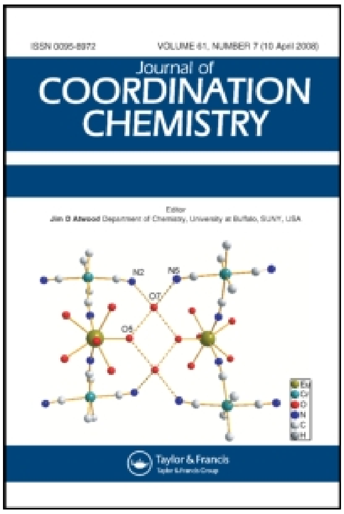

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THE INTERACTIONS BETWEEN PERIPHERAL AND CENTRAL UNITS IN SUPRAMOLECULAR AND METALLOSUPRAMOLECULAR STRUCTURES: THE CHARACTERIZATION OF SOME MONO-, DI- AND TRINUCLEAR COMPLEXES OF A VICINAL OXIME-IMINE LIGAND

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THE INTERACTIONS BETWEEN PERIPHERAL AND CENTRAL UNITS IN SUPRAMOLECULAR AND METALLOSUPRAMOLECULAR STRUCTURES: THE CHARACTERIZATION OF SOME MONO-, DI- AND TRINUCLEAR COMPLEXES OF A VICINAL OXIME–IMINE LIGAND

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The 1 : 1 molar ratio reaction of *p*-phenylenediamine with isonitrosoacetylacetone in chloroform led to the formation of the half unit ligand (HL); (**1**). Two types of the *trans* octahedral $(L)_2Ni \cdot 2H_2O$ complex were characterized; the green molecular complex (**2**) and the associated supramolecular dark brown complex (**3**). Molecular association in (**3**) took place *via* intermolecular hydrogen bonding between the amino group of a molecule and the oxygen sites of an adjacent molecule. The 1 : 1 molar ratio reactions of (**2**) with the metal acetates $M(OAc)_2$ (M = divalent nickel, copper or cobalt) produced the self-assembly structure (**4**) whereby the metal acetate is coordinated to the amino groups of the nickel(II) complex. Reaction of the dinuclear (**4**) with another metal acetate (1 : 1 molar ratio) gave the trinuclear terminated structure (**5**). Similar reactions of (**3**) with nickel acetate (1 : 1 or 1 : 2) led to formation of complexes with metallosupramolecular structures. An antiferromagnetic interaction between the peripheral and central paramagnetic units was observed from those complexes with copper(II) at the peripheral location. In all these cases the metal ions are bridged *via* the aromatic Schiff-base moiety. The suggested structures of the mono-, di- and trinuclear coordination compounds are in accordance with the analytical, spectral and magnetic moment data.

Keywords: Supramolecular and metallosupramolecular structures; mono-, di- and trinuclear complexes; Ni(II), Cu(II) and Co(II) complexes

INTRODUCTION

Recent investigations of metallosupramolecular systems revealed that they have the potential to perform functions and consequently behave as molecular devices.[1] The conversion of light to chemical or electrical energy was considered in relation to the trinuclear Ru(II) complexes of *tris*-bipyridine bridged by cyano groups (Figure 1). In this case (d^6 metal ion) light energy collected by the peripheral units is efficiently funneled to the central one (Figure 2). The significance of this system prompted us to design and characterize comparable (d^8) systems with a high-spin nickel(II) ion as the central unit which is bridged to the peripheral ion (nickel(II), cobalt(II), copper(II) or zinc(II) ions) by the aromatic p_π bridge of the Schiff base. Accordingly, this system comprises homo and hetero di- and trinuclear coordination compounds.

