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## **NEW COORDINATION POLYMERS OF 1,4-BIS(2'-HYDROXYPHENYLAZOMETHINE) PHENYLENE**

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### **ABSTRACT**

Coordination polymers of 1,4-bis(2'-hydroxyphenylazomethine) phenylene have been prepared with the metal ions Ti(III), Cr(III), Fe(III), Mn(II), Ni(II), and Cu(II). They were characterized by elemental analysis, IR, and electronic spectra. The metal contents in all polymers were found to be consistent with a 1:1 (metal:ligand) stoichiometry. The thermal behavior of these coordination polymers has been studied by thermogravimetric analysis in air up to 750°C, and the data showed that they are thermally stable up to 200°C. Physical properties such as the solubility and viscosity of the polymer complexes were also determined. Electrical conductivity measurements of the synthesized polychelated polymers showed that they are insulators except for the Ni(II) complex which shows a semiconducting character. Mössbauer data clearly establish the 3+ oxidation state for the iron complex polymer.

### **INTRODUCTION**

Recently, the development of new polymeric chelates has been of great interest due to their thermal stability, electrical conductivity, and catalytic

action in some chemical reactions occurring in biological materials [1, 3]. Such polymers can be obtained by inclusion of metal ions into the polymer main chain. The polychelates derived from poly-Schiff bases have been studied by numerous workers [4-8]. It was noted that properly designed coordination polymers of transition metals should have semi-conductive properties [9], and semiconductive coordination polymers have been observed [10, 11]. In this work the difunctional Schiff-base ligand 1,4-bis(2'-hydroxyphenylazomethine) phenylene was prepared and interacted with the metal ions  $Ti^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$ . The interaction between these metal ions and the synthesized ligand led to the formation of coordinate polymers. All the chelate polymers were characterized by elemental analysis, electronic and IR spectra, solubility, and viscometry measurements. Furthermore, their thermal stability and electrical properties were studied and are discussed.

## EXPERIMENTAL

### Materials

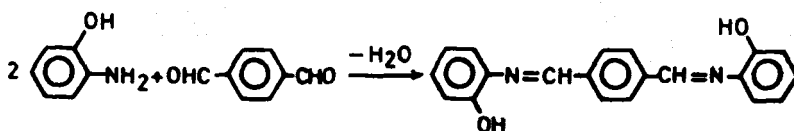
All chemicals were of Analar or chemically pure grade.

### Synthesis of 1,4-Bis(2'-hydroxyphenylazomethine) Phenylene (BHPAP)

A mixture of 0.2 mol *o*-aminophenol and 0.1 mol terephthalaldehyde was dissolved in 100 mL absolute ethanol. The reaction mixture was warmed to 60°C on a water bath for 1/2 h. After this time, shining golden yellow flakes separated. The product was filtered off, washed with ethanol, dried, and recrystallized from ethanol as golden yellow plate crystals, mp 213°C, and had a yield of 95%.

Analysis. Calculated for  $C_{20}H_{16}N_2O_2$ : C, 75.93; H, 5.09; N, 8.86%. Found: C, 75.86; H, 5.11; N, 8.96%. IR (KBr), at 3450-3100  $cm^{-1}$  (br, OH), at 1620  $cm^{-1}$  (s, C=N), and at 1260  $cm^{-1}$  (s, C-O phenolic).  $^1H$  NMR ( $\sigma_1(CD_3)_2$  C=O), at 7-8 (m, 12 H, Ar-H), at 8.1 (5.2 H, N=CH), and at 10.1 (5, 2H, OH phenolic) ppm.

The reaction takes place as follows:



### Preparation of Polychelates

The coordination polymers were prepared by mixing a hot solution of metal chloride (0.01 mol) in ethanol with a solution of the ligand (BHPAP) (0.01 mol) in ethanol in the presence of a few drops of DMF as scavenger for HCl. The resulting mixture was warmed on a water bath at a constant temperature of 70°C for 2 h, whereby the product separated out. The colored products were filtered off, washed thoroughly with ethyl alcohol, then dried under vacuum over phosphorus pentoxide.

