Synthesis and Characterization of Nickel(II) Complexes with Cyclic and Linear Schiff-base Ligands incorporating Sulphur, Nitrogen, and Oxygen Donor Atoms †

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A series of nickel(II) complexes containing macrocyclic and linear Schiff-base ligands has been prepared by condensation of 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, diethylenetriamine, or triethylenetetramine with the thiodiketone, 4-thiaheptane-2,6-dione (D) in the presence of nickel(II) salts. The ligands could not be synthesized in the absence of nickel(II) ions. In the case of 1,2-diaminoethane (en) a purple product and a reddish brown product are formed depending on the reaction conditions. A single-crystal *X*-ray analysis of the purple product $[NiL(en)][NO_3]_2$ [L is the linear Schiff base, $NH_2(CH_2)_2N{=}C(CH_3)CH_2SCH_2COCH_3$] indicates a highly distorted octahedral stereochemistry involving co-ordination of N, N, S, and O atoms of the new quadridentate ligand L. The remaining two positions of the octahedron are occupied by en. The nitrate groups are non-co-ordinating. The reddish brown product is $[NiL^1]X_2$ (L^1 is the macrocyclic sexidentate ligand formed by cyclocondensation of L, X = NO_3^- or Cl^-). Complexes of macrocyclic ligands L^2 and L^3, $[NiL^2]X_2$ and $[NiL^3(CH_3OH)][NO_3]_2$, were obtained by 2 + 2 (L^2) and 1 + 1 (L^3) cyclocondensations of 1,3-diaminopropane and triethylenetetramine respectively with D in the presence of nickel(II) nitrate or chloride. Diethylenetriamine and 1,2-diaminopropane undergo 1 + 1 (L^4) and 2 + 2 (L^5) condensations with D in the presence of nickel(II) salts to form complexes of open-chain Schiff-base ligands, $[NiL^4(C_2H_5OH)][NO_3]_2$ and $[NiL^5][NO_3]_2$ respectively. The failure of ring closure in these cases may be attributed to steric hindrance and/or mismatch of the sizes of the cavities and the nickel(II) ions. From their i.r. and electronic spectra, and the results of electrical conductivity and magnetic susceptibility measurements, these complexes have been assigned distorted six-co-ordinate structures.

The synthesis of complexes of macrocyclic nitrogen donor and macrocyclic mixed nitrogen–oxygen donor ligands *via* metal-template reactions has received much attention in recent years,[1-6] but the synthesis of macrocycles involving nitrogen and sulphur donors *via* the condensation of thiodiketones with amines in the presence of metal ions has not been reported. In attempts to isolate complexes of such macrocyclic ligands, condensations of 2,2′-thiodiketones $(RCOCH_2)_2S$ (R = aryl) with various amines were carried out in the presence of different metal ions, *e.g.* Cu^{II} and Ni^{II}, but products of definite stoicheiometry could not be isolated. The inability of the diarylthiodiketones to undergo cyclocondensation may be attributed to the effect of the bulky, electron-withdrawing aryl groups. A decrease in the reactivity of carbonyl groups adjacent to electron-withdrawing groups has been noted by other workers, for example in the case of CF_3 groups, where attempts to condense hexafluoroacetylacetone and diamines under normal conditions failed.[7-9] It has been well established that the condensations occur exclusively at the carbonyl group adjacent to the methyl group.[9,10] To test this hypothesis, the thiodiketone, 4-thiaheptane-2,6-dione (D), with methyl groups instead of the aryl groups, has been synthesized,[11] and its condensation with various amines in the presence of nickel(II) salts has been found to give a series of nickel(II) complexes with macrocyclic and non-cyclic Schiff-base ligands.