Our earlier studies on supramolecular systems[2–5] indicated that electronic interactions between peripheral units of separate molecules could induce chelate isomerism in the same molecule[2–4] of the nickel(II) complexes of vicinal oxime–imine ligands (Figure 3). Moreover, these interactions could be initiated (switched on) in the case of other nickel(II) complexes.[3] This conclusion was at variance with an earlier interpretation[6] regarding chelate isomerism which ascribed the phenomenon to intramolecular hydrogen bonding. Our argument against this interpretation was simply that if intramolecular hydrogen bonding is considered a stabilizing factor then there is

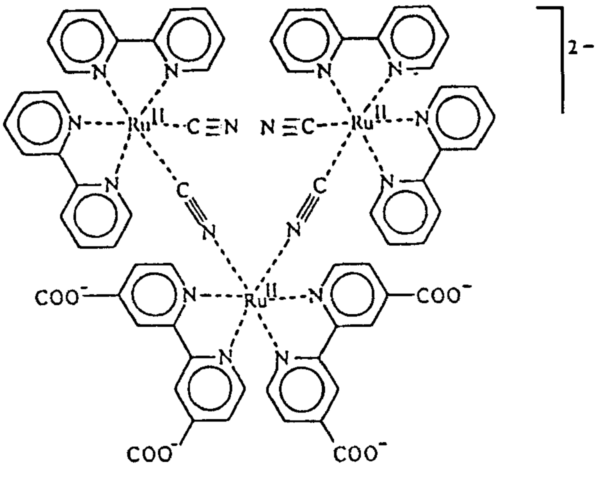

FIGURE 1 Structure of cyano-bridged Ru(II) complex of *tris*-piperidine.

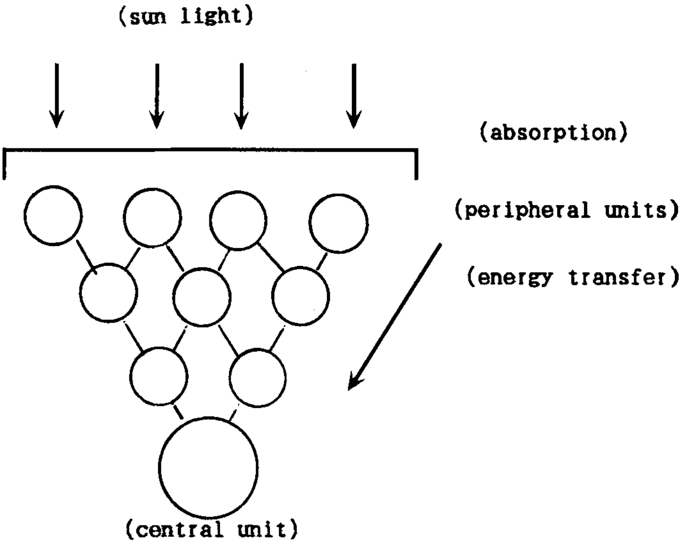

FIGURE 2 Schematic representation for the light harvesting by the peripheral units and the bridged energy transfer to the central unit.

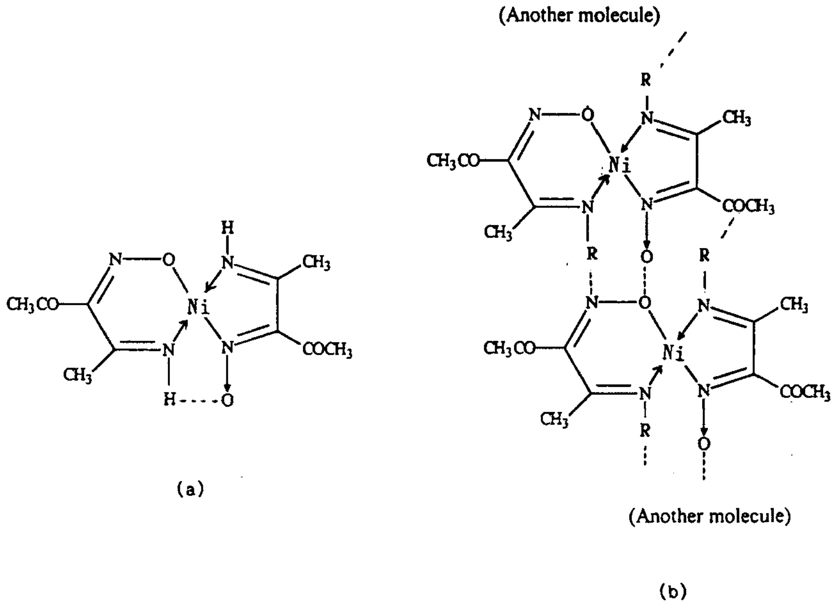

FIGURE 3 (a) Previously suggested intramolecular hydrogen bonding[6] for *bis*(4-iminopentane-2,3-dione-3-oximato)Ni(II). (b) Concluded supramolecular structure[2-5] for the same complex (R = H) as well as R = $-CH_2CH_2OH$ or by transamination of R = $-C_6H_5$ by R = –NH.

