ELSEVIER

Thermochimica Acta 244 (1994) 277–282

thermochimica
acta

Note

Spectral and thermal characterization of mixed-ligand complexes of Cu(II), Ni(II) and Co(II) with 3-methoxy-4-hydroxy benzalidene-2-furoic hydrazide as the primary ligand and with 2-hydroxy-5-chloro-2′-carboxy azobenzene as the secondary ligand

Suresh K. Agarwal [1]

Department of Chemistry, L.R. Postgraduate College, Sahibabad-20 1 005, India

Received 19 November 1993; accepted 14 March 1994

Abstract

The interaction of 3-methoxy-4-hydroxy benzalidene-2-furoic hydrazide and 2-hydroxy-5-chloro-2′-carboxy azobenzene with Cu(II), Ni(II) and Co(II) metal ions has been studied. The analytical data suggest the formation of 1 : 1 : 1 (M–L–L′) complexes (where L is $C_{13}H_{12}N_2O_4$ and L′ is $C_{13}H_8N_2O_3Cl$). Electrolytic conductance data ($\Delta M = 4.9–7.4\ \Omega^{-1}$ cm^2 for the chloro complexes and 69.8–85.4 Ω^{-1} cm^2 for the nitrate complexes) showed that the chloro complexes are non-electrolytes while the nitrate complexes are 1 : 1 electrolytes. Electronic spectra of these complexes show that they possess octahedral geometry. IR spectral studies show that the hydrazide ligand acts as a tridentate ligand, and the azo acts as a bidentate ligand. TG data confirm the above composition for the present complexes.

Keywords: Cobalt compound; Conductance; Copper compound; Ligand; Mixed-ligand complex; Nickel compound; TG

---

[1] Correspondence address: III-E 7/9, Nehru Nagar, Ghaziabad-201 001, India.

SSDI 0040-6031(94)01800-V

1. Introduction

The bactericidal, herbicidal, insecticidal and fungicidal properties of hydrazones are well known [1–6]. In addition, hydrazones have been found to possess analytical applications [7–10]. Azo compounds containing two coordinating groups in the ortho position have also been found to exhibit many analytical applications [11–15]. The synthesis and characterization of some 3d-metal complexes with hydrazones have been recently reported [16–18]. In an attempt to investigate the biological significance (in progress) of ternary complexes with hydrazide and azodye ligands, the study of this type of mixed-ligand complex has been undertaken. Here, the spectral and thermal behaviour of Cu(II), Ni(II) and Co(II) complexes with 3-methoxy-4-hydroxy benzalidene-2-furoic hydrazide and 2-hydroxy-5-chloro-2′-carboxy azobenzene are reported.

2. Experimental

The metal chlorides and nitrates used were of AnalaR grade. 2-Furoic hydrazide and 4-chlorophenol were procured from Aldrich Chemical Co. Inc., USA. IR spectra in the 4000–700 and 650–200 cm^{-1} regions were recorded on a Beckmann IR-20 spectrophotometer. TGA was carried out on a Cahn R.G. electrobalance with a platinum boat in static air, with 5 mg of sample and a heating rate of 6 K min^{-1}. The analytical data (C, H, N) for the compounds were obtained from the Micro-analytical Laboratory, Delhi University, Delhi. The metal contents of the complexes were determined using standard procedures [19].

2.1. Preparation of the ligands

3-Methoxy-4-hydroxy benzalidene-2-furoic hydrazide was prepared by refluxing 2-furoic hydrazide with vanilline (1 : 1 molar ratio) in ethanol (60 ml) for four hours. The resulting solution, on concentration and cooling, yielded the desired compound. 2-Hydroxy-5-chloro-2′-carboxy azobenzene was synthesized by direct coupling of the diazonium chloride of anthranilic acid with 4-chloro phenol in alkaline solution.

2.2. Preparation of the complexes

The complexes were obtained by refluxing an aqueous ethanolic (50%, v/v) solution of the metal salt with an ethanolic solution of the ligands in 1 : 1 : 1 (M : L : L′) molar ratio for 30–45 min on a water bath. The resulting solid compounds were filtered, washed with dry ether, and recrystallized and dried over anhydrous $CaCl_2$.