Experimental

The chemicals used were of AnalaR or BDH grade. All the cyclic and non-cyclic Schiff-base ligands formed in the reactions have not been reported previously, and are denoted as: L = 6-(2′-aminoethylimino)-4-thiaheptan-2-one, L^1 = 3,8,12,17-tetramethyl-1,10-dithia-4,7,13,16-tetra-azacyclooctadeca-3,7,12,16-tetraene] L and L^1 formed respectively from 1 + 1 and 2 + 2 condensation of 1,2-diaminoethane with the thiodiketone D in the presence of nickel(II) salts]; L^2 = 3,9,13,19-tetramethyl-1,11-dithia-4,8,14,18-tetra-azacycloeicosa-3,8,13,18-tetraene; L^3 = 3,14-dimethyl-1-thia-4,7,10,13-tetra-azacyclopentadeca-3,13-diene (L^2 and L^3 obtained from 2 + 2 and 1 + 1 cyclocondensation of 1,3-diaminopropane and triethylenetetramine respectively with D); L^4 = 6-(5′-amino-3′-azapentylimino)-4-thiaheptan-2-one; L^5 = 18-amino-6,8,11,15-tetramethyl-4,13-dithia-7,10,16-triazanonadeca-6,10,15-trien-2-one (L^4 and L^5 formed from 1 + 1 and 2 + 2 condensation of diethylenetriamine and 1,2-diaminopropane respectively with D).

Methods of Preparation.—The complexes were prepared under nitrogen because some decomposition, the nature of which was not established, occurs in solutions exposed to air, and several of the solids are hygroscopic. They were obtained in good yield (*ca.* 70%).

$[NiL(en)][NO_3]_2$. Nickel(II) nitrate hexahydrate (0.66 g, 0.0024 mol) in absolute ethanol (20 cm³) was flushed with nitrogen for about 30 min. To the green solution was added 1,2-diaminoethane (en) (0.28 g, 0.0047 mol) dropwise with constant stirring. A purple complex separated and to the reaction mixture was added an oxygen-free solution of the thiodiketone D (0.67 g, 0.0046 mol) in absolute ethanol (10 cm³), slowly with constant stirring. The reaction mixture was stirred at 70—80 °C for about 30 min when the complex dissolved to give a purple solution. This was filtered while hot to remove any undissolved material, the filtrate was concentrated to about half volume under reduced pressure at *ca.* 40 °C, and allowed to cool slowly. After about 30 min fine purple crystals separated and were filtered off, washed with absolute ethanol and dry benzene (4 × 5 cm³), and dried *in*

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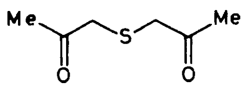
† *Non-S.I. unit employed:* B.M. ≈ 9.27×10^{-24} A m².



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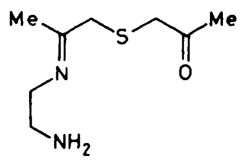

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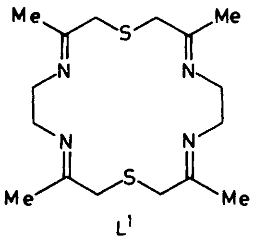

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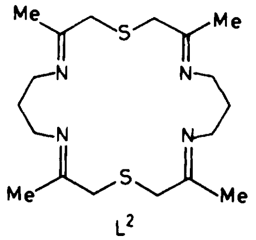

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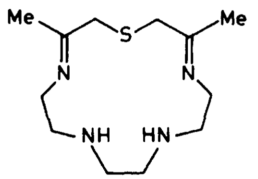

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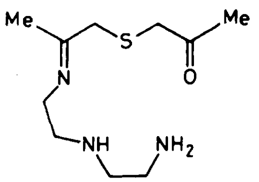

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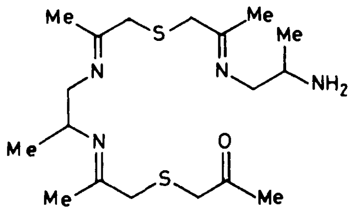
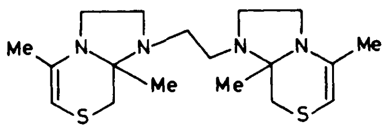


L^5



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vacuo for 3 h at *ca.* 60 °C. This complex is stable to air and moisture.

[NiL^1]X$_2$ (X = NO$_3$ *or* Cl). A mixture of nickel(II) nitrate hexahydrate or nickel(II) chloride hexahydrate (0.001 mol), 1,2-diaminoethane (0.002 mol), and the thiodiketone (0.002 mol) was prepared as described above but in this case the reaction mixture was stirred for much longer, *i.e.* about 4 h, at 70—80 °C, to allow cyclocondensation to occur. Colour changes from green to purple and then to deep red were observed. The reaction mixture was filtered while hot, and the filtrate concentrated under reduced pressure to give a deep red highly hygroscopic semi-solid which was washed repeatedly with dry benzene (4 × 10 cm^3) and dry light petroleum (b.p. 40—60 °C) (4 × 10 cm^3), and kept over concentrated sulphuric acid for 2 d. The powder obtained was dried *in vacuo* at *ca.* 40—50 °C for 3 h and stored in a desiccator because of its highly hygroscopic nature.

