

Iron(III) Chelates of some Schiff Bases Derived from Isatin and Chromone with some Amino Acids and Hydrazine Derivatives

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Summary: Iron(III) complexes of the Schiff bases derived from isatin or chromone with glycine, β -alanine, anthranilic acid, S-methyl hydrazine carbodithioate, ammonium salt of hydrazine carbodithioate, thiosemicarbazide, semicarbazide and benzoyl hydrazine were prepared and characterized by elemental analysis, IR, U.V.-vis spectra and magnetic measurements. Octahedral structures have been assigned to the prepared complexes.

Introduction

In view of the promising importance of isatin and its derivatives as analytical reagents [1-3], and due to the antiviral [4], antibacterial [5], anthelmintic [6] and herbicidal [7] properties of isatins and continuation to our previous work [8,9], we describe here the coordinative properties of these ligands towards Fe(III).

Results and Discussion

The analytical data obtained (Table 1) suggest a (1:2) stoichiometry for Fe(III) chelates of Schiff bases of isatin-amino acids or isatin-substituted hydrazones of the general formula FeL_2Cl . Those derived from 6-formyl-7-hydroxy-5-methoxy-2-methyl chromone (FHMMC) appear to have 1:1 stoichiometry.

Infrared spectra and bonding modes

The tentative assignment of some of the important IR bands of the iron(III) complexes under investigation are collected in (Table 2). A broad band at 3200 cm^{-1} due to νNH of the isatin moiety is exhibited at nearly the same position in spectra of all chelates indicating that this group may probably be uncoordinated. The FHMMC complexes exhibit a broad band around the $3110\text{-}3120\text{ cm}^{-1}$ region attributed to coordinated water [10]. The bands at $1640\text{-}1630\text{ cm}^{-1}$ and $1700\text{-}1690\text{ cm}^{-1}$ due to C=N and C=O group stretching frequencies, respectively, in the ligands shift towards lower values in all complexes ($1600\text{-}1620$ and $1665\text{-}1650\text{ cm}^{-1}$) indicating that the azomethine nitrogen atom and the carbonyl oxygen atom of the isatin residue are coor-

Table 1: Elemental analysis data and magnetic moments for the complexes

Complex	Found (Calc.) %C	Found (Calc.) % N	% Found (Calc.) %H	% μ_{eff} B.M.
1. Fe(isat.-gly.) ₂ Cl	46.46(46.3)	10.4(10.8)	3.6 (3.8)	5.26
2. Fe(isat.- β -alan.) ₂ Cl	48.1(48.3)	10.6(10.2)	3.5(3.6)	5.32
3. Fe(isat.-anth.) ₂ Cl	56.5(56.1)	8.3(8.7)	3.2(3.4)	5.48
4. Fe(isat.-Smhc.) ₂ Cl	39.6(39.3)	13.4(13.7)	3.6(3.2)	5.23
5. Fe(isat.-amsh.) ₂ Cl	37.4(37.1)	14.8(14.4)	2.8(2.4)	5.41
6. Fe(isat.-thios.) ₂ Cl	39.0(39.3)	20.5(20.3)	3.6(3.2)	5.60
7. Fe(isat.-sem.) ₂ Cl	41.4(41.7)	21.9(21.6)	3.4(3.0)	5.29
8. Fe(isat.-benz.) ₂ Cl	56.6(56.2)	13.4(13.1)	3.9(3.7)	5.57
9. Fe(FHMMC-Smhc.)Cl.2H ₂ O	36.4(3.0)	6.4(6.0)	3.9(3.6)	5.62
10. Fe(FHMMC-thios.)Cl.2H ₂ O	35.7(35.9)	6.7(6.4)	4.0(3.9)	5.53

dinated. Appearance of a band in the 1375-1390 cm^{-1} region in the isatin-amino acid complexes is assigned to the sym. COO^- stretching vibration, suggesting that the amino acid carboxyl group is involved in the complex formation. The infrared spectra of Fe(III) complexes of hydrazones lack absorptions due to $\nu(\text{NH})$, but exhibit strong bands at 1618-1605 cm^{-1} due to $\text{C}=\text{N}-\text{N}=\text{C}$. The strong band at 1290-1295 cm^{-1} in the spectrum of the ligands assigned to the phenolic C-OH [11] shows a change in its position to 1275-1280 cm^{-1} in the IR spectra of Fe(III)-FHMMC-hydrazone complexes.

From the foregoing discussion, it is clear for isatin-amino acid or isatin-hydrazone complexes that the anion of each Schiff base is coordinated as a monobasic tridentate ligand to the central Fe(III) ion via the azomethine nitrogen, C=O of the isatin moiety and the oxygen atom of the amino acid carboxylate group (Fig. 1a) or the deprotonated thiol sulphur and enol oxygen for chelates of isatin-hydrazones as shown in Fig. 1b. In the case of FHMMC-hydrazone chelates, the ligand behaves as dinegative tridentate as shown in Fig. 1c.

