CARACTERIZAÇÃO DO Fe (III), Co (II), Ni (II) E DE Cu (II) COMPLEXOS DE HIDRAZONA ÁCIDA SALICILSALICÍLICA POR MÉTODOS FÍSICO-QUÍMICOS

CHARACTERISATION OF Fe(III), Co(II), Ni(II) AND Cu(II) COMPLEXES OF SALICYLSALICYCLICACID HYDRAZONE BY PHYSICO-CHEMICAL METHODS

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RESUMO

Os complexos de Fe(III), Co(II), Ni(II) e Cu(II) com Hidrazona Ácida Salicilsalicílica foram sintetizados. O ligante e os complexos foram caracterizados por análises elementares de espectros UV-Vis, IR e RMN ¹H, bem como por análise térmica, condutividade molar e medições momento magnético. Tentou-se explicar a geometria dos complexos proposta em cada caso e foi proposto que os íons metálicos em estudo formam um complexo 1:1 com o ligante.

Palavras-chave *Hidrazona Ácida Salicilsalicílica; Complexos metálicos, Spectral, térmica, condutividade molar e estudos de momento magnético.*

ABSTRACT

The complexes of Fe(III), Co(II), Ni(II) and Cu(II) with salicylsalicycliacid hydrazone (SSAH) were synthesized. The ligand and the complexes were characterized by elemental analyses, UV-Vis, IR and ¹H NMR spectra, as well as by thermal analysis, molar conductivity and magnetic moment measurements. The tentative geometry of the complexes was proposed in each case and it was proposed that the metal ions under study form 1:1 complex with the ligand.

Keywords: *Salicylsalicycliacid hydrazone, Metal complexes, Spectral, thermal, molar conductivity and magnetic moment studies.*

INTRODUCTION

The chemistry of hydrazones continues to be of interest on account of their unique structural features. Hydrazones play an important role in inorganic chemistry, as they form stable complexes with metal ions (Nawar *et al.*, 1999; Sastry and Rao, 1995; Tsukamoto *et al.*, 1997; Keefe, 1997; Nawar *et al.*, 1994; Gudasi *et al.*, 2006; Kuriakose *et al.*, 2007; Pinto *et al.*, 2004; Terra, 2002). The development of bioinorganic chemistry of hydrazone complexes is due to their wide range of biological applications as antimicrobial (Nawar *et al.*, 1999; Pickart *et al.*, 1982; Mohan *et al.*, 1988; Chohan and Sheazi, 1999; Vicini *et al.*, 2002; Despaigne *et al.*, 2010; Zhu *et al.*, 2002), antifungal (Deepa *et al.*, 2001), antitubercular (Kocyigit-Kaymakcioglu and Rollas, 2002; Bedia *et al.*, 2006), antitumor (Iskander, 2004), anticonvulsant (Ragavendran *et al.*, 2007) and cytotoxic agents (Avaji *et al.*, 2009). The transition metal complexes are expected to play a key role in emerging field namely protein engineering of redox active enzyme systems because the transition metals in these complexes are highly susceptible for oxidation and reduction in varied oxidation states (Kolodziej, 1994; Cervera *et al.*, 1998; Ruiz *et al.*, 1997; Cousins *et al.*, 1999). Hydrazones are also proved to be sensitive analytical reagents for the determination of trace amount of metal ions (Raghavendra Guru Prasad *et al.*, 2010; Srilalitha *et al.*, 2011; Srilalitha *et al.*, 2010). Metal complexes with hydrazones have potential applications in various chemical processes e.g. non linear optics (Basu *et al.*, 2007), catalysis (Fujita *et al.*, 1994; Kimura *et al.*, 1994; Pouralimardan *et al.*, 2007) and as sensors (Bakir *et al.*, 2008). In the context of above mentioned versatile applications of metal complexes of hydrazones, the authors propose to synthesize and characterize certain transition metal complexes of SSAH.

EXPERIMENTAL

All chemicals were of analytical reagent grade procured from Merck, Mumbai, India. Double distilled water was used to prepare the solutions.

Co(II), Ni(II), Cu(II) and Fe(III) solutions were prepared by dissolving appropriate amounts of cobalt(II) sulphate, nickel(II) sulphate, copper(II) sulphate and ferric chloride respectively in double distilled water.