no electronic factor that prevents the other *trans* imino group from behaving similarly. Part of this investigation was briefly reported.[7]

EXPERIMENTAL

Reagent grade chemicals were used. The IR spectra of the metal complexes were measured as KBr pellets using a Schimadzu IR 470 infrared spectrophotometer. The electronic spectra were recorded with a Schimadzu UV3101 UV-vis scanning spectrophotometer. Magnetic susceptibilities were measured at 25°C by the Guoy method as described in our earlier reports[2,8] whereby $Hg[Co(CNS)_4]$ is used as the magnetic susceptibility standard and diamagnetic corrections are effected by employing standard constants.[2,8] The magnetic moments were calculated from the equation $\mu_{\mathrm{eff}} = 2.84\sqrt{\chi_{\mathrm{M}}^{\mathrm{corr}} T}$. C, H, and N analyses were determined at the Analytical Unit of the Kuwait University. Standard methods were used for determination of the metal ions. The metal acetates $M(OAc)_2 \cdot nH_2O$ ($M = Ni$ or Co, $n = 4$; $M = Cu$, $n = 1$ and for $M = Zn$, $n = 2$) and $NiCl_2 \cdot 6H_2O$ were used. The metal complexes were dried *in vacuo* over P_4O_{10}. The half unit ligand (compound (**1**)) was prepared from the 1 : 1 molar ratio reaction of isonitrosoacetylacetone with *p*-phenylenediamine in chloroform using our reported procedure[2] (m.p. 160°C); abbreviated (Hisopphen). Complexes (**2**)–(**19**) were prepared in ethanol from the reactions schematically represented in Figures 4–6.

Preparation of Complexes (2) and (3)

The ethanolic solution ($60\,cm^3$) of sodium hydroxide (0.02 mol) was added to that ($50\,cm^3$) of the ligand (0.02 mol). The ethanolic solution ($40\,cm^3$) of nickel acetate (0.01 mol) was added to the reaction solution which was refluxed for 3 h. The precipitated green complex (**2**) was filtered off and washed with ethanol. The filtrate was concentrated to about half of its volume and left for 20 h to precipitate a dark brown, impure complex. The complex was isolated from the water-soluble impurities by stirring with warm water ($50\,cm^3$) for 1 h before filtering to produce the dark brown complex (**3**) which was washed with ethanol. The green complex (**2**) (0.004 mol) was converted to the dark brown complex (**3**) by refluxing its ethanolic suspension ($50\,cm^3$) with sodium acetate (0.024 mol, $100\,cm^3$) for 5 h. The dark brown complex was filtered off and washed with warm ethanol.

Preparation of Complexes (4)–(10); Figure 4

The dinuclear complex (**4**) was prepared in EtOH by adding a solution of nickel(II) acetate (0.004 mol, 100 cm^3) dropwise while stirring to an equimolar suspension of complex (**2**) (100 cm^3). The reaction solution was refluxed for 5 h, the product collected by filtration, and washed with ethanol. This procedure was applied for preparation of complexes (**5**)–(**10**) (using the molar ratios stated in Figure 4) from reaction of the metal salt with the mono- or dinuclear complex under consideration. Thus, the 1 : 1 molar ratio reaction of the dinuclear complex (**4**) with nickel(II) acetate led to formation of the trinuclear complex (**5**) which was also prepared from a 1 : 2 molar ratio reaction of complex (**2**) with nickel(II) acetate. The 1 : 1 and 1 : 2 molar ratio reactions of (**2**) with nickel(II) acetate were also carried out using the dark brown complex (**3**) to give complexes (**6**) and (**7**), respectively. The trinuclear complex (**8**) was prepared from a 1 : 2 molar ratio reaction of complex (**2**) with nickel(II) chloride. The heterotrinuclear complexes (**9**) and (**10**) were prepared from a 1 : 1 reaction of complex (**4**) with cobalt(II) acetate or copper(II) acetate, respectively.