### Measurements

Elemental analysis for C, H, and N was carried out using an Perkin-Elmer 240 C instrument, and the chlorine content was determined in the Analytical Unit of the Department. The electronic spectra of DMF solutions of the ligand and its different metal complexes were recorded by using a Unicam SP 800 spectrophotometer. The IR spectra were scanned on a Perkin-Elmer 599 B (4000–200  $\text{cm}^{-1}$ ) spectrophotometer by using the KBr disk technique. The inherent viscosities of polymer solutions in DMF were determined at 30°C by using an Ubbelohde Suspended Level Viscometer. Thermogravimetric analysis was carried out in air with Du Pont Models 951, 910 and a Du Pont 1090 Thermal Analyzers at a heating rate of 10°C/min. X-ray diffractograms were obtained with a Philips X-ray PW 1710 diffractometer by using Ni-filtered  $\text{Cu}_\alpha$  radiation. Pellets for electrical conductivity measurements were pressed at a constant pressure of 1000 psi by using an IR die. Silver paste was used to make contact and sandwiched between two standard graphite electrodes. Conductivities were measured over a range of 304–404 K in air by using a 610°C Keithley Electrometer. All calculations were adapted for Arrhenius plots. The iron-57 Mössbauer spectrum was collected on a Austin Science Associates constant acceleration drive with a flyback mode. Isomer shifts were referenced to iron at room temperature.

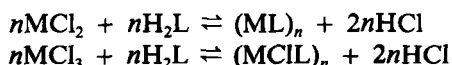
## RESULTS AND DISCUSSION

The interaction of terephthaldehyde and *o*-aminophenol in ethanol yields 1,4-bis(2'-hydroxyphenylazomethine) phenylene (BHPAP), the structure of which is supported by analytical and spectral data. The ligand is freely soluble in sodium hydroxide and gives an orange-colored product which resumes its yellow color on acidification with acetic acid. The desired polymeric chelates, having the stoichiometric ratio 1:1, were

obtained in quantitative yields by the interaction of equimolar amounts of the ligand (BHPAP) with  $Ti^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  cations as metal chlorides in ethanol. A few drops of dimethylformamide were added to the reaction mixture as a scavenger for HCl. The resulting polychelates were found to be quite stable in air. X-ray analysis indicated that all polychelates have halo patterns in the range of  $2\theta = 5-35^\circ$ , and this confirmed the amorphous state of the polychelates. All chelates were colored and insoluble in common organic solvents, partially soluble in *N,N*-dimethylacetamide and formamide, and freely soluble in dimethylformamide (DMF). The inherent viscosity of coordinated polymers solutions (0.5 g/100 mL DMF) was measured at  $30^\circ C$ , and the data are given in Table 1 together with elemental analysis for C, H, N and metal determinations. Table 1 shows that the polychelates have a 1:1 (metal:ligand) stoichiometric ratio and also suggests the presence of coordinated water molecules except for the Cu(II) complex.

Spectrophotometric investigations in the UV and visible region for the DMF solutions of the ligand and related polychelates were performed to inspect the formation of the complexes. The electronic absorption spectrum of the ligand shows two absorption peaks at 295 and 370 nm, which are ascribed to the  $\pi-\pi^*$  transition of the  $-CH=N-$  and intraligand charge transfer transitions [13], respectively. The electronic absorption spectra of DMF solutions of the different polymeric chelates shown in Fig. 1 exhibited no apparent differences from each other, and the values of  $\lambda_{max}$  are given in Table 1. The band appearing in the 245–285 nm region can be assigned to  $\pi-\pi^*$  transitions. The ligand band observed at 370 nm is red shifted (15–58 nm) and deformed to a shoulder. A new band in the 405–452 nm region is observed in the spectra of complexes due to L→M CT transitions from the ligand orbitals to the central metal atom orbitals. These bands are characterized by high molar extinction coefficients in comparison with those of other bands, which reduces absorptions corresponding to transitions within metal ions to non-entities.

