Thermochimica Acta, 111 (1987) 385–389
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

SPECTRAL, MAGNETIC AND THERMAL INVESTIGATIONS ON Cu(II), Ni(II) AND Co(II) COMPLEXES WITH 3-(*p*-DIMETHYL AMINO-ANILINO)-METHYL SALICYLIC ACID HYDRAZIDE

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(Received 23 June 1986)

The systems showing the relationship between thermal stability of metal chelates and structure of chelating agents have been studied only to a limited extent [1]. Wendlandt et al. [2–5] and Hill et al. [6,7] studied the thermal properties of metal chelates with various chelating ligands. Seshagiri and other workers [8–12] reported the thermal stability of metal chelates of oxine. Thorough survey of the literature reveals that much less is known about the chelation behaviour of acid hydrazide Mannich bases. The present note reports the preparation, magnetic susceptibility measurements, spectral behaviour (IR and electronic) and thermal characteristic of Cu(II), Ni(II) and Co(II) complexes of 3-(*p*-dimethyl amino-anilino)-methyl saliylic acid hydrazide.

EXPERIMENTAL

All reagents used were of AnalaR grade. IR spectra of the complexes in KBr pellets and far IR spectra (650–200 cm^{-1}) in nujol mulls were recorded on a Beckmann IR-20 spectrophotometer. Electronic absorption spectra of the complexes in methanol were recorded on a Carl-Zeiss VSU-2P instrument. Thermogravimetric analyses were carried out using a Stanton automatic electrobalance with a heating rate of 6°C min^{-1}.

Preparation of the ligand

Salicylic acid hydrazide was prepared by the action of hydrazine hydrate on ethyl salicylate. The ligand was prepared by condensing the acid hydrazide (in dioxan), *p*-dimethyl amino aniline and HCHO according to the reported procedure [13]; it melts at 172°C.

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Preparation of the chelates

The chelates were prepared by dissolving the ligand in absolute ethanol and refluxing with the metal salts (halides) in aqueous ethanol for 2 h on a water bath. The resulting solid compounds were filtered, washed with ethanol and dried over P_4O_{10}.

RESULTS AND DISCUSSION

Analytical data (Table 1) correspond to the formulae [Cu(L)Cl], Ni · 2L and Co · 2L (where L = $C_{16}H_{19}N_4O_2$) of the isolated complexes. The complexes are non-hygroscopic. They melt above 200 °C. All the complexes are soluble in common organic solvents. All the complexes possess non-electrolytic nature, which is evident from the low conductivity values (Table 1). This is further confirmed by the fact that a solution of the first complex fails to form any precipitate with $AgNO_3$.

Magnetic moment

Magnetic moments (Table 1) indicate that the Cu(II), Ni(II) and Co(II) complexes contain one, two and three unpaired electrons, respectively, accounting for their paramagnetic nature. The magnetic moment of Ni(II) complex is found proximate to its spin-only value. Naturally, orbital contribution is quenched by the crystalline ligand field. The magnetic moments of the Cu(II) and Co(II) complexes are much above their spin-only values. Considerable orbital contribution appears in these complexes. Magnetic moments show that the Ni(II) and Co(II) complexes are octahedral while Cu(II) complex possesses D_{4h} symmetry.

Electronic spectra

The Cu(II) complex exhibits bands at 15 780 and 18 540 cm^{-1}, corresponding to the transitions: $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$. Hence it possesses D_{4h} symmetry.

The absorption peaks at 11 450, 19 200 and 20 500 cm^{-1} in the Ni(II) complex are in accordance with the octahedral geometry. They may be assigned to the transitions: $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$.

The spectra of Co(II) complex shows bands at 9150, 20 570 and 23 400 cm^{-1}, assignable to the transitions: $^4T_{1g} \rightarrow {}^4T_{2g}(F)$, $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(F)$, respectively. The frequencies of the bands are consistent with the octahedral stereochemistry.

TABLE 1

Analytical, conductivity and magnetic moment data of Cu(II), Ni(II) and Co(II) complexes of 3-(*p*-dimethyl amino-anilino)-methyl salicylic acid hydrazide

Complex [a]	Analysis [b]										Conductivity ΛM Ω^{-1} cm^2	Magnetic moment at 300 K ($\mu_{eff.}$ B.M.)
	Metal		C		H		N		Cl			
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.		
Cu·L·Cl	15.18	15.96	47.68	48.24	4.88	4.77	13.54	14.07	8.39	8.90	9.80	2.08
Ni·2L	8.64	8.93	56.90	58.47	6.02	5.78	16.68	17.05	–	–	2.70	2.94
Co·2L	8.66	8.97	59.98	58.45	5.48	5.78	16.57	17.05	–	–	6.80	4.86

[a] Where L = $C_{16}H_{19}N_4O_2$.

[b] Reported as percentages.

IR spectra

The IR spectra results reveal that the ligand molecule possesses three donor sites, viz. the carbonyl group, phenolic OH and hydrazinic amino group.

The strong absorption band (amide I band) which appeared in the ligand at 1670 cm^{-1}, suffers a depression of 20–30 cm^{-1} in the chelated species, indicating the participation of the carbonyl group in bonding to the metal ion through its oxygen atom.

The absorption band, characteristic of the –OH group, observed at 3525 cm^{-1} in the free ligand, is found missing in the complexes, suggesting the involvement of –OH group in chelation.

The band at 3260 cm^{-1} may be due to the superimposed stretching vibrations of –NH bands of the hydrazinic amino and imino groups. The band at 3260 cm^{-1} gets shifted to lower frequency region (3240–3210 cm^{-1}) in the chelated compounds, indicating the hydrazinic $-NH_2$ co-ordination to the metal ions. A ν(M–Cl) vibration band at 245 cm^{-1} appears in the Cu(II) complex.

Thermal behaviour

Thermal investigation on the present set of compounds shows that all the complexes are non-hygroscopic and stable upto 200 °C, showing the absence of crystal and lattice water. The decomposition of the complexes takes place in several steps. The results of thermal analyses are recorded in Table 2.

TABLE 2

Thermal decomposition data for Cu(II), Ni(II) and Co(II) complexes of 3-(*p*-dimethyl amino-anilino)-methyl salicylic acid hydrazide

Complex [a]	Decomp. temp. (°C)		Wt. loss (%)		Species formed
	Initial	Final	Found	Calcd.	
Cu·L·Cl	220	260	22.10	21.00	$CuL_{3/4}Cl$
	270	320	26.08	26.59	$CuL_{1/2}Cl$
	330	390	35.80	36.23	$CuL_{1/4}Cl$
	400	450	45.98	44.65	CuO
Ni·2L	230	280	22.08	22.76	$NiL_{3/2}$
	290	330	29.98	29.47	NiL
	340	400	42.30	41.79	$NiL_{1/2}$
	400	440	65.08	64.12	NiO
Co·2L	220	280	22.10	22.75	$CoL_{3/2}$
	290	330	28.94	29.46	CoL
	340	390	41.06	41.78	$CoL_{1/2}$
	400	450	65.11	64.11	CoO

[a] Where $L = C_{16}H_{19}N_4O_2$.

All these compounds lose weight from about 220 to round about 450°C due to the decomposition of organic ligands. It is observed that the ligand molecule, in all these complexes, is completely lost and the residue is the metallic oxide.

ACKNOWLEDGEMENT

The authors are grateful to Dr. G.D. Sharma, Principal, L.R. College (P.G.), Sahibabad for his keen interest and kind help for the work. S.K.A. is thankful to U.G.C. for providing financial assistance.

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