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Template synthesis and thermal behaviour of some metal complexes of 2,6-diacetylpyridine-mono(carbohydrazone) ligand

F.A. El-Saied [1], Ahmed M. Donia and S.M. Hamza

Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom (Egypt)

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Abstract

The chelating behaviour of neutral and deprotonated 2,6-diacetylpyridine-mono(carbohydrazone) (Hdapc) has been studied in some new complexes of Pd(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ba(II) and UO_2(VI). Spectroscopic, magnetic susceptibility and other analytical studies reveal that the ligand behaves as an NN-chelating agent in the neutral form and as an ONNO- or NNO-chelating agent in the deprotonated form. Molar conductance measurements indicate the presence of coordinated chloride ion and acetate group. The geometry of some of the metal complexes is also discussed. In addition, the thermal behaviour and the nature of the interaction of the water of crystallisation of some of the metal complexes have been studied using DTA, TG, X-ray powder diffraction, IR and solid electrical conductivity techniques.

INTRODUCTION

Metal complexes of 2,6-diacetylpyridine-bis(aroylhydrazone) (aroyl = benzoyl, H_2dapb; picolinoyl, H_2dappc; salicyloyl, H_2daps; 2-thenoyl, H_2dapt; and 2-aminobenzoyl, H_2dapa [1–5]), and 2,6-diacetylpyridine-mono(2-aminobenzoylhydrozone) [6] have been studied. Some interesting aspects involving the hydrazones have arisen from the previous investigations; for example, the versatility for binding metal ions, the tendency to act as quinquedentate planar ligands (except the deprotonated form of 2-thenoylhydrazone which is not planar) and the ability to behave as neutral ligands with metal chlorides and as deprotonated ligands with metal acetates [1–6].

The mononuclear and binuclear La(III) complexes of 2,6-diacetylpyridine-bis(carbohydrazone) (dapcH), 2,6-diacetylpyridine-bis(thiocarbohydrazone) (daptc), and both macrocyclic ligands derived from 2,6-diacetylpyridine and either dapcH or daptc were studied [7]. The Ni(II), Cu(II), Co(II)

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[1] Author to whom correspondence should be addressed.

and Fe(III) complexes of 2,6-diacetylpyridine-mono(thiosemicarbazone) and 2,6-diacetylpyridine-bis(thiosemicarbazone) have been reported [8].

This paper reports the synthesis and characterisation of some metal complexes of 2,6-diacetylpyridine-mono(carbohydrazone) (Hdapc) obtained by template reaction of carbohydrazide with 2,6-diacetylpyridine in the presence of metal salt. A variety of spectral, analytical, thermal and magnetic susceptibility measurements were used to identify the mode of bonding in these complexes.

EXPERIMENTAL

Materials

The 2,6-diacetylpyridine and carbohydrazide used were reagent grade chemicals, used without further purification.

Preparations

The ligand, 2,6-diacetylpyridine-mono(carbohydrazone) (Hdapc), was prepared according to the known method [9] by heating a finely divided mixture of equimolar amounts of 2,6-diacetylpyridine and carbohydrazide in an electric furnace for about 30 minutes at 85 ° C. The very poor solubility of the ligand in all solvents precludes the preparation of metal complexes by direct reaction of the ligand with metal ion.

The template reactions for preparation of the metal complexes were carried out by mixing carbohydrazide, metal salt (metal chlorides, Na_2PdCl_4 or $UO_2(CH_3COO)_2 \cdot 2H_2O$) and 2,6-diacetylpyridine 1 : 1 : 1 molar ratio) in ethanol, or water–ethanol mixture (2 : 1 v/v) in the case of the Ba(II) complex. The resulting solution was refluxed on a water bath for about an hour. The precipitated complexes were filtered off, washed several times with ethanol and dried under a vacuum over phosphorus pentoxide. The Mn(II), Co(II), Ni(II) and Cu(II) acetate complexes were difficult to separate as solids.

Measurements

The elemental analyses (C, H, Cl) were carried out at the microanalytical unit of the University of Cairo; nitrogen analysis was carried out at the analytical unit of the National Research Centre, Dokki; and metal analyses were by standard methods. IR spectra were measured as KBr discs using a Perkin–Elmer 598 spectrophotometer (4000–200 cm^{-1}).

The electronic spectra were run in dimethylformamide and in nujol mull using a Perkin–Elmer 550 S spectrophotometer. The conductivity measurements were made in dimethylformamide solutions (10^{-3} M) using a Tacussel conductimeter, type CD 6 N. Magnetic susceptibilities were measured at 25 °C by the Gouy method; $Hg[Co(CNS)_4]$ was used as the magnetic susceptibility standard. Diamagnetic corrections were effected by employing Pascal's constants [10]. The magnetic moments were calculated from the equation $\mu_{eff} = 2.84(\chi_M^{corr}\ T)^{1/2}$.

