THE STRUCTURE AND ISOMERISM OF SOME NICKEL AND COBALT CHELATES

J. R. MAJER* and A. S. P. AZZOUZ

Chemistry Department, University of Birmingham, P.O. Box 363 Edgbaston, Birmingham B15 2TT, England

(Received 9 June 1980; received for publication 14 November 1980)

Abstract—The mass spectra and fragmentation patterns of a number of nickel and cobalt complexes are described. The ligands used were 2 - hydroxy - 1 - naphthaldoxime, 2 - hydroxy - 1 - naphthylidene aniline and 2 - hydroxy - 1 - naphthylidene ethylene diamine. A structural study was carried out by a combination of mass spectrometry and magnetic susceptibility measurements.

INTRODUCTION

The chelate complexes of many metals are sufficiently volatile to permit their evaporation into an ion source of a mass spectrometer and so thermally stable at temperatures above 200°C that their mass spectra may be successfully recorded[1].

Among the metal chelates which have been studied in this way are the nickel and palladium derivatives of dimethylglyoxime [2], the alkali and alkaline earth metal derivatives of 1,3-diketones [3,4], the transition metal complexes of 8-hydroxyquinoline [5] and of pyridylazo naphthol [6] and the nickel derivative of salicylaldoxime [7].

It has been shown that when the current due to the molecule ion is recorded during the course of the evaporation of a metal chelate, the curve of ion current against time shows fine structure when the metal chelate can exist in the form of isomers [8]. In some cases the difference between the heats of evaporation of the two isomers is large enough to permit the complete separation of the two species. As a result the molecule ion current curve appears as two separate peaks [9].

Recently, an attempt was made to study the energetics of the interconversion of the isomers of nickel salicylaldoximate [10]. This study was made difficult because of the small separation between the peaks due to the two isomers.

An attempt was made to overcome these difficulties by the use of more assymetric ligands derived from 2 hydroxy - 1 - naphthaldehyde, e.g. the oxime, anilide and ethylene diamine [11].

The present paper describes a preliminary study of the structure of the metal derivatives of these ligands by mass spectrometry and magnetic susceptibility measurements.

EXPERIMENTAL

Apparatus. All mass measurements were carried out using an A.E.I. MS902 mass spectrometer fitted with a direct insertion probe. Samples were admitted in pyrex glass tubes 27 mm long and 1 mm internal diameter which were fitted to the end of the probe and discarded after use. The tubes were either packed with small amounts of solid chelate samples or filled with up to $5 \mu l$ of metal chelate solution by means of a Hamilton syringe.

Magnetic susceptibility measurements were carried out using an electromagnet (pole face diameter 1.5 in.) supplied by Newport Instruments.

*Author to whom correspondence should be addressed.

Materials. The following reagents were used as supplied without further purification: cobalt nitrate (Hopkin and Williams), 2-naphthol and nickel nitrate (M and B Chemicals Ltd.), ethylene diamine and hydroxylamine hydrochloride (Fisons Laboratories), o-aminophenol (Aldrich Chemicals).

Salicylaldehyde (Hopkin and Williams). The commercial sample was purified by distillation, b.p. 197°C.

2 - Hydroxy - 1 - naphthaldehyde and 2 - hydroxy - 1 naphthaldoxime were prepared by standard methods [12], while 2 - hydroxy - 1 - napthylidene - aniline, salicylidene o-hydroxyaniline and 2 - hydroxy - 1 - napthylidene ethylene diamine were prepared according to the given procedure [13].

The following procedure was used in the preparation of the metal chelates:

In a 100 ml conical flask, 0.5 g of the reagent is dissolved in about 30 ml of hot methanol. In a second 100 ml conical flask, 1 g of either nickel nitrate or cobalt nitrate is dissolved in distilled water. The two flasks are warmed separately and the contents mixed, stirred and the pH adjusted to neutrality by adding 10% NaOH. The final mixture is left to stand for about 30 min, cooled and filtered. The residue is washed with cold water and crystallised from methanol and the crystalline product dried in air.

 $2 \cdot Hydroxy - 1 \cdot naphthaldehyde$. To a 3-necked litre flask with a separating funnel, mercury sealed mechanical stirrer and a long (double surface) reflux condenser, 50 g of 2-naphthol and 150 ml of ethanol are added, the mixture is stirred and a solution of 100 g of NaOH in 210 ml of water is added rapidly.

