

Novel aspects of the thermo-kinetic properties of cobalt(II), nickel(II) and copper(II) complexes of 2-(benzeneazo)-1,5-dihydroxynaphthalene

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Abstract

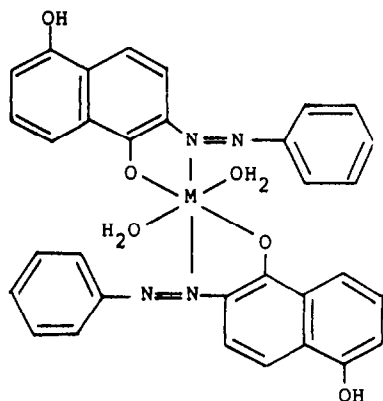
The compound 2-(benzeneazo)-1,5-dihydroxynaphthalene has been isolated and combined with some of the first-row transition metal ions, namely Co(II), Ni(II) and Cu(II). The complexes have been characterised in the solid state by elemental analyses, and infrared and electronic absorption spectral measurements. The thermal behaviour of the complexes has been studied by a combination of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) from ambient temperature up to approximately 550 °C in air. Two thermal processes have been identified: dehydration and decomposition, which interfered with structural rearrangements. The thermal stability of the complexes follows the order Ni(II) > Co(II) > Cu(II). In addition, kinetic data extracted from the DTA thermograms demonstrated that the dehydration process $ML_2 \cdot 2H_2O \rightarrow ML_2$ is simple, whereas the second stage decomposition is complicated and metal-ion dependent.

INTRODUCTION

The potential azo compounds which are the subject of this article, have a rich chemistry which has long been the subject of debate. This class of compounds is involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis, inhibition of azo reduction, monoamine oxidase and in immunochemical affinity labelling [1–4]. In addition, azo ligands with different functional groups were studied extensively in terms of their ability to complex with many metal ions as revealed by complexometric titration [5], and in their application, together with that of their complexes, a dyes of fast, bright shades [6].

The present article reports the synthesis and thermal behaviour of 2-(benzeneazo)-1,5-dihydroxynaphthalene (L) metal complexes with Co(II), Ni(II) and Cu(II) ions.

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EXPERIMENTAL

Preparation of compounds

The 2-(benzeneazo)-1,5-dihydroxynaphthalene (L) was prepared according to the published procedure [7]. Following this procedure, the ligand was prepared by dissolving aniline (0.1 mol) in conc. HCl (0.2 mol) and distilled water (25 cm³). The hydrochloride products were diazotised below 5 °C with a solution of NaNO₂ (0.1 mol) in distilled water (30 cm³), and the resulting diazonium chloride was coupled with an alkaline solution of 1,5-dihydroxynaphthalene (0.1 mol). The crude dye was collected by filtration and crystallised from dioxane; it was then dried in vacuum over P₄O₁₀.

The metal complexes of L were prepared as follows. An alcoholic ammonia (1 : 1, 250 cm³) solution of the divalent metal chloride (Co, Ni and Cu) (0.01 mol) was heated under reflux with L (0.02 mol), dissolved in dioxane, for 30 minutes. The complexes were recrystallised from dioxane. The stoichiometry and identity of the products were confirmed by elemental analyses and spectral measurements.

Physical measurements

All UV-visible absorption spectra were recorded at room temperature on a Shimadzu 240 spectrophotometer using a Nujol mull technique for the solid complexes. Infrared spectra were obtained from KBr pellets using a Perkin-Elmer 683 grating infrared spectrophotometer. Thermogravimetric analyses were performed on test samples using the simple manual thermobalance technique with a high precision of ± 0.2 °C; a 10⁻⁵ g-correction curve was constructed before use and measurements were taken from ambient temperature up to approx. 550 °C in air. Differential thermal

analyses were done using a Du Pont instrument (U.S.A.) in the temperature range 20–550°C at a heating rate of 10°C min⁻¹ (50 mV cm⁻¹) using Al₂O₃ as reference.

