542 and 0.8869	0.7172 and 0.5840
Goodness-of-fit on $F^2$	1.112	1.095
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0861, wR2 = 0.2135	R1 = 0.0564, wR2 = 0.1175
<i>R</i> indices (all data)	R1 = 0.1200, wR2 = 0.2373	R1 = 0.0753, wR2 = 0.1296
Largest diff. peak and hole	0.468 and $-0.432 \text{ e} \text{ Å}^{-3}$	0.507 and $-0.372 \text{ e A}^{-3}$

appropriate dimensions were sealed in a glass capillary, and intensity data were measured at room temperature (293 K) on an Bruker 1-k ccs diffractometer equipped with graphite-monochromated Mo K $\alpha$  ( $\lambda$ =0.71073 Å) radiation. The trial structure was obtained by direct methods using SHELXL-97 and refined by full-matrix least squares on  $F^2$  (SHELXS-97) [14]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Absorption corrections were employed using  $\psi$ -Scan. The crystallographic data along with details of structure solution refinements are given in Table 1.

# 3. Results and discussion

The complex is dark brown and readily soluble in polar organic solvents. From the analytical data it can be formulated as either  $[Fe(Pranthas)_2]FeCl_4$  or [FePranthasCl<sub>2</sub>] but the crystallographic and spectroscopic as well as spectroscopic data indicated that the  $\text{FeCl}_4^-$  anion was formed in the reaction. The compound was found to be a 1:1 electrolyte [15] in DMF with  $\Lambda_m$  value near to  $105 \ \Omega^{-1} \ \mathrm{cm}^2 \ \mathrm{mol}^{-1}$ . The cation centre of the complex is expected to contain two deprotonated ligands attached to low-spin iron(III). Magnetic moment has been determined for the complex at room temperature in the polycrystalline state, which was found to be 4.35 BM, on a per ion basis, which is consistent with one high-spin iron and one low-spin iron(III) in the molecule [7,16]. The complete assignment of the two spin states of the complex was done on the basis of EPR and Mössbauer measurements.

#### 3.1. Molecular and crystal structure of HPranthas

Fig. 1 shows the molecular structure of HPranthas and Table 2 lists the selected bond lengths and angles. There are

two crystallographically independent molecules A and B in the asymmetric unit of the compound HPranthas with bond lengths and angles which agree with each other and are within normal ranges. Both molecules are related by a local pseudo-twofold rotation axis and exist in an E configuration about the C6-N3 and C5-N2 bonds relative to the N3-N2 bond. The S and hydrazine N3 atoms are in Z configuration with respect to the C5-N2 bond. In both molecules the five membered pyrrolidine ring is not planar and tends towards an envelope conformation. In both molecules, the relative conformations of the pyridine ring and the methyl group with respect to the plane of the thiosemicarbazone are conditioned by the  $sp^2$  hybridized carbon atom. The C5–S1 (1.692(4) Å) and C6-N3 (1.293(6) Å) bond lengths are typical of double bond character in agreement with previously reported thiosemicarbazone derivatives [17,18].

# 3.2. Molecular and crystal structure of [Fe(Pranthas)<sub>2</sub>][FeCl<sub>4</sub>]

Fig. 2 shows the molecular structure of the compound along with atom numbering scheme. Table 3 presents selected bond lengths and angles. The low-spin iron(III) ion has a distorted octahedral coordination in the complex. The pattern of coordination is similar to that observed in complexes of similar type [9,19,20]. The two molecules of monodeprotonated ligand, coordinate to iron via pyridyl nitrogens, azomethine nitrogens and thiolato sulfurs in a meridional arrangement to form four five membered chelate rings. The crystallographic asymmetric unit contains a [Fe(Pranthas)<sub>2</sub>] cation and a tetrachloroferrate [FeCl<sub>4</sub>]<sup>-</sup> anion.

There is a slight shortening of the Fe–N(azomethine) bond distance compared to Fe–N(py) distances; this may be attributed to the fact that the azomethine nitrogen is a stronger base compared with the pyridyl nitrogen. The two azomethine nitrogen atoms are *trans* to each other, while the pyridyl nitrogen atoms and thiolato sulfur atoms are in



Fig. 1. ORTEP diagram of the compound HPranthas, with 50% ellipsoidal probability. Hydrogen atoms are shown as smaller spheres of arbitrary radii.

