PREPARATION OF NOVEL NON-SYMMETRICAL SCHIFF BASES USING SOLID STATE REACTIONS

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ABSTRACT

The Schiff bases **I**, **II** and **III** were prepared using a solid state reaction technique. Their structures were studied using elemental analysis, IR and electronic spectra. The solid state reactions of preparation were also studied by differential thermal analysis (DTA), X-ray diffraction and IR spectroscopy. The energies of activation and the orders of the reactions were determined.
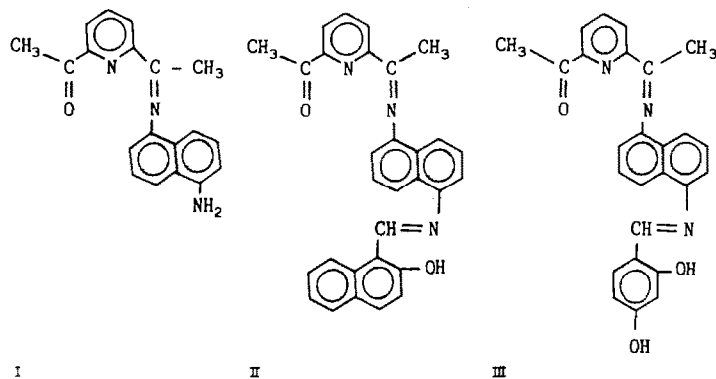
INTRODUCTION

Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate systems. In the complexes containing π-conjugated macrocyclic ligands the reactivity and the redox potential of the central metal are very sensitive to the nature of the chelate ring. However, few studies have been devoted to complexes involving non-symmetrical bases. In general, the known non-symmetrical diimines have been obtained by a template synthesis and have not been isolated in the free (non-coordinated) state [1–4]. Recently, Costes et al. [5] have reported a reliable procedure in solution for obtaining non-symmetrical diimines involving ethylenediamine, acetylacetone, salicylaldehyde and 2-hydroxyacetophenone. The redox potential $E_{1/2}$ related to the reaction $Co^{III} \rightarrow Co^{II}$ in the non-symmetrical complexes obtained was measured [5]. The data emphasize the usefulness of non-symmetrical ligands in affording a convenient way of varying the properties of complexes. Because of our interest in solid reactions, in this work, a reliable, simple and economic method for obtaining non-symmetrical diimines is reported using a solid state reaction. The thermal behaviour of the reaction and the products obtained are investigated.

EXPERIMENTAL

Preparation of ligands

The Schiff bases **I**, **II** and **III** were prepared using a solid state reaction technique as follows.

CH$_3$—C≡N—C—CH$_3$
‖ ‖
O N

NH$_2$

I

CH$_3$—C—N—C—CH$_3$
‖ ‖
O N

CH=N
OH

II

CH$_3$—C—N—C—CH$_3$
‖ ‖
O N

CH=N
OH

OH

III

Ligand **I** was prepared by mixing equimolar ratios (1:1) of 1,5-di-aminonaphthalene and 2,6-diacetylpyridine. The mixture was heated to 90°C for 15 min in a drying oven. A green compound was obtained. Analysis gave: C, 75.5%; H, 5.4%; N, 13.6%. Calculated for $C_{19}H_{17}N_3O$: C, 75.2%; H, 5.6%; N, 13.9%. Ligands **II** and **III** were prepared by mixing equimolar ratios (1:1) of ligand **I** with 2-hydroxy-1-napthaldehyde and 2,4-dihydroxybenzaldehyde respectively. The mixtures were heated to 90°C for ligand **II** and to 110°C for ligand **III** for 30 min. Red and orange compounds were obtained respectively. Analysis of ligand **II** gave: C, 79.4%; H, 5.1%; N, 8.9%. Calculated for $C_{30}H_{23}N_3O_2$: C, 78.7%; H, 5.0%; N, 9.2%. Analysis of ligand **III** gave: C, 72.9%; H, 5.0%; N, 9.6%. Calculated for $C_{26}H_{21}N_3O_3$: C, 73.7%; H, 5.0%; N, 9.9%.

The elemental analyses were carried out at National Research Centre Dokki, Cairo, Egypt. IR spectra were measured as KBr discs using a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer. Electronic spectra were recorded in CHCl$_3$ using a Unicam SP 100 spectrophotometer. Thermal analysis was carried out using a Shimadzu XD-30 thermal analyser. X-ray powder diffraction was recorded with a Shimadzu XD-3 diffractometer using the Cu $K\alpha$ line.