Physico-chemical measurements

Conductivity measurements were made on Conductivity Meter-303, Systronics, India. The electronic spectra were recorded using Shimadzu UV-160 Spectrophotometer. The infrared spectra were recorded in KBr pellets on Perkin Elmer-283 Spectrometer. The scanning time was 5 minutes and the range was 3800-300 cm^{-1} . AV₂-2A Dupont 9900 model thermo gravimetric equipment was employed for recording the thermal analysis data. The heating rate was maintained at 10° per minute and the experiments were carried out in nitrogen atmosphere.

The elemental analysis data was obtained from CDRI, Lucknow, India. Thermal analysis data, magnetic susceptibility data and ¹H NMR spectra were obtained from RSIC, IIT, Chennai, India.

Synthesis of SSAH

Appropriate concentrations of salicylic hydrazide (Srilalitha *et al.*, 2010) and salicylaldehyde in dimethylformamide were taken in a round bottom flask, 50 ml of methanol was added and the contents were heated for about 1 hour at 30°C. Yellow product obtained after cooling was recrystallised from 1:1 dimethylformamide. (Melting Point: 285°C).

Figure 1. Structure of salicylsalicylicacid hydrazone.

Synthesis of Metal-SSAH complexes

Solutions containing equal volumes of equimolar solutions of SSAH and metal solution were heated for about 2 hours in a round bottom flask at about 70°C. The crystalline metal-SSAH complexes (Co(II)-SSAH: Light orange, Ni(II)-SSAH: Light green, Cu(II)-SSAH: Green and Fe(III)-SSAH: Black) obtained were washed with water and dried in vacuo.

RESULTS AND DISCUSSION

Elemental analysis

The analytical data pertaining to elemental analysis of the SSAH (1) and metal complexes (2-5) under investigation are presented in the [Table 1](#). The data was in agreement with the theoretically calculated values shown in the parenthesis.

Molar conductivity data

The molar conductivity values of the metal complexes 2-5 determined in dimethylformamide solutions of concentration 1×10^{-3} M is given in [Table 1](#). The molar conductivity values were in the range $1.90 - 8.90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ normally recommended for non electrolytes (Geary, 1971). Hence complexes 2-5 are non electrolytic in nature.

Electronic spectral studies

The electronic spectral data and magnetic moment of the compounds 1-5 are given in the [Table 2](#).

The Fe(III)-SSAH complex exhibits an intense charge transfer band in the region $25000-20000 \text{ cm}^{-1}$. Generally the d-d absorption in octahedral Fe(III) complexes is rarely observed because the intense charge transfer absorptions obscure it. Further high spin Fe(III) complexes are not stabilized by crystal field effects. The μ_{eff} value of 5.66 BM was in agreement with the expected value for the high spin Fe(III)-SSAH complex (Hankare *et al.*, 2004) and indicated the high spin octahedral geometry for the complex (Cotton and Wilkinson, 1980).

Table 2. Electronic spectral and magnetic moment data of the complexes

Complex	μ_{eff} (BM)	Band positions $\nu \text{ (cm}^{-1}\text{)}$
Fe(III)-SSAH	5.66	31746 25000-20000
Co(II)-SSAH	Diamagnetic	33112 24390 22200
Ni(II)-SSAH	3.75	33100 24390 21100
Cu(II)-SSAH	2.60	31760 29110 25000

The electronic spectra of Co(II)-SSAH complex contains three distinct bands at 33112, 24390 and 22200 cm^{-1} . The first two bands were assigned to charge transfer and the third to d-d transfer of ${}^5\text{T}_{2g} \rightarrow {}^5\text{T}_{2g}$ favoring an octahedral structure. The spectrum contains two principle absorption bands (Ferguson *et al.*, 1963). A band near $8000-10000 \text{ cm}^{-1}$ was attributed to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ transition. A multiple band at 20000 cm^{-1} was attributed to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition. These transitions were consistent with the characteristic octahedral geometry (Lever, 1984). The complex was found to exhibit diamagnetic property corresponding to low spin Co(III) complexes (Levason, 1974). Probably cobalt was in the +3 oxidation state in the complex (Huheey, 1983).

The electronic spectrum of Ni(II)-SSAH complex contains an intense charge transfer band at 33100 cm^{-1} . However two separate bands observed at 24390 cm^{-1} and 21100 cm^{-1} were attributed to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) transitions respectively (Figgis, 1960). The appearance of ν_3 and ν_2 bands suggests an octahedral structure for the complex. The μ_{eff} value of 3.75 BM also suggests an octahedral geometry with ${}^3\text{A}_{2g}$ ground state (Lever, 1965; Agarwal *et al.*, 2006).

