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Thermochromic phase transitions in manganese(II) and cobalt(II) Schiff base complexes

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Abstract

Mn(II) and Co(II) complexes of salicylidene-4-aminoantipyrine display a change of colour upon heating. The change is reversible in air. The thermochromism in these complexes has been attributed to a first-order phase transition. The phase transition obtained was investigated by means of DTA, TG, X-ray powder diffraction and solid electrical conductivity. The kinetic and thermodynamic parameters of the obtained phase transition were determined.

INTRODUCTION

Various chemical species display reversible or irreversible colour changes with temperature, referred to as thermochromism. They are of increasing importance in various practical applications (temperature indicator devices, temperature sensitive light filters, imaging systems, storage of energy, etc.) [1–4]. The study of these materials has been very useful in helping to understand the competitive nature of various factors which influence colour change. For inorganic compounds this transition is most often due to a change in crystalline phase, to a change in ligand geometry, or to a change in the number of molecules of solvent in the coordination sphere [1]. The thermochromic behaviour of a number of metal chelates (in the solid state) has recently been reported by us [5–7]. The present study aims to investigate the reversible thermochromic phase transition in Mn(II) and Co(II) complexes with salicylidene-4-aminoantipyrine.

EXPERIMENTAL

Complexes **I** and **II** (Scheme 1) were prepared and investigated by the method reported earlier [8].

The thermal investigation (DTA and TG) was carried out in air on Shimadzu XD-30 and DT-30 thermal analysers respectively, with a heating

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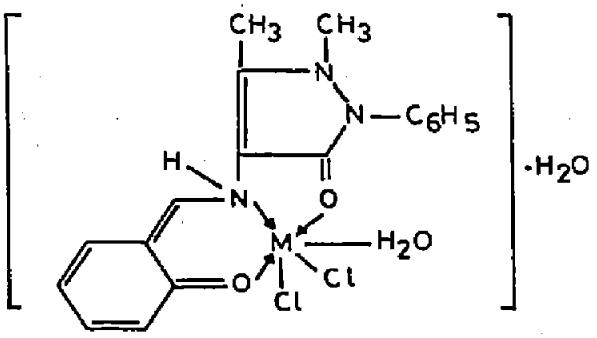

Scheme 1. M = Mn, (**I**); M = Co, (**II**).

rate of 10°C min^{-1}. Benzoic acid was used as a calibrant for the evaluation of enthalpy changes. X-ray powder diffraction was recorded using a Shimadzu XD-3 diffractometer with Cu Kα radiation. The high temperature phases were measured as a paste with paraffin oil, which were already heated up to 140°C. The electronic spectra were measured in nujol mulls on a Perkins–Elmer Lambda 4B spectrophotometer. The solid electrical conductivity was measured in air using a two probe method, and a Keithley 175 autoranging multimeter (applied potential 200 V). The discs were pressed under 7000 kg cm^{-2}.

RESULTS AND DISCUSSION

The yellow Mn(II) complex **I** and the red Co(II) complex **II** change to orange and brown respectively upon heating up to 90–140°C. The corresponding orange and brown forms are hereafter known as **Ia** and **IIa** respectively. The change in colour is reversible in air below 90°C, demonstrating thermal hysteresis again. This reversibility can be delayed for a few hours if the high temperature form is immersed in paraffin oil [1]. The above phenomenon has been studied and confirmed by DTA, TG, X-ray, electrical conductivity and electronic spectra. The DTA curves (Fig. 1) of **I** and **II** show an endothermic peak in the temperature range 90–150°C. This peak was assigned to a thermochromic phase transition on the basis of the TG measurements, which show no weight loss in that temperature range (Fig. 1). Upon cooling below 90°C, the original colours return, and the cold samples give the phase transition DTA peak again (Fig. 1). This indicates the reversibility of the transition. The phase transition obtained (colour change) is also accompanied by drastic changes in X-ray patterns (Fig. 2). The patterns of **Ia** and **IIa** are characterized by a number of reflections of low intensity, suggesting a low degree of crystallinity. Solid electronic spectra of **I** and **II** and their corresponding phases **Ia** and **IIa** are almost the same, indicating that the thermochromism in these compounds is not due to a change in coordination geometry. Rather, it is caused by a change in ligand field strength due to a structural phase transition [2, 7]. The energy of activation E_a and the order of this phase transition