RESULTS AND DISCUSSION

The structures of the free ligand (L) and its metal complexes have been discussed previously [8]. To follow the structural changes taking place during thermal analysis, which is the subject of this article, we choose to study those aspects of the structure that showed pronounced changes. The IR spectra of the free ligand and its complexes show similar patterns in the region 3500–600 cm⁻¹, except for the appearance of the N=N stretching frequencies at 1570–1535 cm⁻¹ and the decrease in the $\nu(\text{C}=\text{O})$ in the complexes, demonstrating the involvement of the azo group in the complex

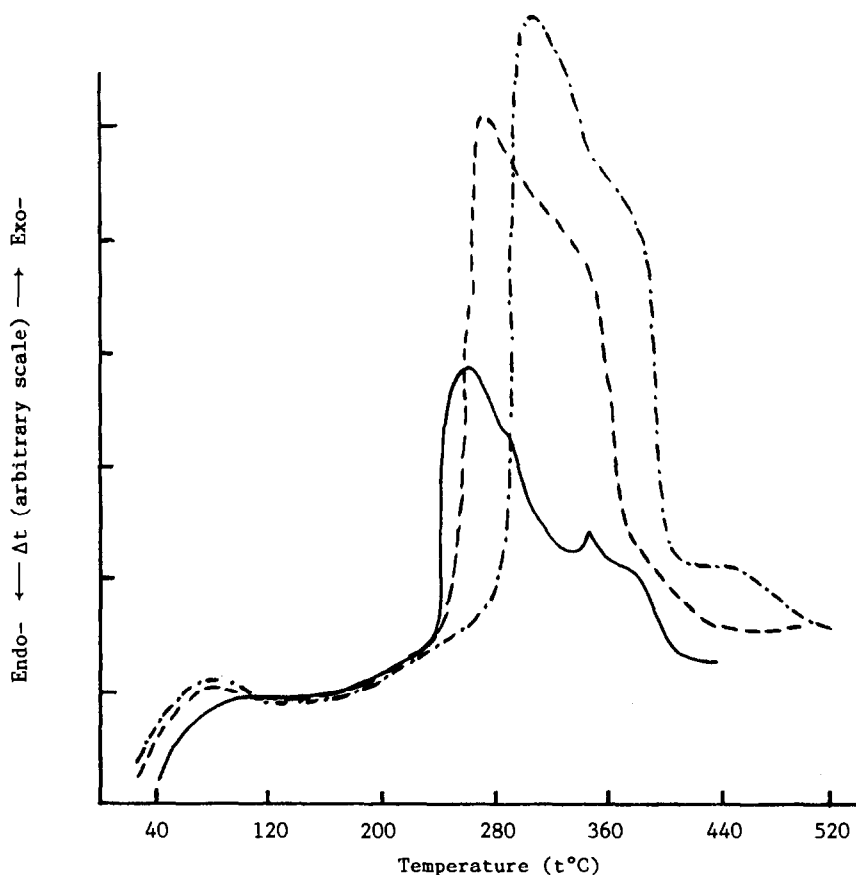


Fig. 1. DTA curves of the transition metal complexes of 2-(benzeneazo)-1,5-dihydroxynaphthalene. — CuL₂·2H₂O ····· NiL₂·2H₂O --- CoL₂·2H₂O.

formation and ruling out the possibility of hydrazone tautomerism in the complex formation. The implication that there are two water molecules in the core of the complex has been verified from elemental analysis, from the appearance of broad bands in the IR spectra of the complexes at around 3500 cm^{-1} and from the electronic spectra of the solid complexes where distorted octahedral geometries have been reported [8]. Therefore, the complexes are formulated as $\text{ML}_2 \cdot 2\text{H}_2\text{O}$.

