Thermochimica Acta, 131 (1988) 1–6
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOCHROMISM IN Ni(II) COMPLEXES WITH SCHIFF BASE DERIVATIVES OF 4-AMINOANTIPYRINE

AHMED M. DONIA

Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom (Egypt)

EL-ZEINY M. EBEID

Department of Chemistry, Faculty of Science, Tanta University, Tanta (Egypt)

(Received 8 October 1987)

ABSTRACT

Ni(II) complexes of 2-hydroxy-1-naphthylidene-4-aminoantipyrine (**I**) and salicylidene-4-aminoantipyrine (**II**) display a change of colour upon heating. The change in **II** is reversible in the presence of moisture. The thermochromism in crystalline **I** and **II** has been studied using differential thermal analysis (DTA), electronic and IR spectroscopy, X-ray powder diffraction and electrical conductivity. Thermochromism in these complexes has been attributed to dehydration.

INTRODUCTION

Antipyrine and its derivatives have diverse medical uses [1,2] e.g. antipyretic, analgesic and antirheumatic [2]. Antipyrines have also been used as analytical reagents in the estimation of some metal ions [3–6]. Their complexing abilities have been modified by the preparation of Schiff base derivatives [4–7]. A number of transition metal complexes of some Schiff base derivatives of antipyrine have recently been prepared and characterized by a variety of spectral and analytical methods to clarify the structure and the nature of bonding in these complexes [8].

In this paper, we report the thermal behaviour of Ni(II) complexes with some Schiff base derivatives of 4-aminoantipyrine. The observed thermochromism in these complexes is discussed in terms of structural and spectroscopic changes.

EXPERIMENTAL

The ligands 2-hydroxy-1-naphthylidene-4-aminoantipyrine (HL1) and salicylidene-4-aminoantipyrine (HL2) were prepared by condensation of

0040-6031/88/$03.50

4-aminoantipyrine with the corresponding aldehyde The condensation was carried out by refluxing ethanolic mixtures for about 15 min and the precipitate obtained upon cooling was collected and recrystallized from ethanol. Ni(II) complexes were prepared by adding the stoichiometric amounts (1 1 metal ligand) of hot ethanolic solutions of $NiCl_2$ $6H_2O$ to hot ethanolic solutions containing the ligand and sodium acetate in 1 1 molar ratio A precipitate was obtained upon refluxing the mixtures for approximately 2 h The precipitate was filtered off, washed with ethanol several times and dried over $CaCl_2/P_2O_{10}$

Thermal analysis of the complexes was carried out using a Shimadzu XD-30 thermal analyzer X-ray powder diffraction was recorded using a Shimadzu XD-3 diffractometer by applying the Cu $K\alpha$ line Electronic spectra were measured in Nujol mulls using a Perkin–Elmer 550S spectrophotometer IR spectra were measured in KBr discs using a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer Conductivity measurements were taken using a Super Megohmmeter Model RM 170 with an applied voltage of 50 V

RESULTS AND DISCUSSION

Thermal behaviour

The Ni(II) complexes with HL1 ($\mathbf{I}_a$) and HL2 ($\mathbf{II}_a$) are yellowish-green and change to orange upon heating to approximately 160 °C for about 5 min The corresponding orange form are hereafter known as $\mathbf{I}_b$ and $\mathbf{II}_b$, respectively The change in colour in system **II** is reversible and the orange $\mathbf{II}_b$ form changes to the yellowish-green $\mathbf{II}_a$ form on leaving in air at room temperature This reversibility is not observed in system **I** The temperature range of thermochromism coincides with the endothermic peaks of the differential thermal analysis (DTA) curves as shown in Fig 1 The DTA curve of $\mathbf{I}_a$ shown in Fig 1, consists of an endothermic peak at about 160 °C, followed by a relatively sharp exothermic peak at about 307 °C that is assigned to material decomposition Other analytical techniques (see below) indicate that the endothermic peak at about 160 °C is assigned to dehydration of $\mathbf{I}_a$ giving the orange form $\mathbf{I}_b$ This endothermic peak is absent in the DTA curve of the orange form $\mathbf{I}_b$ The exothermic peaks at 320 and 380 °C appearing in the DTA curve of $\mathbf{I}_b$ are also assigned to decomposition processes The energies of activation (E_a) of the dehydration processes of $\mathbf{I}_a$ and $\mathbf{II}_a$ have been evaluated from the DTA curves using the formula of Thomas and Clarke [9] The thermal dehydration follows a first-order kinetic law for which the rate constant (K) is obtained from the DTA curves at a certain temperature T by the relation [9]