Differential thermal analyses (DTA) were carried out in air using a Shimadzu XD-30 thermal analyser. The heating rate was 15 °C min^{-1} and the sample weight was 10 mg. The electrical conductivity measurements were taken on a Keithley 175 autoranging multimeter with an applied voltage of 200 V and a rate of heating of 1 °C min^{-1}. The TG measurements were carried out by recording the weights of the samples before and after heating up to 100–140 °C.

RESULTS AND DISCUSSION

The analytical data (Table 1) show that the reaction of 2,6-diacetylpyridine with carbohydrazide in the presence of a metal salt produces 1 : 1 metal complexes. These air-stable metal complexes are non-hygroscopic, and are soluble in dimethylformamide and acetonitrile, except the Ba(II) complex which is partially soluble. The molar conductances of the metal complexes measured in dimethylformamide indicate their non-electrolytic nature, and the coordination of the chloride ions or acetate group.

Infrared spectra

Table 2 lists selected vibrational bands and assignments of Hdapc ligand and its metal complexes. The infrared spectrum of the ligand shows two bands at 3410 and 3350 cm^{-1}, along with a strong broad band at 3190 cm^{-1}, which were assigned [8] to $\nu(NH_2)$ and $\nu(N-H)$, respectively. The spectrum of the ligand also reveals bands at 1690, 1655 and 1645 cm^{-1}, assigned [7–9,11,12] to $\nu(C=O)$, amide I, and $\nu(C=N)$, respectively. The appearance of the band characteristic of $\nu(C=O)$ in the spectrum of the ligand indicates that the ligand is a 1 + 1 condensation product, i.e. one mole of 2,6-diacetylpyridine was condensed with one mole of carbohydrazide to produce 2,6-diacetylpyridine-mono(carbohydrazone).

The pyridine ring vibrations most affected by pyridine nitrogen coordination to a metal atom are those of the pyridine ring deformation, in-plane ring deformation and out-of-plane deformation [13,14]. In the spectra of all the metal complexes, the band at 1480 cm^{-1} disappears, whereas the bands at 600 and 410 cm^{-1} shift to higher frequencies compared to that of the free ligand, indicating coordination of the pyridine nitrogen to the metal atom. In the spectra of all the metal complexes, the bands characteristic of

TABLE 1

Analytical [a] and conductance data for the ligand and its complexes

Compound	Colour	C (%)	H (%)	N (%)	Cl (%)	M (%)	Λ_M (ohm^{-1} cm^2 mol^{-1})	DTA exothermic peak (°C) [b]
Hdapc	Yellow	51.7 (51.1)	5.7 (5.5)	29.5 (29.8)	–	–	–	
Pd(Hdapc)$Cl_2 \cdot 2H_2O$	Orange	26.5 (26.8)	3.6 (3.8)	16.1 (15.6)	15.5 (15.9)	24.1 (23.7)	48.1	260 m
Mn(Hdapc)$Cl_2 \cdot 2H_2O$	Yellow	30.7 (30.2)	4.1 (4.3)	16.9 (17.6)	17.5 (17.9)	13.6 (13.9)	22.1	350 d
Fe(Hdapc)Cl_3	Dark brown	30.6 (30.2)	3.7 (3.3)	17.2 (17.6)	26.5 (26.8)	14.4 (14.9)	50.0	308 d
Co(Hdapc)$Cl_2 \cdot H_2O$	Green	30.8 (31.3)	3.9 (3.9)	17.8 (18.3)	18.9 (18.5)	15.7 (15.4)	18.2	300 d
Ni(dapc)(H_2O)Cl$\cdot 2H_2O$	Orange	31.6 (31.4)	4.4 (4.7)	18.5 (18.3)	10.1 (9.3)	15.8 (15.4)	33.8	255 d
Cu(dapc)(H_2O)Cl	Purple	34.8 (34.2)	4.2 (4.0)	19.5 (19.9)	10.0 (10.1)	18.4 (18.1)	28.5	–
UO_2(dapc)($OOCCH_3$)	Orange	25.7 (25.6)	3.1 (2.7)	11.8 (12.4)	–	41.6 (42.3)	10.1	240 d
Ba(dapc)(H_2O)Cl	Yellow	28.7 (28.3)	3.4 (3.3)	15.9 (16.5)	7.9 (8.4)	32.6 (32.9)	33.2	310 d

[a] Calculated values in parentheses.

[b] m, melting; d, decomposition.