[NiL^2]X$_2$ (X = NO$_3$ *or* Cl). These complexes were prepared as above by stirring a mixture of nickel(II) nitrate hexahydrate or nickel(II) chloride hexahydrate (0.001 mol), thiodiketone (0.002 mol), and 1,3-diaminopropane (0.002 mol) in absolute ethanol (25 cm^3) at 60—70 °C for about 1 h when colour changes from blue to violet to greenish brown, and finally to reddish brown (X = NO$_3$) or light green (X = Cl) occurred. The solution was filtered while hot and concentrated nearly to dryness under reduced pressure at about 40 °C when a reddish brown/light green compound separated which was washed with dry benzene (5 × 10 cm^3) and then with dry light petroleum (b.p. 40—60 °C) by decantation. Each complex was dried *in vacuo* at about 50 °C for 3 h and is highly hygroscopic.

[NiL^3(CH$_3$OH)][NO$_3$]$_2$·CH$_3$OH. Nickel(II) nitrate hexahydrate (0.001 mol) was dissolved in methanol (20 cm^3) to give a green solution. Triethylenetetramine (0.001 mol) was added dropwise with constant stirring. A bluish white complex separated. To the reaction mixture was added a solution of the thiodiketone (0.001 mol) in methanol (10 cm^3) with constant stirring, and after about 5—10 min at 70—80 °C the solid dissolved to give a reddish brown solution. The stirring was continued for 15 min, the solution filtered while hot, and the filtrate concentrated under reduced pressure at 40—50 °C to an oily mass which was washed with dry benzene (4 × 10 cm^3) and dry light petroleum (5 × 10 cm^3) to give the complex as a fine powder. The complex was finally dried *in vacuo* at 40—50 °C for 3 h. It is highly hygroscopic.

[NiL^4(C$_2$H$_5$OH)][NO$_3$]$_2$. The complex was synthesized by the method used for the complex of L, by stirring a mixture of nickel(II) nitrate hexahydrate (0.001 mol), thiodiketone (0.001 mol), and diethylenetriamine (0.001 mol) in absolute ethanol for 4—5 h at 80—85 °C, when the colour of the reaction mixture changed to greyish brown. It was filtered while hot, and the filtrate was concentrated nearly to dryness under reduced pressure; the oily mass obtained was treated with dry benzene (4 × 10 cm^3), then with dry light petroleum (b.p. 40—60 °C), and dried *in vacuo* at 40—50 °C for 3 h. The complex is highly hygroscopic.

[NiL^5][NO$_3$]$_2$. This hygroscopic complex was prepared by the same procedure as the complex of L^1, *i.e.* from nickel(II) nitrate hexahydrate (0.001 mol), 1,2-diaminopropane (0.002 mol), and the thiodiketone (0.002 mol) in absolute ethanol (40 cm^3).

Analysis and Physical Measurements.—Because of their hygroscopic nature, the samples for various investigations were kept in ampoules in a glove-box with a gas recirculation and purification system obtained from Faircrest Engineering Ltd., Croydon. Nickel was determined both volumetrically and gravimetrically. Carbon, hydrogen, and nitrogen analyses were carried out by the Micro-analytical Unit, University of Surrey. Conductivity measurements were carried out with a Wayne Kerr Autobalance Universal Bridge B642 and a dip-type cell which was calibrated with aqueous potassium chloride solution. Magnetic measurements were carried out by the Gouy method on solid samples sealed in nitrogen in stoppered quartz tubes. The magnetic balance was supplied by Newport Instruments, Newport Pagnell. The field was calibrated with Hg[Co(NCS)$_4$]. Diffuse-reflectance spectra were recorded on a Beckman MIV spectrophotometer provided with a reflectance attachment. Infrared spectra (200—5 000 cm^{-1}) were recorded on a Perkin-Elmer 577 spectrophotometer. The Nujol mulls (KBr or Polythene plates) were made up in the glove-box under nitrogen.

