Journal of Thermal Analysis, Vol. 36 (1990) 1033-1038

THERMAL AND ELECTRICAL BEHAVIOUR OF NICKEL(II) AND COPPER(II) COMPLEXES OF 4-ACETYLAMINO-2-HYDROXY-5-METHYL AZOBENZENE

*M. S. Masoud**, *E. A. Khalil*, *E. El-Sayed El-Shereafy*** and *S. A. El-Enein***

DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, ALEXANDRIA UNIVERSITY
ALEXANDRIA, EGYPT
**DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, MENOUFIA UNIVERSITY,
SHEBIN EL-KOM, EGYPT

(Received September 13, 1989)

The thermal behaviour of the entitled nickel(II) and copper(II) complexes of 4-acetylamino-2-hydroxy-5-methyl azobenzene has been studied by means of differential thermal analysis (DTA), thermogravimetry (TG), X-ray powder diffraction, IR and electrical conductivity. A light has been thrown on the nature of interaction of the solvents of crystallization with the host complex. Some of the kinetic parameters are calculated and discussed.

Thermal analysis plays an important role in studying the structure and the properties of metal complexes. Nowadays a number of solid state reactions (e. g., thermal isomerization, conformational changes, polymorphic transformations, thermal phase transitions, thermochromism, etc...) of some metal chelates have been studied by means of thermal analysis [1-10]. In our laboratory, the structural chemistry of some transition metal chelates of simple substituted-azobenzenes was characterized [11-15] based on spectral and magnetic susceptibility techniques, but no work has been done on their thermal properties. The major goal of the present manuscript is conducted to study the thermal behaviour of some of these complexes to throw more light on the solid state reactions present.

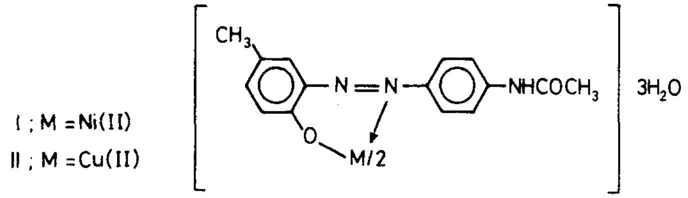
---

*Author to whom correspondence should be directed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

The investigated complexes (I, II) were prepared as reported and their structures were proposed as in scheme 1 [11-15]. The differential thermal analysis (DTA) was carried out using Shimadzu XD-30 thermal analyzer. The thermogravimetric analysis (TG) was obtained by recording the weight of the sample before and after a DTA run up to 140°. The measurements were repeated for accuracy. The conductivity measurements were taken on a Keithley 175 autoranging multimeter with an applied volt 200 V. The x-ray powder diffraction was recorded using a Shimadzu XD-3 diffractometer by applying CuK$_\alpha$ line. KBr-IR spectra were recorded using a Perkin-Elmer 598 (4000-200 cm^{-1}) spectrophotometer.



Results and discussions

The investigated complexes (I, II) display a desolvation heating up to 130° for 15 min to give the anhydrous forms I$_a$ and II$_a$, respectively. The desolvation reaction and the nature of interaction of the solvent with the host molecule have been studied by thermal and spectral methods. The DTA curves of (I) and (II), (Fig. 1), show an endothermic peak in the temperature ranges 60-110° and 90-140°C, respectively. This peak is assigned to desolvation of the complexes as evident from the TG measurements, which show a weight loss corresponding to three molecules of water. This goes parallel to the elemental analyses of the complexes [11]. Such reaction is irreversible as indicated from the disappearance of its peak in the DTA curves of (I$_a$) and (II$_a$) Fig 1. The energies of activation (ΔE) of desolvation reaction of the nickel and copper complexes are 77 kJ/mol and 102.7 kJ/mol, respectively, calculated based on Piloyan *et al.* [16] method (Fig 2). In turn, the order values calculated from the peak asymmetry method of Kissinger [17] are 1.6 and 1.1, respectively. The X-ray diffraction patterns of both hydrated and dehydrated forms (Fig. 3) show no significant differences, in-