$\nu(NH_2)$ persist, indicating non-coordination of the terminal amino-group, whereas the band due to ν(C=N) appears at lower frequencies in the spectra of the metal complexes, indicating the coordination of the azomethine nitrogen atom [15]. The band corresponding to ν(C=O) persists in the spectra of Pd(II), Mn(II), Fe(III), Co(II) and Cu(II) complexes, but shifts to lower frequencies in the spectra of Ni(II), UO_2(VI) and Ba(II) complexes, indicating non-coordination of the carbonyl group to the metal atom in the former complexes and its coordination to the metal atom in the latter. In the spectra of Pd(II), Mn(II), Fe(III) and Co(II) complexes, the amide I band (ν(C=O)) persists, indicating the non-coordination of amide oxygen to the metal atom, however, in the spectra of Ni(II), Cu(II), UO_2(VI) and Ba(II) complexes, the amide I band undergoes a remarkable shift ($\Delta\nu \approx 65$ cm^{-1}) towards lower frequency values. The band at 1600–1590 cm^{-1} in the spectra of the latter complexes can also be attributed [1] to the presence of the $>C{=}N{-}N{=}C<$ group, suggesting that the amide oxygen atom coordinates in its enolic form upon deprotonation. This is supported by the presence of a strong band near 1545 cm^{-1} which is characteristic [1] of the δ(NCO) vibration.

Bidentate coordination of the acetate group in the UO_2(VI) acetate complex is suggested as the ν_{as} (at 1535 cm^{-1}), ν_{sym} (at 1445 cm^{-1}) and δ(OCO) (at 675 cm^{-1}) were at comparable frequencies to those reported [16] for the bidentate acetates of UO_2(VI). The spectrum of the UO_2(VI) complex shows a strong band at 920 cm^{-1} and a weak band at 255 cm^{-1}, assigned [16,17] to antisymmetric ν_3(O–U–O) and bending ν_2(O–U–O), respectively. The appearance of the latter band indicates that the UO_2(VI) ion is linear [16].

The infrared spectra of Pd(II), Mn(II), Co(II) and Ni(II) complexes show a broad band near 3500 cm^{-1} which is assigned to uncoordinated water, whereas the spectra of the Ni(II), Cu(II) and Ba(II) complexes show a band near 3450 cm^{-1} assigned to coordinated water.

Electronic spectra and magnetic moment

The electronic spectral features are summarised in Table 3. The electronic spectral bands of all the metal complexes in dimethylformamide are very close to those in nujol mull.

The broad shoulder appearing at 490 nm indicates that the Pd(II) complex is square-planar [18].

The spectrum of the Co(II) complex shows a multi-component band (ν_3). The observed splitting and high intensity of this band suggest a tetrahedral arrangement around the Co(II) ion [19–21]. Further support for this geometry is provided by the high solubility of the complex in water to form an orange solution [22].

TABLE 2

Infrared spectral data [a]

Compound	$\nu(H_2O)$	$\nu(NH_2)$	$\nu(NH)$	ν(CH (alkyl))	$\nu(C=O)$	Amide I	$\nu(C=N)$	Ring	δ(NCO)	$\delta_{as}(CH_3)$, $\delta_s(CH_3)$	$\nu(C{-}O)$
Hdapc	–	3410 (m) 3350 (m)	3190 (s, br)	2910 (w) 2880 (w)	1690 (s)	1655 (s)	1645 (sh)	1565 (s) 1480 (s) 600 (m) 410 (m)	–	1440 (s), 1355 (s)	1245 (s) 1260 (sh)
Pd(Hdapc)-$Cl_2 \cdot 2H_2O$	3500 (br)	3370 (sh)	3190 (m)	2915 (w)	1685 (sh)	1655 (s)	1625 (s, br)	1560 (sh) 620 (w) 420 (w)	–	1440 (m) 1350 (m)	1250 (w) 1270 (w)
Mn(Hdapc)-$Cl_2 \cdot 2H_2O$	3500 (br)	3360 (br)	3180 (sh)	2915 (w)	1685 (m)	1655 (sh)	1630 (s)	1555 (s) 615 (m) 418 (w)	–	1445 (s), 1365 (s)	1250 (s) 1265 (sh)
Fe(Hdapc)Cl_3	–	3380 (br)	3180 (m)	2920 (w)	1690 (sh)	1655 (sh)	1625 (s)	1565 (s) 620 (m) 418 (w)	–	1440 (m, br), 1370 (m, br)	1255 (s) 1275 (s)