The electronic spectrum of the Cu(II)-SSAH complex in dimethylformamide showed intense charge transfer bands at 31760 cm^{-1} and 29110 cm^{-1} . A distinct band at 25000 cm^{-1} was due to the d-d transitions and this suggests square planar geometry for the complex (Sacconi and Ciampolini, 1964; Blum, 1974). The μ_{eff} value of the complex 2.60 BM was higher than the value

calculated on the basis of spin only formula for a single unpaired electron (Agarwal *et al.*, 2006). This may be attributed to the absence of metal-metal interaction and monomeric nature of the complex.

IR Spectral Studies

To ascertain the ligand-metal bonding in the complexes under study (2-5), the infrared spectra of the complexes were compared with that of the free ligand. The IR spectra of the SSAH and complexes (2-5) taken in KBr pellet are shown in the [Figures 2 – 6](#) and the spectral data is given in the [Table 3](#).

The ligand shows absorption bands at 3325, 1625, 1615 and 1090 cm^{-1} due to $\nu_{(\text{N-H})}$, $\nu_{(\text{C=O})}$, $\nu_{(\text{C=N})}$ and $\nu_{(\text{N-N})}$ respectively. The band observed at 3410 cm^{-1} was attributed to the intramolecular hydrogen bonding between the hydrogen of the phenolic OH and the nitrogen of the azomethine group and /or between the nitrogen of the amide-II NH and the carbonyl oxygen of the amide-I CO group. Ligand behaves in dibasic tetradentate manner through the involvement of both the phenolic OH groups after deprotonation and coordination through azomethine nitrogen and amide-II NH nitrogen with metal. The mode of complexation with the metal was suggested by the negative shifts observed by about 14-52 cm^{-1} and 30-120 cm^{-1} in case of $\nu_{(\text{C=N})}$ and $\nu_{(\text{N-H})}$ respectively. (Ibrahim, 1995; Krishnan and Indrasenan, 1989; Agarwal and Prakash, 1991; Agarwal, *et al.*, 1992) However a positive shift by about 13-53 cm^{-1} observed in the case of $\nu_{(\text{N-N})}$ was in agreement with that observed in similar metal complexes (Pickart *et al.*, 1982). Further the disappearance of bands near 3500 to 3300 cm^{-1} was due to the complexation of deprotonated phenolic OH group with the metal (Iskandar *et al.*, 1980; Mustafa *et al.*, 1983).

New bands observed at 572-587 and 419-430 cm^{-1} in the spectra of metal complexes were attributed to the $\nu_{(\text{M-O})}$ (Gosavi and Rao, 1967) and $\nu_{(\text{M-N})}$ (Mikami *et al.*, 1967) vibrations respectively.

Thermal studies

The thermograms obtained are presented in the [Figures 7-10](#).

The thermograms indicate a sharp initial decomposition. All the complexes were found to

be thermally stable up to 300°C. This clearly suggests the absence of water molecules in the metal complexes. This fact was further confirmed by the absence of endothermic peaks in the DTA curves in the temperature range 0 to 200°C.

Pyrolysis data of the anhydrous complexes at 500°C are presented in the [Table 4](#). The data reveals that, in case of Fe(III) and Co(II) complexes, the pyrolysis data corresponds approximately to that of metallic oxide state, while in the case of Ni(II) and Cu(II) complexes, the data corresponds to the metallic state.

The initial decomposition data presented in the [Table 4](#) indicate that the thermal stabilities of the complexes are in the order Ni(II) > Cu(II) > Co(II) > Fe(III). The horizontal portion of the thermograms of the complexes extends up to 300°C. In the case of Cu(II) and Ni(II) complexes, the thermal decomposition may occur by the scission of metal ligand bond. However in the case of Co(II) and Fe(III) complexes the thermal decomposition does not occur by the scission of metal ligand bond and hence it corresponds to the oxide state of the metal.

¹H NMR spectral studies

The ¹H NMR spectral data of the ligand and complexes recorded in DMSO-d₆ using TMS as an internal reference is given in the [Table 5](#).

The ¹H NMR spectrum of the ligand exhibits a broad signal around δ 5.40 ppm due to –OH proton. Area under the peak corresponds to two protons indicating two –OH groups in the ligand. A sharp peak noticed at δ 10.90 ppm was due to –NH proton. A multiplet observed at about δ 6.90-7.89 was attributed to –CH protons of benzene ring.

