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Thermal and spectral studies on Co(II), Ni(II) and Cu(II) complexes of sulfamethazine Schiff base

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Abstract

The thermal behavior of sulfamethazine Schiff base complexes with Co(II), Ni(II) and Cu(II) ions has been studied. The thermal stability of these complexes is discussed in terms of the type of metal ions. The energies of activation were determined and discussed in relation to the structure of the complex which is characterized by elemental analysis and IR spectra.

INTRODUCTION

Schiff bases and their metal complexes are known to be biologically important [1–6], and of interest in the catalysis [7–9] of various chemical and photochemical reactions. Although the work on Schiff base complexes drew the attention of many workers [10–13], yet it seems that little attention has been paid to thermal studies of Co(II), Ni(II) and Cu(II) complexes of sulfamethazine Schiff base. Thus the present study describes the thermal behavior of these complexes. The structure and the nature of the complexes are investigated by elemental analysis and IR spectroscopy.

EXPERIMENTAL

All chemicals used in the present investigation were of high grade purity from Bayer and were used without further purification.

Preparation of ligand

The ligand was prepared by the method of Diehl and Hach [14]. The ligand has the formula shown.

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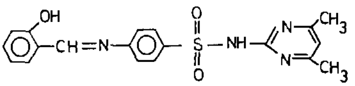


Formula of the ligand.

Preparation of complexes

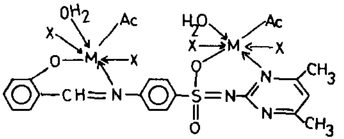
A stirred solution of the ligand (0.01 mol) dissolved in 50 ml of ethanol was mixed with metal salts (0.01 or 0.02 mol) dissolved in 20 ml ethanol. The mixture was stirred for ≈ 1 h during which time the solid complex separated and was then filtered off, washed with hot ethanol, then with ether and dried in vacuo.

Apparatus and working procedures are the same as those previously described [15–17].

RESULTS AND DISCUSSION

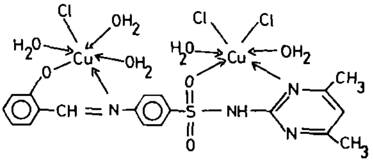
All the solid complexes were subjected to elemental analysis (Table 1). The low conductance values (8.9–12.3 Ω^{-1} cm^2 mol^{-1}) indicate the non-ionic character of the complexes [18] (Table 1).

The IR spectra of the complexes **1–3** show the disappearance of the ν(NH) band of the free ligand, whereas for complexes **4** and **5** the ν(NH) band is still observed. This indicates that the ligand in complexes **1–3** reacts through the phenolic and enolic OH resulting from the tautomeric shift within the sulfonamide group [5]. Also, the IR spectra of complexes **1–4** show the shift of the C=N band to higher values indicating coordination through the azomethine nitrogen. For complex **5**, the C=N band is still observed at the same position indicating that the C=N grouping is not involved in complex formation. The above data indicate that the ligand behaves as a dibasic tetradentate ligand for complexes **1–3**, monobasic tetradentate for complex **4** and neutral bidentate for complex **5**.



X = H_2O for M = Co^{2+}, Ni^{2+}

X = Zero for M = Cu^{2+}



Complex **4**.

TABLE 1

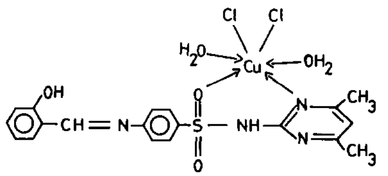
Analytical data and conductance values of the complexes **1–5**