Co(Hdapc)- $Cl_2 \cdot H_2O$	3520 (br)	3360 (br)	3180 (sh)	2915 (w)	1685 (sh)	1655 (sh)	1630 (s)	1555 (s) 620 (m) 418 (w)	–	1435 (s), 1370 (sh)	1255 (s) 1275 (sh)
Ni(dapc)(H_2O)- $Cl \cdot 2H_2O$	3500 (sh) 3440 (br)	3350 (br)	3180 (sh)	2920 (w)	1600 (s)	1590 (m)	1630 (s)	1570 (sh) 615 (w) 420 (m)	1545 (s)	1440 (m), 1365 (m)	1255 (sh) 1275 (m)
Cu(dapc)- (H_2O)Cl	3450 (br)	3380 (br)	3180 (w)	2915 (w)	1690 (m)	1590 (m)	1625 (s)	1560 (w) 620 (m) 415 (w)	1545 (s)	1440 (m), 1365 (m)	1260 (br)
UO_2(dapc)- ($OOCCH_3$)	–	3380 (br)	3180 (w)	2920 (w)	1655 (sh)	1590 (s)	1620 (s)	1550 (sh) 618 (w) 415 (w)	1545 (s)	1460 (s, br), 1370 (s, br)	1260 (br)
Ba(dapc)- (H_2O)Cl	3440 (sh)	3380 (br)	3180 (m)	2920 (w)	1660 (s)	1600 (sh)	1615 (m, br)	1560 (sh) 610 (m) 415 (w)	1545 (s)	1443 (s), 1370 (s, br)	1280 (m)

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[a] Key: s = strong; m = medium; br = broad; sh = shoulder; w = weak.

TABLE 3

Magnetic and electronic spectral [a] data

Compound	μ_{eff} (BM) (298 K)	λ_{max}/nm ($\epsilon \times 10^3$/dm^3 mol^{-1} cm^{-1}) [b]	
		d–d bands	Other bands
Hdapc			420 (sh), 360 (sh), 300 (s)
Pd(Hdapc)$Cl_2 \cdot 2H_2O$	Diamagnetic	490 (sh, br) (0.96)	415 (sh) (2.4), 360 (sh) (3.4), 280 (s) (8.4)
Mn(Hdapc)$Cl_2 \cdot 2H_2O$	5.8		415 (sh) (1.8), 350 (s) (5.8), 280 (s) (8.4)
Fe(Hdapc)Cl_3	5.9		420 (sh) (3.3), 360 (sh) (15.7), 300 (s) (42)
Co(Hdapc)$Cl_2 \cdot H_2O$	4.6	670 (s, br) (0.23) 655 (sh) (0.21) 630 (sh) (0.14) 605 (s) (0.16) 595 (sh) (1.5)	420 (sh) (5.6), 360 (s, br) (14.5)
Ni(dapc)(H_2O)Cl$\cdot 2H_2O$	2.9	670 (w) (0.09) 500 (sh) (1.12)	370 (s, br) (8.5) 290 (s) (12.2)
Cu(dapc)(H_2O)Cl	–	670 (w, br) (0.04)	420 (sh) (2.06) 365 (sh) (3.43) 300 (s, br) (10.58)
UO_2(dapc)($OOCCH_3$)	–		560 (sh) (33.58) 530 (s) (41.04) 500 (sh) (38.81) 380 (s, br) (59)
Ba(dapc)(H_2O)Cl	–		420 (sh), 390 (s) 310 (s, br)

[a] In dimethylformamide.

[b] sh = shoulder; br = broad; s = strong; w = weak.

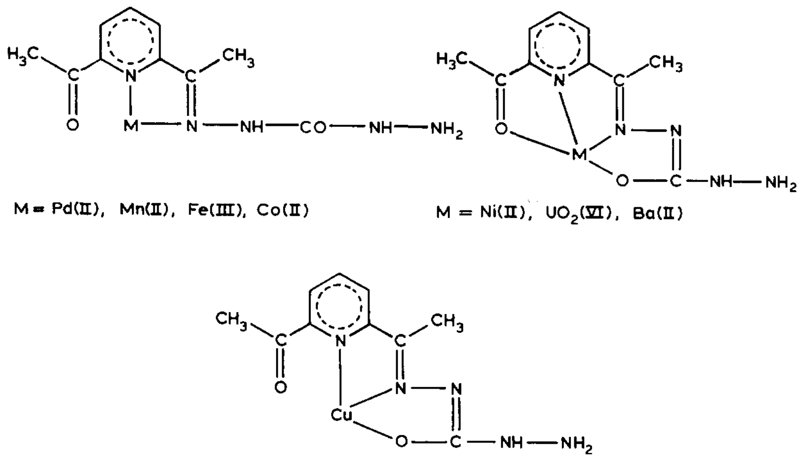
The electronic spectrum of the Ni(II) complex shows two absorption bands at 670 and 500 nm. The appearance of these bands indicate an octahedral structure for the Ni(II) complex [23–25].

The literature is not overly specific with regard to the geometry of five-coordinate Cu(II) complexes. However, it is possible to distinguish six-, five- and four-coordinate Cu(II) complexes from each other [26]. The spectrum of the Cu(II) complex shows a broad, weak band at 670 nm, indicating a distorted square-pyramidal geometry [26–30].