RESULTS AND DISCUSSION

IR spectra

Table 1 shows the IR spectra and their assignment for ligands **I**, **II** and **III**. For ligand **I** the well-defined bands at about 3200–3410 cm^{-1}, 1690 cm^{-1} and 1635 cm^{-1} are assigned to $\nu(NH_2)$, $\nu(C=O)$ and $\delta(NH_2)$ respectively [6]. This indicates the formation of a "half unit" of Schiff base with a free NH$_2$ group (see structure above). The spectra of ligands **II** and **III** show characteristic bands at 3400 cm^{-1}, 1690 cm^{-1} and 1610 cm^{-1}. These are

TABLE 1

IR spectra of Schiff bases (cm^{-1})

Assignment	I	II	III
$\nu(NH_2)$	3410 m 3310 m 3200 m	–	–
$\nu(OH)$	–	3400 br	3400 br
$\nu(=CH)$	3060 w	3060 w	3060 vw
$\nu(C=O)$	1690 s	1690 s	1690 s
$\delta(NH_2)$	1635 vs	–	–
$\nu(C=N)$	covered by $\delta(NH_2)$	1610 vs	1610 vs
Aromatic rings	1580 m	1580 w	1580 sh
$\delta_{as}(CH_3)$	1420 m	1420 sh	1430 w
$\delta_s(CH_3)$	1350 s	1350 m	1350 m

m, medium; w, weak; s, strong; vs, very strong; sh, shoulder.

assigned to $\nu(OH)$, $\nu(C=O)$ and $\nu(C=N)$ respectively [6,7]. The disappearance of the NH_2 from the spectra of II and III (Table 1) confirms the formation of the "half unit" of the Schiff base (I), while the appearance of OH and C=O in their spectra confirm the formation of non-symmetric Schiff bases II and III (see structures above).

Electronic spectra

The electronic spectra of the ligands show two bands (Table 2, Fig. 1) around 315–320 nm and 365–390 nm. These are assigned to n–π^* [6] and charge transfer (CT) [8,9]. The appearance of a new band at 365–395 nm (CT band) in the spectra of the ligands in comparison with the bands in the spectra of the reactants emphasizes the formation of ligands. Elemental analysis, IR and electronic spectra measurements confirm the structures given in the experimental section.

Thermal studies

The solid state reactions for the preparation of ligands I, II and III were studied using a differential thermal analyser. Figure 2 shows the thermo-

TABLE 2

The electronic spectra of the Schiff bases in $CHCl_3$ (nm)

Assignment	I	II	III
n–π^*	320 s	315 m	315 sh
CT	365 sh	390 m 475 sh	365 sh
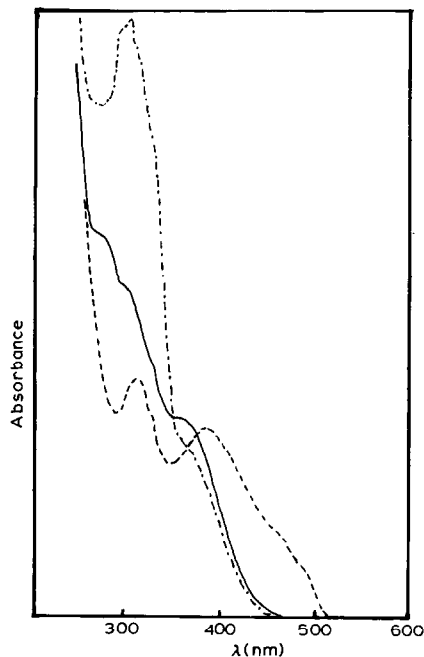
Fig. 1. Electronic spectra of ligands I, II and III: $-\cdot-$, I; $---$, II; ———, III.

grams of the reactant mixtures of ligands I, II and III, hereafter known as I_a, II_a and III_a, and those of the previously prepared ligands I, II and III. The thermogram of I_a displays a sharp endothermic peak at 77°C, followed by other endothermic peaks at 160°C, 180°C and 206°C. These can be assigned to phase transformation and material decompositions as indicated by other spectroscopic measurements (IR and X-ray). The peak at 77°C can be assigned to the formation of ligand I through the melting of diacetyl-pyridine (melting point, 78–79°C). This assignment is confirmed by the disappearance of this peak in the thermogram of I and by its temperature which matches the temperature range of preparation of I (ca. 90°C).

The thermograms of II_a and III_a show endothermic peaks at ca. 72°C and ca. 95°C respectively. These can be assigned to the formation of ligands II and III. The assignments are confirmed by the disappearance of these peaks in the thermograms of II and III and by their temperatures which correspond to the temperature range of preparation of II and III (ca. 90°C and 110°C) respectively. The thermogram of II_a also shows two sharp exothermic peaks at ca. 250°C and 290°C. These can be assigned to material decompositions. The thermogram of III_a shows a broad endother-mic peak around 230°C and this can be attributed to material decomposi-tion.