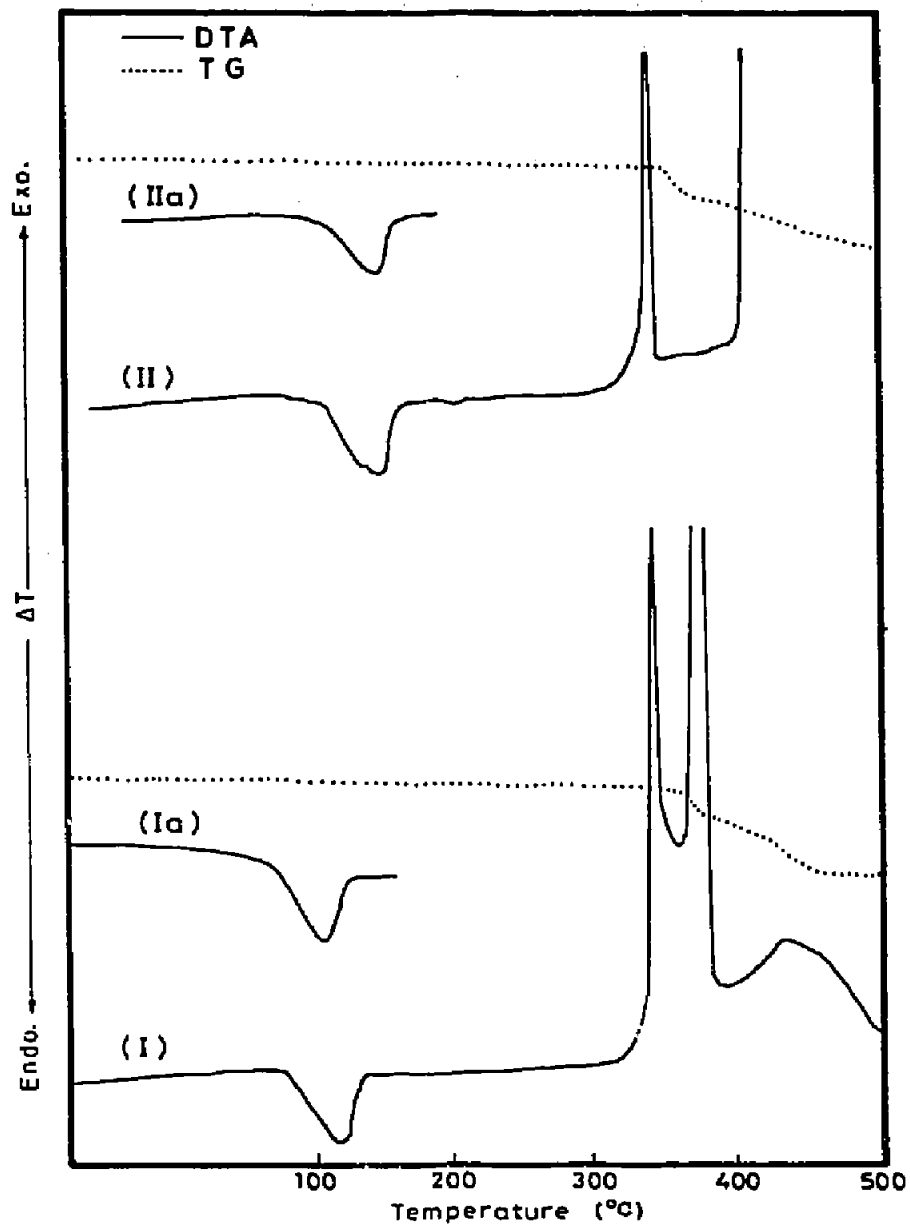

Fig. 1. DTA and TG curves of the investigated complexes.

have been evaluated from the DTA peak. The values of E_a as obtained from the method of Piloyan et al. [9] (Fig. 3) are 58.4 and 139 kJ mol^{-1} for **I** and **II** respectively. The order values (Table 1) as obtained from the peak asymmetry method of Kissinger [10] are nearly first order.