A. Sreekanth et al. / Journal of Molecular Structure 737 (2005) 61-67

Table 2Selected bond lengths and angles of HPranthas

Bond lengths		Bond angles	
S(1A)–C(5A)	1.692(4)	C(5A)-N(1A)-C(4A)	124.0
N(1A)-C(5A)	1.347(6)	C(5A)-N(2A)-N(3A)	121.4
N(2A)-C(5A)	1.349(6)	C(6A)-N(3A)-N(2A)	118.6
N(2A)-N(3A)	1.364(5)	C(2A)-C(3A)-C(4A)	105.3
N(3A)-C(6A)	1.293(6)	N(1A)-C(5A)-N(2A)	114.7
C(1A)-C(2A)	1.511(9)	N(2A)-C(5A)-S(1A)	124.0
X–H···Cg	H…Cg (Å)	X…Cg (Å)	$\angle X - H \cdots$
			Cg (°)
C9–H9BA–Cg $(4)^a$	2.8854	3.6978	146.67
a = x, 1/2 - y, 1/2 + z	Cg(4)=N4B,C7B,C8B, C9B, C10B, C11B		
D–H···A	H…A (Å)	D…A (Å)	$\angle D - H \cdots$
			A (°)
N2A-H2AC…N4A	1.93	2.6184	136
N2B-H2Bc…N4B	1.95	2.6249	135
C3B–H3BC···S1A <sup><math>b</math></sup>	2.83	3.7531	160
b=1+x, y, z			

*cis* positions. The tetrachloroferrate anion present in the molecule is in a slightly distorted tetrahedral geometry with equal bond lengths ( $\sim 2.187$  Å) and angles ( $\sim 109.46^{\circ}$ ).

#### 3.3. IR and electronic spectra

Table 4 lists the assignments of IR bands most useful for the establishment of the mode of coordination of the thiosemicarbazone and its iron(III) complex. Coordination of the azomethine nitrogen is indicated by the lowering of the band at 1604 to 1597 cm<sup>-1</sup>. The band is not a pure vibrational C=N stretching, but it contains also a contribution from C=C vibrations of the pyridyl ring [21]. Two bands at ≈1380 and 843 cm<sup>-1</sup> were assigned to the C-S stretching and bending mode of vibrations. These bands are observed at lower energy in the complex, indicating



Fig. 2. ORTEP diagram of the compound [Fe(Pranthas)<sub>2</sub>]FeCl<sub>4</sub> with 50% ellipsoidal probability. Hydrogen atoms are omitted for clarity.

Table 3		
Selected bond lengths	and angles	of complex

Bond lengths (Å)		Bond angles (°)		
Fe(1)–N(7)	1.918(3)	N(7)–Fe(1)– N(3)	176.48(16)	
Fe(1)–N(3)	1.928(3)	N(7) - Fe(1) - N(8)	80.47(15)	
Fe(1)–N(8)	1.986(3)	N(3) - Fe(1) - N(3)	103.03(15)	
Fe(1)–N(4)	1.986(3)	N(7) - Fe(1) - N(4)	98.98(14)	
Fe(1)–S(1)	2.2151(13)	N(7) - Fe(1) - S(1)	95.42(11)	
Fe(1)–S(2)	2.2194(13)	N(3)-Fe(1)- S(1)	85.12(11)	
Fe(2)–Cl(2)	2.1820(19)	N(8)-Fe(1)- S(1)	89.18(10)	
Fe(2)–Cl(3)	2.1831(19)	N(4)-Fe(1)- S(1)	164.56(11)	
Fe(2)–Cl(4)	2.187(2)	N(7)-Fe(1)-S(2)	85.52(11)	
Fe(2)–Cl(1)	2.1929(17)	N(3)-Fe(1)- S(2)	90.97(11)	
S(1)–C(5)	1.741(4)	N(8)-Fe(1)- S(2)	165.57(11)	
$C-H\cdots\pi$ interactions	H····Cø	X····Co	X-H···Co	
$C(12)-H(12A)\cdots Co(4)^{a}$	2.7738	3 1062	102.19	
$C(23) - H(23A) \cdots Cg(1)^{a}$	3,0009	3 2959	100.24	
$C(23) - H(23A) \cdots Cg(3)^{a}$	2.9469	3.2420	100.10	
$C(22) = H(22A) \cdots Cq(7)^{b}$	3 0917	3 9134	148 28	
$C(13)-H(13B)\cdots Cg(8)^{c}$	3.0146	3.8528	145.42	
H-bonding interactions	DA	Η…Δ	D_H…A	
$C(9)-H(9A)\cdots Cl(3)$	2.82	3 6626	152	
Equivalent position code		Cg(1) = Fe(1), S(1), C(5),		
		N(2), N(3)		
a=x, y, z, b=-1+x, y, z, c=1+x, y, z		Cg(3) = Fe(1), N(4), C(8), C(6), N(3)		
		Cg(4) = Fe(1), N(8), C(20),		
		C(18), N(7)		
		$C_{g}(7) = N(4), C(12), C(11)$		
			C(10) C(9) C(8)	
		Cg(8) = N(8)	C(20), C(21)	
		C(22), C(23), C	C(24)	
		( )) - ( + )) -	· /	

coordination of thiolato sulfur. Another band which is considered to be sensitive to coordination is v(N-N) which is raised in energy due to coordination because of the increased double bond character. The newly formed C=N bond due to the deprotonation of the ligand is also observed  $\approx 1648 \text{ cm}^{-1}$ .