Complex	Formula	% yield	Ω [a]	% C [b]	% H [b]	% N [b]	% M [b]	Δ*E* [c] (kcal mol^{-1})
1 $[Co_2L(Ac)_2(H_2O)_6]$	$C_{23}H_{34}N_4O_{13}SCo_2$	75	9.8	38.2(38.13)	4.6(4.7)	7.4(7.75)	15.8(16.28)	27.2
2 $[Ni_2L(Ac)_2(H_2O)_6]$	$C_{23}H_{34}N_4O_{13}SNi_2$	76	8.9	37.8(38.2)	4.4(4.7)	7.39(7.74)	15.9(16.24)	–
3 $[Cu_2L(Ac)_2(H_2O)_2]H_2O$	$C_{23}H_{28}N_4O_{10}SCu_2$	82	10.1	42.8(42.7)	4.25(4.33)	8.1(8.66)	19.3(19.63)	4.46
4 $[Cu_2LCl_3(H_2O)_5]$	$C_{19}H_{27}N_4O_8SCu_2Cl_3$	70	12.3	31.6(32.4)	4.0(3.83)	7.3(7.95)	17.8(18.03)	26.4
5 $[CuLCl_2(H_2O)_2]$	$C_{19}H_{22}N_4O_5SCuCl_2$	72	11.1	42.4(41.3)	3.6(3.98)	10.2(10.14)	11.0(11.49)	23.8

[a] Ω^{-1} cm^2 mol^{-1} in 10^{-3} M DMF.

[b] Percentage found (calc.).

[c] Thermal decomposition.



Complex **5**.

The application of thermal methods of analysis in coordination chemistry drew the attention of some investigators [19–23] to solving the problem concerning the bonding and structure of coordination compounds and to calculating the kinetic and thermodynamic data for the solid state reactions [24–26].

The DTA thermogram of complex **1** consists of a weak endothermic peak at 110°C consistent with the loss of water from the surface of the crystals [27]. An exothermic peak at 205°C is probably assigned to the phase change of the complex. The exothermic peak at 275°C is assigned to the melting of the complex which is consistent with the microscopic observation of melting point. The strong broad exothermic peak at 395°C includes the decomposition [28] of the complex with subsequent loss of the organic portion leading to the final product CoO. The energy of activation (E_a) of this thermal decomposition was evaluated from the DTA thermogram as in previous work [19,26]. From Arrhenius plots (Fig. 1). E_a is obtained from the slope as 27.2 kcal mol^{-1} (Table 1).

The thermogram of complex **3** shows a broad endothermic peak at 124°C correlated with the loss of water molecules [27]. The appearance of a

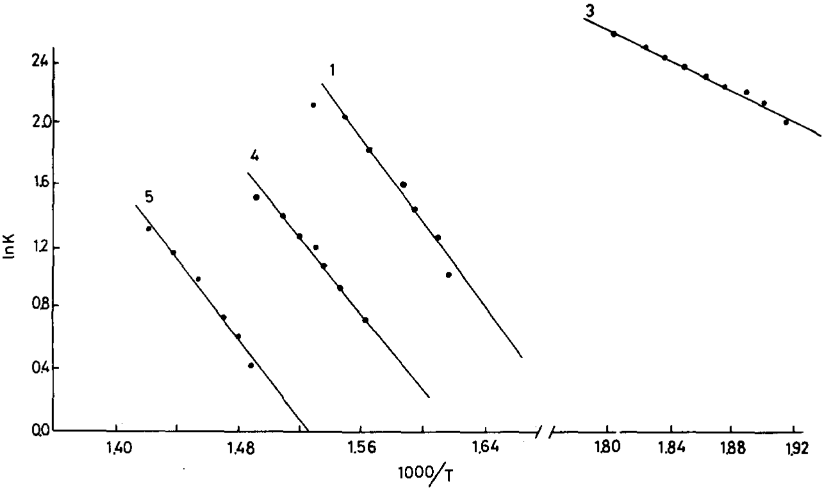


Fig. 1. Arrhenius plots of complexes **1**, **3**, **4** and **5** constructed from DTA thermograms.

strong broad exothermic peak at 295°C with a shoulder at 352°C may be correlated with an overlap between two adjacent processes, presumably melting and subsequent decomposition along the chelate bond and loss of the organic molecule. This process may lead to the formation of a stable oxidation product namely CuO [29]. The energy of activation of the thermal decomposition was calculated from an Arrhenius plot as 4.46 kcal mol^{-1} (Table 1).

