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SOLID-STATE THERMAL POLYMORPHIC TRANSFORMATIONS FOR SOME SOLVATES OF 2-HYDROXY-5-METHYLAZOBENZENE-4′-CARBOXYLIC ACID COMPLEXES

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ABSTRACT

The polymorphic and pseudo-polymorphic transformation of some solvates of 2-hydroxy-5-methylazobenzene-4′-carboxylic acid complexes have been studied using thermal analytical and spectral methods. The nature of the interaction of the water of crystallisation in the complexes has been characterised. Some of the kinetic parameters of the desolvation reaction have also been calculated.

INTRODUCTION

Thermal studies play an important role in investigating solid-state properties as well as the reactions in the solid state [1–5]. It is known that, in general, different polymorphs of some compounds exist as different structures and possess variable properties, e.g. density, hardness, crystal shape, optical and electrical properties, vapour pressure, etc. The crystals probably occur with different structures [6]. However, the phenomenon of polymorphism in the compounds needs more investigation. Some very interesting forms of crystalline matter that display this phenomenon are crystal solvates containing solvents of crystallisation. The nature of the interaction of the solvent with the host molecule plays an important role in explaining the wide range of behaviour of these solvates [7]. Crystal solvates display polymorphic and pseudo-polymorphic transformation upon desolvation, according to the nature of the interaction of the solvent [7]. The solid-state thermal polymorphism and thermal isomerisation of some inorganic complexes have recently been studied [8]. The present work studies the polymorphism as well as the nature of the interaction of the water molecules in the

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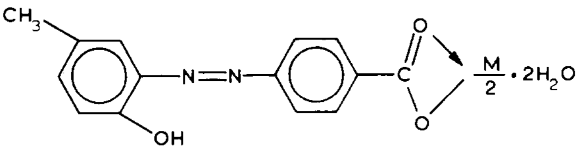
2-hydroxy-5-methylazobenzene-4′-carboxylic acid complex solvates (**I** and **II**)



I, M = Ni^{II}.
II, M = Co^{II}.

EXPERIMENTAL

The investigated metal chelates **I** and **II** were prepared as previously reported [9]. The thermal analysis was measured using a Shimadzu XD-30 thermal analyser with a heating rate of 10 ° C min^{-1}. The thermogravimetric analysis (TG) was performed by recording the weight of the dry samples before and after heating up to 190 ° C and 120 ° C in a drying oven for 45 min and 15 min, for **I** and **II**, respectively. The measurements were repeated several times for accuracy. Conductivity measurements were taken on a Keithley 175 autoranging multimeter with an applied voltage 200 V and a heating rate 1° C min^{-1}. X-ray powder diffraction was recorded using a Shimadzu XD-3 diffractometer by applying Cu $K\alpha$ radiation. The IR spectra were measured in KBr discs using a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer.

RESULTS AND DISCUSSION

The investigated solvates (**I** and **II**) exhibit a solid-state polymorphic transformation on heating in the temperature range 50–180 ° C, giving their corresponding polymorphs **Ia** and **IIa**. This solid state reaction has been studied by thermal and spectral methods. The DTA curves of both **I** and **II**. Fig. 1, show an endothermic peak in the temperature ranges 50–190 ° C and 50–130 ° C, respectively. This peak is assigned to a polymorphic transformation through desolvation, as is clear from the TG measurements. The weight loss corresponds to two molecules of water. This is in good agreement with the suggested formula of the complexes. It is interesting to note that the desolvation of **I** takes place at a higher temperature and more vigorously (190 ° C for 45 min) than that of **II** (120 ° C for 15 min). Also, it is obvious that the rate of desolvation and the rate of polymorphic transformation of **I** is very slow, as indicated by the nature of its endothermic DTA peak which