The far-IR spectrum of the complex has a broad split band assignable to  $v_3$ (FeCl<sub>4</sub>) at 376 cm<sup>-1</sup>. This splitting may be due to the steric factors which reduce the symmetry from tetrahedral [22,23]. Similarly the band corresponding to  $v_4$  at 123 cm<sup>-1</sup> is also found to be split due to site effects. The other two stretching modes  $v_1$  and  $v_2$  are found at 325 and 100 cm<sup>-1</sup>, respectively. Bands at 526 and 353 cm<sup>-1</sup> were assigned to the Fe–N vibrations of the azomethine and pyridyl nitrogen coordination, respectively. The Fe–S bond stretching vibrations is found at 419 cm<sup>-1</sup>.

Table 4 IR spectral data of the ligand and it's iron(III) complex

Compound	$\nu(C=N)$	$\nu(N=C)$	$\nu(N=N)$	$\nu/\delta(C=S)$
HPranthas Fe(Pranthas) <sub>2</sub> - FeCl <sub>4</sub> Fe(Pranthas) <sub>2</sub> - FeCl <sub>4</sub>	1604 s 1597 s ν(Fe–N <sub>azo</sub> ) 526 w	- 1648 s v(Fe-N <sub>py</sub> ) 353 s	1118 s 1193 s ν(Fe–S) 419 m	1380 s, 843 w 1239 m, 839 w v(FeCl <sub>4</sub> ) 376 s, 325 s, 123 s, 100 s

All values are in  $cm^{-1}$ .

The electronic spectra of the ligand and its iron(III) complex in the UV region are dominated by two intense intraligand bands around 37,030 and 29,850 cm<sup>-1</sup> assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, while coordination has little effect on these bands. Usually  $n \rightarrow \pi^*$  transitions involving N and S occur at a lower energy than  $\pi \rightarrow \pi^*$ . The bands at 14,990 and 24,210 cm<sup>-1</sup> in the spectrum of the complex were assigned to  $d \rightarrow \pi^*$  transitions. These transitions also involve  $S \rightarrow Fe$  and other ligand to metal charge transfer transitions. The band at 10,250 cm<sup>-1</sup> is due to  $d \rightarrow d$  band which correspond to  ${}^2T_{2g} \rightarrow {}^2T_{1g}$  transition of the d<sup>5</sup> spin-paired systems [24].

#### 3.4. Electron paramagnetic resonance spectrum

The EPR spectrum of the complex was recorded at 110 K in DMF glass and spin Hamiltonian parameters were obtained after the spectral simulations performed by Easy-Spin package [25]. The spectrum was resolved into well-defined rhombic symmetry with three g values viz. 2.20, 2.15 and 1.99. Fig. 3 shows the EPR spectrum of the complex recorded in a DMF glass. This type of feature is



Fig. 3. EPR spectrum of the complex in a solution of DMF at 110 K: experimental spectrum (blue), simulated best fit spectrum (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

common for low spin octahedral complexes [26]. The observed anisotropic character is due to rhombic distortion common for spin paired iron(III) complexes. The small deviation of the anisotropic g values from 2.0 suggests that the unpaired electrons is in the  $d_{xy}$  orbital with a  $d_{xz}^2 d_{yz}^2 d_{xy}^1$  ground state configuration. It is interesting to note a sharp but small signal corresponding to g=4.264 indicating the presence of high spin species which was identified as [FeCl<sub>4</sub>]<sup>-</sup> anion. The absence of ligand hyperfine splitting of the highest g-values indicate no interaction of the unpaired electron with the imine nitrogen.

#### 3.5. Mössbauer spectrum

The Mössbauer spectrum of the complex was recorded at 298 K in order to understand and confirm the spin behavior of the system. The Mössbauer parameters calculated from the spectra were compared with  $\alpha$ -iron as a standard. The positive  $\delta_{is}$  value shows that the excited state is not necessarily larger than the ground state. The high intensity doublet in the spectrum the complex with an isomer shift approximately at  $-0.13 \text{ mm s}^{-1}$ , characterized by a quadrupolar splitting  $\Delta E_q \approx 2.21 \text{ mm s}^{-1}$ , is ascribed to the  ${}^2T_{2g}$ ground state of low spin iron(III) [27]. The 1:1 ratio between the quadrupole split spectra is not strictly observed due to the anisotropic absorption known as Goldansky-Karyagin effect. The spectrum also showed of another broad, less intense signal corresponding to  $\delta_{is} \approx 0.12 \text{ mm s}^{-1}$ ,  $\Delta E_{\rm q} \approx 0.675 \text{ mm s}^{-1}$  ascribed to tetrahedral high spin iron(III) species [28]. Similar features were observed in the spectrum of an iron(III) complex reported elsewhere [9], where it was found that there was no change in the spectral features even when the temperature was lowered to 20 K. The observation of the broad line with unresolved quadrupolar splitting is assumed to be due to much slower spin relaxation due to the orbital electrons of iron (Fig. 4).