The technique of differential thermal analysis (DTA) has been reviewed elsewhere [9]. Figure 1 shows the DTA thermograms for $\text{ML}_2 \cdot 2\text{H}_2\text{O}$. The curves indicate very weak endothermic peaks at around $120\text{--}180^\circ\text{C}$, which mostly correspond to partial loss of chemically combined water molecules. The products obtained by heating $\text{ML}_2 \cdot 2\text{H}_2\text{O}$ to 180°C for 30 minutes

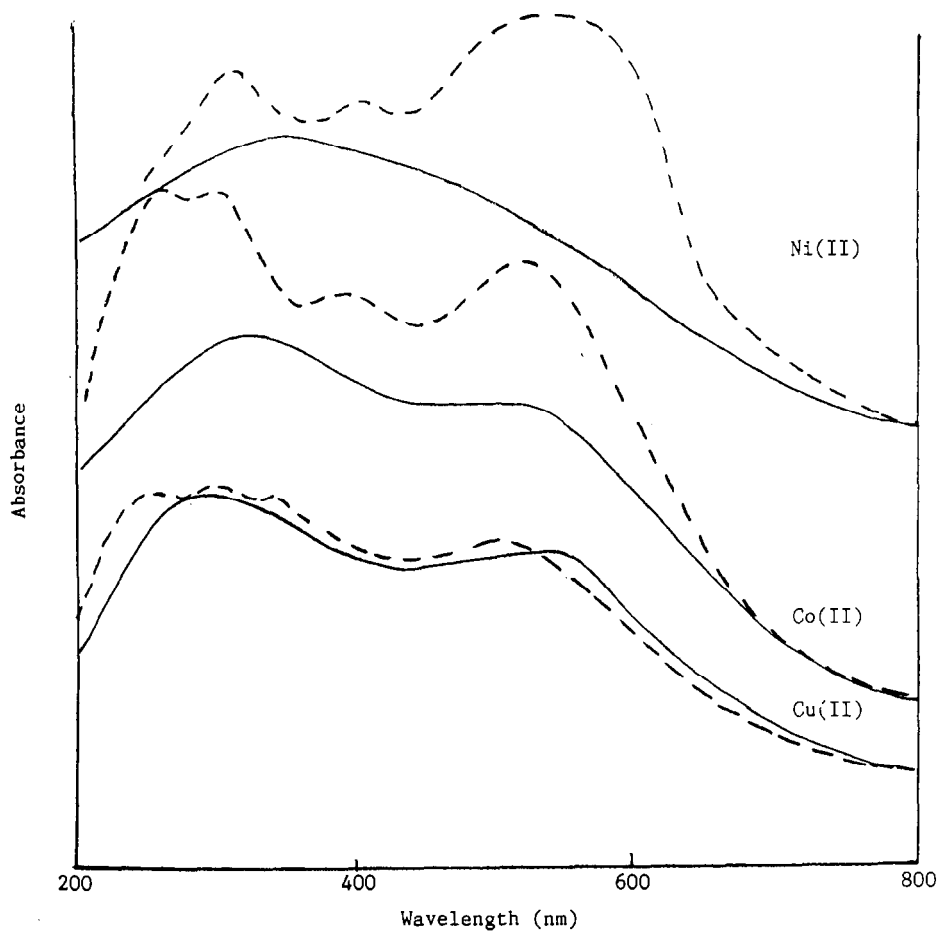


Fig. 2. Solid state electronic spectra of 2-(benzeneazo)-1,5-dihydroxynaphthalene complexes before (a) ----- and after (b) ——— heating at 180°C .

have solid state electronic spectra (Fig. 2) similar to those reported for square-planar or distorted square-planar geometries [10,11]. In addition, the attenuation of the IR absorption frequencies at 3500 cm^{-1} for the products presents supportive evidence for the vaporisation of two water molecules from the complex core at 180°C . The copper complex thermogram displays