Preparation of Complexes (11)–(14); Figure 5

These complexes were prepared in EtOH from reaction of a solution of the metal of salt with a suspension of either the mono- or dinuclear complex (0.004 mol) using the procedure detailed above for complex (**4**) with molar ratios stated in Figure 5. Thus, the 1 : 1 reaction of complex (**2**) with cobalt(II) acetate gave heterodinuclear complex (**11**). The latter complex reacted with either nickel(II) acetate or copper(II) acetate (1 : 1 molar ratio) to produce the heterotrinuclear complexes (**12**) and (**14**), respectively. Complex (**13**) was prepared from the 1 : 2 molar ratio reaction of complex (**2**) with cobalt(II) acetate.

Preparation of Complexes (15)–(19); Figure 6

These complexes were prepared in EtOH, using the procedure described above for complex (**4**), from reaction of a solution of the metal salt with an ethanolic suspension of the metal complex under consideration (0.004 mol) using the molar ratios listed in Figure 6. Thus, the 1 : 1 reaction of complex (**2**) with coper(II) acetate led to formation of the heterodinuclear complex (**15**) which reacted with either nickel(II) acetate or cobalt(II) acetate (1 : 1 molar ratio) to produce the heterotrinuclear complexes (**16**) and (**17**), respectively. Reaction of complex (**2**) with either copper(II) acetate (1 : 2 molar ratio) or