$$K = \frac{dH/dt}{A - a}$$

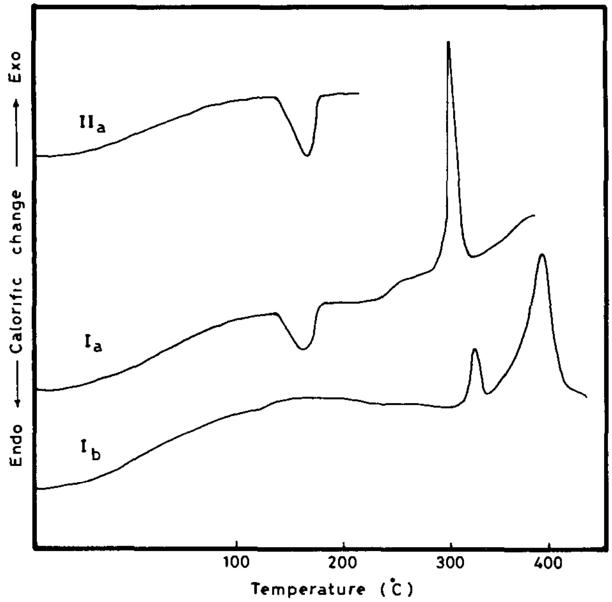

Fig 1 DTA of the solid complexes I_a, I_b and II_a

where dH/dt is the deviation of the curve peak from the base line, A is the total area of the dehydration peak and a is the area swept up to a temperature T Arrhenius plots were then constructed as shown in Fig 2 and the energies of activation E_a were obtained from the slopes as $E_a = 139\ 6$ kJ mol^{-1} for I_a and $E_a = 167\ 6$ kJ mol^{-1} for II_a

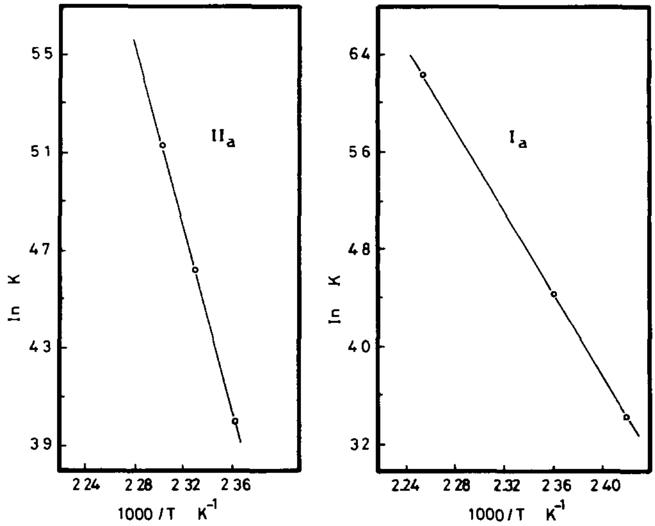

Fig 2 Arrhenius plots constructed from DTA curves of I_a and II_a

The endothermic peak at about 160 °C is obtained in the DTA curves of both II_a and II_b forms This is due to the hygroscopic nature of the orange II_b form which undergoes reversible hydration giving the original yellowish green (II_a) form (Fig 1) This process can be used as a quick and simple method for testing the dryness of some organic solvents