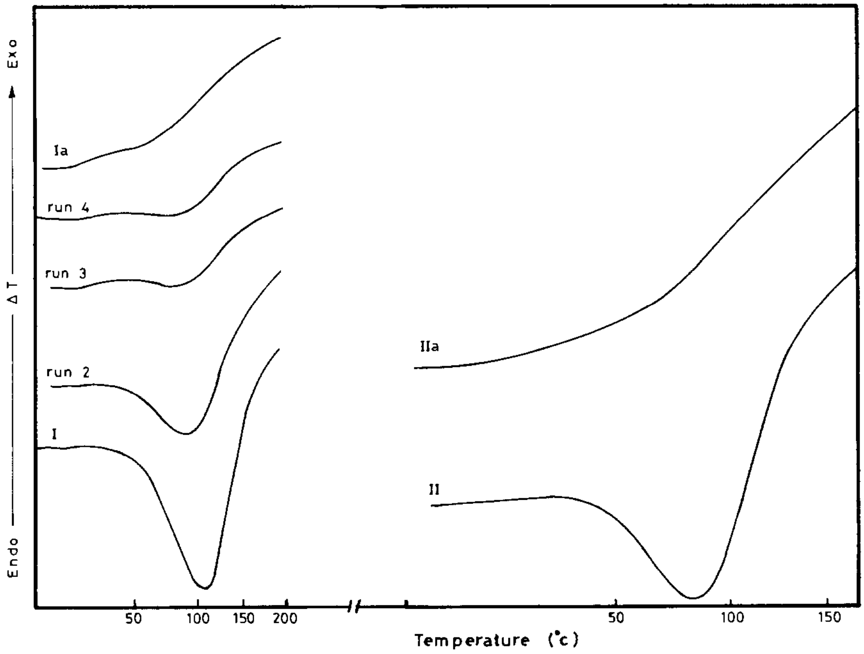


Fig. 1. DTA curves of **I**, **Ia**, **II** and **IIa**.

shows a gradual decrease in area through several successive runs, see Fig. 1. This is not the case for **II**; the broad endothermic peak in the DTA curve of **IIa** is assigned to the lattice rearrangement as demonstrated by the X-ray powder diffraction results. Thus, the kinetic parameters of the desolvation and polymorphic transformation reaction of **I** can be determined by the isothermal technique rather than the dynamic one. On the other hand, the desolvation reaction is irreversible, as indicated by the disappearance of its DTA peak in the DTA curves of **Ia** and **IIa**, Fig. 1. Also, neither **Ia** nor **IIa** revert to **I** and **II** on standing in air. The X-ray diffraction patterns of **I** and **Ia** (Fig. 2) are significantly different, indicating the presence of two polymorphs with strikingly different structures. This result, together with the fact of the vigorous desolvation, leads to the conclusion that water plays an important role in holding the crystal together (lattice water), through a hydrogen-bonding network between water and the host molecule, resulting in a polymorphic transformation upon desolvation [7]. For complex **II**, the X-ray powder diffraction patterns of **II** and **IIa** (Fig. 2) show a multitude of reflections of low intensity, indicating a lower degree of symmetry and crystallinity [10] and confirming the lattice-rearrangement assignment of the broad DTA peak of **IIa**. Again, the ease of desolvation of **II**, in addition to the X-ray diffraction data, suggest a weak interaction of water, i.e. water plays little or no role in holding the crystal together. In this case, water occupies the crystal voids, desolvation resulting in a pseudo-polymorphic

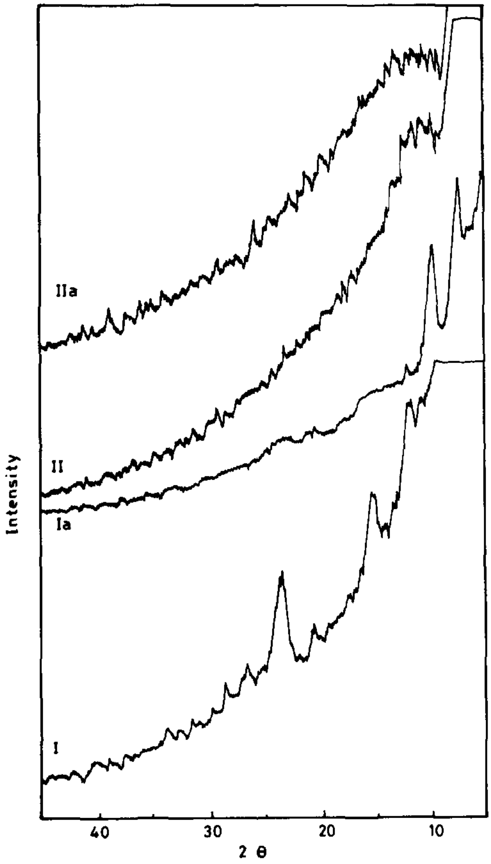


Fig. 2. X-ray power diffraction of **I**, **Ia**, **II** and **IIa**.

transformation [7]. The energy of activation (ΔE) of this pseudo-polymorphic transformation, as given by the method of Piloyan et al. [11] (Fig. 3), is 54.6 kJ mol^{-1}. The order value is 0.76, as given by Kissinger's peak assymetry method [12].