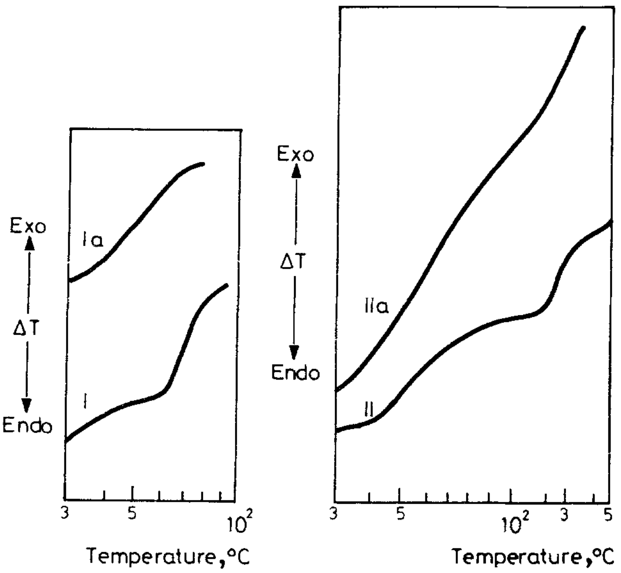


Fig. 1 DTA curves of I, Ia, II and IIa

dicating the presence of pseudopolymorphic transformation rather than polymorphic one through desolvation [9].

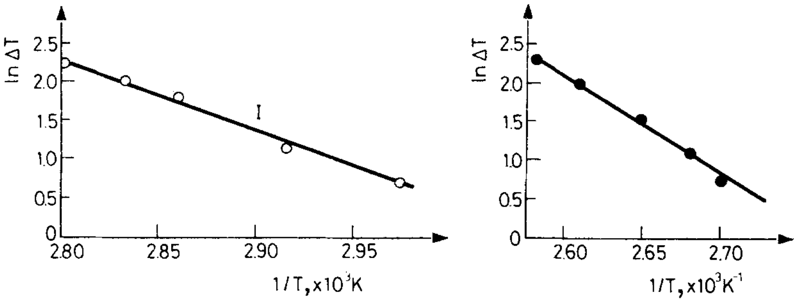


Fig. 2 A plot constructed from the DTA curves of (I) and (II)

The IR spectra of both the hydrated and dehydrated forms are identical, to assign that these complexes are with no conformational or configurational changes during desolvation [9]. In summary, the spectral results in addition

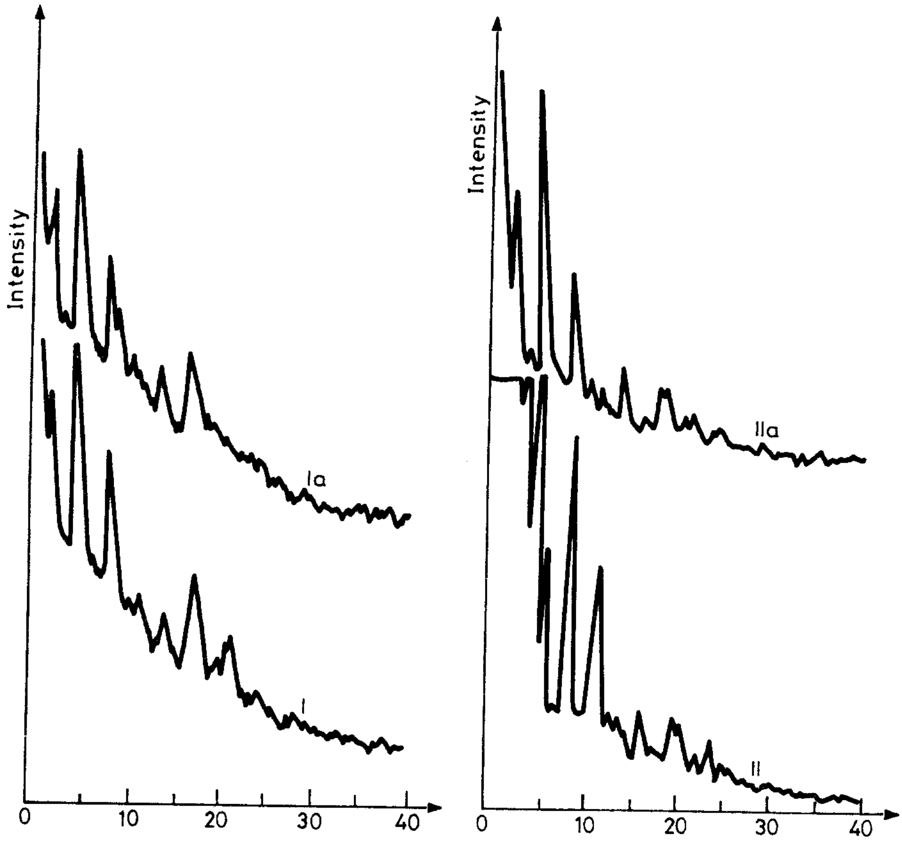


Fig. 3 X-ray powder diffraction of I, Ia, II and IIa

to the ease of desolvation process suggest the very little contribution of water molecules in the crystal network.

