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THERMOCHROMISM OF THE COBALT(II)–ISONIAZID COMPLEX IN THE SOLID STATE

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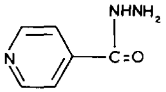
ABSTRACT

The cobalt(II) complex of isoniazid (I_a) shows the thermochromism in the solid state. This thermochromism has been attributed to dehydration and was studied using differential thermal analysis (DTA), electronic and IR spectroscopy and X-ray powder diffraction. The energy of activation E_a of the dehydration process and the reaction order were evaluated.

INTRODUCTION

Isoniazid (see below) is a useful tuberculostatic agent as was reported by Farbenfabriken Bayer.



It forms metal chelates with many bivalent ions. These complexes have been used in the determination of the structure of isoniazid [1,2]. Copper, cobalt and zinc complexes have anti-tubercular effects [3]. The structure, stability and consecutive formation constants of metal chelates of isoniazid with different metal ions, particularly Cu^{II} and Cd^{II}, have been studied previously [4,5]. More recently the thermochromism in some Ni^{II} and V^{III} complexes has been investigated [6,7]. In this work, we report the thermal behaviour of the Co^{II} complex with isoniazid. The observed thermochromism in this complex is discussed in terms of structural and spectroscopic changes. The kinetic parameters of the thermal reaction are also determined.

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EXPERIMENTAL

The metal complex was prepared by mixing the ligand (0.1 mol) and the metal chloride (0.1 mol) in an ethanol solution. After evaporation of most of the solvent, a pink precipitate was obtained. The precipitate was filtered off, washed with ethanol several times and dried over $CaCl_2$–P_2O_{10}.

The elemental analysis was carried out at the National Research Centre Dokki, Cairo, Egypt. IR spectra were measured using KBr discs and a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer. Electronic spectra were measured as Nujol mulls using a Unicam SP 100 spectrophotometer. The differential thermal analysis (DTA) was carried out using a Shimadzu XD-30 thermal analyser. X-ray powder diffraction was measured using a Shimadzu XD-3 diffractometer by applying the Cu $K\alpha$ line.

RESULTS AND DISCUSSION

The structure of the pink complex obtained was checked and confirmed as follows: elemental analysis: C, 24.1%; H, 3.5%; N, 14.1%; calculated for $[Co(C_6H_7N_3O)Cl_2 \cdot 2H_2O]$: C, 23.8%; H, 3.6%; N, 13.9%. The IR band assignments of isoniazid and some of its metal complexes have been reported elsewhere [8]. Figure 1 shows the IR spectra of isoniazid and its Co^{II} complex. The spectrum of the complex displays a broad band near 3400 cm^{-1} and a medium band near 3200–3000 cm^{-1} which are assigned to ν(OH) of water and bonded ν(NH) respectively. The spectrum also shows a strong band at 1645 cm^{-1} which is assigned to ν(C=O); this band is shifted to lower frequency (approximately 20 cm^{-1}) relative to that of the ligand (1665 cm^{-1}), indicating the coordination through the C=O group. The electronic spectrum of the complex (Fig. 2) shows a band at 500 nm,

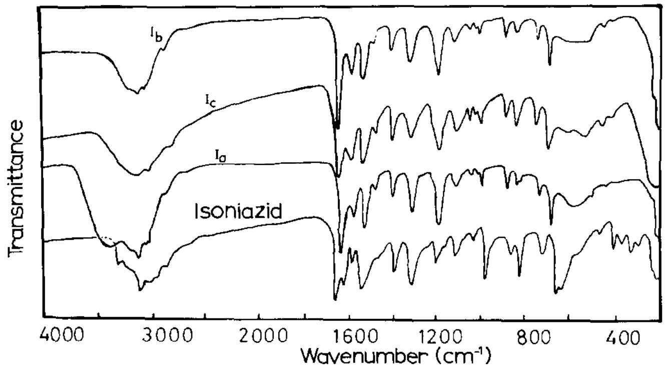


Fig. 1. IR spectra of isoniazid, I_a, I_b and I_c.