The spectrum of the UO_2(VI) complex shows a strong, very broad band at 530 nm, ascribed to a charge-transfer transition(s) from the equatorial ligands to the uranium atom [16].

The higher energy bands displayed by all the metal complexes are due to charge transfer(s) and internal ligand transitions.

The room-temperature magnetic moments (μ_{eff} BM) of some metal complexes are reported in Table 3. The diamagnetic nature of the Pd(II) complex confirms the suggested square-planar geometry around the Pd(II)



Scheme 1.

ion, whereas the values observed for Mn(II), Fe(III), Co(II) and Ni(II) complexes indicate high-spin metal complexes. The observed values for the Co(II) and Ni(II) complexes confirm the suggested tetrahedral [31] and octahedral [32] structures, respectively.

The above arguments and analytical data (Table 1) indicate that the ligand behaves as an NN-chelating agent in the neutral form (Pd(II), Mn(II), Fe(III) and Co(II) complexes), whereas, in the Ni(II), UO_2(VI), Ba(II) and Cu(II) complexes, the ligand behaves as an ONNO- or ONN-chelating agent in the deprotonated form. Thus, the modes of bonding illustrated in Scheme 1 are suggested.

Thermal studies

The thermal studies on some of the investigated complexes suggest their structures as well as their thermal behaviour. The nature of the interaction of the water of crystallisation has also been characterised. The crystal solvates of the Mn(II), Co(II) and Ni(II) complexes, I, II and III respectively, exhibit a solid-state pseudo-polymorphic transformation on heating in the temperature range 50–120 °C. This transformation was studied by thermal and spectral methods. The DTA curves of I, II and III (Fig. 1) show a broad endothermic peak in the temperature range 50–120 °C, assigned to the pseudo-polymorphic transformation through desolvation, as indicated from the TG, X-ray powder diffraction and IR measurements.

The TG curves show a weight loss corresponding to two molecules of water for I and III, and one molecule for II. This is in good agreement with the suggested formulae. The desolvation reaction is irreversible as shown from the disappearance of its DTA peak in the DTA curves of the desolvated products, Ia, IIa and IIIa. The very broad endothermic peak