Fig. 4. Mössbauer spectrum of the complex (298 K).

### 4. Supplementary information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data center, CCDC 228088 for compound HPranthas and CCDC 228089 for compound [Fe(Pranthas)<sub>2</sub>]FeCl<sub>4</sub>. Copies of this information maybe obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

#### Acknowledgements

One of the authors A.S. would like to thank the Cochin University of Science and Technology for a Research Fellowship. The authors are thankful to Dr Ajay Gupta, Interuniversity Consortium, Indore, India, for Mössbauer spectral experiments. HKF thanks the Malaysian Government and Universiti Sains Malaysia for the fundamental research grant No. 304/PFIZIK/670011.

#### References

- [1] S. Padhye, G.B. Kauffmann, Coord. Chem. Rev. 63 (1985) 127.
- [2] D.X. West, S.B. Padhye, P.B. Sonawane, Struct. Bonding 76 (1991) 1.
- [3] A.E. Liberta, D.X. West, Biometals 5 (1992) 121.
- [4] R. Raina, T.S. Srivastava, Inorg. Chim. Acta 67 (1982) 83.
- [5] D.L. Klayman, J.F. Bartoserich, T.S. Griffin, C.J. Mason, J.P. Scovill, J. Med. Chem. 22 (1979) 885.
- [6] B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, Transition Met. Chem. 13 (1988) 247.
- [7] B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, Synth. React. Inorg. Met.-Org. Chem. 28 (1998) 1415.

- [8] A. Sreekanth, M.R.P. Kurup, Polyhedron 22 (2003) 3321.
- [9] A. Sreekanth, M.R.P. Kurup, Polyhedron 23 (2004) 1225.
- [10] A. Sreekanth, S. Sivakumar, M.R.P. Kurup, J. Mol. Struct. 655 (2003) 47.
- [11] R.P. John, A. Sreekanth, M.R.P. Kurup, S.M. Mobin, Polyhedron 21 (2002) 2515.
- [12] A. Sreekanth, U.L. Kala, C.R. Nayar, M.R.P. Kurup, Polyhedron 23 (2004) 41.
- [13] J.P. Scovill, Phosphorous Sulfur Silicon Relat. Elem. 60 (1991) 15.
- [14] G.M. Sheldrick, SHELXL 97, Program for the Solution of Crystal Structures, University of Göttingen: Göttingen, Germany, 1997; G.M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structures, University of Göttingen: Göttingen, Germany, 1997.
- [15] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [16] S.A. Cotton, Coord. Chem. Rev. 8 (1978) 185.
- [17] S. Sivakumar, PhD Thesis, Cochin University of Science and Technology, Kochi, India, 2003.
- [18] J. Garcia-Tojal, J.L. Pizarro, L. Lezama, M.I. Arriortua, T. Rojo, Inorg. Chim. Acta 278 (1998) 150.
- [19] N.C. Saha, A. Saha, R.J. Butcher, S. Chaudhuri, N. Saha, Inorg. Chim. Acta 339 (2002) 348.
- [20] N.C. Saha, R.J. Butcher, S. Chaudhari, N. Saha, Polyhedron 22 (2003) 375.
- [21] D.X. West, P.M. Ahrweiler, G. Ertem, J.P. Scovill, D.L. Klayman, J.L.F. Anderson, R. Gilardi, C. George, L.K. Pannel, Transition Met. Chem. 10 (1985) 264.
- [22] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Wiley, NY, 1997.
- [23] J.S. Avery, C.D. Burbridge, D.M.L. Goodgame, Spectrochim. Acta, Part A 24 (1968) 1721.
- [24] A.H. Ewald, R.L. Martin, E. Sinn, A.H. White, Inorg. Chem. 8 (1968) 1837.
- [25] St. Stoll, Spectral Simulations in Solid-State EPR, PhD Thesis, ETH, Zurich, 2003.
- [26] Y. Nishida, A. Sumita, K. Hayashida, H. Olishima, S. Kida, Y. Maedo, J. Coord. Chem. 9 (1979) 261.
- [27] S. Floquet, M.L. Boillot, E. Riviere, F. Varret, K. Boukheddaden, D. Morineau, P. Negrier, New J. Chem. 27 (2003) 341.
- [28] N.A. Bell, J.S. Brooks, J.K. Robinson, S.C. Thrope, J. Chem. Soc., Faraday Trans. 94 (1998) 3155.