3. Results and discussion

The analytical data (Table 1) suggest the formulae $[MLL'Cl] \cdot 2H_2O$ for the chloro complexes and $[MLL'(H_2O)]NO_3$ for the nitrate complexes. The complexes

Table 1
Analytical and conductivity data of Cu(II), Ni(II) and Co(II) complexes

Complex [a]	Analysis [b]										Conductivity $\Delta M/(\Omega^{-1}\ cm^2)$
	Metal/%		C/%		H/%		N/%		Cl/%		
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	
[CuLL′Cl] · $2H_2O$	9.42	9.47	46.21	46.53	3.55	3.57	8.39	8.35	10.49	10.57	4.9
[CuLL′(H_2O)]NO_3	9.31	9.35	45.64	45.94	3.21	3.24	10.22	10.30	5.26	5.22	69.8
[NiLL′Cl] · $2H_2O$	8.90	8.82	46.47	46.87	3.62	3.60	8.47	8.41	10.56	10.65	7.4
[NiLL′(H_2O)]NO_3	8.63	8.70	46.68	64.27	3.29	3.26	10.30	10.38	5.21	5.25	85.4
[CoLL′Cl] · $2H_2O$	8.76	8.85	46.48	46.85	3.58	3.60	8.48	8.41	10.71	10.64	6.2
[CoLL′(H_2O)]NO_3	8.69	8.73	46.70	46.26	3.24	3.26	10.30	10.37	5.22	5.25	81.3

[a] L is $C_{13}H_{12}N_2O_4$ and L′ is $C_{13}H_8N_2O_3Cl$. [b] Reported percentage.

are soluble in common organic solvents. The chloro complexes are non-electrolytic while the nitrate complexes are 1 : 1 electrolytes, which is evident from the conductivity data (Table 1).

3.1. Electronic spectra

The copper(II) complexes exhibit a single broad band at around 15 200 cm^{-1} suggesting a distorted octahedral geometry. The electronic spectra of Ni(II) complexes show three bands at 10 000–9680, 15 850–15 700 and 25 750–25 700 cm^{-1} which may tentatively be assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$, respectively. Two bands in the 8150–8100 and 19 350–19 200 cm^{-1} regions are found in the spectra of Co(II) complexes assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(P)$ (ν_3) transitions, respectively. These spectral bands observed for the Ni(II) and Co(II) complexes are consistent with the octahedral geometry.

3.2. IR spectra

The sharp band due to ν(C=N) present at 1630 cm^{-1} in the hydrazide shows a negative shift of 20–30 cm^{-1} in the spectra of the complexes, showing that the