The solution is heated to 70-80°C on a water bath and 42 ml of pure chloroform is added until reaction commences (indicated by the formation of a deep blue colour). The water bath is removed and addition of chloroform continued at such a rate that the mixture refluxes gently (about 1.5 hr). The sodium salt of the phenolic aldehyde separates near the end of the addition. The stirring is continued for a further 1 hr. The excess chloroform and ethanol is distilled off on a water bath and under vacuum (using a water pump). The residue is treated with stirring, concentrated HCl dropwise until the contents of the flask are acid to Congo red paper (about 88 ml are required); a dark oil accompanied by a considerable amount of sodium chloride separates. Sufficient water is added to dissolve the salt, the oil is extracted with diethyl ether and the ethereal solution is washed and dried with anhydrous magnesium sulphate. The ether is distilled off and the residue distilled under reduced pressure, b.p. 163-166°C at 8 mm Hg. The distillate solidifies on cooling. The solid is recrystallised from 38 ml ethanol to yield 28 g 2 - hydroxy - 1 - naphthaldehyde, m.p. 80°C.

The IR spectrum for the product shows peaks at 3400 cm^{-1} (m), 1650–1630 cm⁻¹ (s) and 1600 cm⁻¹ (s), which are assigned to the stretching frequencies of the phenolic hydroxyl group, the strongly hydrogen bonded carbonyl group and the aromatic structure, respectively.

The mass spectrum shows a peak at m/e 172. Exact mass measurement of this peak reveals the presence of $C_{11}H_8O_2$.

2 - Hydroxy - 1 - naphthylidene aniline. 4 g of 2 - hydroxy - 1 - naphthaldehyde is dissolved in methanol in a 50 ml round bottom flask. 2.1 g of pure aniline is added to the mixture. The flask contents are refluxed for about 1 hr, followed by cooling, filtration of the precipitate, washing with distilled water and finally recrystallisation from hot methanol. The orange product collected has m.p. 85°C. The IR spectrum shows the following stretching frequencies, 3400 cm^{-1} (s) 1640 cm^{-1} (s) and 1600 cm^{-1} (s) corresponding to the phenolic group, the azomethine group and the aromatic structure respectively. Exact mass measurement for the molecular ion peak at m/e 247 shows the presence of $C_{17}H_{13}ON$. Elemental Anal. calc.: C, 82.60; H, 5.26; N, 5.7. Found: C, 82.90; H, 5.40; N, 5.5.

2 - Hydroxy - 1 - naphthaldoxime. 2g of 2 - hydroxy - 1 - naphthaldehyde is dissolved in 8 ml ethanol. A solution of 2.5 g hydroxylamine hydrochloride in 5 ml water is added and the mixture made alkaline with 10% sodium carbonate solution. The mixture is allowed to stand overnight and acidified with acetic acid. The ethanol is distilled off under reduced pressure (15 mm Hg) and the residue diluted with twice the volume of water. The crude precipitate is filtered and recrystallised from 40 ml of 2:1 v/v methanol water. A white precipitate, m.p. 143°C is obtained.

The IR spectrum has strong absorption peaks at about 3300 cm^{-1} (m), 1640 cm⁻¹ (s) and 1600 cm⁻¹ (s), corresponding to the stretching frequencies for the phenolic group, the azomethine group and the aromatic structure, respectively. The mass spectrum shows a molecular ion peak at m/e 187. Precise mass measurement shows that the molecular formula is $C_{11}H_9O_2N$. Anal. Calc. for C, 70.50; H, 4.81; N, 7.49. Found: C, 70.30; H, 4.80; N, 7.50%.

2 - Hydroxy - 1 - naphthylidene ethylene diamine. This reagent is prepared by condensation of 0.02 mol of 2 - hydroxy - 1 naphthaldehyde with 0.01 mol of ethylene diamine.

3.44 g 2 - hydroxy - 1 - naphthaldehyde is dissolved in 15 ml methanol in a 100 ml round bottom flask. 0.7 ml ethylene diamine is added and the mixture *gently* refluxed for 1 hr. The mixture is cooled and filtered and the crude yellow product recrystallised from hot methanol, m.p. $282-286^{\circ}C$ (decomp.).

The IR spectrum shows the following absorptions, 3400 cm^{-1} (m), 1642 cm^{-1} (s) and 1600 cm^{-1} (s). These are assigned to the phenolic hydroxy group, the azomethine group and the aromatic structure respectively. The mass spectrum shows a molecular ion peak at m/e 368. Precise mass measurement for this peak gives the elemental composition for the sample as $C_{24}H_{20}O_2N_2$.

