

SYNTHESIS AND SPECTRAL PROPERTIES OF CHROMIUM (III) COMPLEX OF SEMICARBAZONE DERIVED FROM ISATIN

NARAYAN T. AKINCHAN

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ABSTRACT

A Chromium(III) complex was prepared by reacting isatin-3-semicarbazone (ISSCH) with chromium(III) chloride. The complex was characterized by molar conductance, magnetic moment, infrared, far-infrared and electronic spectra and elemental analysis. The ligand exists in keto tautomeric form and it coordinates through imino nitrogen and two carbonylo oxygen atoms. Octahedral structure for $[Cr(ISSC)_2Cl]$ is suggested.

Keywords: Semicarbazone, chromium(III), magnetic moment, IR, electronic spectra.

INTRODUCTION

The metal complexes of semi- and thiosemi-carbazones have been studied and the articles published on them have been reviewed (Campbell 1975, Padhye and Kauffman 1985). Chromium (III) complexes of semicarbazones (Garg and Tandon 1990, Patil et al 1983, Shukla et al 1993 Singh et al 1996) and thiosemi-carbazones (Garg and Tandon 1990 and Shukla et al 1993) have been extensively investigated. Furthermore the metal complexes of isatin-3-semicarbazones (Akinchan et al 1994 and, Chatterjee et al 1989) and isatin-3-thiosemicarbazones (Akinchan et al 2002 and, Ivanov et al 1988, 1989) have also been reported. It appears from the literature search that chromium (III) complexes with these ligands have not been studied. The present article describes the preparations and the magnetic and spectral properties of chromium (III) complex with semicarbazone derived from isatin abbreviated as ISSCH

MATERIALS AND METHODS

Materials:

Indoline 2,3 -dione (Isatin) (L. R, BDH) semicarbazide hydrochloride, (Anala R, BDH) Chromium (III) Chloride hexa hydrate (L. R., Aldrich) were used as supplied. The other chemicals used were chemically pure laboratory reagents (L. R).

Preparation of isatin 3-semicarbazone (ISSCH)

To a boiling solution of isatin (1.47g, 10mmol) in ethanol (50ml) was added dropwise a solution of (a) semicarbazide hydrochloride (1.12g, 10 mmol) and (b) sodium acetate (0.82g, 10 mmol) in aqueous ethanol (50ml). After adding

five drops of acetic acid, the resulting solution was refluxed for a period of two hours on a water bath. On cooling to room temperature a light yellow microcrystalline product was filtered and washed with ethanol and then diethyl ether and dried over silica gel. Yield: 76% FAB (POS) MS, M/Z 205

(MH 100%). Anal Calcd for $C_9 H_8 N_4 O_2$ (204.19) C 52.94; N27.44, H3.95 Found. C52.82, N27.38 H3.98.

ANALYSIS

Carbon, hydrogen and nitrogen were determined by the standard micro method at Central Drug Research Institute, Lucknow, India.

Preparation of bis(isatin 3- semicarbazonato) Chromium(III)chloride: $Cr(ISSC)_2Cl$:

Warm ethanolic solution of the 3-isatin semicarbazone (20 mmol), chromium (III) chloride hexahydrate (10 mmol) and sodium acetate (20 mmol) were mixed and refluxed on a water bath for 6 hours. The resulting solution on concentration and cooling gave microcrystalline yellowgreen solid which was washed with ethanol, diethylether and dried over silica gel. Yield, 46%. Anal Calcd for $Cr C_{18}H_{14} N_8O_4Cl$. Cr, 10.53 C,43.78 N; 22.69 H 2.86., Cl, 7.19% Found, Cr 10.46; C43.66; N22.58; H. 2.91. Cl, 7.06%

Physical Measurements;

Infrared spectra were recorded on Perkin Elmer 1600 and 2000 instruments using standard KBr pellet and nujol mull techniques for middle and far infrared region respectively. The uv-visible reflectance spectra were obtained on Cary-500 scan uv- vis- NIR instrument.