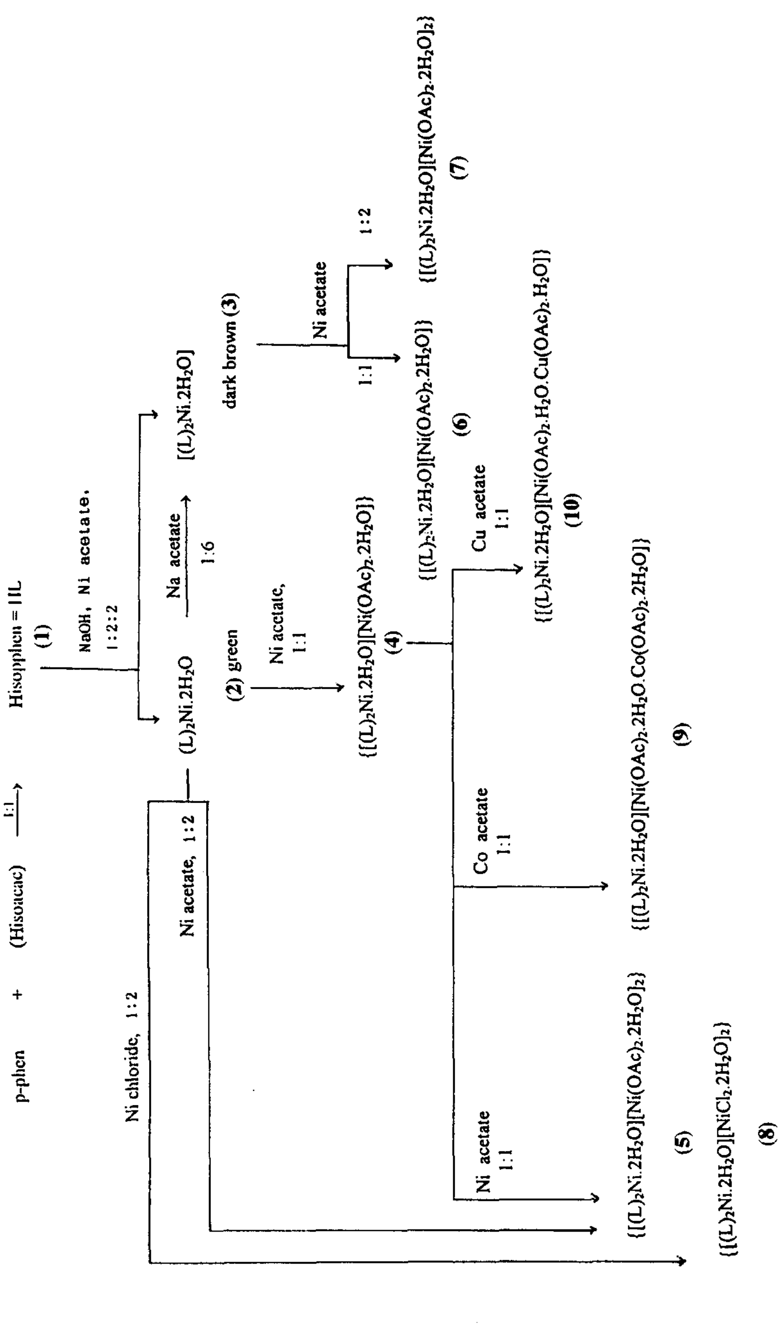

FIGURE 4 Schematic representation for the reactions of the ligand and its nickel(II) complexes.

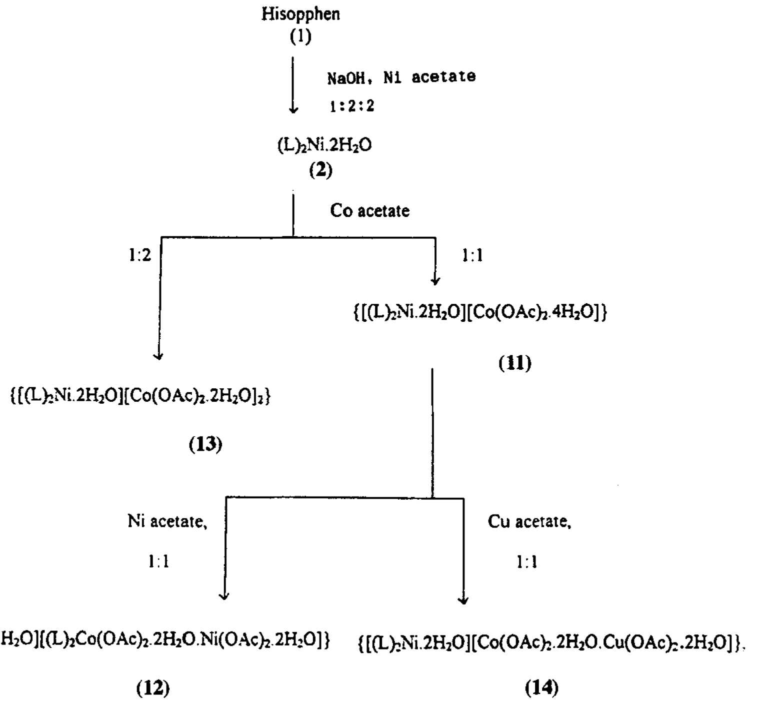

FIGURE 5 Schematic representation for the reactions of the green nickel(II) complex (**2**) with cobalt(II) acetate and the reactivity of the formed complexes.

zinc(II) acetate (1 : 1 or 1 : 2 molar ratios) led to formation of complexes (**18**) and (**19**), respectively.

Compound (**1**), HL, yellow. *Anal.* Calcd. for $C_{11}H_{13}N_3O_2$ (%): C, 60.26; H, 5.98; N, 19.17. Found: C, 59.92; H, 6.03; N, 19.32.

Complex (**2**), $(L)_2Ni \cdot 2H_2O$, green. *Anal.* Calcd. for $C_{22}H_{28}N_6O_6Ni$ (%): C. 49.74; H, 5.31; N, 15.82; Ni, 11.05. Found: C, 49.20; H, 5.10; N, 15.52; Ni, 11.00.

Complex (**3**), $(L)_2Ni \cdot 2H_2O$, dark brown. *Anal.* Calcd. for $C_{22}H_{28}N_6O_6Ni$ (%): C, 49.74; H, 5.31; N, 15.82; Ni, 11.05. Found: C, 49.64; H, 5.23; N, 15.94; Ni, 11.36.

Complex (**4**), $\{[(L)_2Ni \cdot 2H_2O][Ni(OAc)_2 \cdot 2H_2O]\}$, green. *Anal.* Calcd. for $C_{26}H_{38}N_6O_{12}Ni_2$ (%): C, 41.97; H, 5.15; N, 11.30; Ni, 15.78. Found: C, 41.94; H, 5.10; N, 10.98; Ni, 16.10.

