

Co (II) AND Fe (III) COMPLEXES OF SCHIFF BASES DERIVED FROM ISATIN WITH SOME AMINO ACIDS

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SUMMARY: Co (II) and Fe (III) chelates of Schiff bases derived from isatin with α -alanine, valine, β -phenyl- α -alanine, serine, threonine, aspartic acid, glutamic acid, histidine and tryptophan have been synthesized and identified on the basis of their chemical analysis, IR, UV-Vis. spectra and magnetic moment measurements. All the complexes are suggested to possess octahedral structures.

Key Words: Cobalt, ferrum.

INTRODUCTION

In view of the importance of isatins (1-6) and amino acids (7, 8) in many scientific fields and due to the scarcity of literature on the complexation of Schiff bases derived from isatin with amino acids, we report herein the chelating behavior of some of these ligands towards Co (II) and Fe (III).

EXPERIMENTAL

Materials

All chemicals used in the present work viz, isatin, amino acids, metal chlorides were of Analytical Reagent (A.R.) grade (E. Merck or B. D. H.).

Preparation of the ligands

Ethanol solution of isatin (1 mol) was added to H₂O solution of amino acids (1 mol). The mixtures were heated under reflux for ca. 1 h. The resulting ligands were precipitated, filtered off, washed with EtOH and dried.

Preparation of the metal complexes

The metal complexes were prepared by adding a hot H₂O solution of CoCl₂.6H₂O and FeCl₃.6H₂O (1 mol) to an EtOH solution of the ligands (2 mol) and heating under reflux for 1 h. The reaction mixtures were concentrated to a small volume by evaporation. On cooling the complexes which precipitated, were filtered off, washed with ethanol and dried over P₄O₁₀ in a desiccator.

Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out in the micro analysis laboratory of Faculty of Science,

Cairo University. Infrared spectra were measured as KBr pellets on a model 408 Shimadzu spectrophotometer over the 4000-650 cm⁻¹ range. Electronic spectra in ethanol were recorded using a Spectronic 2000 spectrophotometer in 200-850 nm range. The magnetic measurements were made at room temperature by the Gouy method using Hg (Co(NCS)₄) as calibrant.

RESULTS AND DISCUSSION

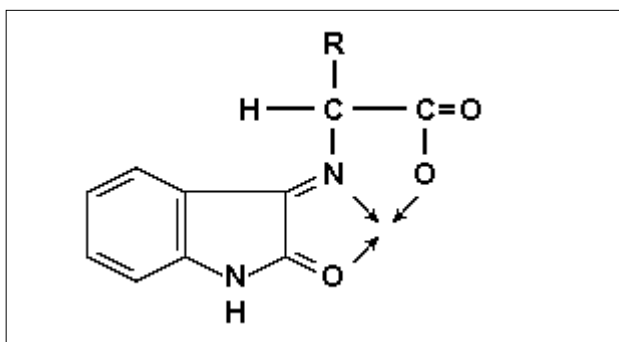
The chemical analysis data of the different synthesized cobalt (II) and iron (III) complexes (Table 1) suggest that the proposed formulas are CoL₂ and FeL₂.Cl where L = isatin-amino acid Schiff bases.

Infrared spectra and mode of coordination

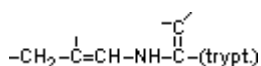
The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligands to the central metal ions (Co²⁺ and Fe³⁺) are given in Table 2. Generally, the IR spectra of the free ligands show a broad band around 3200 cm⁻¹ which can be attributed to NH stretching vibration of isatin, histidine and tryptophan moieties. The position of this band remains at nearly the same frequency in spectra of the metal complexes suggesting the uncoordination of this group. A 1360-1380 cm⁻¹ band in the complexes spectra is assigned to stretching vibration of the symmetric amino acids carboxyl group, suggesting the involvement of this group in the complex formation. The band appearing in the 1630-1620 cm⁻¹ region in the spectra of all complexes can be considered as an overlapped band due to two stretching vibrations of anti-symmetric coordinated COO and C=N.

