Thermochimica Acta, 152 (1989) 335–339
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL ISOMERIZATION OF SQUARE-PLANAR Ni(II) COMPLEX IN THE SOLID STATE

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(Received 25 January 1989)

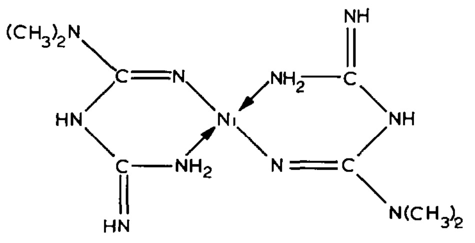
ABSTRACT

The thermal behaviour of the biologically active square-planar Ni(II) metformin complex was studied. The phase change obtained has been investigated by differential thermal analysis (DTA), thermogravimetry (TG), electrical conductivity, X-ray powder diffraction and infrared spectroscopy. This phase change was attributed to geometrical isomerization and/or conformational changes in the chelate rings.

INTRODUCTION

The solid state thermal isomerization of octahedral diamine complexes of nickel(II) has recently been studied [1–3]. The mechanisms of the thermal isomerization in such complexes have been previously reported [2–6].

The biologically active square-planar Ni(II) complex of metformin (**I**) has recently been synthesized and characterized by different analytical and spectral methods [7]. In the present work, the thermal and electrical behaviour of this complex were studied. In addition, the kinetic parameters of the obtained phase transition were determined.



(I)

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EXPERIMENTAL

The complex (**I**) was prepared by the method reported earlier [7]. The thermal analysis was measured using a Shimadzu XD-30 thermal analyser. The TG curve was measured by recording the weight of the sample before and after a DTA run up to 130 ° C. The conductivity measurements were taken on a Keithley 175 autoranging multimeter with 250 V applied voltage. X-ray diffraction was recorded using a Shimadzu XD-3 diffractometer with Cu *Kα* radiation. IR spectra were measured quantitatively in KBr discs using a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer.

RESULTS AND DISCUSSION

Thermal studies

The investigated Ni(II) complex (**I**) transforms to its isomer ($\mathbf{I}_a$) upon heating in the temperature range 70–130 ° C. This transformation has been studied and confirmed by DTA, TG, X-ray powder diffraction, electrical conductivity and IR spectroscopy. The DTA curve of **I** (Fig. 1) shows a broad endothermic peak in the temperature range 70–130 ° C. This peak was assigned to the phase transition on the basis of the TG measurements which show no mass loss in that temperature range. The obtained phase transition is irreversible as is evident from the disappearance of its DTA peak in the

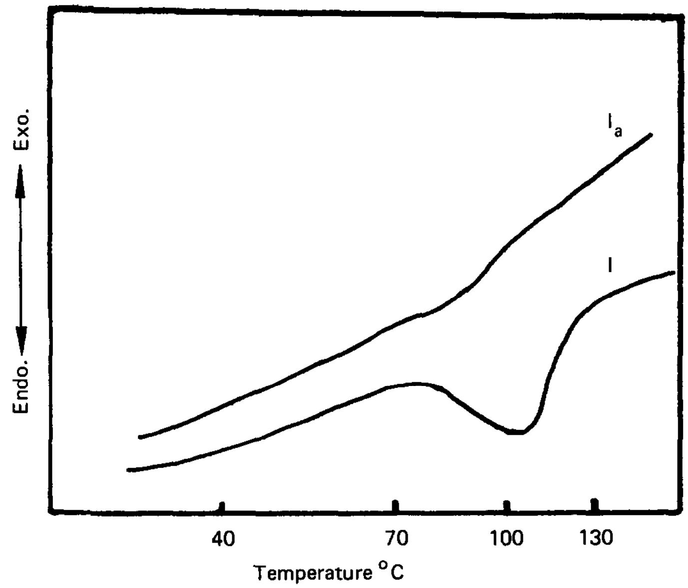

Fig. 1. DTA curves of **I** and $\mathbf{I}_a$.

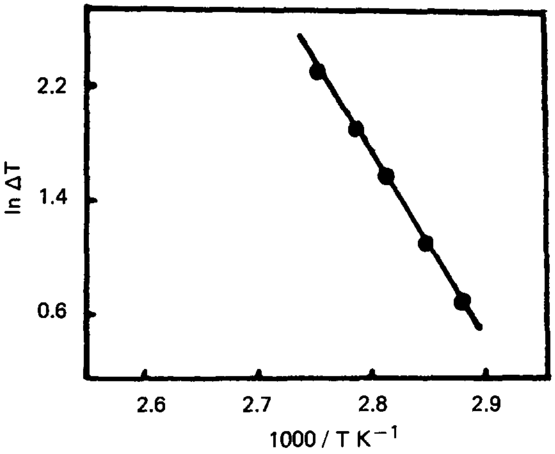

Fig. 2. A plot constructed from the DTA curves of I.

DTA curve of I_a. Also, I_a does not revert to I on standing in air. The energy of activation (E_a) as well as the order of this phase transition reaction have been evaluated from the DTA peak. The value of (E_a) as obtained using the method of Piloyan et al. [8] (Fig. 2) is 104.75 kJ mol^{-1}. Whilst the order value as obtained from the peak asymmetry method of Kissinger [9] is 2/3.