The absence of broad peak corresponding to –OH proton in the ¹H NMR spectra of metal complexes was attributed to the involvement of deprotonated phenolic –OH groups in the complexation process. The signal of –NH proton was slightly shifted towards lower values. This is attributed to (1) the complexation of amide (II) nitrogen with metal and (2) a probable existence of hydrogen bonding between oxygen of amide-I carbonyl group and nitrogen of amide-II –NH group. It can also be seen from the [Table 5](#) that the signals of aromatic protons were not disturbed in the spectra of metal complexes.

On the basis of above discussion, the proposed geometry for the metal complexes are depicted in [Figure 11](#) a and b.

CONCLUSION

Fe(III), Co(II), Ni(II) and Cu(II) complexes of SSAH have been synthesized and characterized by elemental analyses, molar conductivity, UV-Vis spectral, IR spectral, ^1H NMR spectral, thermal analysis data and magnetic moment measurements. Co(II), Ni(II) and Fe(III) complexes of SSAH were found to have octahedral geometry whereas Cu(II)-SSAH complex has square planar geometry.

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Table 1. Analytical data of ligand and complexes

S.No.	Compound	Color	Mol. Wt.	Melting point (°C)	Found (Cal) %				Molar conductance (ohm ⁻¹ cm ² mole ⁻¹)
					C	H	N	Metal	
1	SSAH	Light yellow	256	285	65.53 (65.60)	4.60 (4.70)	10.82 (10.90)	---	----
2	Fe(III)-SSAH	Black	309.85	267	54.12 (54.20)	3.10 (3.20)	8.92 (9.00)	17.74 (18.00)	8.90
3	Co(II)-SSAH	Light orange	312.93	241	53.55 (53.70)	3.10 (3.20)	8.70 (8.90)	18.70 (18.80)	3.20
4	Ni(II)-SSAH	Light green	312.71	234	53.60 (53.70)	3.10 (3.20)	8.85 (9.00)	18.65 (18.80)	3.32
5	Cu(II)-SSAH	Green	317.54	212	52.70 (53.90)	3.10 (3.20)	8.75 (8.80)	19.80 (20.20)	1.90

Table 3. Important frequencies (cm^{-1}) observed in the IR spectra of the compounds and their assignments

SSAH	Fe(III)-SSAH	Co(II)-SSAH	Ni(II)-SSAH	Cu(II)-SSAH	Assignment
3410	---	---	---	---	$\nu_{\text{O-H}}$
3325	3275	3200	3195	3225	$\nu_{\text{N-H}}$
1650	1607	1608	1610	1625	$\nu_{\text{C=O}}$
1615	1563	1571	1575	1601	$\nu_{\text{C=N}}$
1090	1143	1103	1117	1124	$\nu_{\text{N-N}}$
---	580	580	572	575	$\nu_{\text{M-O}}$
---	431	419	430	428	$\nu_{\text{M-N}}$

Table 4. Thermal analysis data of the metal-SSAH complexes

Complex	Percent pyrolysed			Initial decomposition temperature (°C)
	Theoretical		Experimental	
	M (metallic state)	MO (metal oxide state)		
Fe(III)-SSAH	82.00	76.80	74.00	356.41
Co(II)-SSAH	81.20	76.00	72.00	380.77
Ni(II)-SSAH	80.90	75.70	84.00	390.85
Cu(II)-SSAH	80.10	75.00	84.00	385.90

Table 5. Important ^1H NMR spectral data (δ ppm) of the compounds and their assignments

Compound	Aldehydic proton	-NH proton	-OH proton	Aromatic proton
SSAH	8.600	10.900	5.400	6.900-7.890
Fe(III)-SSAH	8.690	11.350	---	6.900-7.890
Co(II)-SSAH	8.114	11.180	---	6.900-7.890
Ni(II)-SSAH	8.700	11.200	---	6.900-7.890
Cu(II)-SSAH	8.670	11.300	---	6.900-7.890

Figure 2. IR spectrum of SSAH

Figure 3. IR spectrum of Fe(III)-SSAH complex

Figure 4. IR spectrum of Co(II)-SSAH complex

Figure 5. IR spectrum of Ni(II)-SSAH complex

Figure 6. IR spectrum of Cu(II)-SSAH complex

Figure 7. TGA and DTG of Fe(III)-SSAH complex

Figure 8. TGA and DTG of Co(II)-SSAH complex

Figure 9. TGA and DTG of Ni(II)-SSAH complex

Figure 10. TGA and DTG of Cu(II)-SSAH complex

Figure 11. (a) and (b)-Proposed structure of Metal-SSAH complexes