Anal. cal. for C, 78.26; H, 5.42; N, 7.60. Found: C, 78.20; H, 5.50; N, 7.40%.

Cobalt bis - (2 - hydroxy - 1 - naphthylidene aniline). 0.5 g of 2 - hydroxy - 1 - naphthylidene aniline is dissolved in 15 ml methanol and 1 g of cobalt nitrate in 40 ml of 1:1 v/v methanol water. The solutions were heated to 90°C mixed, stirred and methanol added to dissolve the precipitate. The pH was adjusted to 7 with dilute NaOH solution. The green precipitate was filtered and washed with water and methanol. On standing the filtrate deposits an orange precipitate which is also filtered and washed with water and methanol. The melting point of green and orange precipitates are 98-99 and 130°C (decomp.), respecteively.

The mass spectrum for both compounds are identical, with a base molecular ion peak at m/e 551. Precise mass measurement of this ion gives an atomic constitution of $CoC_{34}H_{24}O_2N_2$.

Nickel bis - (2 - hydroxy - 1 - naphthylidene aniline). 0.5 g of 2hydroxy - 1 - naphthylidene aniline is dissolved in 15 ml methanol. 1 g of nickel nitrate is dissolved in 30 ml of a mixture 3:1 v/v of methanol water. The two solutions are warmed separately mixed and stirred. To complete precipitation for the complex the pH is adjusted to 7 with hot dilute sodium hydroxide solution. The mixture is cooled and the greenish yellow precipitate is filtered washed with water and recrystallised from hot methanol, m.p. 280°C (decomp.). The mass spectrum for the complex shows a molecule ion peak of the type ML₂ at m/e 550. Precise mass measurement for this peak gives the molecular formula of the complex as NiC₃₄H₂₄O₂N₂.

Cobalt 2 - hydroxy - 1 - naphthaldoximate. 0.4 g of 2 - hydroxy - 1 - naphthaldoxime is dissolved in 30 ml methanol and 1 g of cobalt nitrate in 30 ml of a mixture 1:2 v/v methanol water. The two solutions are heated separately, mixed and stirred. The pH is adjusted to 7 with dilute sodium hydroxide solution. The brown precipitate is filtered, washed with water and cold methanol. (m.p. 340°C (decomp)). The mass spectrum for the crude product shows a molecular ion peak at m/e 431. Precise mass measurement for this peak gives the formula as $CoC_{22}H_{16}O_4N_2$.

Nickel 2 - hydroxy - 1 - naphthaldoximate. The procedure was the same as that described for the cobalt complex. A green precipitate m.p. 275°C (decomp) exhibited a mass spectrum with a molecule ion peak at m/e 430. This peak is identified as being due to the presence of NiC₂₂H₁₆O₄N₂ by precise mass measurement.

Nickel (bis N,N - 2 - hydroxy - 1 - naphthylidene ethylene diamine). Although a small amount of precipitate was produced by mixing solutions of nickel nitrate and 2 - hydroxy - 1 - naphthylidene ethylene diamine, the complex was obtained in greater yield by mixing 0.69 g of 2 - hydroxy - 1 - naphthaldehyde in 20 ml methanol and 0.14 ml of 1,2-ethylene diamine with 0.5 g nickel nitrate dissolved in 30 ml distilled water. After 90 min the precipitate was filtered washed with methanol and recrystallised from methanol to give an orange-brown powder, m.p. 290°C (decomp). The mass spectrum has a molecular ion peak at m/e 424, corresponding to a complex of the type ML. Precise mass measurement shows that the formula for the complex is NiC₂₄H₁₈O₂N₂.

Cobalt (bis N,N - 2 - hydroxy - 1 - naphthylidene ethylene diamine). A similar procedure has been followed in the synthesis of this complex. The brown precipitate formed was filtered and recrystallised from methanol, m.p. $205-207^{\circ}$ C (decomp). The mass spectrum has a molecular ion peak at m/e 425. Precise mass measurement for the molecular ion peak reveals that the complex has a composition of $CoC_{24}H_{18}O_2N_2$.

RESULTS AND DISCUSSION

The physical properties of the 6 metal chelates and their suggested structures are summarised in Table 1.

Mass spectrometry

Mass spectra of nickel and cobalt 2 - hydroxy - 1 - naphthaldoximates. Satisfactory mass spectra have been recorded for the nickel and cobalt 2 - hydroxy - 1 - naphthaldoximate complexes as shown in Fig. 1. The molecular ion peaks at m/e 430 and 431 show a complex of the type ML₂.