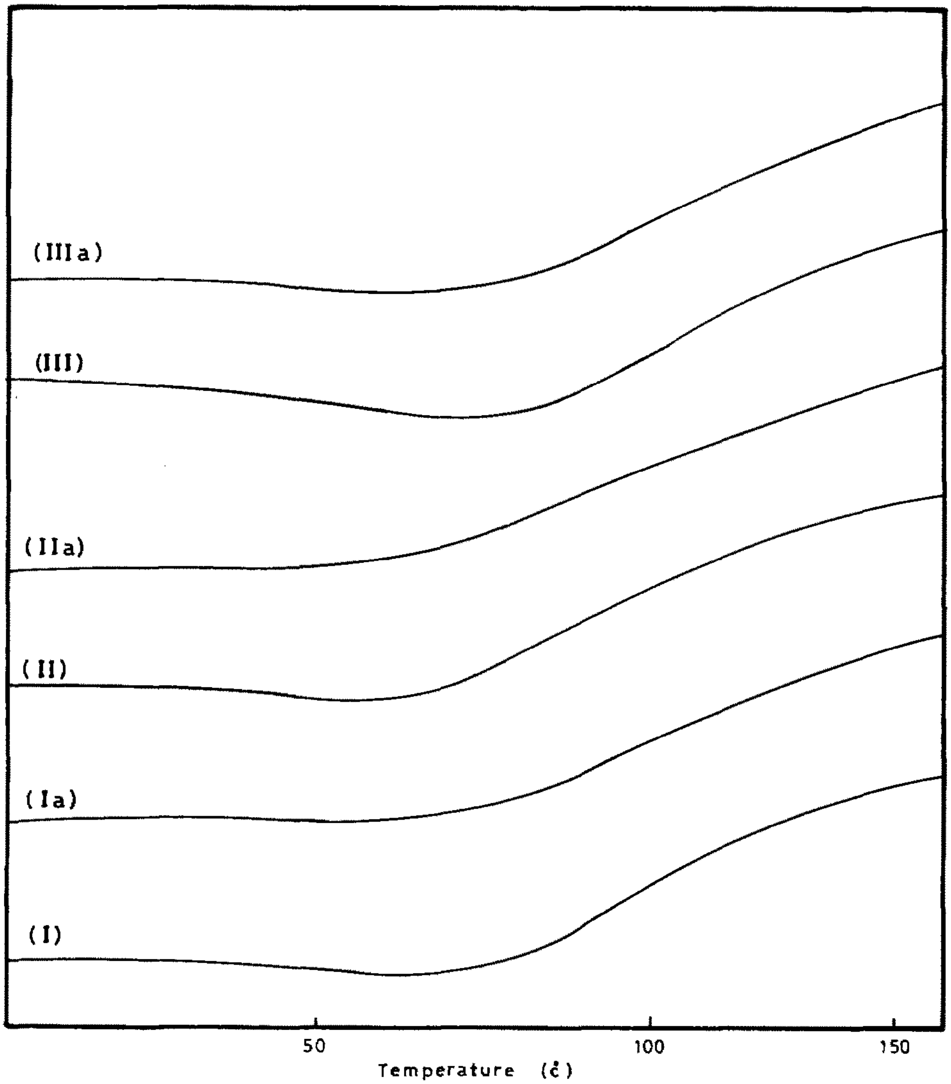


Fig. 1. DTA curves of solvated and desolvated complexes.

observed is assigned to lattice rearrangements, as seen from the X-ray measurements. The X-ray diffraction patterns of both solvated and desolvated species (Fig. 2) are characterised by a multitude of reflections of low intensity, indicating a low degree of symmetry and crystallinity [33,34]. This confirms the lattice rearrangements assigned to the very broad DTA peaks of Ia, IIa and IIIa. Again the ease of the desolvation (80 °C for 15 min), together with the X-ray diffraction data, suggest the weak interaction of water, i.e. water plays little or no role in holding the crystal together, occupying the crystal voids and leading to a pseudo-polymorphic transformation upon desolvation [35]. The energies of activation (ΔE) of the

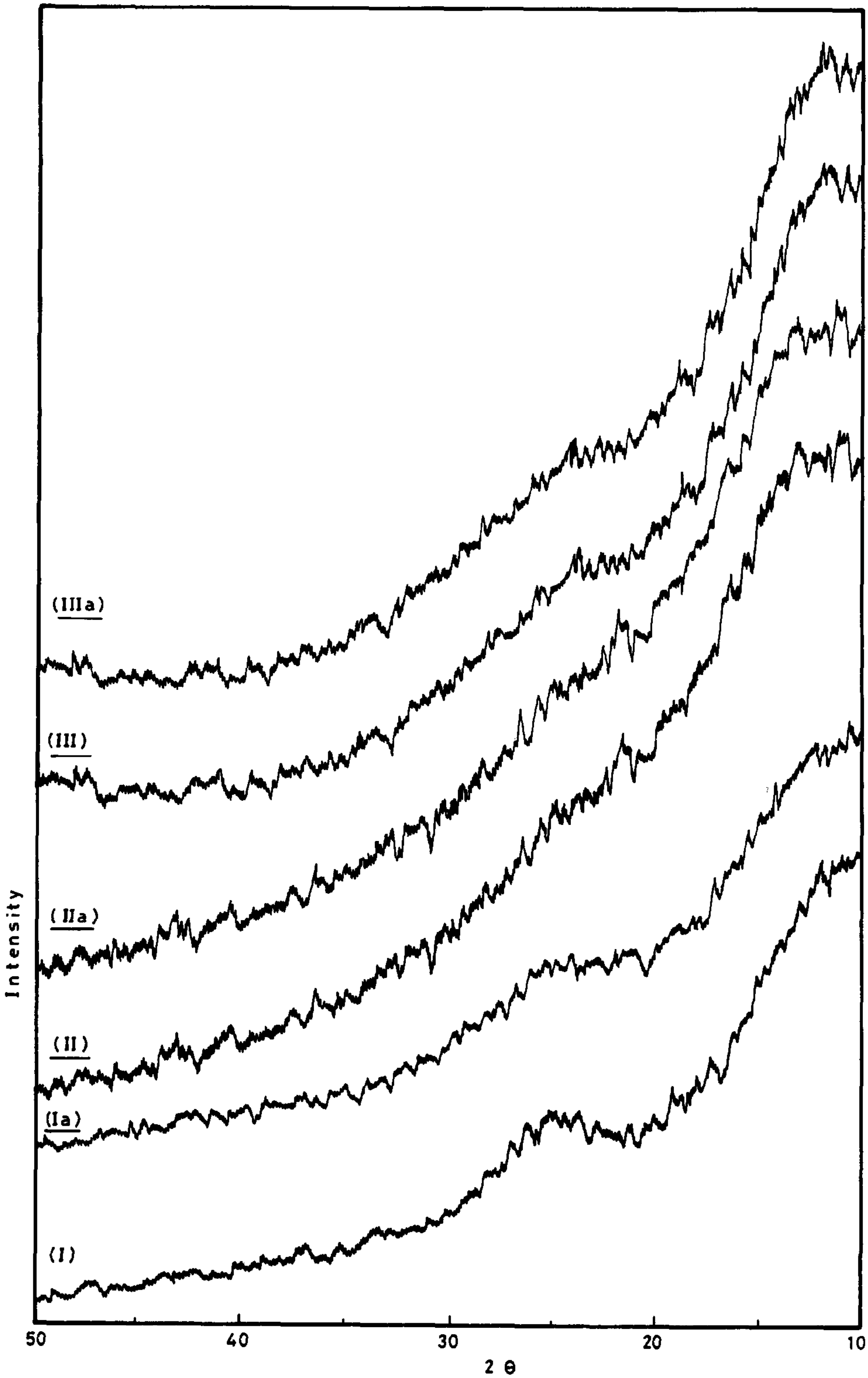


Fig. 2. X-ray power diffraction of solvated and desolvated complexes.