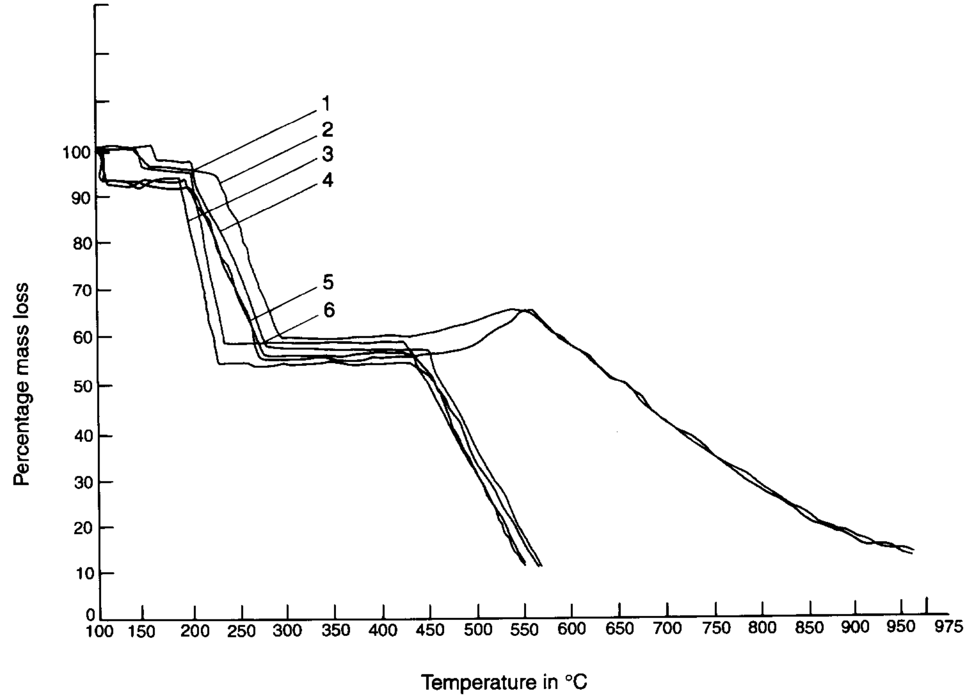

Fig. 1. Thermolysis curves of Cu(II), Ni(II) and Co(II) mixed-ligand complexes: 1, [CuLL'Cl] · $2H_2O$; 2, [CuLL'(H_2O)]NO_3; 3, [NiLL'Cl] · $2H_2O$; 4, [NiLL'(H_2O)]NO_3; 5, [CoLL'Cl] · $2H_2O$; 6, [CoLL'(H_2O)]NO_3.

azomethine nitrogen is involved in coordination. The bands appearing at 1670, 1510 and 1290 cm^{-1} in the spectrum of hydrazide assignable to the amide I, amide II and amide III bands, respectively, exist at 1640–1635, 1540–1530 and 1330–1325 cm^{-1} in the spectra of the mixed ligand complexes under study, which indicates the coordination of carbonyl oxygen. The hydrazide ligand shows strong bands at 610 and 590 cm^{-1}, assigned to furan ring-deformation modes [20]. These bands show a red shift of 20–30 cm^{-1} on complexation, indicating metal–ligand bonding through the furyl oxygen atom.

A bathochromic shift of the –N=N– band [21], located at 1610 cm^{-1} in the azo ligand, is observed on complexation (1595–1585 cm^{-1}) showing the metal–azo link. The appearance of bands at ≈1590 and 1400 cm^{-1} corresponding to antisymmetric and symmetric COO stretchings shows chelation through the oxygen atom of the deprotonated carboxyl group.

Some non-ligand bands also exist in the far-infrared spectra of the complexes in the 400–370 and 510–500 cm^{-1} regions, assignable to ν(M–N) and ν(M–O) vibrations respectively. The band appearing at 250 cm^{-1} in the chloro complexes is assigned as ν(M–Cl). The presence of coordinated water in the nitrate complexes is indicated by a broad band at around 3400 cm^{-1}, and by somewhat weaker bands at around 850 and 700 cm^{-1}.

Table 2
Thermal decomposition data for the mixed-ligand Cu(II), Ni(II) and Co(II) complexes

Complex [a]	Decomp. temp/°C		Weight loss/%		Decomp. product
	Initial	Final	Found	Calcd.	
1. [CuLL'Cl] · $2H_2O$	95	110	5.32	5.36	[CuLL'Cl]
	210	240	43.75	44.15	CuL'Cl
	440	550	87.34	88.13	CuO
2. [CuLL'(H_2O)]NO_3	160	180	2.67	2.65	[CuLL']NO_3
	210	240	40.62	40.94	CuL'NO_3
	440	550	87.49	88.28	CuO
3. [NiLL'Cl] · $2H_2O$	90	110	5.36	5.40	[NiLL'Cl]
	220	270	44.12	44.47	NiL'Cl
	450	560	88.07	88.77	NiO
4. [NiLL'(H_2O)]NO_3	160	180	2.63	2.66	[NiLL']NO_3
	220	270	41.01	41.23	NiL'NO_3
	450	560	88.08	88.91	NiO
5. [CoLL'Cl] · $2H_2O$	95	110	5.37	5.40	[CoLL'Cl]
	230	290	44.10	44.45	CoL'Cl
	450	970	88.12	88.74	CoO
6. [CoLL'(H_2O)]NO_3	160	180	2.69	2.66	[CoLL']NO_3
	230	290	40.84	41.22	CoL'NO_3
	450	970	88.09	88.88	CoO

[a] L is $C_{13}H_{12}N_2O_4$ and L' is $C_{13}H_8N_2O_3Cl$.