The spectra of these compounds exhibit almost identical dissociation patterns. The first fragmentation pathway for nickel is by the loss of a water molecule giving the fragment M-18⁺, followed by loss of NO. The second fragmentation pathway is via a loss of one ligand to produce the ML⁺ fragment at m/e 244. Further frag-



$$C_{11}H_8NO_2 \xrightarrow{-H_2O} C_{11}H_6NO \xrightarrow{-CO} C_{10}H_6NO$$

186 168 140

Table 1. The physical properties and structure of metal chelates



* (D) = Decomposition

** Two separated isomers



Fig. 1(a). Mass spectrum of nickel 2 - hydroxy - 1 - naphthaldoximate.



Fig. 1(b). Mass spectrum of cobalt 2 - hydroxy - 1 - naphthaldoximate.

mentation of the ML⁺ ion is through the loss of another water molecule to produce ML-18⁺ at m/e 226. The fragment ion of the ligand L⁺ loses a further water molecule to give L-18⁺, followed by loss of carbon monoxide to produce L-46⁺. Finally the metal ion appears in the spectrum at m/e 58 and 60.

Fragmentation scheme for nickel 2 - hydroxy - 1 - naphthaldoximate

The fragmentation pattern for the cobalt complex is similar, although the spectrum is made simpler by the mono isotopic nature of the cobalt atom.

Mass spectra of nickel and cobalt bis(2 - hydroxy - 1 - naphthylidene aniline). The mass spectra for the nickel and cobalt complexes were recorded at a temperature of 290°C (Fig. 2). The base peaks correspond to the molecule ion peaks and the general formula of these complexes are of the type ML₂, in which the central metal atom forms part of two six membered rings.

The fragmentation scheme for nickel bis(2 - hydroxy - 1 - naphthylidene aniline) has three different pathways. Scheme one involves the loss of NO and H₂O to produce M-48⁺ fragments, possibly as a result of thermal decomposition prior to ionisation, because it is unusual for an odd electron molecule ion to lose an even electron molecule. The second pathway is the successive loss of C₆H₅ and HCN to produce M-77⁺ and M-104⁺. Here, the even electron molecule HCN is lost from the even electron radical ion M-77⁺. The third pathway is the loss of a ligand to produce ML⁺. This even electron ion undergoes further fragmentation by the loss of an NO molecule. Finally, there are peaks due to the ligand fragment and to

the metal ion at m/e 169, 58 and 60. The fragmentation scheme is as follows:

$$Ni(C_{17}H_{13}NO) \xleftarrow{-(C_{17}H_{13}NO)} Ni(C_{17}H_{13}NO)_2 \xrightarrow{-(NO+H_2O)} Ni(C_{17}H_{11}N)(C_{17}H_{13})$$

$$304 \qquad 550 \qquad 502$$

$$\downarrow -NO \qquad \qquad \downarrow -C_6H_5$$

$$Ni(C_{17}H_{13}) \qquad Ni(C_{17}H_{13}NO)(C_{11}H_8NO)$$

$$274 \qquad 473 \qquad \qquad \qquad \downarrow -HCN$$

$$Ni(C_{17}H_{13}NO)(C_{10}H_7O)$$

$$446$$

Cobalt (bis - 2 - hydroxy - 1 - naphthylidene aniline) was prepared in the form of both orange and green precipitates. These precipitates have the same mass spectrum and were shown to be isomers. The mass spectra and fragmentation scheme for cobalt (bis - 2 hydroxy - 1 - naphthylidene aniline) isomers are similar to that for the nickel complex, with the exception of fragmentation scheme one for the former.

Mass spectra of nickel and cobalt (bis - N,N - 2 hydroxy - 1 - naphthylidene ethylene diamine). The mass spectrum of nickel (bis - N,N - 2 - hydroxy - 1 naphthylidene ethylene diamine) was recorded at a temperature of 310°C as shown in Fig. 3. The general formula for the complex is ML in which the nickel atom forms part of two six membered rings. The molecular ion peak is at m/e 424 and its relative intensity is 68%. The fragmentation scheme for the complex is shown below. The first fragment corresponds to M-56⁺ due to the substitution of the nickel atom by two protons. These protons may be generated from the water molecules in the crystal lattice of the compound which are lost under the action of heat during the injection of the sample into the jon source. Therefore, the first fragment peak in the spectrum will result in the regeneration of the molecular ion for the ligand molecule. This observation was further supported by comparing the mass spectrum of the ligand with the dissociation pattern generated in the mass spectrum of the complex. Other successive fragmentation peaks correspond to L-C₁₁H₈NO⁺, L-C₁₂H₁₀NO⁺, L- $C_{13}H_{12}NO^+$, L- $C_{14}H_{13}N_2O^+$ and L- $C_{14}H_{14}N_2O_2^+$ which are at m/e 198, 184, 170, 143 and 126 respectively. Finally, there are further fragments corresponding to the metal ion at m/e 58 and 60. The fragmentation scheme for the complex is as follows:



Fig. 2(b). Mass spectrum of cobalt - 2 - hydroxy - 1 - naphthylidene animine.

spectrum and fragmentation scheme are similar to that for the nickel complex.