The reaction between the 1,4-bis(2'-hydroxyphenyleneazomethine) bidentate ligand and Ti(III), Cr(III), Fe(III), Mn(II), Ni(II), and Cu(II) chlorides occurs as follows:



The infrared spectrum of BHPAP shows a broad band at 3450–3100  $cm^{-1}$  with a maximum at 3250  $cm^{-1}$ , attributed to the OH group. The

TABLE 1. Analytical Data, Inherent Viscosity, Electronic Spectra, and Physical Properties of Polychelates

Chelate	MW <sup>a</sup>	Analysis, % C/(F) <sup>b</sup>				mp, °C	$\lambda_{\max}$ , nm	Color	$\eta_{\text{inh}}$ , dL/g
		M	C	H	Cl				
[TiClC <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> · H <sub>2</sub> O] <sub>n</sub>	415.72	11.52 (11.64)	57.78 (57.43)	3.88 (3.75)	8.53 (8.41)	> 360	245 sh 422 sh 452	Brown	0.34
[CrClC <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> · H <sub>2</sub> O] <sub>n</sub>	419.82	12.38 (12.51)	57.22 (57.36)	3.84 (3.74)	8.44 (8.56)	> 360	250 sh 430 sh 450	Dark brown	0.5
[FeClC <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> · H <sub>2</sub> O] <sub>n</sub>	423.69	13.18 (13.27)	56.69 (56.51)	3.81 (3.94)	8.37 (8.50)	> 360	252 sh 380 sh 405	Dark brown	0.42
[MnC <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> · 2H <sub>2</sub> O] <sub>n</sub>	405.32	13.55 (13.60)	59.27 (59.12)	4.47 (4.56)	—	> 360	256 sh 425 sh 450	Black	—
[NiC <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> · 2H <sub>2</sub> O] <sub>n</sub>	409.09	14.35 (14.22)	58.72 (58.91)	4.43 (4.57)	—	> 360	285 sh 385 sh 412	Black	0.61
[CuC <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> ] <sub>n</sub>	377.69	16.81 (16.96)	63.57 (63.39)	3.73 (3.81)	—	> 360	285 sh 280 sh 410	Dark green	0.38

<sup>a</sup>MW = molecular weight of repeat unit estimated from elemental analysis,<sup>b</sup>C = calculated, (F) = found.

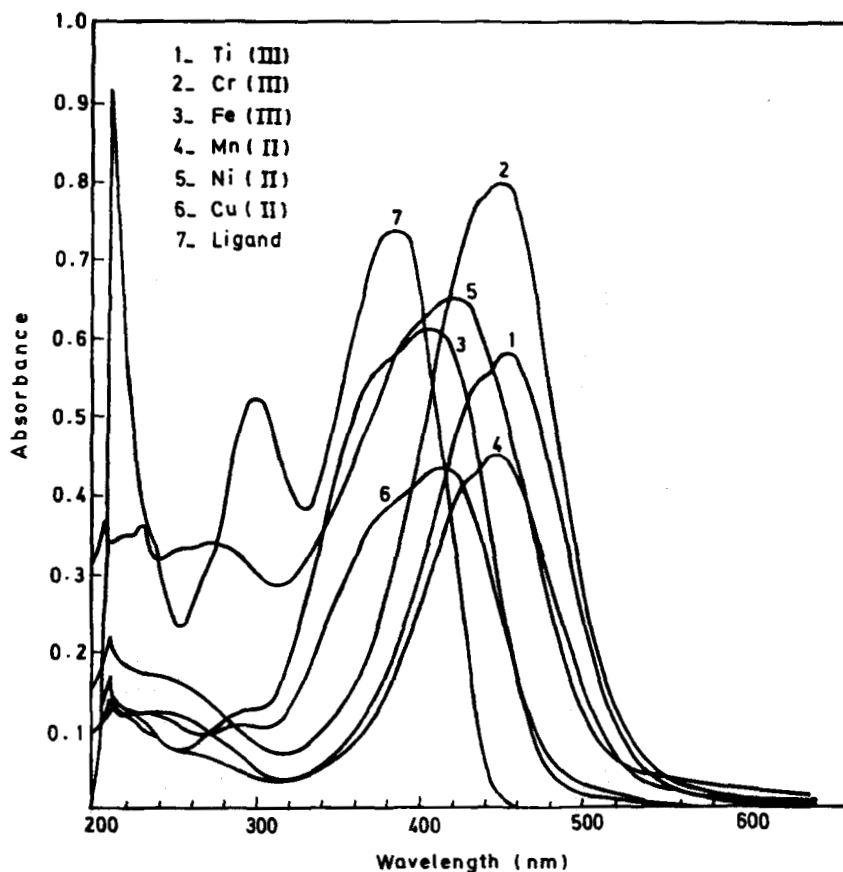


FIG. 1. UV-visible spectra of the ligand and its polymer complexes.