Results and Discussion

A series of nickel(II) complexes of macrocyclic and non-cyclic Schiff-base ligands, incorporating nitrogen, sulphur, and in some cases oxygen donor atoms, derived from the template condensation of amines and the thiodiketone (D) has been

Table 1. The colours, melting points, molar conductances, and analytical data for nickel(II) complexes with sulphur- and nitrogen-containing Schiff bases

				Analysis [b] (%)			
Complex	Colour	M.p./°C	$\Lambda_M{}^a$/ohm^{-1} cm^2 mol^{-1}	C	H	N	Ni
$[NiL(en)][NO_3]_2$	Purple	180—182	172	27.80 (27.90)	5.50 (5.60)	19.15 (19.55)	14.00 (13.65)
$[NiL^1][NO_3]_2 \cdot H_2O$	Reddish brown	185—190	148	35.35 (35.55)	5.95 (5.55)	14.90 (15.55)	11.20 (10.85)
$[NiL^2][NO_3]_2 \cdot C_2H_5OH$	Reddish brown	103—108 (decomp.)	135	40.60 (40.25)	6.45 (6.40)	15.45 (14.10)	10.20 (9.85)
$[NiL^3(CH_3OH)][NO_3]_2 \cdot CH_3OH$	Reddish brown	78—85 (decomp.)	162	34.00 (33.35)	5.85 (6.75)	16.85 (16.65)	10.90 (11.65)
$[NiL^1]Cl_2 \cdot C_2H_5OH$	Reddish brown	100—105 (decomp.)	166	41.15 (41.85)	6.60 (6.60)	10.75 (10.85)	11.65 (11.35)
$[NiL^2]Cl_2 \cdot H_2O$	Light green	108—110 (decomp.)	121	42.10 (41.95)	6.45 (6.60)	8.60 (10.85)	10.90 (11.40)
$[NiL^4(C_2H_5OH)][NO_3]_2$	Greyish brown	88—95 (decomp.)	138	33.70 (32.65)	5.35 (5.65)	16.15 (15.85)	13.10 (13.30)
$[NiL^5][NO_3]_2$	Reddish brown	88—92 (decomp.)	154	38.10 (38.00)	5.90 (6.00)	13.25 (14.80)	9.90 (10.35)

[a] In methanol (*ca.* 10^{-3} mol dm^{-3}); Λ_M = 121—172 ohm^{-1} cm^2 mol^{-1} for 2 : 1 electrolytes, W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
[b] Calculated values given in parentheses.

Table 2. Magnetic moments and i.r. spectral data

Complex	Magnetic moment $\mu_{eff.}$*/B.M.	Far-i.r. spectra (cm^{-1})	Other i.r. bands
$[NiL(en)][NO_3]_2$	3.10	525m, 425w, 330m, 320w	3 310vs, 3 265vs, 3 180s, 1 750w, 1 697vs, 1 680 (sh), 1 600s, 1 350vs, 1 170s, 1 074m, 1 045vs, 1 025m, 830s, 738m, 690s
$[NiL^1][NO_3]_2 \cdot H_2O$	3.11	—	3 380 (sh), 3 240sbr, 1 745w, 1 690m, 1 650m, 1 600m, 1 320sbr, 1 165w, 1 110m, 1 037s, 980w, 825w, 730w
$[NiL^2][NO_3]_2 \cdot C_2H_5OH$	2.82	340m, 335m, 312w	3 360 (sh), 3 260sbr, 3 170s, 1 745w, 1 660 (sh), 1 605vs, 1 105m, 1 035m, 1 017m, 930w 730m, 675vw
$[NiL^3(CH_3OH)][NO_3]_2 \cdot CH_3OH$	3.08	530mbr, 440m, 338vw, 315vw, 280w, 220m	3 400 (sh), 3 240mbr, 1 695s, 1 600s
$[NiL^1]Cl_2 \cdot C_2H_5OH$	2.89	382vw, 320w, 302 (sh), 235w	3 400 (sh), 3 220sbr, 3 120sbr, 1 690s, 1 650 (sh), 1 590s, 1 290mbr, 1 240w, 1 155w, 1 110w, 1 040w, 980m, 720w, 675s
$[NiL^2]Cl_2 \cdot H_2O$	2.99	470m, 430w, 335w, 308w, 255 (sh), 230s	3 400 (sh), 3 220mbr, 3 140mbr, 1 705s, 1 660s, 1 600s, 1 282m, 1 240
$[NiL^4(C_2H_5OH)][NO_3]_2$	2.96	515m, 385w, 305s, 290s, 225sbr	3 400 (sh), 3 245sbr, 3 160 (sh), 1 742w, 1 690vs, 1 601s, 1 295sbr, 1 165m, 1 090m, 1 025m, 970m, 823m, 725w, 668s
$[NiL^5][NO_3]_2$	2.97	443s, 312s, 280m, 245w, 233w, 220w	3 400 (sh), 3 250s, 3 160s, 1 740 (sh), 1 694vs, 1 602s, 1 290 (sh), 1 162m, 1 110m, 1 017m, 825m, 730w, 680w