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Figure 1: Structure of the ligands. Schiff base derivative of isatin with aminoacids. R represents side chain of Ala, Val, Ser, Thr, Phe, Asp, Glu, His or Trp. The arrows indicate the sites of coordination.



R = -CH₃ (α -alan.), -CH₂ (CH₃)₂ (Val.), -CH₂OH (ser.) - CH (OH) CH₃ (threon.), -CH₂-C₆H₅ (β -ph- α -alan.), -CH₂-COOH (asp.), -CH₂-CH₂-CooH (glut.), -CH₂-C=CH-N+CH-NH (hist.), and



Appearance of a band at 1720-1740 cm⁻¹ due to stretching vibration of un-ionized and un-coordinated COO⁻ in spectra of isatin-glutamic and isatin aspartic acid complexes suggest that the β - and μ carboxyl groups of the amino acid moieties do not take part in the complexation.

Bands at 1700-1690 and 1640-1630 cm⁻¹ due to C=O and C=N stretching frequencies respectively in the free ligands shift towards lower values in all complexes (1685-1670 and 1620-1600 cm⁻¹) indicating that the carbonyl oxygen atom of the isatin residue and the azomethine nitrogen atom are coordinated.

In case of isatin-serine or -threonine complexes, the binding ability of the alcoholic OH is relatively weak in acid or neutral media (10), therefore, the probability of coordination of the hydroxyl group of serine or threonine moieties is excluded.

Table 1: Analytical data and magnetic moments of the complexes..

Complexes	Found (calc.) %	Found (calc.) %	Found (calc.) %	μ_{eff} B.M.
	C	N	H	
Co (isat.- α -alan.) ₂	53.8 (53.5)	11.6 (11.3)	3.8 (3.6)	4.60
Co (isat.- val.) ₂	56.6 (56.8)	10.5 (10.2)	5.0 (4.7)	4.62
Co (isat.- ser.) ₂	50.5 (50.3)	10.8 (10.6)	3.8 (3.4)	4.59
Co (isat.- threo.) ₂	52.3 (52.1)	10.0 (10.1)	4.0 (3.9)	4.56
Co (isat.- β -Ph- α -al.) ₂	63.6 (63.2)	8.8 (8.6)	4.3 (4.0)	4.63
Co (isat.- asp.) ₂	49.3 (49.5)	9.5 (9.6)	3.3 (3.0)	4.68
Co (isat.- glut.) ₂	51.3 (51.5)	9.6 (9.2)	3.4 (3.6)	4.62
Co (isat.- hist.) ₂	53.9 (53.7)	17.6 (17.9)	3.9 (3.5)	4.68
Co (isat.- trypt.) ₂	62.6 (62.9)	11.3 (11.5)	3.5 (3.8)	4.59
Fe (isat.- α -alan.) ₂ .Cl	50.0 (50.2)	10.4 (10.6)	3.6 (3.4)	5.62
Fe (isat.- val.) ₂ .Cl	53.8 (53.6)	9.5 (9.6)	4.7 (4.4)	5.43
Fe (isat.- ser.) ₂ .Cl	48.5 (48.3)	10.4 (10.2)	3.6 (3.2)	5.63
Fe (isat.- threo.) ₂ .Cl	52.4 (52.1)	10.0 (9.5)	4.0 (3.7)	5.59
Fe (isat.- β -Ph- α -al.) ₂ .Cl	60.5 (60.2)	8.5 (8.2)	3.6 (3.8)	5.48
Fe (isat.- asp.) ₂ .Cl	46.8 (46.9)	9.0 (9.1)	3.0 (2.9)	5.39
Fe (isat.- glut.) ₂ .Cl	49.0 (48.9)	9.1 (8.7)	3.7 (3.4)	5.63
Fe (isat.- hist.) ₂ .Cl	51.5 (51.1)	17.3 (17.0)	3.6 (3.3)	5.61
Fe (isat.- trypt.) ₂ .Cl	60.6 (60.2)	11.4 (11.0)	3.4 (3.6)	5.60

Table 2: Infrared and electronic spectra of the complexes.