Further evidence for the polymorphic and pseudo-polymorphic transformations can be found in the electrical conductivity behaviour with temperature. For **I**, Fig. 4 shows a semiconducting behaviour with two activation energies ΔE of 0.67 and 0.73 eV, in the temperature ranges 21–107 ° C and 212–273 ° C, respectively. The temperature range 110–200 ° C over which the conductivity is lowered coincides to a large extent with that of the endothermic DTA peak. This means that the energy of the system was devoted to the desolvation; thus the polymorphic transformation rather than the thermal agitation of electrons gives the lower conductivity values. This confirms the phenomenon of polymorphic transformation. The electrical conductivity of **II** (Fig. 4) shows a semiconducting and metallic behaviour in the temperature ranges 21–93 ° C and 127–190 ° C, respectively, with activation energies,

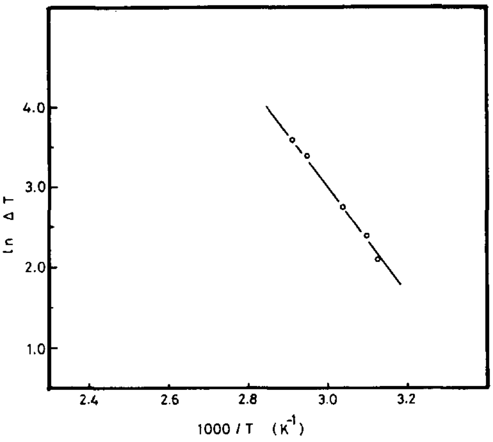


Fig. 3. A plot constructed from the DTA curve of **II**.

ΔE, of 0.71 eV and 1.4 eV, respectively. As with **I**, the temperature range of lowering conductivity (100–122° C) corresponds to the pseudo-polymorphic transformation as indicated by the DTA endothermic peak of **II**. The metallic behaviour observed may be due to the creation of some crystal-void defects that function as traps for current carriers [5].

The IR spectra of **I** and **Ia** and of **II** and **IIa** are identical. This indicates that the chemical structure of the molecule in each corresponding poly-

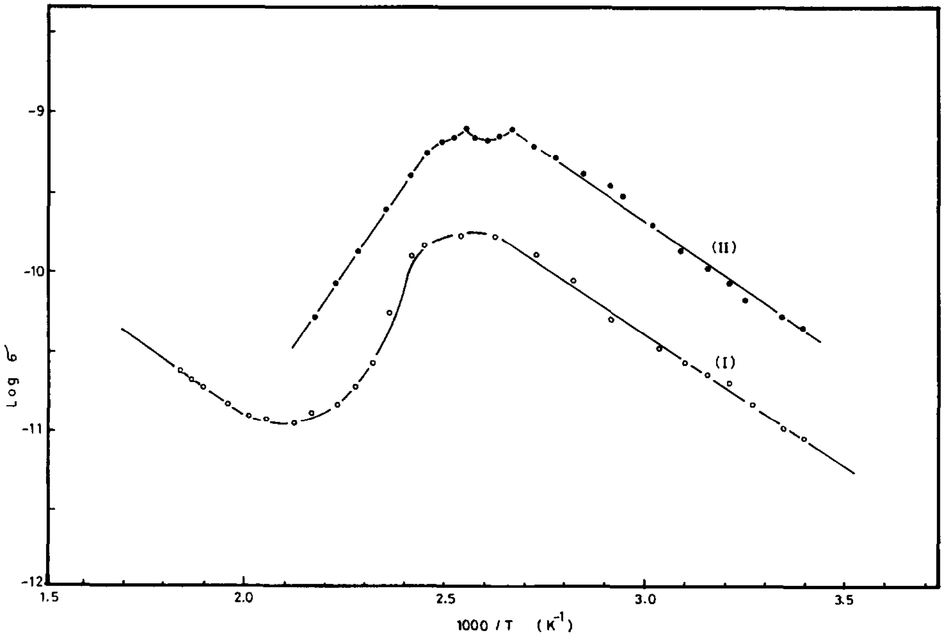


Fig. 4. Temperature dependence of electrical conductivity of **I** and **II**.

morph is the same and undergoes no conformational or configurational changes [7].

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