Isomerism of nickel and cobalt complexes

It has been shown that the green and orange precipitates obtained in the preparation of cobalt bis - 2 hydroxy - 1 - naphthylidene aniline have the same composition and are probably isomers rather than different crystal forms. When a compound can exist in two isomeric forms there is often a slight difference in their

$$NiC_{24}H_{18}N_{2}O_{2} \xrightarrow{-Ni^{2+}}_{+2H^{+}} C_{24}H_{20}N_{2}O_{2} \xrightarrow{-C_{11}H_{8}NO} C_{13}H_{12}NO \xrightarrow{-CH_{2}} C_{12}H_{10}NO$$

$$424 \qquad 368 \qquad 198 \qquad 184$$

$$C_{10}H_{6} \xleftarrow{-OH} C_{10}H_{7}O \xleftarrow{-HCN} C_{11}H_{8}NO$$

$$126 \qquad 143 \qquad 170$$

The mass spectrum for cobalt (bis - N,N - 2 - hydroxy - 1 - naphthylidene ethylene diamine) is also shown in Fig. 3. This spectrum is recorded at a temperature of 350° C. The molecular ion peak for the complex is at m/e 425. The mass

heats of sublimation. As a result, when a mixture of the two isomers is evaporated into the ion source of a mass spectrometer one isomer appears in the vapour phase before the other. This effect has been detected by con-



Fig. 3(b). Mass spectrum of cobalt (bis - N,N - 2 - hydroxy - 1 - naphthylidene ethylene diamine).

tinuously recording the ion current at a specific m/e value during the course of the evaporation. An ion current curve showing structure or divided completely into two peaks gives an indication of the existence of two isomeric species, more particularly so if the m/e value chosen is that of the molecule ion.

This technique was first applied in a study of the nickel and cobalt complexes of 2 - hydroxy - 1 - naphthaldoxime. 10 μ l of a 0.2% solution of nickel 2 - hydroxy - 1 naphthaldoximate in dimethyl sulphoxide (200 μ g of metal chelate) was placed in the insertion probe of the mass spectrometer and evaporated into the ion source at a temperature of 310°C. The ion current at m/e 430 was recorded continuously and the resulting curve is shown in Fig. 4. It can be seen that the two peaks are almost completely resolved and the separation compares favourably with that obtained previously for nickel salicylaldoximate[10]. In addition, the first peak is much larger than the second (ratio 5:1) suggesting that the isomers are sufficiently different in structure to ensure preferential formation of one isomer during precipitation.

Similar results were observed for cobalt 2 - hydroxy -1 - naphthaldoximate when it was evaporated under similar conditions at a temperature of 340°C, Fig. 4, but the tailing of the second peak suggests that the molecule ion is being formed as a result of a chemical reaction associated with an energy of activation. One possible reaction is the thermal decomposition of a hydrate.

The case of the metal derivatives of bis, N, N - 2 hydroxy - 1 - naphthylidene ethylene diamine is an interesting one. When $5 \mu l$ of a 0.2% acetone solution of the nickel chelate was evaporated into the ion source at a temperature of 300°C the ion current curve at m/e 424 showed only a single broad maximum indicating the presence of only one isomer. Figure 5, in earlier studies with the corresponding chelate nickel (bis, N, N - salicylidene ethylene diamine) it was shown that the molecule ion current curve has two distinct peaks. Figure 6. Despite the fact that only one ligand is involved it was shown that this could be attached to the central nickel



Fig. 4. Integrated ion current curves for (a) nickel 2 - hydroxy -1 - naphthaldoximate, (b) cobalt 2 - hydorxy - 1 - naphthaldoximate.



Fig. 5. Integrated ion current curves for (a) nickel (bis - N,N - 2 hydroxy - 1 - naphthylidene ethylene diamine), (b) cobalt (bis - N,N -2 - hydroxy - 1 - naphthylidene ethylene diamine).