For ligand I the phase transformation and decomposition peaks at 160°C and 180°C respectively are confirmed using IR spectroscopy and X-ray diffraction. Figure 3 shows the IR spectra of ligand I and samples heated to
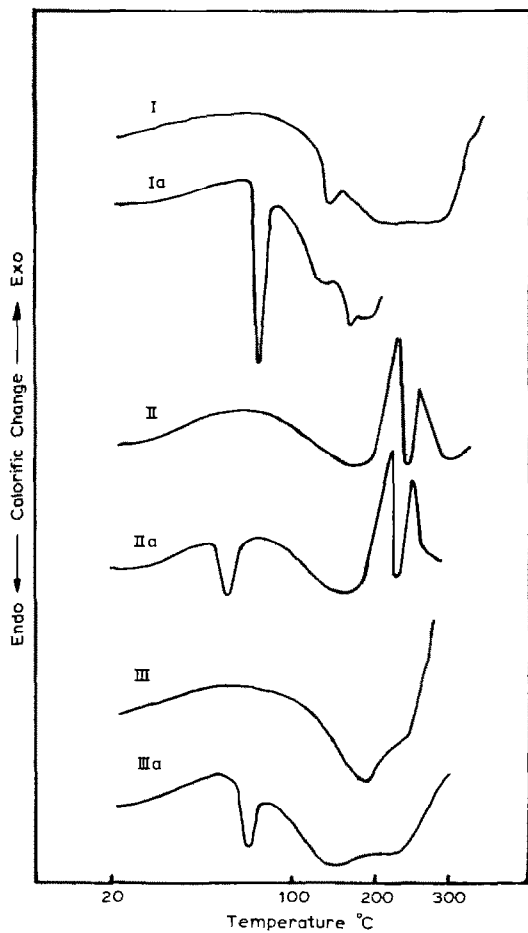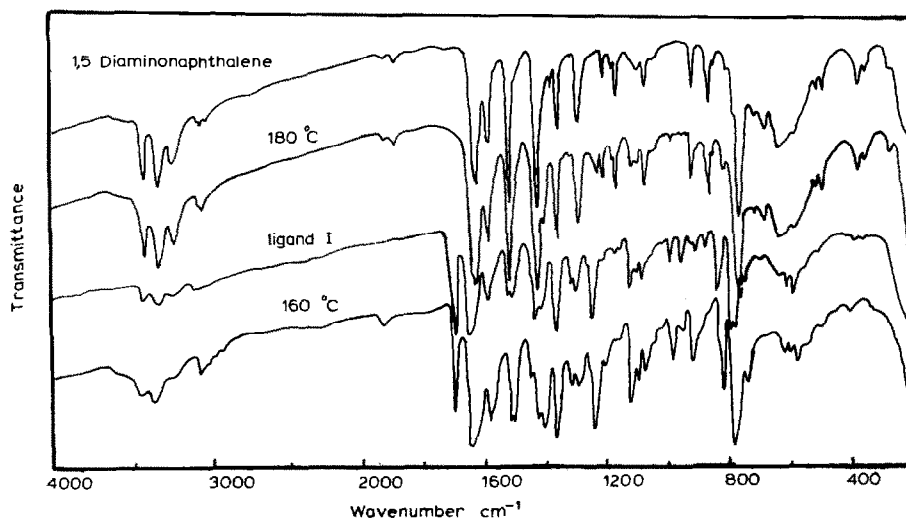
Fig. 2. DTA thermograms of ligands.

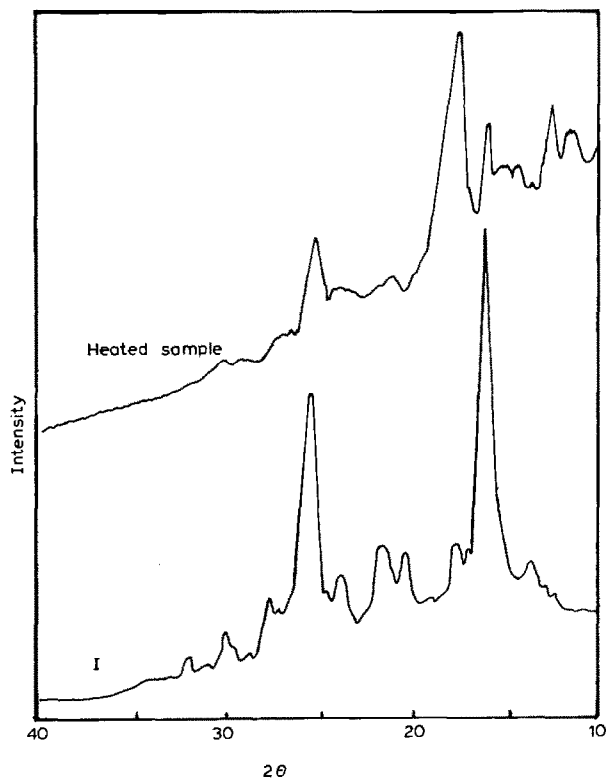Fig. 3. IR spectra of ligand I and samples heated to 160°C and 180°C.

