

## Mössbauer and other spectral studies of Fe(III) complexes of benzothiazolines

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**Abstract.** Different molar reactions of  $\text{Fe}(\text{OPr}')_3$  and  $\text{FeCl}_3$  with benzothiazolines having an NSH donor system, derived by the condensation of *o*-aminothiophenol with heterocyclic aldehydes, viz. pyridine-2-aldehyde, furfuraldehyde and thiophene-2-aldehyde, lead to the formation of  $[\text{Fe} \cdot \text{OPr}'(\text{NS})_2]_2$ ,  $[\text{Fe}(\text{NS})_3]$  and  $[\text{Fe}(\text{NS})_2\text{Cl}]$  type of complexes. The resulting derivatives have been characterized by elemental analysis, conductivity measurements, molecular weight determinations and magnetic studies. IR, electronic, Mössbauer and ESR spectral data have been used to deduce the structures of the resulting derivatives.

**Keywords.** Low spin Fe(III) complexes; benzothiazolines; IR spectra; Mössbauer spectra; ESR spectra.

### 1. Introduction

The condensation of *o*-aminothiophenol with a carbonyl compound often results in the formation of a heterocyclic compound. It is reported that even in the absence of a metal ion an equilibrium may exist between the two forms as shown in chart 1 (Jadamus *et al* 1964a).

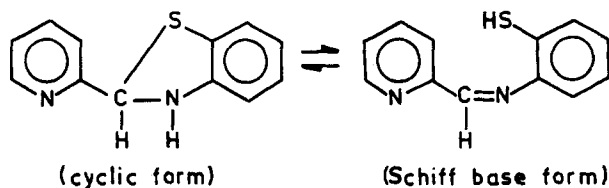


Chart 1.

However, the present work shows that the metal ion acts as a template and favours the formation of a Schiff base rather than the cyclic form as reported in a similar study (Thompson and Busch 1964).

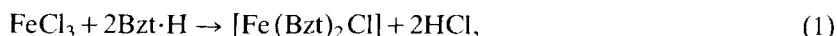
A careful survey of the literature reveals that several transition metal complexes of this type have been reported (Lindoy 1971). However, complexes of iron(III) with benzothiazolines derived from heterocyclic aldehydes which have great

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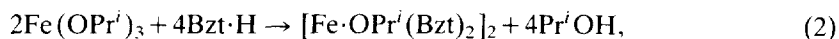
biological importance have not been studied so far. In the present paper, we report the synthesis and characterization of iron(III) complexes with this type of ligand.

## 2. Discussion

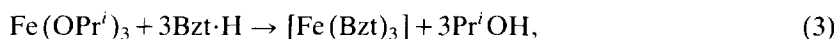
The reactions of  $\text{Fe}(\text{OPr}^i)_3$  and  $\text{FeCl}_3$  with the benzothiazolines can be represented by the following equations:



I



II



III

where BztH = benzothiazoline;  $\text{Fe}(\text{OPr}^i)_3$  = iron(III) isopropoxide.

All the resulting derivatives are coloured solids and soluble in alcohol, DMF and DMSO. Complexes I and III are monomeric while complex II is dimeric as determined by the Rast-camphor method. The low molar conductivities ( $10\text{--}15 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) of the resulting complexes in anhydrous DMF show that they are nonelectrolytic in nature.

### 2.1 IR spectra

In the IR spectra of the ligands, a strong band at  $\sim 3400\text{--}3200 \text{ cm}^{-1}$  may be assigned to the stretching vibrations of the NH group (Sharma *et al* 1980). A strong band at  $1660 \pm 10 \text{ cm}^{-1}$  is possibly due to the N–H deformation vibrations (Consiglio *et al* 1978). The absence of  $\nu\text{SH}$  and  $\nu\text{C}=\text{N}$  are indicative of the benzothiazoline structure of the ligands and not the Schiff base form. In the spectra of metal complexes, bands due to N–H vibrations disappear, indicating the chelation of nitrogen with the metal atom, and a new band is observed at  $\approx 1585 \text{ cm}^{-1}$  which can be assigned to  $>\text{C}=\text{N}$  vibrations (Varshney and Tandon 1985). The presence of the  $>\text{C}=\text{N}$  band suggests that the resulting metal complexes are metal Schiff base derivatives as the benzothiazoline ring rearranges to give the Schiff base derivatives in the presence of metal ions.