Fig. 6. Integrated ion current curve for nickel bis - N,N - salicylidene ethylene diamine showing two maxima.

atom in two different conformations to form two isomeric chelates. It is assumed that the substitution of the phenyl group by the bulkier 1 - naphthyl groups reduces the possibility of formation of the chelate in the *cis* configuration. A similar result was obtained when evaporating $2 \mu l$ of an 0.2% acetone solution of cobalt (bis - N,N - 2 - hydroxy - 1 - naphthylidene ethylene diamine) (40 μg of chelate) into the ion source at a temperature of 330°C.

It was suggested previously that when the chelate, cobalt (bis - 2 - hydroxy - 1 - naphthylidene aniline) was formed, the green and orange precipitates obtained were two distinct isomers. When a sample of the green precipitate was dissolved in methanol and $10 \,\mu$ l of an 0.2% solution was injected into the ion source at a temperature of 270°, the curve of ion current at m/e 551 with time showed only a single maximum indicating that only one isomeric species was present (Fig. 7a).

The nature of the orange precipitate depended upon the rate of precipitation and temperature of the solution and was frequently contaminated with a small amount of the green isomer. When a sample of the pure orange form was dissolved in methanol and $10 \,\mu$ l of an 0.2% solution injected into the ion source at a temperature of 270°C the ion current curve at m/e 551 showed only a single maximum (Fig. 7b).

When however a sample of the impure orange form was used or a mixture of the green and orange forms was treated in the same way, the resulting ion current curve at m/e 551 showed two maxima. (Fig. 7c). The areas of the two separate peaks were proportional to the amount of the two isomers used to make up the mixture.

The result was confirmed by studying the absorption spectra of the isomers (Fig. 8) in the near UV region. The green isomer exhibited a spectrum with a characteristic absorption maximum at 390 nm while the orange isomer had this maximum shifted to a wavelength of 432 nm. In the impure samples of the orange precipitate the spectrum showed both absorption maxima. It was found that although there was no thermal interconversion of the isomers in the ion source of the mass spectrometer while the samples were being evaporated at a temperature of 270°C, isomerisation did take place in solution.

A sample of the green isomer was dissolved in methanol to give a 1% solution. An aliquot of this solution was heated at a temperature of 50°C for 30 min. During this time the green solution gradually acquired an orange colour and a small amount of solid material was precipitated. This was shown to be the orange isomer by its absorption spectrum and by the position of its maximum in the ion current curve at m/e 551.

In the case of the nickel derivative of 2 - hydroxy - 1 naphthylidene aniline only one precipitate was formed and this was yellow/green in colour. The presence of two



Fig. 7. (a) Ion current curve for green precipitate, (b) ion current curve for pure orange precipitate and, (c) ion current curve for mixture of impure orange form.

separate forms was demonstrated by their differential solubility in organic solvents. When the sample was shaken with diethyl ether a yellowish green solution was produced and the residue was almost totally green in colour. When however, cyclohexane was substituted for diethyl ether a pure yellow solution was formed and the residue was green. Evaporation of the cyclohexane solution gave a yellow crystalline solid. An examination of the absorption spectra of methanol solutions of the yellow and green forms revealed characteristic differences in absorption maxima in the near UV. That for the yellow form occurring at 434 nm and that for the green form at 420 nm. The spectrum of a solution of the original precipitate exhibited both maxima (Fig. 9).

The three samples were then examined in the mass spectrometer by injecting $10 \ \mu l$ of a 5% solution and evaporating the chelates at a temperature of 290°C. The results given in Fig. 10 show that the ion current curve at m/e 550 exhibits a single maximum for the green and yellow forms but two separate maxima for the sample of the original precipitate.

The isomerisation of this chelate was demonstrated by dissolving a sample of the yellow form in acetone and heating an aliquot of the 2% solution at a temperature of 30°C for 2 hr. During this time the colour of the solution gradually changed from yellow to green and a precipitate of green crystals was formed. Samples were removed at 15 min intervals and examined by mass spectrometry. After 20 min the ion current curve at m/e 550 showed a small second maximum and this increased in size in



Fig. 8. Absorption spectra for orange (----) and greed (-----) isomers for cobalt 2-hydroxynaphthylidene aniline in methanol.



Fig. 9. Absorption spectra for green (----), yellow (-----) and mixture from yellow-green (-----) isomers for nickel 2-hydroxynaphthylidene aniline in methanol.

subsequent samples becoming predominant after 90 min. The ion current curve at m/e 550 for a sample of the green crystalline precipitate dissolved in acetone showed only a single maximum.