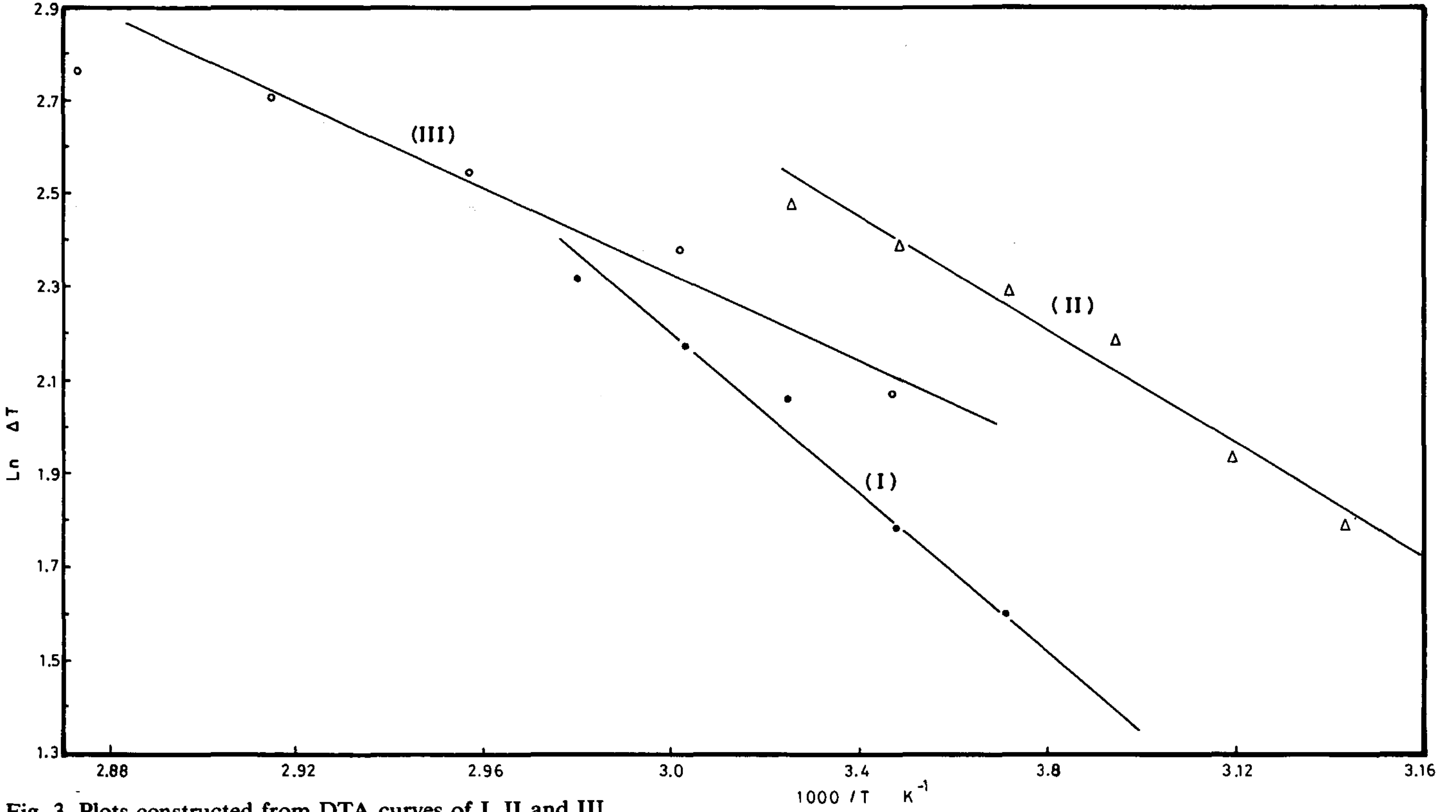


Fig. 3. Plots constructed from DTA curves of I, II and III.

desolvation reactions as given by the method of Piloyan et al. [36] (Fig. 3) are 71.72, 50.54 and 38.49 kJ mol^{-1} for I, II and III, respectively.