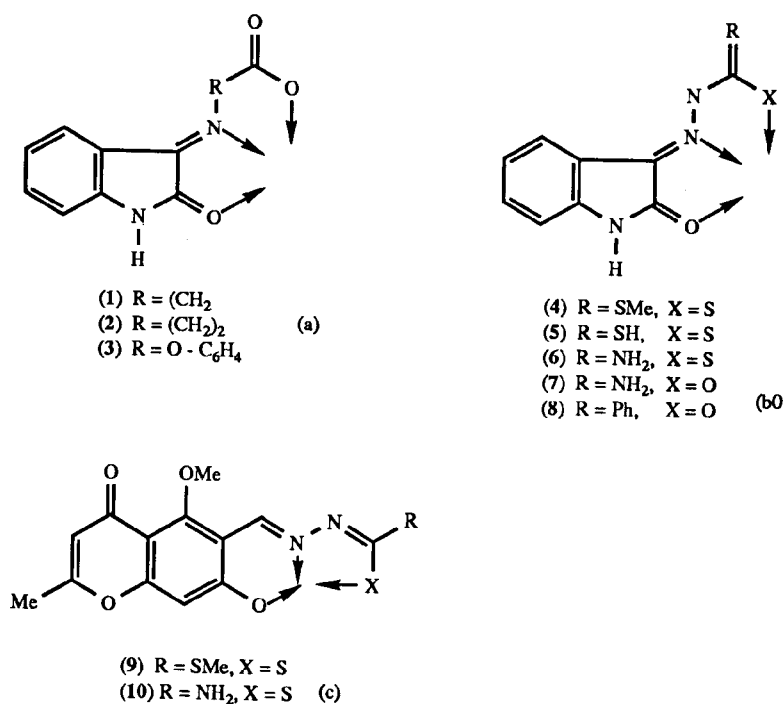


Figure 1. Structure of the ligands. The arrows indicate the suggested coordination sites.

Table 2: Infrared and electronic spectra of the complexes.

Complex	$\nu(\text{C}=\text{O})$ cm^{-1}	$\nu(\text{C}=\text{N})$ cm^{-1}	$\nu(\text{OH})$ cm^{-1}	$\nu(\text{C}-\text{O})$ cm^{-1}	$\nu(\text{Sym. COO}^-)$ cm^{-1}	λ_{max} nm
1. Fe(isat.-gly.) ₂ Cl	1660	1610	-	-	1380	300,420
2. Fe(isat.- β -anal.) ₂ Cl	1665	1605	-	-	1375	300,425
3. Fe(isat.-anth.) ₂ Cl	1658	1600	-	-	1390	320,450
4. Fe(isat.-Smhc.) ₂ Cl	1655	1600	-	-	-	240,400
5. Fe(isat.-amsh.) ₂ Cl	1650	1615	-	-	-	230,420
6. Fe(isat.-thios.) ₂ Cl	1660	1600	-	-	-	250,425
7. Fe(isat.-Sem.) ₂ Cl	1665	1618	-	-	-	260,430
8. Fe(isat.-benz.) ₂ Cl	1658	1609	-	-	-	260,435
9. Fe(FHMMC-Smhc.).Cl.2H ₂ O	1665	1620	3110	1275	-	320,420
10. Fe(FHMMC-thios.).Cl.2H ₂ O	1663	1620	3120	1280	-	310,430

Electronic spectra and magnetic measurements

The magnetic moments at room temperature for the complexes are given in (Table 1). The values of the magnetic moments suggest an octahedral geometry around Fe(III). This is confirmed by the electronic spectra which showed two broad absorption bands in the 240-310 and 420-450 nm regions (Table 2). These may be assigned to the charge-transfer [12] and ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition of the octahedral configuration [13] respectively.

Experimental

All chemicals used in the present work were of A.R. grade (E.Merck or B.D.H.). The synthesis of ligands under investigation was described elsewhere [8].

Preparation of Fe(III) complexes

The complexes were prepared by adding 50 ml of an aqueous solution of FeCl₃.6H₂O (0.1 mol) to 100 ml of ethanolic solutions of isatin Schiff base ligands (0.2 mol) and FHMMC-hydrazone solution (0.1 mol) and heating under reflux for 1 hour. The reaction mixture was concentrated to a small volume by evaporation. On cooling, the Fe(III) complexes which precipitated were filtered off, washed with EtOH and dried over P₄O₁₀ in a desiccator.

Physical measurements

Elemental analyses were carried out at the microanalysis laboratory of the Faculty of Science, Cairo University. A Shimadzu 408 spectropho-

tometer was used for recording the KBr IR spectra over the 4000-650 cm^{-1} range. Electronic spectra were measured in EtOH or DMF using a Spectronic 2000 spectrophotometer in the 200-850 nm range. The magnetic measurements were made at room temperature (298 K) by the Gouy method using Hg [Co(NCS)₄] as calibrant.

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