When a sample of the yellow isomer was dissolved in cyclohexane and an aliquot of the 2% solution was heated at 70°C for 2 hr there was no detectable change in the colour of the solution and the ion current curve at m/e 550 for a sample showed only a single maximum indicating that no isomerisation had taken place. This suggests that the polarity of the solvent has an important effect on the rate of isomerisation.

Magnetic susceptibility measurements

For paramagnetic substances the molar magnetic susceptibility X_m is related to the magnetic moment m by the equation:

$$X_m = \frac{NE_0 m^2}{3kT} \tag{1}$$

where $X_m = \text{molar}$ magnetic susceptibility (m³ mol⁻¹), $E_0 = \text{permeability}$ of vacuum = $4\Pi \times 10^{-7}$ (kg m s⁻² A⁻²), $N = 6.0249 \times 10^{23}$ (atoms mol⁻¹), m = magnetic moment, $k = 1.38062 \times 10^{-23}$ (J K⁻¹), and T = absolute temperature. The magnetic moment can be expressed in terms of the number of unpaired electrons

$$m = m_B \mathcal{N}[n(n+2)] \tag{2}$$

where m_B is Bohr magneton = 9.27×10^{-24} A m².

The magnetic susceptibility of the 6 complexes was measured by using the Gouy method [14, 15] using the following equation

$$X_m = (a\Delta_w + X_0)\frac{V}{W} \cdot M \tag{3}$$

where a is a constant, Δ_w = apparent change in mass on applying the magnetic field, X_0 = magnetic susceptibility of atmosphere = 0.364×10^{-6} , V = specific volume of the



Fig. 10. Ion current curves at m/e 550 showing: (a) single maximum for green precipitate, (b) single maximum for yellow precipitate, and (c) 2 separate maxima for sample of original precipitate.

substance, W = mass of the sample, and M = molecular weight of sample.

The value of the constant a in eqn (3) was determined by calibrating the sample tube. This calibration was made using a reference compound of known molar magnetic susceptibility such as $CuSO_4 \cdot 5H_2O$ which has a value of $1.838 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$. *a* was found to be = 3.06.

The results of the measurements of magnetic susceptibility for the 6 complexes and the calculations of the number of unpaired electrons are given in Table 2. It was considered that from these calculations the hybridisation in the central metal atom could be determined and hence the shape of the molecule. The shape identified in this way should allow the possibility of the existence of isomeric structures and therefore should be in accord with the results of the mass spectrometric investigations. The complexes of nickel with all three chelating agents are shown to have 2 unpaired electrons per molecule and the hybridisation is therefore sp^3d^2 . This is not in accord with a planar configuration and suggests that the molecules of nickel 2 - hydroxy - 1 - naphthaldoximate and cobalt - 2 hydroxy - 1 - naphthylidene aniline must have an octahedral configuration. This is only possible if the two additional coordination centres are occupied by water molecules, i.e. the metal chelate is in the form of a hydrate. No trace of the molecule ions of such hydrated metal chelates appear in the mass spectra but it is accepted that the hydrated molecules do not survive ionisation by electron impact. There are no examples of peaks due to the molecule ions of hydrated metal chelates in electron impact mass spectra in Ref. [1]. It was considered possible that the demonstration of the existence of these hydrates might be achieved with a less energetic form of ionisation. The chelates were examined using field desorption mass spectrometry.

Samples of the chelates in methanol solution were coated onto tungsten wire filaments previously activated with benzonitrile and their spectra recorded at a voltage of 13 kV.

The resulting spectra are shown in Fig. 11. Once again there is no evidence for the existence of the molecule ion of a hydrated metal chelate.

The results of the magnetic susceptibility measurements on the chelates of cobalt show that for all three

Complex	Kolar suscept- ility	Corrected molar susceptib- ility	Magnetic moment	No. of unpaired electrons	No. Of Maxima observed in mass spec.	Suggested bond orbital	Suggested orbital shape
	X _m x10 ⁻⁸ m ³ .mol ⁻¹	X _m x10 ⁻⁸ m ³ .mol ⁻¹	B.M	(n)			
N _{ickel} 2-hydroxy- l-naphthylidene aniline	4.29	4.35	2.84	2	2	sp ³ d ²	octshedral
Cobalt 2-hydroxy- 1-naphthylidene aniline	16.72	16.78	5.58	5	2	sp ³ d ²	octahedral
Nickel 2-hydroxy- 1-naphthaldoximete	4.26	4.34	2.84	2	2	sp ³ d ²	octahedral
Cobalt 2-hydroxy- 1-naphthaldoximate	7•97	8.00	3 .8 6	3	2	3;2 spd	octahedral
Nickel (bis-N,N- 2-hydroxy-l-naphthy) idene ethylene diamine)	1- 4.39	4.52	2.90	2	1	sp ³	tetrahedra]
Cobalt (bis-N,N- 2-hydroxy-1-naphthy) idene ethylene dismine)	L- 8.0	8.14	3.90	3	1	ap ³	tetrahedral