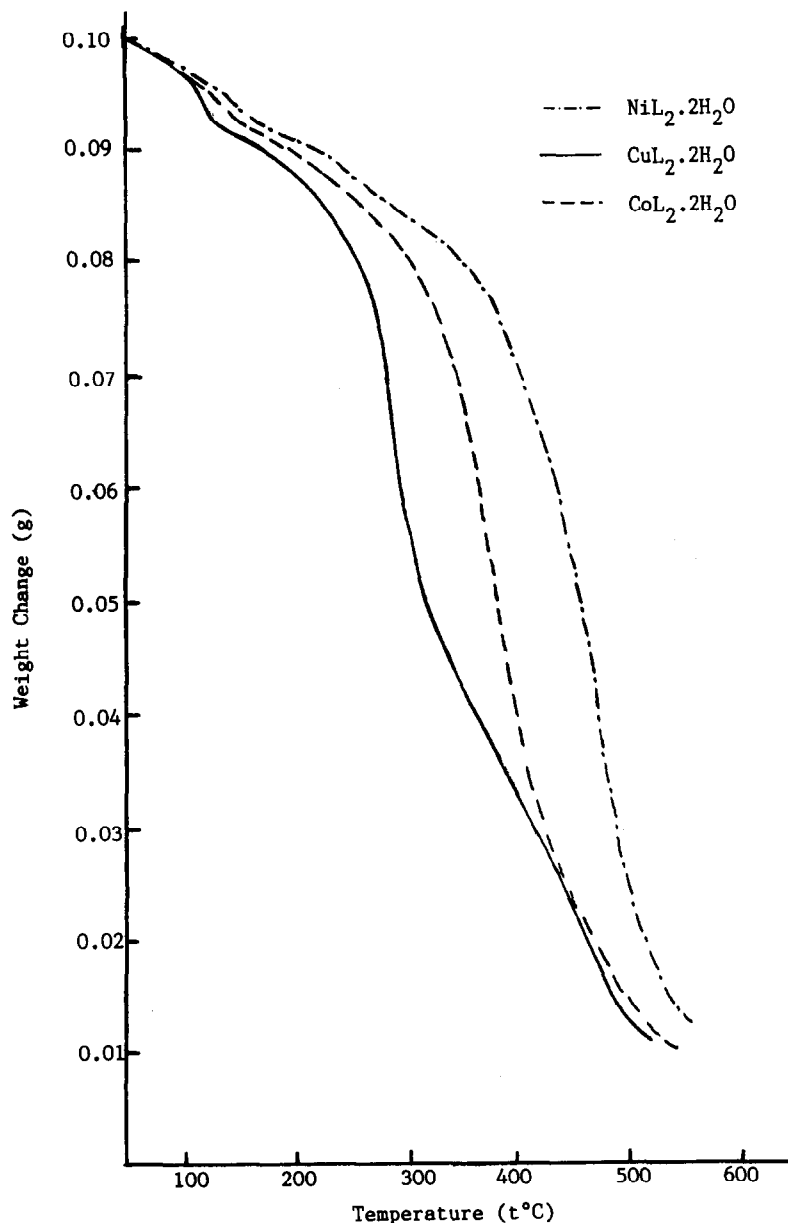


Fig. 3. TGA curves of 2-(benzeneazo)-1,5-dehydroxynaphthalene complexes.

a broad exotherm at 280 °C which is immediately followed by a shoulder at 297 °C corresponding to decomposition and structural rearrangement of the complex. This assignment is clearly justified by the TGA measurements; the tracing curve, Fig. 3, for the copper complex shows a plateau covering the temperature range 180–225 °C, corresponding to ML_2 . The appearance of