Table 1: IR spectra * (Cm^{-1}) of ISSCH and $\text{Cr}(\text{ISSC})_2\text{Cl}$

ISSCH	$\text{Cr}(\text{ISSC})_2\text{Cl}$	Assignments
3623(55)	3470(40)	$\text{V}_s(\text{NH}_2)$
3351(46)	3308(51)	$\text{V}_s(\text{NH}_2)$
3290(47)	---	$\text{V}(\text{NH})$
3172(45)	3240(48)	$\text{V}(\text{NH})$
	3127(50)	
1725(24)	1704(23)	$\text{V}(\text{C}=\text{O})$
1698(21)	---	$\text{V}(\text{C}=\text{O})$
--	1624(32)	$\text{V}(\text{C}=\text{O})$
1609(27)	1575(33)	$\text{V}(\text{C}=\text{N})+\text{V}(\text{C}=\text{C})$
1511(68)	---	
1470(51)	1466(26)	$\text{V}(\text{C}=\text{C})$
1454(48)	---	
1397(55)	1395(42)	$\text{V}(\text{C}=\text{C})$
1354(46)	1348(45)	$\text{V}(\text{C}=\text{NH})$
---	1305(58)	$\text{V}(\text{CH})$
---	1277(69)	$\text{V}(\text{CC})$
1236(71)	1213(48)	$\text{V}(\text{NH})+\text{V}(\text{CN})$
1193(43)	---	
1164(54)	1166(46)	$\text{V}(\text{CH})$
1110(34)	1112(43)	$\text{V}(\text{NN})$
1053(68)	1029(73)	$\text{V}(\text{CH})$
---	1009(74)	$\text{V}(\text{CC})$
951(68)	951(69)	$\text{V}(\text{CNNC})$

* % transmittance is given in parenthesis

RESULTS AND DISCUSSION

The results of the elemental analysis and other physical properties are reported in experimental section. On the basis of analytical data and the conductance measurement the complex could be formulated as $[\text{Cr}(\text{ISSC})_2]\text{Cl}$.

INFRARED SPECTRA:

The observed IR spectral bands for the ISSCH and $[\text{Cr}(\text{ISSC})_2]\text{Cl}$ are presented in Table 1. The proposed assignments are based on the earlier reported data and previously quoted literature. (Akinchan et al 1994, 2002). The spectrum of chromium (III) complex, $[\text{Cr}(\text{ISSC})_2]\text{Cl}$ differs from the spectrum of isatin-3-semicarbazone. (ISSCH) in whole 4000-900 cm^{-1} region (Table 1). Among the four highest energy bands, only that observed in the ligand at 3290 cm^{-1} does not have counterpart in the spectrum of chromium (III) complex, where the ligand deprotonation has been suggested (Akinchan et al 1994). Thus the IR spectral band at 3290 cm^{-1} is attributed to $\text{v}(\text{NH})$ vibration of semicarbazone moiety. Three remaining IR bands at 3623, 3351 and 3172 cm^{-1} result from vibrations of the $\text{V}_{\text{as}}(\text{NH}_2)$, $\text{V}_s(\text{NH}_2)$ and indoline $\text{v}(\text{NH})$ stretching vibrations. (Akinchan et al 1994, 2002). The IR spectral band at 1725 cm^{-1} assigned to $\text{V}(\text{C}=\text{O})$ of indoline moiety in the spectrum of ISSCH shifts to 1704 cm^{-1} in the spectrum of the $[\text{Cr}(\text{ISSC})_2]\text{Cl}$ indicating the coordination through carbonyl