Table 2. Regults of mass spectrometry and magnetic susceptibility measurements



Fig. 11. Field desorption spectra for (a) nickel 2 - hydroxy - 1 - naphthaldoximate, (b) cobalt 2 - hydroxy - 1 - naphthaldoximate, and (c) cobalt 2 - hydroxy - 1 - naphthylidene aniline.

chelating agents the number of unpaired electrons in the molecule of the chelate is 3 corresponding to a hybridisation of sp^3d^2 . This suggests that as before the cobalt atom must have an octahedral configuration in order that the chelate may exist in two isomeric forms. This can only occur if the metal chelate exists in the form of a hydrate. Once again there is no evidence in either the electron impact or the field desorption mass spectra for the existence of the molecule ion of a hydrated metal chelate.

CONCLUSION

The complexes of cobalt and nickel with 2 - hydroxy - 1 - naphthaldoxime and 2 - hydroxy - 1 - naphthylidene aniline are of the type ML_2 . The ligand molecule (L) is acting as a bidentate donor and as a result these complexes should have a coordination number 4. If sp^3

hybridisation occurred the geometrical structure would be tetrahedral and the complexes should have only one isomer and there would be only one maximum in the molecule ion current curve. The experimental ion current curves show two maxima. This behaviour can only be explained if it is supposed that coordination numbers 5 and 6 are occupied by water molecules. The bonding orbital will be converted from sp^3 to sp^3d^2 and the favoured geometrical structure will be octahedral. This is in accord with the experimental results taken from mass spectrometry and magnetic susceptibility measurements, but the hydrated molecules have not been positively identified. In the case of the nickel and cobalt derivatives of 2 - hydroxy - 1 - naphthylidene ethylene diamine the complexes are of the form ML and the number of unpaired electrons are 2 and 3 respectively. The fact that one isomer only is detected by mass spectrometry suggests that the hybridisation is sp³ and that the configuration is tetrahedral. However, this result conflicts with earlier studies on nickel salicylidene ethylene diamine which was shown to have two isomers by mass spectrometry.

Acknowledgements—The authors are indebted to Mr. D. Carter of the School of Pharmacy, London, for helpful advice and assistance and to the University of Mosul, Iraq, for the grant of study leave for one of us (A.S.P.A.).

REFERENCES

- 1. J. Charalambous, *Mass Spectrometry of Metal Compounds*. Butterworths, England (1975).
- 2. A. E. Jenkins and J. R. Majer, Talanta 14, 777 (1967).
- 3. R. Perry, Ph. D. Thesis, Birmingham University (1968).
- R. Belcher, C. R. Cranley, J. R. Majer, W. I. Stephen and P. C. Uden, Anal. Chim. Acta 60, 109 (1972).
- 5. A. E. Jenkins, J. R. Majer and M. J. A. Reade, *Talanta* 14, 1213 (1967).
- 6. D. Betteridge and D. John, Talanta 15, 1227 (1968).
- 7. K. T. I. Al-Kuwaity, M.Sc. Thesis, Birmingham University (1977).
- 8. J. R. Majer and M. J. A. Reade, Chem. Commun. 58 (1970).
- R. Belcher, J. R. Majer, R. Perry and W. I. Stephen, Anal. Chim. Acta 43, 451 (1968).
- J. R. Majer and K. Al-Kuwaity, Proc. Analyt. Div. Chem. Soc. pp. 98-101 (1978).
- 11. A. S. P. Azzouz, M.Sc. Thesis, Birmingham University (1979).
- 12. A. I. Vogel, A Text Book of Practical Organic Chemistry. Longmans Green, London (1964).
- M. E. El-Bayoumi, M. El-Aasser and F. Abdel Halim, J. Am. Chem. Soc. 93, 586 (1971).
- 14. G. Pass and H. Sutcliffe, *Practical Inorganic Chemistry*, Chapman & Hall, London 2 edn. (1974).
- 15. R. S. Nyholm, Chem. Soc. Quart. Rev. 7, 377 (1953).