* At room temperature.

isolated and characterized. The structures of the Schiff-base ligands shown have been deduced from the elemental analyses and i.r. spectra of the complexes; the ligands have not been isolated. Four isomers of L^5 are possible arising from the methyl groups of the amine, 1,2-diaminopropane, and they are arbitrarily shown in the 11,15 positions. The nickel(II) complexes have been assigned distorted octahedral stereochemistries from their elemental analyses (Table 1), i.r. and electronic spectra, electrolyte type, and magnetic behaviour (Tables 2 and 3).

The analytical data (Table 1) show that the condensation of 1,2-diaminoethane and D in the presence of nickel(II) nitrate hexahydrate results in the formation of two products, one purple and one dark red, according to the reaction conditions. The purple crystalline product $[NiL(en)][NO_3]_2$ was obtained by stirring the reaction mixture for about 30 min. It is stable to air and moisture, and single-crystal *X*-ray analysis [12] shows distorted octahedral stereochemistry around the nickel ion in which four of the co-ordination sites are occupied by the Schiff-base ligand L (N,N,S,O) and the remaining octahedral positions are occupied by two nitrogen atoms of an ethylenediamine molecule (Figure). The nitrate ions are non-co-ordinating.

The dark red complex obtained by stirring the reaction mixture at 70—80 °C for about 4 h has the formula $[NiL^1][NO_3]_2 \cdot H_2O$, where L^1 is the macrocyclic, sexidentate Schiff-base ligand obtained by cyclocondensation of L. In the presence of nickel(II) chloride, 2 + 2 cyclocondensation of 1,2-diaminoethane and the thiodiketone also occurs to form the complex $[NiL^1]Cl_2 \cdot C_2H_5OH$.

1,3-Diaminopropane and triethylenetetramine in the presence of nickel(II) nitrate or chloride undergo cyclodehydrative

Table 3. Electronic (reflectance) spectra (cm^{-1})

Complex	$^3A_{2g}\rightarrow{}^3T_{2g}$	$^3A_{2g}\rightarrow{}^3T_{1g}$	Charge transfer and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transitions
$[NiL(en)][NO_3]_2$	11 700s (vbr)	18 700s (vbr)	32 800vs (vbr)
$[NiL^1][NO_3]_2\cdot H_2O$	11 800s (vbr)	—	25 000vs (br), 36 350vs (br)
$[NiL^2][NO_3]_2\cdot C_2H_5OH$	10 750s, 11 360 (sh)	—	27 800vs (br), 40 000vs (br)
$[NiL^3(CH_3OH)][NO_3]_2\cdot CH_3OH$	11 100s (vbr)	18 200 (sh)	27 800vs (br), 36 900vs (br)
$[NiL^1]Cl_2\cdot C_2H_5OH$	11 800s (vbr)	19 050 (sh), 23 800 (sh)	33 900vs (br)
$[NiL^2]Cl_2\cdot H_2O$	10 500s (vbr)	17 400s (br)	28 550vs (br), 37 050vs (br)
$[NiL^4(C_2H_5OH)][NO_3]_2$	11 250s (vbr)	18 200m (br)	24 700 (sh), 36 400vs (br)
$[NiL^5][NO_3]_2$	11 700s (vbr)	20 000 (sh)	24 100vs (br), 33 300vs (br), 41 650s (br)