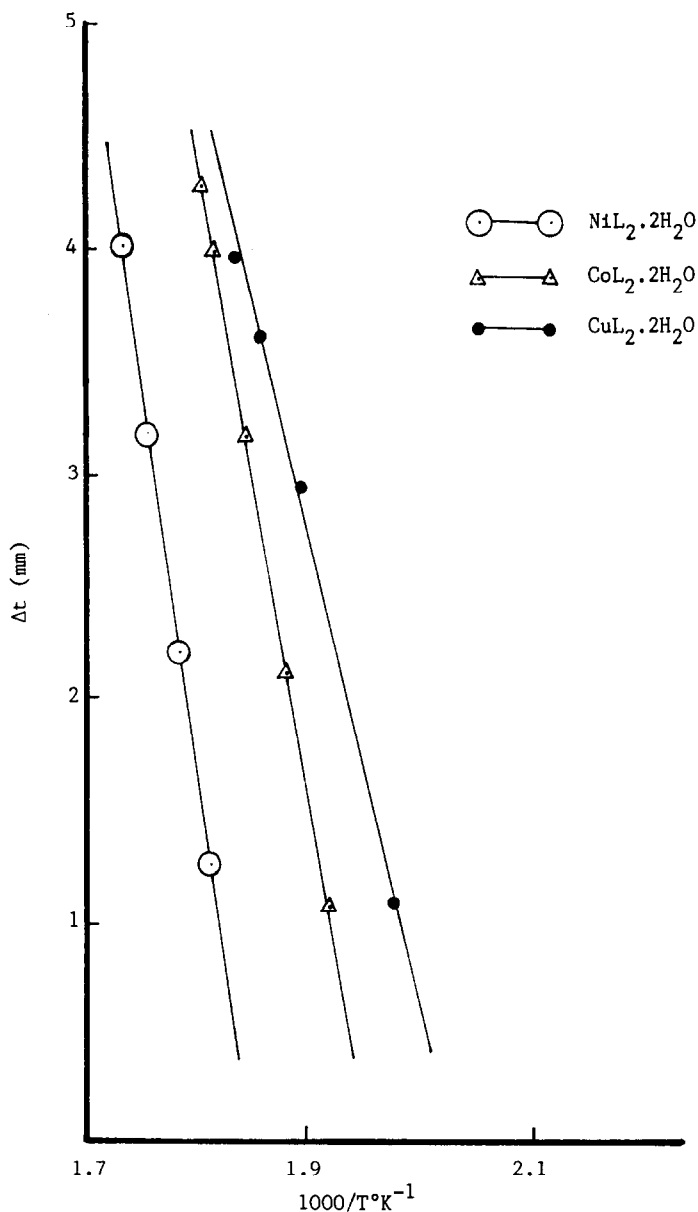


Fig. 4. Plots constructed from DTA curves of the complexes.

this plateau is due to structural changes and emphasises the well-known plasticity of copper(II) complexes [12]. However, this plateau is replaced by shoulders at 195 °C and 200 °C for the cobalt and nickel complexes, respectively, demonstrating that the copper complex is more susceptible to structural transformation than the other two transition metal complexes. The other exotherms in the DTA curves of all the complexes are due to their thermal decomposition to the metal oxide. Briefly, the thermal stability of the complexes under investigation can be arranged in the order: Ni(II) > Co(II) > Cu(II).

Kinetic parameters

Various methods have been proposed for determining kinetic parameters from differential thermal analysis (DTA) measurements [13–16]. However, only one of these provides a direct method for determining the activation energy (ΔE) of the chemical reaction. Following Piloyan's [16] treatment, ΔE can be determined simply using the equation

$$\Delta t = C - \frac{\Delta E}{RT} \quad (1)$$

where R and T have the usual meaning and C is a constant. Values of Δt are taken directly from the DTA curve in units of length (cm or mm) and plotted against the reciprocal of absolute temperature. A straight line should be obtained (Fig. 4) whose slope is related to the activation energy (ΔE) by

$$\Delta E = \text{slope} \times R = \text{slope} \times 8.31 \text{ (kJ mol}^{-1}\text{)} \quad (2)$$

The order of the solid-state chemical reaction can be calculated from the shape of the thermogram using Reich's [17] empirical relation of the type

$$n = 1.26\sqrt{S} \quad (3)$$

where n is the reaction order and S is the peak shape factor. The results are presented in Table 1. The activation energy of the complexes shows two sets of values. The lower values fall within the values for bonding of the metal

TABLE 1
Kinetic parameters of the metal complexes

Complex	ΔE (kJ mol ⁻¹)	Order n
CoL ₂ ·2H ₂ O	16.29	1.16
	193.90	1.80
NiL ₂ ·2H ₂ O	15.91	1.12
	274.23	1.32
CuL ₂ ·2H ₂ O	15.58	1.19
	148.39	2.03

centre to H_2O , and suggest that these dehydrations are simple processes [18]. This is also inferred from the order of such processes which tend to limit to 1. There are, however, large differences in the second set of activation energy values. Nor is the order of the reaction so simple. This suggests that the second stage of the decomposition of the organic compound is not a straightforward process: it most probably interferes with structural rearrangements due to the chelate effect and the different binding power of the metal ions.

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