oxygen atom. The -IR band at 169 cm^{-1} in the spectrum of 3-isatin semicarbazone (ISSCH) had been previously assigned to $\text{v}(\text{C}=\text{O})$ of semicarbazone moiety and it shifted to 1684 cm^{-1} in the spectrum of Copper (II) complex. (Akinchan et al, 1994) Patil et al (1983) reported $\text{v}(\text{C}=\text{O})$ at 1660 cm^{-1} in the spectrum of 2-hydroxy-1-naphthaldehyde semicarbazone and it changed to lower energy on metal coordination. During the present investigation, this band has been located at 1698 cm^{-1} and it disappeared in the spectrum of chromium(III) complex. It provides a supporting evidence of the deprotonation of NH group and coordination involving carbonyl oxygen atom of semicarbazone moiety. A new band at 1624 cm^{-1} in the complex's spectrum could be assigned to $\delta(\text{NH}_2)$. Similar observations have been reported by Ivanov et al (1988). The IR spectral band at 1609 cm^{-1} assignable to $\text{v}(\text{C}=\text{N})+\text{V}(\text{C}=\text{C})$ changed to 1575 cm^{-1} in the spectrum of the chromium (III) complex supporting the coordination involving imino nitrogen atom of the semicarbazone. (Akinchan et al. 2002). Thus the, deprotonated form of 3-isatin semicarbazone acts as ONO-tridentate chelating ligand.

In the far infrared region most spectral bands retain their position upon metal coordination demonstrating their origin from the ligand out-of-plane deformations (Table 2). Only three new spectral bands recorded at 518, 453 and 412 cm^{-1} can be considered as candidates for chromium-nitrogen [$\text{v}(\text{Cr}-\text{N})$] chromium-oxygen [$\text{v}(\text{Cr}-\text{O})$] stretching vibrations (Figure 1). Thomas

and Parmeswaran (1992) have reported $\nu(\text{Cr-N})$ at $500\text{-}540\text{cm}^{-1}$ and $\nu(\text{Cr-O})$ at $340\text{-}350\text{cm}^{-1}$ for chromium (III) complexes with schiff bases. Mishra and Purohit (1988) have reported $\nu(\text{Cr-N})$ at 470cm^{-1} and $\nu(\text{Cr-O})$ at 410cm^{-1} for salicylaldehyde thiosemicarbazone complexes of chromium(III). Thus higher energy band observed at 518cm^{-1} be assigned to $\nu(\text{Cr-N})$ stretching

vibration and the lower energy bands at 453 and 412cm^{-1} represent the two $\nu(\text{Cr-O})$ stretching vibrations in the spectrum of $[\text{Cr}(\text{ISSC})_2]\text{Cl}$.

Electronic spectra:

The uv-visible reflectance spectra of ISSCH and $\text{Cr}(\text{ISSC})_2\text{Cl}$ were taken using Li_2CO_3 matrix.

Table 2. Far-IR Spectra (cm^{-1}) of ISSCH and $\text{Cr}(\text{ISSC})_2\text{Cl}$

ISSCH	$\text{Cr}(\text{ISSC})_2\text{Cl}$
---	---
533	535
---	518
490	491
---	453
428	429
---	412
396	381
353	---
---	323
301	---
274	270
---	258
242	242
---	225
208	---
185	174
167	159
138	138
109	116