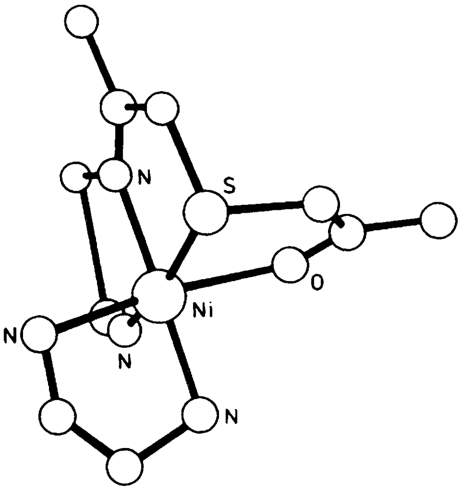

Figure. The structure of the cation in $[NiL(en)][NO_3]_2$

condensation with the thiodiketone resulting in the formation of complexes having formulae $[NiL^2][NO_3]_2\cdot C_2H_5OH$, $[NiL^2]Cl_2\cdot H_2O$, and $[NiL^3(CH_3OH)][NO_3]_2\cdot CH_3OH$. Ligands L^2 and L^3 are macrocyclic Schiff bases and are potentially sexidentate (four nitrogen and two sulphur) and quinquedentate (four nitrogen and one sulphur) ligands respectively.

The condensations of diethylenetriamine and 1,2-diaminopropane with the thiodiketone in the presence of nickel(II) nitrate hexahydrate result in the formation of complexes which have been assigned the formulae $[NiL^4(C_2H_5OH)][NO_3]_2$ and $[NiL^5][NO_3]_2$ respectively on the basis of analytical data. Ligands L^4 and L^5 are non-cyclic potentially quinque- and hepta-dentate Schiff-base ligands respectively if the uncondensed carbonyl groups act as donors. No macrocyclic products either of the 1 + 1 or 2 + 2 cyclocondensation types were isolated from diethylenetriamine or 1,2-diaminopropane even when longer reaction times or higher temperatures were used.

The thiodiketone D has a very broad and strong band at 1 700 cm^{-1} in its i.r. spectrum due to the carbonyl groups. That condensation of the carbonyl groups had occurred in the formation of the nickel(II) complexes was judged from the absence or relative weakness of bands in this region. The spectra (Table 2) of $[NiL(en)][NO_3]_2$, $[NiL^4(C_2H_5OH)][NO_3]_2$, and $[NiL^5][NO_3]_2$ contain an intense band at 1 690—1 697 cm^{-1} which is slightly shifted to lower frequency and much less broad compared to the band at 1 700 cm^{-1} of the free thiodiketone. This indicates the presence of a carbonyl group in the ligands L, L^4, and L^5, possibly co-ordinated to the metal ion. A shoulder at about 1 680 cm^{-1} in the spectrum of $[NiL(en)][NO_3]_2$ can be assigned to an imine band ν(C=N), but in the spectra of the other two complexes it is apparently completely obscured by the strong carbonyl band. In the spectra of the remaining complexes, an absorption band in the range 1 650—1 705 cm^{-1} of medium to strong intensity can be assigned to ν(C=N) in macrocyclic systems.[13-15]

Owing to the presence of ligand bands it was not possible to determine from the i.r. spectra of the nitrates whether or not the anions are co-ordinated, but the electrical conductance measurements show that they are ionic. The ionic nature of $[NiL(en)][NO_3]_2$ is confirmed by its crystal structure. It appears that in the complexes of L^3 and L^4 solvent molecules complete the co-ordination. In the electronic spectrum of $[NiL(en)][NO_3]_2$, known to contain distorted octahedral complex cations from its crystal structure, there are three bands at 11 700, 18 700, and 32 800 cm^{-1} (Table 3) which are assigned to the expected $^3A_{2g}\rightarrow{}^3T_{2g}$, $\rightarrow{}^3T_{1g}$, and $\rightarrow{}^3T_{1g}$ (P) transitions of octahedral nickel(II). In the remaining spectra the $^3A_{2g}\rightarrow{}^3T_{2g}$ transition is clearly defined, but more broad through increased distortion. The $^3A_{2g}\rightarrow{}^3T_{1g}$ transition cannot always be distinguished because it lies on broad absorption rising to peaks in the 30 000 cm^{-1} region which are ascribed to charge transfer and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transitions. Thus, the electronic spectra are generally indicative of distorted octahedral stereochemistry for these complexes. In agreement,[13] the effective magnetic moments at 293 K (Table 2) lie in the range 2.82—3.11 B.M.

All these complexes decompose in water to give several products (t.l.c.) indicating that the macrocyclic and the open-chain Schiff bases are stable only in the presence of metal ions.[1] This has been confirmed by unsuccessful attempts to synthesize the Schiff bases by treating the thiodiketone with various amines in the absence of metal ions under different conditions. No products were identified except with triethylenetetramine when E was formed.[11]

Acknowledgements

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