spectrum also shows sharp bands at  $1620\text{ cm}^{-1}$  due to the  $\text{C}=\text{N}$  bond, at  $1260\text{ cm}^{-1}$  due to phenolic  $\text{C}-\text{O}$  stretching vibrations, and at  $1590\text{ cm}^{-1}$  which is attributed to  $\text{C}=\text{C}$  stretching vibrations of the aromatic ring system [14].

The IR spectra of polychelates are not significantly different from each other, and their assignments are given in Table 2. New IR bands are observed in the spectra of coordinated polymers appearing at  $455\text{--}438\text{ cm}^{-1}$ , and they are due to the  $\text{M}-\text{O}$  bonds [15]. The band at  $1260\text{ cm}^{-1}$  for  $\text{C}-\text{O}$  stretching vibration was shifted to a higher frequency ( $1290\text{--}1280$

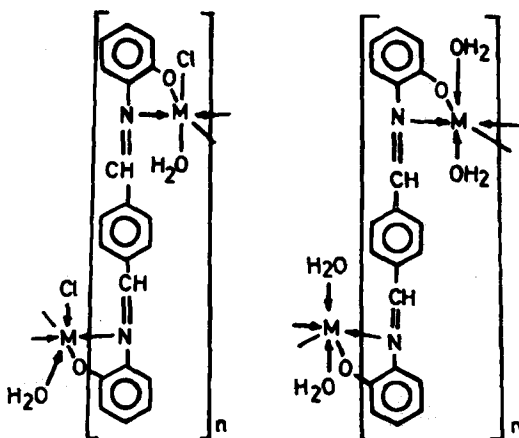
TABLE 2. Significant Infrared Bands ( $\text{cm}^{-1}$ ) of the Ligand ( $\text{H}_2\text{L}$ ) and Different Polymeric Chelates

Ligand	Ti(III)	Cr(III)	Fe(III)	Mn(II)	Ni(II)	Cu(II)	Assignment
$\text{H}_2\text{L}$	$\text{C1LH}_2\text{O}$	$\text{C1LH}_2\text{O}$	$\text{C1LH}_2\text{O}$	$\text{L}_2\text{H}_2\text{O}$	$\text{L}_2\text{H}_2\text{O}$	L	
3450	—	—	—	—	—	—	OH group
3100	—	—	—	—	—	—	—
1590	1590	1590	1590	1590	1590	1590	C=C aromatic st. vibration
1260	1290	1290	1285	1280	1280	1280	C—O phenolic st. vibration
1620	1618	1615	1615	1610	1612	1610	C=N st. vibration
—	438	455	438	445	440	440	M—O st. vibration
—	515	510	510	510	520	515	M—N st. vibration
—	370	350	345	—	—	—	M—Cl
—	850	855	850	850	855	—	Rocking vibration of coordinated $\text{H}_2\text{O}$



$\text{cm}^{-1}$ ) whereas the band for the  $\text{C}=\text{N}$  group at  $1620\text{ cm}^{-1}$  shifted to a lower frequency ( $17\text{--}25\text{ cm}^{-1}$ ) in all polychelates. This behavior is consistent with the wider delocalization of the electronic charge in the chelate ring [16]. The IR spectra show that all the chelate polymers possess coordinated water except for  $\text{Cu}(\text{II})$ . The  $\text{Ti}(\text{III})$ ,  $\text{Cr}(\text{III})$ ,  $\text{Fe}(\text{III})$ ,  $\text{Mn}(\text{II})$ , and  $\text{Ni}(\text{II})$  chelates exhibit weak bands at  $\sim 860\text{ cm}^{-1}$  which are ascribed to the rocking vibrations of coordinated water [17]. The IR spectra of trivalent metal chelated polymers showed a band at  $370\text{--}345\text{ cm}^{-1}$  which is due to the  $\text{M}\text{--}\text{Cl}$  bond as well as vibrational bands at  $515\text{ cm}^{-1}$  which are assigned to the  $\text{M}\text{--}\text{N}$  stretching vibrations. There were other characteristic absorption bands for the rest of the molecules. The infrared spectral data of the ligand and metal chelates are given in Fig. 2.