The behaviour of the electrical conductivity property of the nickel and copper complexes with temperature (Fig. 4) gives a good evidence for desolvation and pseudo-polymorphic transformation. The nickel complex shows a semiconducting behaviour with two activation energies (ΔE) 0.22 eV and 6.14 eV in the temperature ranges 20-77° and 111-147°, respectively. The temperature range 77-107° of lower conductivity values coincide with that of the endothermic DTA peak, indicating the consumption of an energy in the desolvation process rather than the thermal agitation of electrons [18]. For the copper complex, the conductivity data are of a semiconducting and a

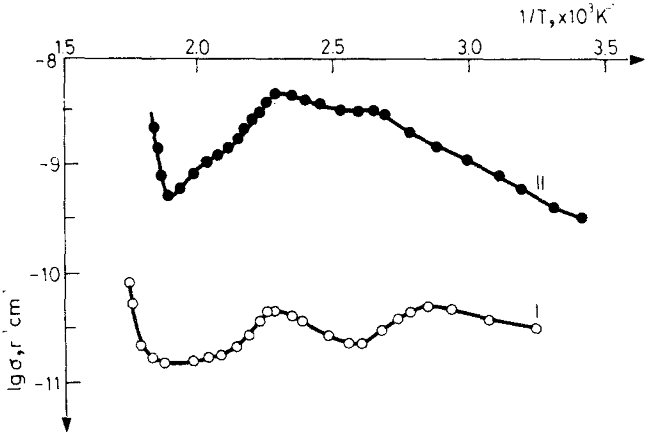


Fig. 4 Temperature dependence of electrical conductivity of I and II

metallic behaviour with ΔE 0.57 eV and 6.00 eV within the temperature ranges 20-100° and 135-167°, respectively. The observed metallic behaviour may be attributed to the creation of crystal voides and defects as a result of desolvation [9, 18]. Again the temperature range 100-135° of nearly constant conductivity values is in good correlation to the desolvation process.

References

1 C. Duval, Inorganic and Thermogravimetric Analysis, Elsevier, Amsterdam, 1953.
2 W. W. Wendlandt, Anal. Chem., 27 (1955) 1277; Anal. Chim. Acta 15 (1956) 109; 17 (1957) 274.
3 W. W. Wendlandt and I. M. Bryant, Anal. Chim. Acta, 13 (1955) 550.
4 G. De, P. K. Biswas and N. R. Chaudhuri, J. Chem. Soc. Dalton trans. (1984) 259.
5 J. R. Lusty, H. S. Chan, E. Khar and J. Pecling, Inorg. Chim. Acta, 106 (1985) 209.
6 K. Miyokawa and I. Masuda, J. Phys. Chem. Solids, 47 (1986) 13.
7 A. Ghosh, G. De and N. R. Chaudhuri, J. Chem. Res., 1 (1987) 104.
8 L. Deuschle and U. Weser, Inorg. Chim. Acta, 135 (1987) 5.
9 A. M. Donia and E. M. Ebeid, Thermochim. Acta, 131 (1988) 1.
10 S. R. Byrn, Solid State Chemistry of Drugs, Acad. Press. N. Y., London, 1982.
11 M. S. Masoud, M. M. Osman, T. M. Salem and E. A. Khalil, Ind J. Chem., 20 A (1981) 584.
12 M. S. Masoud, S. Abou Ali, G. Y. Ali and M. A. El-Dessouky, J. Chem. Eng. Data, 28 (1983) 297.
13 M. S. Masoud, M. A. Goher and A. M. Heiba, Rev. Inorg. Chem., 5 (1983) 407.
14 M. S. Masoud and M. M. El-Essawi, J. Chem. Eng. Data, 29 (1984) 363.
15 M. S. Masoud, H. M. El-Nahas and E. A. Khalil, Ind. J. Chem., 24 A (1985) 347.
16 G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, Nature, (1966) 1229.
17 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
18 M. S. Masoud, M. Kassem and E. A. Khalil, React. Solids, 2 (1986) 269.

Zusammenfassung — Mittels DTA, TG, Röntgendiffraktionsuntersuchungen, IR und elektrischen Leitfähigkeitsmessungen wurde das thermische Verhalten der Titelverbindungen untersucht. Bei diesen 4-Acetylamino-2-hydroxy-5-methyl-azobenzolkomplexen von Nickel(II) und Kupfer(II) wurde auch die Natur der Wechselwirkung des Lösungsmittels der Kristallisierung mit der Komplexverbindung ergründet. Einige der kinetischen Parameter wurden berechnet und diskutiert.