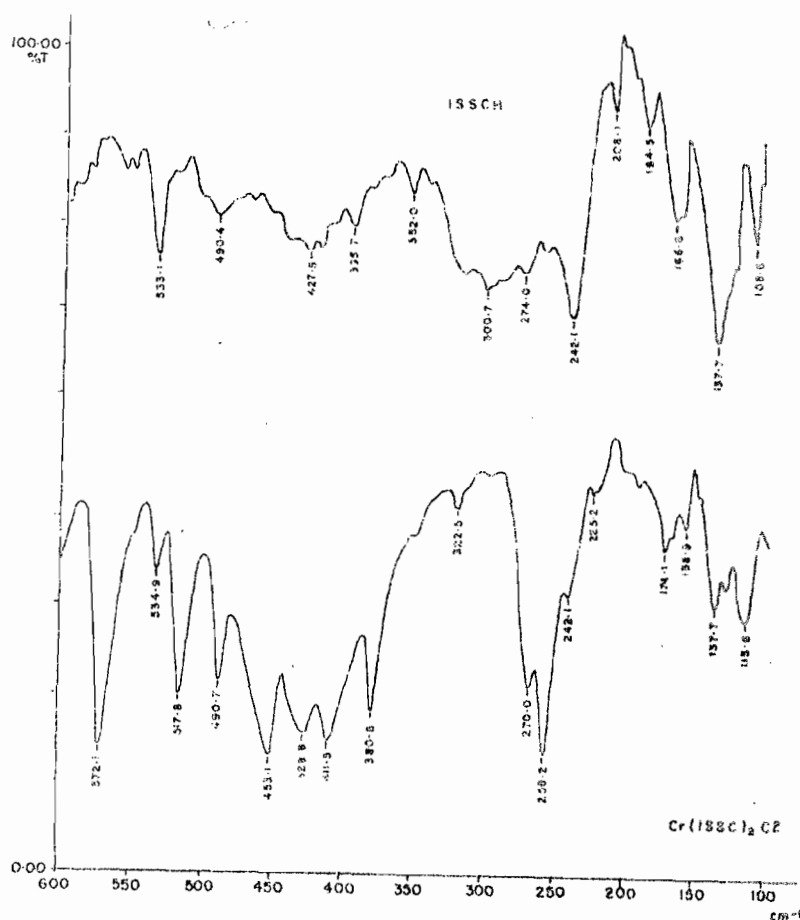


Fig. 1: Far IR Spectra of ISSCH and $\text{Cr}(\text{ISSC})_2\text{Cl}$

Table 3: Electronic spectra of ISSCH and Cr (ISSC)₂Cl

Nature of Spectrum	ISSCH Cm ⁻¹	Cr (ISSC) ₂ Cl Cm ⁻¹	Assignments
Reflectance Spectrum	40980	37037	$\Pi-\Pi^*$ (arom)
	31250	30303	$\Pi-\Pi^*$ (Semicarb)
	25000	24691	
	---	21276	$4A_{2g}(F) \rightarrow 4T_{2g}(F)$
	----	15385	$4A_{2g}(F) \rightarrow 4T_{1g}(F)$
Solution Spectrum (DMSO)	40980	39936	$\Pi-\Pi^*$ (arom)
	37760	37578	$\Pi-\Pi^*$ (arom)
	31690	31726	$\Pi-\Pi^*$ (Semicarb)
	27100	26667	
	-	21978	$4A_{2g}(F) \rightarrow 4T_{2g}(F)$
	-	15544	$4A_{2g}(F) \rightarrow 4T_{1g}(F)$

Spectral bands located above 35,000cm⁻¹ results from the $\Pi-\Pi^*$ transitions of aromatic ring system. (Akinchan et al 2002). Their sensitivity to metal coordination suggests the delocalization of electron density over conjugated band system consisting of Π -orbitals of the semicarbazone moiety and the aromatic rings system. The spectral bands between 25,000 and 35,000 cm⁻¹ are assigned to the $\Pi-\Pi^*$ transitions of semicarbazone group. (Akinchan et al 1994). Patil et al (1983) have reported the electronic spectra of chromium (III) complex with 2-hydroxy-1-naphthaldehyde semicarbazone at 22,730 and 17,290 cm⁻¹ and the magnetic moment value of 3.83 BM. Mishra and Purohit (1988) have also reported these electronic transitions at 23,200-23400 and 18,500-19200 cm⁻¹ with magnetic moment value in the range of 3.7-3.85 BM. The spectral bands in the complex's spectrum under investigation have been observed at 21,000 and 15,000cm⁻¹ assignable to $4A_{2g}(F) \rightarrow 4T_{2g}(F)$ and $4A_{2g}(F) \rightarrow 4T_{1g}(F)$ electronic transitions (Table 3). The magnetic moment value has been found to be 3.78 BM. These experimental observations are able to suggest an octahedral structure for Cr(ISSC)₂Cl. The electronic spectra in dimethyl sulphoxide are somewhat similar to the solid state spectra of this chromium(III) complex. It is probably due to substitutially inert nature of the Chromium (III) complex. (Table 3)

CONCLUSION

The isatin 3-semicarbazone exist in keto tautomeric form and it acts as anionic tridentate chelating agent and it coordinates through imino nitrogen and two carbonyl oxygen atoms. The Cr(ISSC)₂Cl complex appears to have octahedral structure.

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