Based on what was stated above, the polymeric structures are



where  $\text{M} = \text{Ti}(\text{III})$ ,  $\text{Cr}(\text{III})$ , or  $\text{Fe}(\text{III})$  in the left-hand structure, and  $\text{M} = \text{Mn}(\text{II})$  or  $\text{Ni}(\text{II})$  in the right-hand structure.

Thermogravimetric analysis of polychelates and their weight loss at different temperatures are reported in Table 3. The TG curves confirm the presence of water molecules in all the chelates, except that of  $\text{Cu}(\text{II})$ . According to the literature [17], water eliminated below  $150^\circ\text{C}$  can be considered as crystalline water, and water eliminated above  $150^\circ\text{C}$  may be due to its coordination to the metal atom in chelates. In our study, the removal of water from  $\text{Ni}(\text{II})$  and  $\text{Mn}(\text{II})$  chelates is complete at nearly

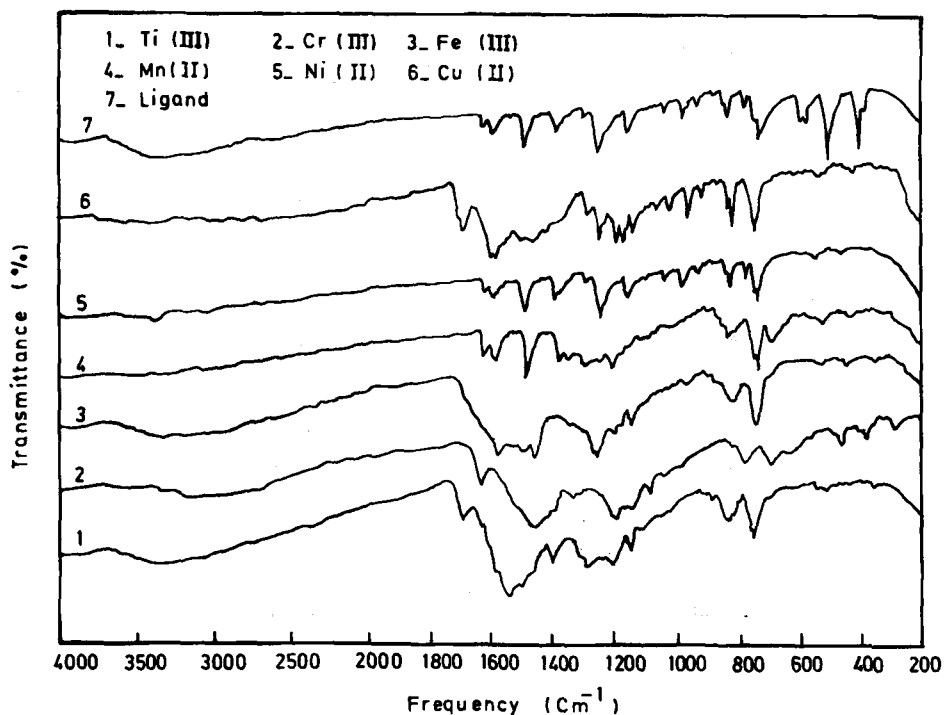


FIG. 2. IR spectra of the ligand and its polymer complexes.