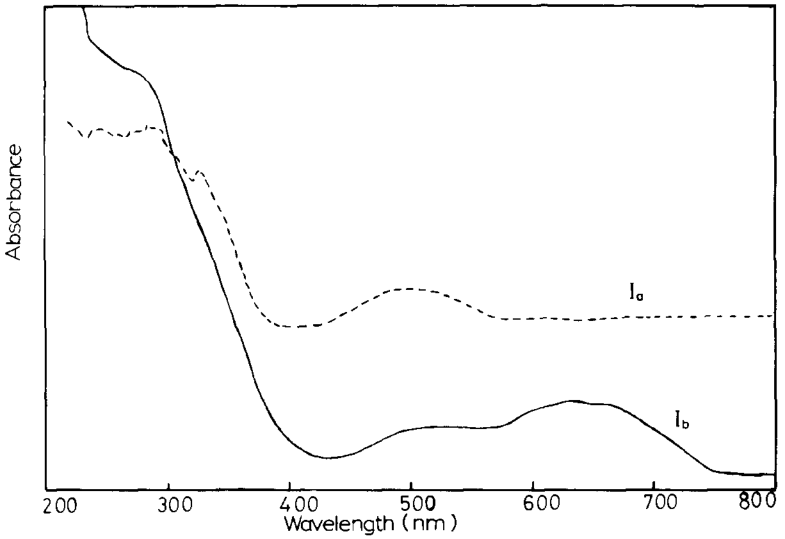
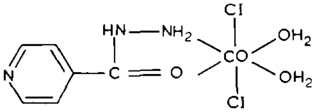


Fig. 2. Electronic spectrum of I_a and I_b.

indicating octahedrally coordinated cobalt [9]. The above argument suggests the following structure



Thermal studies

The cobalt(II)-isoniazid complex (I_a) is pink and changes to blue on heating to approximately 145 ° C for about 10 min. The corresponding blue complex is referred to hereafter as I_b. The change in colour is reversible and the blue form changes to pink again on standing in air at room temperature for 1 h. This reversibility can be prevented for several days if the blue form is kept under paraffin oil. If the blue form (I_b) is heated to 190 ° C, the colour changes to dark blue (I_c). The dark blue colour is also reversible and changes to blue and then to pink, but only very slowly (approximately 24 h). The DTA curve (Fig. 3) consists of two endothermic peaks at 145 ° C and 190 ° C followed by an exothermic peak at 230 ° C. These peaks are assigned as indicated by other analytical measurements to the dehydration of I_a, the phase change $I_b \rightarrow I_c$ and decomposition of the material respectively. The temperature range of thermochromism coincides with the endothermic peak at approximately 145 ° C, indicating that the thermochromism can be attributed to the dehydration process. The energy of activation E_a of the

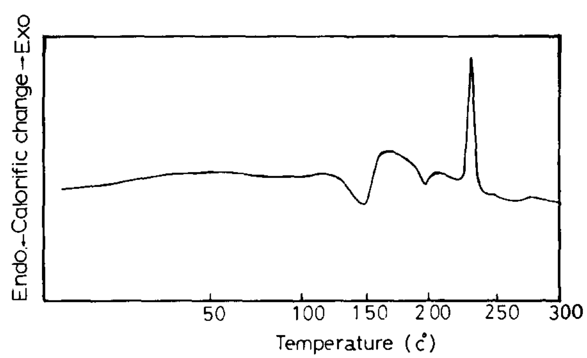


Fig. 3. DTA curve of I_a.

dehydration process can be evaluated from the DTA curve using the method of Wendlandt [10] (Fig. 4); by assuming first-order kinetics, the value of E_a is 181 kJ mol^{-1}. The order of the dehydration reaction as obtained from the asymmetry of the DTA peak using the Kissinger method [11] is 0.86, confirming the first-order assumption for the process. The hygroscopic nature of the blue form (I_b) which gives the original pink form (I_a) can be used as a quick and simple method for testing the dryness of some organic solvents.