Further evidence for the pseudo-polymorphic transformation and the nature of the interaction of the water of crystallisation was provided by the electrical conductivity behaviour of the solid complexes with temperature. Figure 4 shows the semiconducting and metallic behaviour of all the

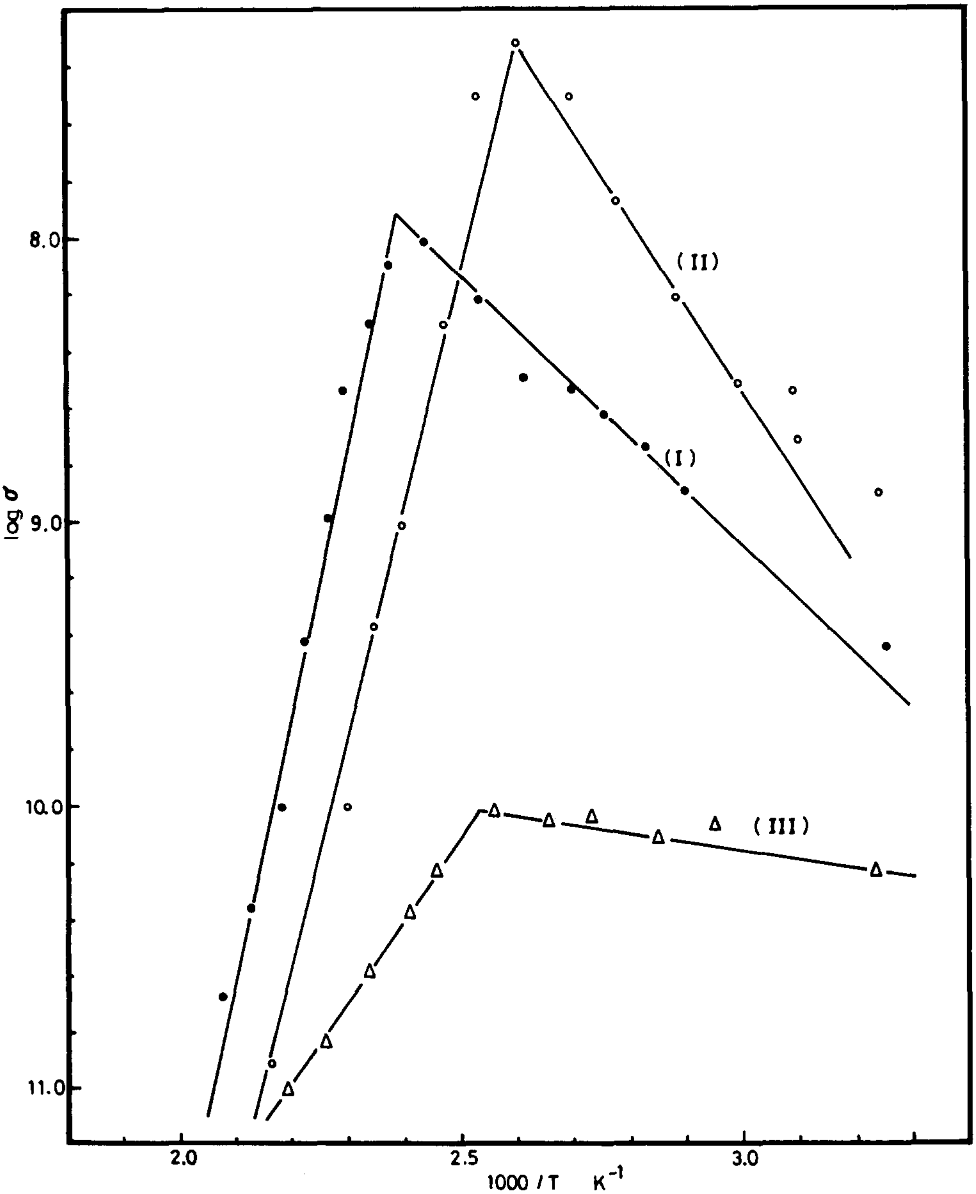


Fig. 4. Temperature dependence of electrical conductivity of I, II and III.

complexes in the temperature ranges 35–(137, 112, 117 °C) and (137, 112, 177)–184 °C, respectively. The temperature range of the semiconducting behaviour (≈ 35–137 °C) coincides, to a great extent, with that of the desolvation DTA peak (50–120 °C). This means that not all the submitted energy was consumed in the desolvation reaction due to the weak interaction of the water molecules. The metallic behaviour observed beyond the temperature range of complete desolvation confirmed the pseudo-polymorphic transformation and may be attributed to the creation of some crystal voids and defects that function as traps for the current carriers [37]. The IR spectra of both solvated and desolvated species show no significant changes. This indicates that the molecules in both species suffer no conformational or configurational changes [35]. The DTA curves of all investigated complexes show an exothermic peak within the temperature range (240–310 °C) (Table 1). This peak is assigned to material decomposition.

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