TABLE 3. Thermogravimetric Analysis of Polychelates

Compound	Wt% loss at temperature, °C						
	150	200	300	400	500	600	700
Ti-BHPAP	7	10	22	35	60	68	85
Cr-BHPAP	3.5	7	18	30	65	77	80
Fe-BHPAP	4.5	9	25	32	62	77	82
Mn-BHPAP	8	10	20	35	60	72	83
Ni-BHPAP	2.5	9	17.5	30	59	65	84
Cu-BHPAP	—	8.5	15	38	55	65	83

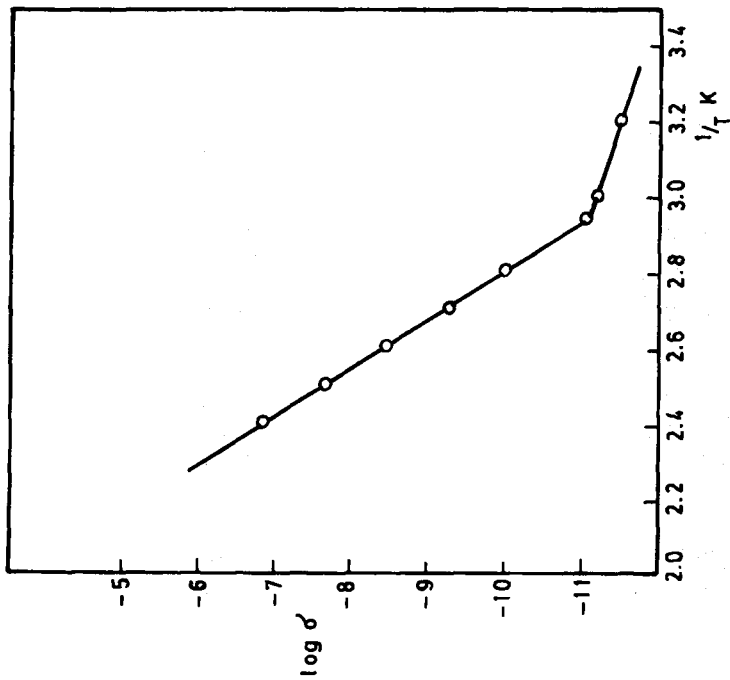


FIG. 3. Arrhenius plot for the electrical conductance of the chelate polymer of Ni(II).

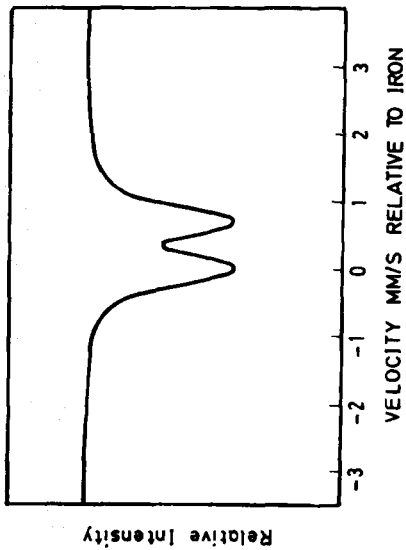


FIG. 4. Mössbauer spectrum of the Fe(III) complex.

130°C. This water is probably crystalline water. The removal of water from Ti(III), Cr(III), and Fe(III) chelates above 150°C indicates the presence of coordinated water molecules. Most of the polychelates start to decompose with a weight loss of from 7 to 10% at 200°C except for elimination of water molecules. The TG thermograms indicate that the polychelates decompose in two stages, and that the rate of degradation in the first stage is fast compared to the second stage. Table 3 indicates that the thermal stabilities of polycoordinates are in the order of Ni > Cu > Mn, Cr > Ti > Fe. Moreover, decomposition is complete at about 750°C in all chelates.

Electrical conductivity measurements were made over a wide range of temperatures (304–404 K). All the polychelates are insulator materials with values of  $10^{-11}$  to  $10^{-12}$  (ohm · cm)<sup>-1</sup> except the Ni(II) complex which has a value of  $7.1 \times 10^{-5}$  (ohm · cm)<sup>-1</sup>. A typical plot of  $\log \sigma$  vs  $1/T$  for Ni(II) chelate is shown in Fig. 3.

For further confirmation of our results, Mössbauer measurements of the iron polychelate sample are presented in Fig. 4. The Mössbauer spectrum consists of a broad quadrupole doublet with an isomer shift ( $\delta$ ) of 0.35 mm/s relative to iron and quadrupole splitting (QS) of 0.7 mm/s attributed to a high-spin Fe(III) species. The broad line indicates that the Fe nuclei were situated in two sites of slightly different chemical environment. This is consistent with what has been reported [18]. The aromatic azomethine linkage is found in *syn-anti* isomerism.

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