Both ΔH and ΔS have also been evaluated from the DTA curves using the relations [11, 12]

$$A = \pm K \Delta H m; \qquad \Delta S = \Delta H / T_m$$

where A is the peak area, K is the calibration constant, m is the mass of the sample and T_m is the peak temperature in kelvin. Values of ΔH and ΔS are found in Table 1.

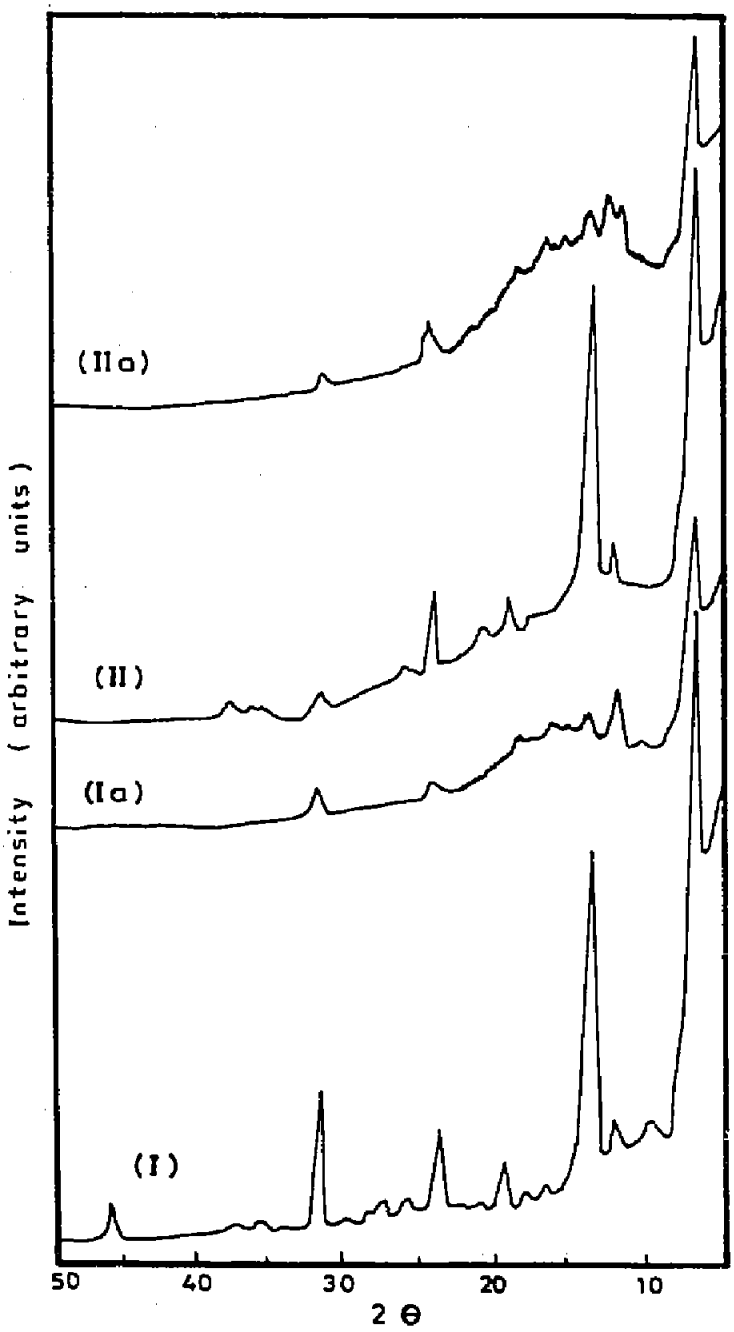

Fig. 2. X-ray diffraction patterns of the complexes before and after heating.