Spectroscopic study

The yellowish-green Ni(II) complex I_a and its orange thermoproduct I_b were investigated by means of UV and IR spectra. The electronic spectrum of I_a (Fig 3) shows bands of relatively low intensity around 605 nm (16 528 cm^{-1}) and 420 nm (23 809 cm^{-1}) These bands were assigned to $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transitions, respectively, indicating an octahedral geometry for I_a [10] The spectrum of I_b shows a band with strong intensity near 450 nm (22 222 cm^{-1}) indicating a square planar geometry [10]

The IR spectrum of I_a has been discussed previously [8] The IR spectra of both I_a and I_b (shown in Fig 4) are nearly the same with an extra broad band appearing at about 3400 cm^{-1} in the spectrum of I_a that is assigned to ν(OH) of water. This supports the view that the transformation from I_a to I_b is associated with dehydration Both ring stretching and out-of-plane π-CH bands at 1280 cm^{-1} and 755 cm^{-1} [5], respectively, are less intense and are slightly shifted (by about 5 cm^{-1}) in the spectrum of I_b compared with I_a This might be due to the structural change accompanying dehydration. The analytical and spectral data that have been described previously [8] indicate the following chemical formulae for the complexes I_a and II_a I_a

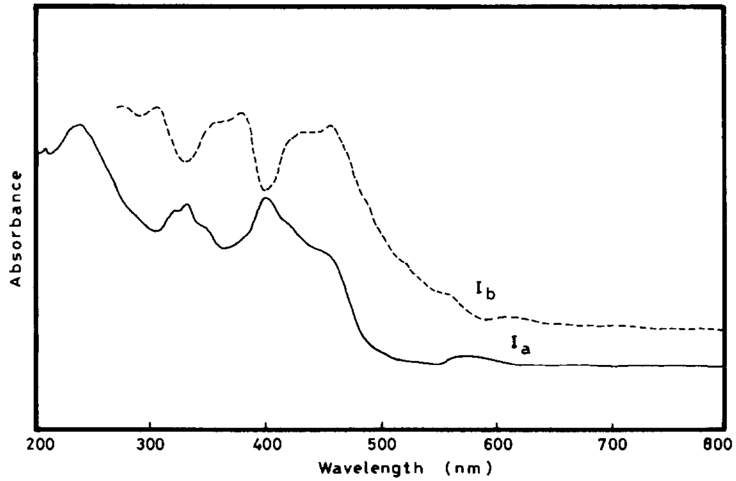

Fig 3 Electronic spectra of the complexes I_a and I_b

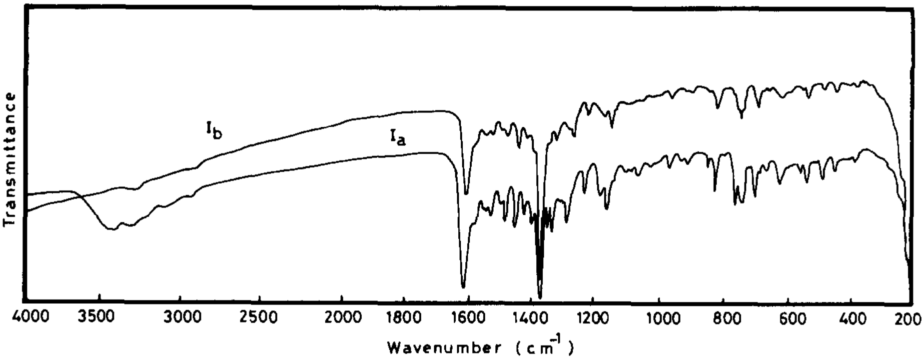

Fig 4 IR spectra of the complexes I_a and I_b

(yellowish-green), $[Ni(HL1)(H_2O)_4]Cl_2$ $3H_2O$, II_a (yellowish-green), $[Ni(HL2)(H_2O)_2Cl_2]$ H_2O

The thermal dehydration of I_a (octahedral structure) leads to a product of square planar geometry The process involves the diffusion of Cl^- ions from the outer sphere of the complex to satisfy the coordination number This is not the case in **II** Since mass transfer in the form of Cl^- is difficult in the condensed phase, the back reaction $I_b \rightarrow I_a$ is largely prohibited in **I** compared with the corresponding transformation in **II**