The far-IR spectra of the complexes give a number of new bands, which are absent in the spectrum of the ligand. In the spectra of complexes (II) a new band is observed at  $870 \text{ cm}^{-1}$  which may be assigned to Fe–O–Fe vibrations (Marini *et al* 1981). The presence of this band suggests the dimeric nature of these complexes involving bridging oxygen atoms. Some new bands observed at  $370 \text{ cm}^{-1}$ ,  $300 \text{ cm}^{-1}$ ,  $260 \text{ cm}^{-1}$  are due to  $\nu(\text{Fe-N})$ ,  $\nu(\text{Fe-S})$  and  $\nu(\text{Fe-Cl})$  respectively, which further support the bonding of the ligand with the metal atom (Marini *et al* 1981).

### 2.2 Electronic spectra

The electronic spectra of the ligands consists of two bands around 250 and 315 nm characteristic of the typical spectrum of benzothiazolines (the cyclic form) and

these may be attributed to the  $\phi-\phi^*$  and  $\pi-\pi^*$  benzenoid transitions (Jadamus *et al* 1964b). In the spectra of metal complexes one band is observed between 460 and 480 nm suggesting that iron is in a low spin state.

### 2.3 Magnetic moments

The magnetic moments of all the complexes at room temperature are in the range 1.7–2.1 B.M. suggesting a low spin state for these complexes. Low values obtained for complexes(II) may be due to dimer formation where antiferromagnetic interactions can lead to low  $\mu_{\text{eff}}$  values. Values obtained for complexes I and III are consistent for the low spin five-coordinate and low spin six-coordinate complexes respectively (Cotton 1972).

### 2.4 Mössbauer spectra

The chemical isomer shift values,  $\delta$ , relative to natural iron foil, which are sensitive to both the oxidation and spin states of iron, are in agreement with the structural assignments made on the basis of electronic, IR and magnetic measurements (table 1). The isomer shift (0.20–0.25  $\text{mm s}^{-1}$ ) with respect to iron and quadrupole splitting (1.63–1.75  $\text{mm s}^{-1}$ ) at room temperature are characteristic of six-coordinate low spin iron(III) complexes (Burman and Sathyanarayana 1981).

### 2.5 ESR spectra

The complexes give a signal in their ESR spectra in the X-band region at room temperature in the polycrystalline state from which the Lande splitting factors ( $g$  values) have been calculated. The data shows that the  $g$  values lie in the range 1.99 to 2.00 characteristic of an  $S = \frac{1}{2}$  system (Cotton and Gibson 1971).

Thus on the basis of the above studies the following structures can be suggested for the different types of complexes.

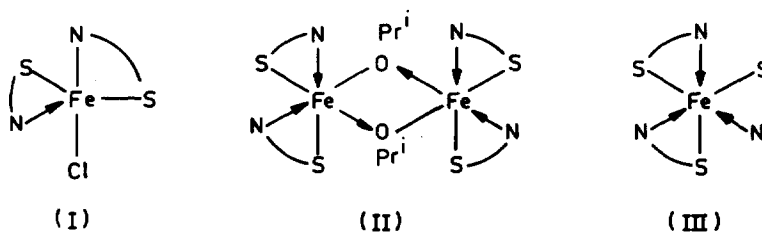


Chart 2.

Table 1. Mössbauer spectral data.

Complex	Isomer shift ( $\text{mm s}^{-1}$ )	Quadrupole splitting ( $\text{mm s}^{-1}$ )
$[\text{Fe}(\text{C}_{27}\text{H}_{25}\text{N}_4\text{S}_2\text{O})_2]$	$0.20 \pm 0.03$	$1.63 \pm 0.06$
$[\text{Fe}(\text{C}_{12}\text{H}_6\text{N}_2\text{S})_3]$	$0.25 \pm 0.05$	$1.75 \pm 0.06$

Table 2. Physical properties and analysis of Fe(III) complexes.