Complex (**5**), $\{[(L)_2Ni \cdot 2H_2O][Ni(OAc)_2 \cdot 2H_2O]_2\}$, green. *Anal.* Calcd. for $C_{30}H_{48}N_6O_{18}Ni_3$ (%): C, 37.66; H, 5.06; N, 8.78; Ni, 18.40. Found: C, 37.50; H, 4.97; N, 9.00; Ni, 18.92.

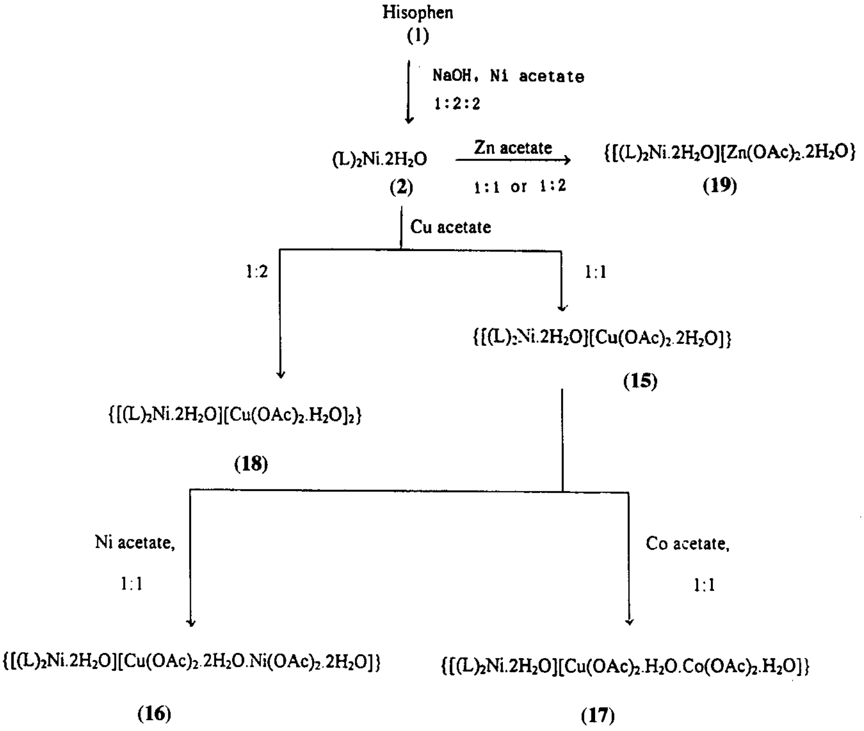

FIGURE 6 Schematic representation for the reactions of the green nickel(II) complex (**2**) with copper(II) acetate and the reactivity of the formed complexes.

Complex (**6**), $\{[(L)_2Ni \cdot 2H_2O][Ni(OAc)_2 \cdot 2H_2O]\}$, brown-green. *Anal.* Calcd. for $C_{26}H_{38}N_6O_{12}Ni_2$ (%): C, 41.97; H, 5.15; N, 11.30; Ni, 15.78. Found: C, 42.46; H, 5.06; N, 11.43; Ni, 16.17.

Complex (**7**), $\{[(L)_2Ni \cdot 2H_2O][Ni(OAc)_2 \cdot 2H_2O]_2\}$, brown-green. *Anal.* Calcd. for $C_{30}H_{48}N_6O_{18}Ni_3$ (%): C, 37.66; H, 5.06; N, 8.78; Ni, 18.40. Found: C, 38.05; H, 5.10; N, 8.63; Ni, 18.62.

Complex (**8**), $\{[(L)_2Ni \cdot 2H_2O][NiCl_2 \cdot 2H_2O]_2\}$, green-yellow. *Anal.* Calcd. for $C_{22}H_{36}N_6O_{10}Cl_4Ni_3$ (%): C, 30.64; H, 4.21; N, 9.74; Cl, 16.44; Ni, 20.42. Found: C, 31.23; H, 4.43; N, 10.11; Cl, 16.02; Ni, 20.33.