Complexes Found (calc.) %	ν sym.COO ⁻ cm ⁻¹	ν C=N cm ⁻¹	ν COOH cm ⁻¹	ν NH cm ⁻¹	ν C=O cm ⁻¹	λ max nm
Co (isat.- α -alan.) ₂	1365	1615	-	3200	1670	500, 350, 230
Co (isat.- val.) ₂	1360	1605	-	3200	1672	530, 300, 250
Co (isat.- ser.) ₂	1370	1600	-	3200	1675	535, 290, 260
Co (isat.- threo.) ₂	1362	1600	-	3200	1680	550, 320, 245
Co (isat.- β -Ph- α -al.) ₂	1370	1618	-	3200	1685	550, 340, 230
Co (isat.- asp.) ₂	1370	1620	1720	3200	1680	500, 325, 240
Co (isat.- glut.) ₂	1380	1619	1735	3200	1670	520, 330, 250
Co (isat.- hist.) ₂	1365	1620	-	3200	1670	525, 330, 260
Co (isat.- tryp.) ₂	1360	1600	-	3200	1675	530, 350, 240
Fe (isat.- α -alan.) ₂ .Cl	1368	1608	-	3200	1680	380, 310
Fe (isat.- val.) ₂ .Cl	1369	1610	-	3200	1685	390, 320
Fe (isat.- ser.) ₂ .Cl	1367	1610	-	3200	1683	420, 300
Fe (isat.- threo.) ₂ .Cl	1369	1620	-	3200	1670	430, 290
Fe (isat.- β -Ph- α -al.) ₂ .Cl	1373	1600	-	3200	1675	395, 290
Fe (isat.- asp.) ₂ .Cl	1375	1609	1730	3200	1680	440, 300
Fe (isat.- glut.) ₂ .Cl	1380	1614	1740	3200	1685	438, 295
Fe (isat.- hist.) ₂ .Cl	1365	1620	-	3200	1679	380, 310
Fe (isat.- tryp.) ₂ .Cl	1369	1615	-	3200	1680	435, 315

It can be deduced, from the above argumentation, that the isatin-amino acid Schiff base ligand behaves as a monobasic tridentate chelating agent towards the central Co (II) and Fe (III) via the three bonding sites of the azomethine nitrogen atom, carbonyl oxygen atom of the isatin residue and the negatively charged oxygen atom of the amino acid α -carboxyl groups as shown in Figure 1.

Electronic spectra and magnetic moments

The magnetic moment values measured at room temperature and electronic spectra bands of the complexes which were studied are given in Tables 1 and 2. The magnetic moments of Co (II) complexes (4.68-4.56 B.M) suggest a high-spin octahedral configuration (11). The high values of μ_{eff} may be due to orbital contribution.

The Co (II) complexes exhibit two bands at 550-500, 350-290 nm in the electronic spectra. The bands can be assigned to ${}^4T_{1g}(F) - {}^4A_{2g}$ and ${}^4T_{1g}(F) - {}^4T_{1g}(P)$ transitions respectively, which are in accordance with Co (II) high-spin octahedral geometry (12). The band observed in the 260-230 nm region can be assigned to charge transfer transition.

The magnetic moments obtained for Fe (III) complexes (5.63-5.39 B.M) are in favor to infer the presence of octahedral geometry around the central iron (III). The electronic spectra of Fe (III) complexes exhibit two bands at 440-380 and 320-290 nm assignable to the spin allowed electronic absorption of ${}^5T_{2g}(F) - {}^5E_g$ transition in octahedral configuration and charge transfer transition respectively.

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