Spectroscopic study

The pink Co^{II} complex (I_a) and its blue thermoproduct (I_b) were investigated using electronic and IR spectra. The electronic spectrum of I_a (Fig. 2) displays a band near 500 nm, indicating octahedrally coordinated cobalt [9] as mentioned above. The spectrum of I_b shows two bands near 635 nm and 525 nm, indicating pseudotetrahedrally coordinated cobalt [12].

The IR spectra of I_a and I_b (Fig. 1) are nearly the same, except for some minor differences in the shape, intensity and position of some peaks,

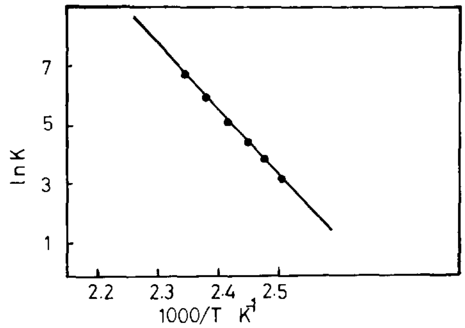


Fig. 4. Arrhenius plot constructed from DTA curve of I_a.

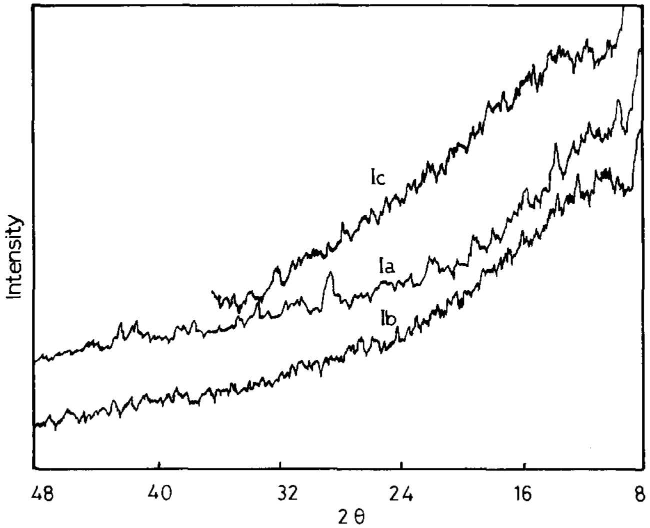


Fig. 5. X-ray diffraction patterns of I_a, I_b and I_c.

especially the out-of-plane CH deformation near 850 cm^{-1} and the in-plane CH-bending mode near 1210 cm^{-1}. This may be due to structural change (geometrical change) accompanying dehydration [6,7]. The dehydration of I_a is also confirmed by the disappearance of ν(OH) of water near 3400 cm^{-1} from the spectrum of I_b. The IR spectrum of I_c (Fig. 1) shows lower intensity and broader peaks relative to I_b, especially ν(NH) near 3200–300 cm^{-1} and the in-plane CH-bending mode at 1200 cm^{-1}; the ring breathing near 1060–1020 cm^{-1} and the out-of-plane CH deformation at 850 cm^{-1} have a sharp shape. These minor changes in the shape and intensity of the peaks may be due to some phase changes (blue $I_b \rightarrow$ dark blue I_c). This result confirms the assignment of the DTA peak at 190 °C to phase change.

The structural change accompanying the dehydration process ($I_a \rightarrow I_b$) was also examined by X-ray powder diffraction (Fig. 5). The pattern of I_a, which has a number of reflections with low intensity, suggests a low degree of symmetry and crystallinity [12,13]. The patterns of I_b and I_c are not clear due to the very low intensity of the reflections. These patterns are similar to those of amorphous materials.

This work and our previous studies [6,7] of thermochromism in metal complexes may lead to new uses of these metal complexes for energy storage.

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