The structural change accompanying the dehydration process $I_a \rightarrow I_b$ has also been examined by X-ray powder diffraction as shown in Fig 5 The dehydrated specimen I_b possesses broader diffraction peaks indicating a lower degree of crystallinity and a possible existence of microstrains [11,12]

The changes in electrical conductivity σ of I_a as a function of heating are shown in Fig 6. At temperatures lower than the dehydration temperature,

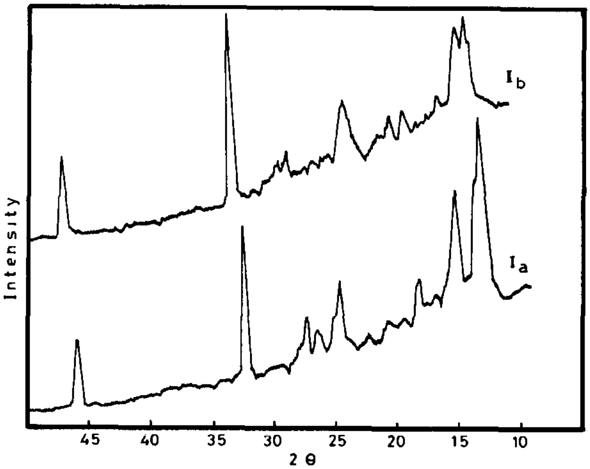

Fig 5 X-ray powder diffraction patterns of the complexes I_a and I_b

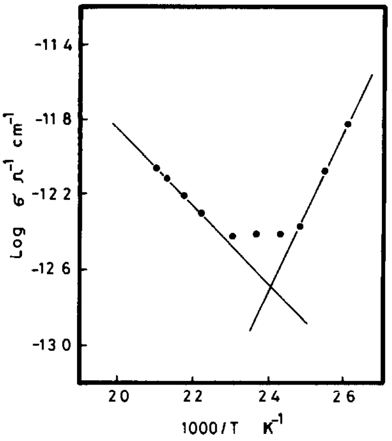

Fig 6 Temperature dependence of electrical conductivity of I_a

the conductivity σ decreases as the temperature increases This is characteristic of metallic behaviour It seems that the loss of water of crystallization at some lattice sites creates some voids and defects that function as traps of current carriers When the dehydration process is over, however, the material shows a semiconducting behaviour The inflection temperature between the metallic and semiconducting behaviours coincides with the dehydration temperature of $I_a \rightarrow I_b$

REFERENCES

1 P J Meffin, R L Williams, T F Blaschke and M Rowland, J Pharm Sci, 66 (1977) 135

2 E V Schmidt, T P Priskchep and N A Chernova, Izv Tomsk Politekh Inst (1975) 156, M M Shoukry, A Kh Ghoneim, E M Shoukry and M H El-Nagdi, Synth React Inorg Met Org Chem, 12 (1982) 815

3 N L Olenovich and L I Koval Chuk, Zh Anal Khim, 28 (1975) 2162

4 Sh T Talipov, A T Tashkhodzhaev, L E Zel'tser and Kh Khilkmatov, Izv Vyssh Uchebn Zaved Khim Tekhnol, 15 (1975) 1109

5 V V Savant, P P Ramamurthy and C C Patel, J Less-Common Met, 22 (1970) 479

6 B Janik and S Sawicki, Mikrochim Acta, (1970) 1050

7 V L Letunov, Zh Org Khim, 20 (1984) 162

8 A M Donia and F A El-Saied, J Polyhedron, submitted for publication

9 J Thomas and T A Clarke, J Chem Soc A, (1968) 457

10 L E Orgel, J Chem Phys, 23 (1955) 1004

11 W W Beeman, P Kasberg and M B Webb, in S Flugge (Ed), Handbuch der Physik, Springer-Verlag, Berlin, 1957, p 321, Band XXXII, Chemistry of Solid State, W E Garner, London, 1985, p 109

12 A R Tourky, M S Farag, T M Salem and Z M Hanafi, Z Phys Chem, 227 (1964) 145