Reactants		Molecular formula, colour & state	M.P. (°C)	% Analysis					Magnetic moments (B.M.)
Iron compound	Ligand			Molar ratio	Fe Found (Calc)	C Found (Calc)	H Found (Calc)	N Found (Calc)	
FeCl <sub>3</sub>	Py-2-al-Bzt	Fe(C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> S) <sub>2</sub> Cl (Dark brown solid)	64	10.5 (10.7)	55.4 (55.6)	3.5 (3.4)	10.6 (10.8)	1.78	
Fe(OPr') <sub>3</sub>	Py-2-al-Bzt	[Fe(C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> S) <sub>2</sub> .OC <sub>3</sub> H <sub>7</sub> ] <sub>2</sub> (Brown solid)	128	10.0 (10.3)	60.0 (59.7)	4.9 (5.0)	10.2 (10.3)	1.71	
Fe(OPr') <sub>3</sub>	Py-2-al-Bzt	Fe(C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> S) <sub>3</sub> (Brown solid)	121	7.8 (8.0)	62.0 (62.2)	4.0 (3.8)	12.0 (12.1)	2.12	
FeCl <sub>3</sub>	Furf-Bzt	Fe(C <sub>11</sub> H <sub>8</sub> NSO) <sub>2</sub> Cl (Dark brown solid)	43	11.0 (11.2)	53.1 (53.3)	3.3 (3.2)	15.4 (15.6)	1.81	
Fe(OPr') <sub>3</sub>	Furf-Bzt	[Fe(C <sub>11</sub> H <sub>8</sub> NSO) <sub>2</sub> .OC <sub>3</sub> H <sub>7</sub> ] <sub>2</sub> (Yellow solid)	83	10.5 (10.7)	57.5 (57.6)	4.9 (4.8)	5.1 (5.4)	1.74	
Fe(OPr') <sub>3</sub>	Furf-Bzt	Fe(C <sub>11</sub> H <sub>8</sub> NSO) <sub>3</sub> (Brown solid)	79	8.4 (8.4)	59.7 (59.8)	3.7 (3.6)	6.2 (6.3)	2.08	
FeCl <sub>3</sub>	Thioph-2-al-Bzt	Fe(C <sub>11</sub> H <sub>8</sub> NS <sub>2</sub> ) <sub>2</sub> Cl (Dark green solid)	60	10.4 (10.5)	49.9 (50.0)	2.9 (3.03)	5.2 (5.3)	1.73	
Fe(OPr') <sub>3</sub>	Thioph-2-al-Bzt	[Fe(C <sub>11</sub> H <sub>8</sub> NS <sub>2</sub> ) <sub>2</sub> .OC <sub>3</sub> H <sub>7</sub> ] <sub>2</sub> (Orange solid)	70d	10.0 (10.1)	54.0 (54.3)	4.5 (4.5)	4.9 (5.1)	1.79	
Fe(OPr') <sub>3</sub>	Thioph-2-al-Bzt	Fe(C <sub>11</sub> H <sub>8</sub> NS <sub>2</sub> ) <sub>3</sub> (Orange solid)	230d	8.0 (7.9)	55.7 (55.8)	3.5 (3.4)	5.7 (5.9)	2.00	

d = decomposed.

### 3. Experimental

All the reactions were carried out under strictly anhydrous conditions and chemicals of analytical grade were used.

Benzothiazolines were prepared by methods reported earlier (Garg and Tandon 1987). Iron(III) isopropoxide was prepared by treating sodium isopropoxide with anhydrous  $\text{FeCl}_3$  (Sharma and Mehrotra 1969).

#### 3.1 Synthesis of Fe(III) complexes

$\text{Fe}(\text{OPr}^i)_3$  and the ligand were mixed in 1 : 2 and 1 : 3 molar ratios in dry benzene as the reaction medium. The resulting solution was refluxed on a column for 3–4 hours and the progress of the reaction was monitored by the estimation of isopropanol in the azeotrope. The solvent was removed and the product was repeatedly washed with dry cyclohexane or/and dry ether. It was finally dried *in vacuo*.

Anhydrous  $\text{FeCl}_3$  and ligand were mixed in 1 : 2 molar ratio in methanol. The resulting solution was refluxed on a column for 2 h. The solution was concentrated by removing the solvent *in vacuo*. It was then kept in a refrigerator overnight. The solid mass thus obtained was washed with benzene and cyclohexane and finally dried *in vacuo*.

#### 3.2 Analytical methods and physical measurements

Iron was estimated complexometrically (Garg and Tandon 1987). Nitrogen was estimated by Kjeldahl's method and sulphur by Messenger's method, carbon and hydrogen analyses were performed at the microanalytical laboratory of the department. The results are shown in table 2.

Electronic spectra were recorded in methanol on a Pye Unicam SP 8–100 spectrophotometer. IR spectra were recorded in the form of KBr pellets on a Perkin Elmer 577 grating spectrophotometer.  $^{57}\text{Fe}$  Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer with a multichannel data store.  $^{57}\text{Co}$  in a rhodium matrix was used as the source. EPR spectra were obtained on Varian E-4X Band spectrometer with diphenylpicrylhydrazyl (DPPH) as the reference substance.

Molar conductance measurements were made using a Systronics conductivity bridge (model 305). Molecular weight determinations were carried out by the Rast-camphor method. Magnetic susceptibilities were determined by Gouy's method.

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