Other evidence for this phase transition was demonstrated by the electrical conductivity behaviour of I with temperature. Figure 3 shows a semiconducting behaviour with two different activation energies, ΔE, 0.15 eV and 1.38 eV at two different temperature ranges, 30–68 °C and 130–149 °C, respectively. On the other hand, the temperature range (70–128 °C) of the lowering conductivity between the two semiconducting regions coincides exactly with that of the endothermic DTA peak. This means that the energy of the system was consumed in the phase transformation rather than the

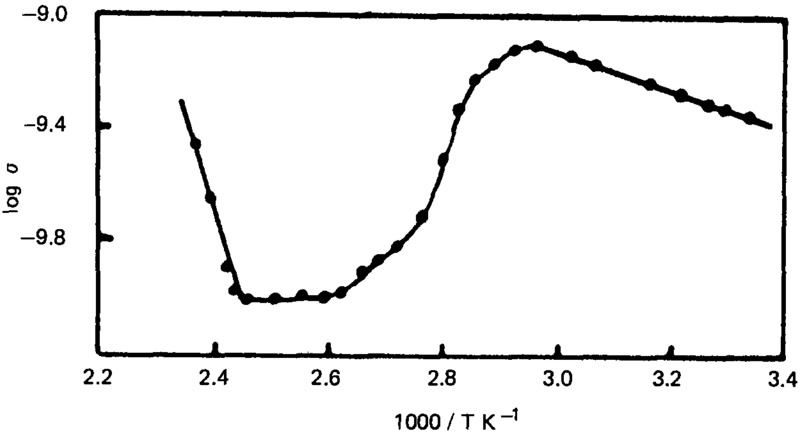

Fig. 3. Temperature dependence of electrical conductivity of I.

thermal agitation of electrons giving lower conductivity values. This conductivity behaviour confirms the phase transition assignment of the DTA peak.

Spectroscopic studies

The obtained phase transition (I → I_a) has also been confirmed by X-ray powder diffraction and IR measurements. The two species (I) and (I_a) show significantly different X-ray diffraction patterns (Fig. 4), indicating the presence of two phases. On the other hand, the IR spectra of (I) and (I_a) (Fig. 5) are mainly the same, confirming that the two species are chemically

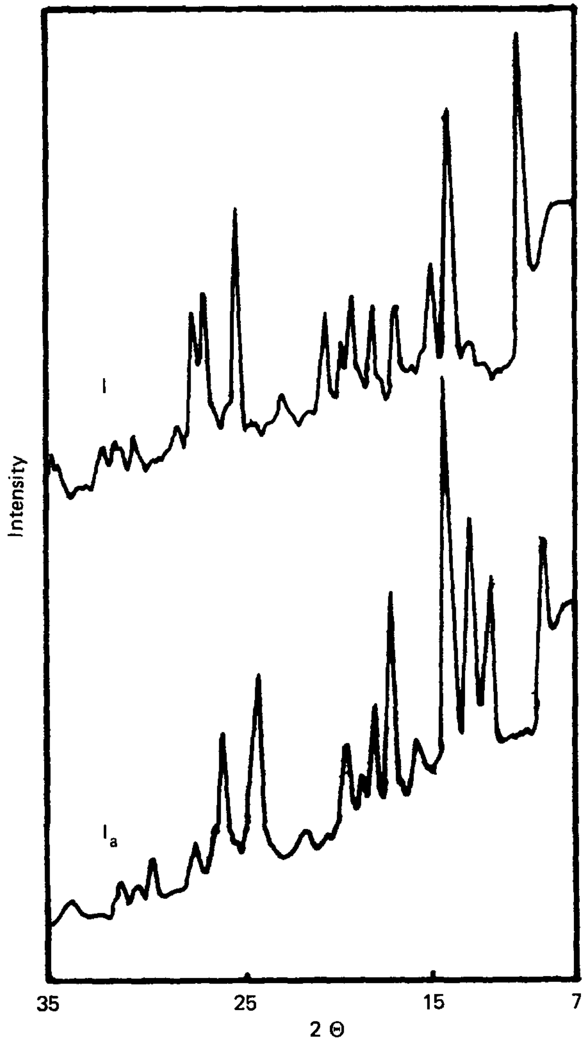

Fig. 4. X-ray diffraction patterns of I and I_a.

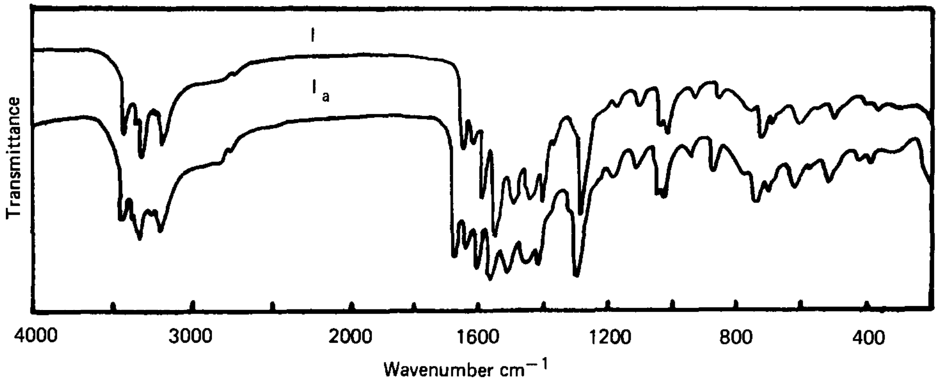

Fig. 5. IR spectra of I and I_a.

identical. The observed minor changes in the shape, relative intensities and, sometimes, the position (5–10 cm^{-1}) of some peaks, especially ν_{NH_2}, might be attributed to the phase change [3,10,11].

Finally, the data obtained are in good agreement with those of the previous work [3]. So, either of the following two factors are likely to be effective in the obtained phase change: geometrical isomerization (*cis–trans*) of the two chelate rings around the metal ion [3,12]; and/or conformational changes (boat–chair) of the individual six-membered chelate rings [3,4].

A clearer picture would have been obtained if single-crystal analysis could have been performed for both I and I_a.

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