Fig. 4. X-ray diffraction patterns of ligand I and sample heated to 160 °C.
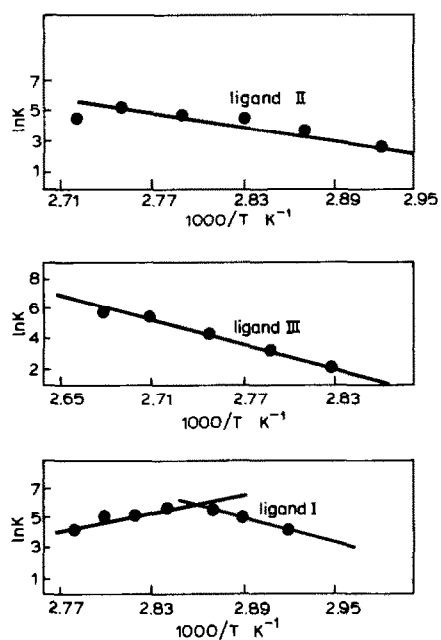

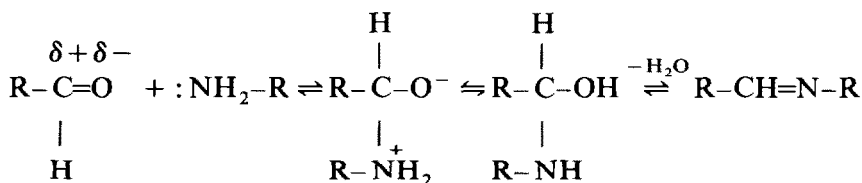Fig. 5. Arrhenius plots constructed from DTA thermograms.

TABLE 3

Reaction orders and activation energies

Ligand	E_a (kJ mol^{-1})	Order
I	218 acceleratory period	0.94
	168 deceleratory period	
II	122	0.96
III	233	1.2

160°C and 180°C. The spectrum of the sample heated to 180°C is similar to that of 1, 5-diaminonaphthalene (Fig. 3), indicating the decomposition of ligand I. Whilst the spectrum of the sample heated to 160°C is similar to ligand I some minor differences can be seen in the shape, intensity and frequency of some peaks, e.g. those of the antisymmetrical CH_3 deformation and the CH_3 deformation (1350–1450 cm^{-1}) [10], and the out-of-plane deformation of aromatic CH (700–950 cm^{-1}) [10]. This may be due to a change in crystal packing as a result of the phase change [11,12]. This phase change is also confirmed by the different X-ray diffraction patterns obtained for ligand I and the sample heated to 160°C (Fig. 4).

The energies of activation of the solid state formation reactions were determined using the method described in ref. 13 assuming first-order reactions. The Arrhenius plots are given in Fig. 5. The assumption of first-order reaction kinetics appears to be valid in this case as confirmed by the asymmetry of the peaks [14] (Table 3). The activation energies E_a were obtained from the slopes of the plots (Table 3). The Arrhenius plot of ligand I (Fig. 5) shows first-order kinetics, with two different activation energies in the acceleratory and deceleratory periods of the reaction. The break point of the curve at 78°C, which matches the melting point of diacetylpyridine (78–79°C), confirms our assignment of the DTA peak at ca. 77°C. From the study of the kinetic parameters it can be seen that the activation energy of the formation of ligand III is greater than that of ligand II (111 kJ mol^{-1}). This indicates the greater reactivity of 2-hydroxy-1-naphthaldehyde

$$\overset{\delta+}{R}-\overset{\delta-}{C}=O \quad + :NH_2-R \rightleftharpoons R-\overset{\overset{H}{|}}{\underset{\underset{R-\overset{+}{N}H_2}{|}}{C}}-O^- \rightleftharpoons R-\overset{\overset{H}{|}}{\underset{\underset{R-NH}{|}}{C}}-OH \overset{-H_2O}{\rightleftharpoons} R-CH=N-R$$

with R–C=O having an additional H below.

R = residual part of molecule

compared with 2,4-dihydroxybenzaldehyde for Schiff base condensation with the same amine. This result is in good agreement with a reaction mechanism for Schiff base condensation as follows:

It is clear that the reaction is nucleophilic, and is dependent on the value of the partial positive charge on the carbon of the aldehyde. Therefore, the electron-withdrawing substituents on the carbon facilitate the condensation. Accordingly, 2-hydroxy-1-napthaldehyde is more reactive than 2,4-dihydroxybenzaldehyde (see structures).

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