The positive values of entropy are consistent with the lattice disordering obtained during the phase transition. This is also confirmed by the lower degree of crystallinity of the high temperature phases (Fig. 2). Further evidence for the phase transition was provided by the variation of the electrical conductivity of the cobalt complex with temperature (upon heating and cooling). Figure 4 shows metal-like behaviour in the temperature range 50–88°C (red phase predominant). Semiconductor-like behaviour with an activation energy ΔE of 0.18 eV was observed in the

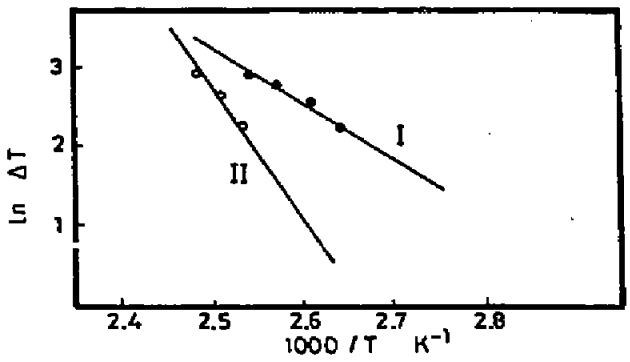

Fig. 3. Plots constructed from the phase transition DTA peak of **I** and **II**.

TABLE 1

Kinetic and thermodynamic parameters of the phase transition

Complex	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})	Order
I	55.98	142.4	58.38	0.9
II	75.79	183.5	139	0.95

temperature range 143–187°C (brown phase predominant). The temperature range 105–143°C (of decreasing or constant conductivity) coincides with that of the endothermic DTA peak. This means that the energy of the system was consumed in the phase transition rather than the thermal agitation of the electrons. Moreover, the great similarity observed in the

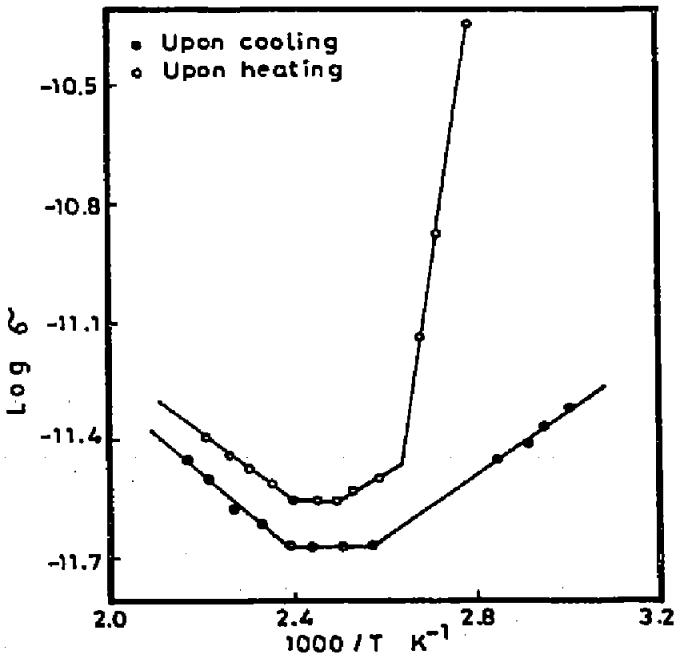

Fig. 4. Temperature dependence of electrical conductivity of **II**.

behaviour of the conductivity upon both heating and cooling confirms the reversibility of the phase transition. Unfortunately, we were unable to succeed in measuring the conductivity of the Mn(II) complex. In all trials the measurements were faced by the destruction of the pressed disc of the sample at the transition temperature. However the complexes showed higher thermal stabilities above 300°C. The exothermic DTA peaks and TG weight loss in the temperature range 300–400°C suggest decomposition of the material. This indicates that water of crystallization is tightly bound in the lattice.

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