3.3. Thermal behaviour

The TG curves of the chloro complexes (Fig. 1) show the presence of lattice water. The decomposition starts in these compounds at 90–95°C and the mass loss observed at 110°C corresponds to the elimination of two water molecules. The nitrate complexes, however, decompose in the 160–180°C range showing a mass loss of 2.63–2.69% which is consistent with the removal of one water molecue. Furthermore, the removal of water in this temperature range shows that the water molecule has a coordinated nature in the nitrate complexes of Cu(II), Ni(II) and Co(II) (2, 4 and 6 in Table 2). Further decomposition of all the complexes takes place at 210–230°C and the hydrazide ligand is practically eliminated from the complexes at 240–290°C (1–6, Table 2). In the final stage of decomposition, both the ligand molecules are eliminated and a metallic oxide residue is left at 550–560°C in the case of the copper and nickel complexes, and at 970°C in the cobalt complexes. Thermogravimetric data and the possible end products are listed in Table 2.

Acknowledgements

The U.G.C. authorities, New Delhi, are thanked for providing financial assistance. Dr. G.D. Sharma, Principal L.R.P.G. College, Sahibabad, is thanked for providing the necessary laboratory facilities.

References

[1] W. Hoyle and G.A. Howarth, Chem. Abstr., 78 (1973) 1608h.
[2] J.R. Dilworth, Coord. Chem. Rev., 21 (1976) 29.
[3] J.P. Alcock, H.J. Baker and A.A. Diamautis, Aust. J. Chem., 25 (1972) 289.
[4] S.K. Sahni, S.P. Gupta, S.K. Sangal and V.B. Rana, J. Inorg. Nucl. Chem., 39 (1977) 1098.
[5] W.O. Foye and R.N. Duvall, J. Am. Pharm. Assoc. Sci. Ed., 47 (1958) 285.
[6] N.K. Sing, R.C. Aggarwal and N. Aggarwal, Indian J. Chem., 23A (1984) 1011.
[7] M. Katyal and Dutty, Talanta, 22 (1975) 151.
[8] M.L. Hett and D.E. Ryan, Anal. Chim. Acta, 34 (1966) 407.
[9] R.E. Jenson and R.T. Ptvaum, Anal. Chim. Acta, 37 (1967) 397.
[10] K. Dey, S.B. Ray, P.K. Bhattacharya, A. Gangopadhyay, K.K. Bhasin and R.D. Verma, J. Indian Chem. Soc., 62 (1985) 809.
[11] T. Sasumu, Q. Fernando and H. Freiser, Anal. Chem., 37 (1965) 1249.
[12] S.I. Gusev and E. Nikolaeva, Zh. Anal. Khim (USSR), 21 (1966) 281.
[13] R.A. Chalmers, Talanta, 14 (1967) 527.
[14] H.L. Mahalaha, M.K. Dove and D.D. Sharma, J. Indian Chem. Soc., 45 (1968) 413; 48 (1971) 1179.
[15] M.S. Goher, M.S. Masoud and A.M. Heiba, Pol. J. Chem., 55 (1981) 1491.
[16] Sheesh Bhardwaj, M.N. Ansari and M.C. Jain, Indian J. Chem., 28A (1989) 81.
[17] R.L. Dutta and Kuntala De, Indian J. Chem., 28A (1989) 807.
[18] K. Raja Reddy, K. Laxma Reddy and K.A. Reddy, Indian J. Chem., 28A (1989) 916.
[19] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longmans, London, 4th edn., 1978, p. 462, 678, 461.
[20] J.D. Donaldson, J.F. Knifton and S.D. Ross, Spectrochim. Acta, 21 (1965) 275.
[21] M.S. Masoud, T.M. Salem and M.A. El-Henawi, Synth. React. Inorg. Met. Org. Chem., 11 (1981) 577.