The exothermic peaks at 252 and 286°C are assigned to bond breaking between the metal ions and coordinated water molecules in complexes **4** and **5** respectively. This assignment is confirmed by the observation that the relative areas of these peaks with respect to their preceding exothermic peaks are different. These ratios are consistent with the higher water content in complex **4** compared with complex **5**. The exothermic peaks at 430–480°C combined with a broad shoulder near 570°C include various processes of decomposition with the loss of the organic portion and the subsequent oxidation of Cu_2O to the final CuO product. The energies of the thermal decomposition and melting of the complexes **4** and **5** are 26.4 and 28.5 or 23.8 and 21.6 kcal mol^{-1}, respectively. For complex **4** metal ion centers are more rich in positive charge compared with complex **5**. This makes the coordination bond stronger in the first complex (**4**) and this is reflected by the observed energies of activation, that is, higher in complex **4** compared with the corresponding thermal process in complex **5**.

REFERENCES

1 J.L. Hoard and J.V. Silverton, Inorg. Chem., 2 (1963) 235.
2 T.R. Felthause and D.N. Hendricheson, Inorg. Chem., 17 (1978) 2636.
3 J.H. Eapason and G.W. Kirker, Inorg. Chim. Acta, 40 (1980) 105.
4 S.C. Bhatia, J.M. Bindlish, A.R. Saini and P.C. Jain, J. Chem. Soc. Dalton Trans., (1981) 1773.
5 M.A. El-Ries, S.M. Abu-El-Wafa and S.M. El-Kousy, J. Pharm. Belg., 43 (1988) 93.
6 W.E. Rudzinsk, I.M. Aminbhavi and N.S. Biradur, Inorg. Chim. Acta, 67 (1982) 177.
7 R.H. Holm, G.W. Everette and A. Chakrovty, Prog. Chem., 7 (1966) 83.
8 G.M. Mockler, G.W. Chaffey, E. Sinn and H. Wong, Inorg. Chem., 11 (1972) 1308.
9 M.A. Elmorsi, M. Gaber, R.M. Issa and M.M. Ghoneim, Bull. Electrochem. (India), 4 (1988) 959.
10 P. Souza, J.A. Garcia-Vazquez and J.R. Masaguer, Transition Met. Chem., 11 (1986) 229; 9 (1984) 318; Synth. React. Inorg. Met. Org. Chem., 15 (1985) 247.
11 M.B. Drew, S.M. Nelson and J. Reedijk, Inorg. Chim. Acta, 64 (1982) 189.
12 C.A. McAuliffe and W.E. Hill, Inorg. Chim. Acta, 45 (1980) L115.
13 F.A. Aly, M. Gaber, R.M. Issa and F.A. El-Said, Bull. Soc. Chim. Fr., 4 (1988) 661.
14 H. Diehl and C.C. Hach, Synthesis, 4 (1950) 196.
15 S.A. Amer, M. Gaber and R.M. Issa, Polyhedron, 7 (1988) 2635.
16 M. Gaber, R.M. Issa, F.A. Aly and M.I. Ayad, Thermochim. Acta, 155 (1989) 309.
17 M. Gaber, H.E. Mabrouk and M. Mounir, Thermochim. Acta, 186 (1991) 89.
18 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
19 W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 833.

20 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition Metal Ammine Complexes, Elsevier, Amsterdam, 1967.
21 R. Lozano, J. Martinez, A. Martinez and A. Doadrio Lopes, Polyhedron, 2 (1983) 977.
22 A.M. Donia, S.A. Amer and M.M. Ayad, Thermochim. Acta, 137 (1989) 189.
23 M. Gaber, M.M. Ayad and M.I. Ayad, Thermochim. Acta, 176 (1991) 21.
24 J.E. House, Thermochim. Acta, 40 (1980) 225.
25 C.E. Bamberger, K. Brookhart and P.P. Robinson, Inorg. Chim. Acta, 57 (1982) 161.
26 J. Thomas and T.A. Clarke, J. Chem. Soc. A, (1968) 457.
27 C.F. Bell and D.R. Rose, Inorg. Chem., 7 (1968) 325.
28 T.H. Chang, T.J. Yang and M.W. Yen, J. Chin. Chem. Soc. (Peking), 23 (1976) 181.
29 M.M. Abou-Sekkina and M.G. Abou El-Azm, Thermochim. Acta, 79 (1984) 47.