Complex (**9**), $\{[(L)_2Ni \cdot 2H_2O][Ni(OAc)_2 \cdot 2H_2O \cdot Co(OAc)_2 \cdot 2H_2O]\}$, green-yellow. *Anal.* Calcd. for $C_{30}H_{48}N_6O_{18}CoNi_2$ (%): C, 37.65; H, 5.06; N, 8.78; Co, 6.16; Ni, 12.27. Found: C, 38.21; H, 5.01; N, 8.36; Co, 6.32; Ni, 12.03.

Complex (**10**), $\{[(L)_2Ni \cdot 2H_2O][Ni(OAc)_2 \cdot H_2O \cdot Cu(OAc)_2 \cdot H_2O]\}$, green-brown. *Anal.* Calcd. for $C_{30}H_{44}N_6O_{16}Ni_2Cu$ (%): C, 38.93; H, 4.79;

N, 9.08; Ni, 12.68; Cu, 6.86. Found: C, 39.29; H, 4.91; N, 9.00; Ni, 13.10; Cu, 6.90.

Complex (**11**), {[(L)$_2$Ni · 2H$_2$O][Co(OAc)$_2$ · 4H$_2$O]}, green-brown. *Anal.* Calcd. for $C_{26}H_{42}N_6O_{14}CoNi$ (%): C, 40.02; H, 5.43; N, 10.77; Co, 7.55; Ni, 7.52. Found: C, 40.37; H, 5.32; N, 10.67; Co, 7.41; Ni, 7.12.

Complex (**12**), {[(L)$_2$Ni · 2H$_2$O][Co(OAc)$_2$ · 2H$_2$O · Ni(OAc)$_2$ · 2H$_2$O]}, green-brown. *Anal.* Calcd. for $C_{30}H_{48}N_6O_{18}CoNi_2$ (%): C, 37.65; H, 5.06; N, 8.78; Co, 6.16; Ni, 12.27. Found: C, 37.22; H, 5.10; N, 8.48; Co, 6.41; Ni, 12.48.

Complex (**13**), {[(L)$_2$Ni · 2H$_2$O][Co(OAc)$_2$ · 2H$_2$O]$_2$}, green-brown. *Anal.* Calcd. for $C_{30}H_{48}N_6O_{18}Co_2Ni$ (%): C, 37.65; H, 5.05; N, 8.78; Co, 12.31; Ni, 6.13. Found: C, 37.11; H, 5.13; N, 8.61; Co, 12.64; Ni, 6.55.

Complex (**14**), {[(L)$_2$Ni · 2H$_2$O][Co(OAc)$_2$ · 2H$_2$O · Cu(OAc)$_2$ · 2H$_2$O]}, green-brown. *Anal.* Calcd. for $C_{30}H_{48}N_6O_{18}CoNiCu$ (%): C, 37.46; H, 5.03; N, 8.74; Co, 6.13: Ni, 6.10; Cu, 6.61. Found: C, 37.19; H, 5.10; N, 8.62; Co, 6.47; Ni, 6.23; Cu, 6.90.

Complex (**15**), {[(L)$_2$Ni · 2H$_2$O][Cu(OAc)$_2$ · 2H$_2$O]}, green-brown. *Anal.* Calcd. for $C_{26}H_{38}N_6O_{12}NiCu$ (%): C, 41.70; H, 5.11; N, 11.22; Ni, 7.84; Cu, 8.49. Found: C, 41.56; H, 5.21; N, 11.30; Ni, 8.00; Cu, 8.69.

Complex (**16**), {[(L)$_2$Ni · 2H$_2$O][Cu(OAc)$_2$ · 2H$_2$O · Ni(OAc)$_2$ · 2H$_2$O]}, green-brown. *Anal.* Calcd. for $C_{30}H_{48}N_6O_{18}Ni_2Cu$ (%): C, 37.47; H, 5.03; N, 8.74; Ni, 12.21; Cu, 6.61. Found: C, 37.13; H, 5.09; N, 8.34; Ni, 12.09; Cu, 6.32.

Complex (**17**), {[(L)$_2$Ni · 2H$_2$O][Cu(OAc)$_2$ · H$_2$O · Co(OAc)$_2$ · H$_2$O]}, green-brown. *Anal.* Calcd. for $C_{30}H_{44}N_6O_{16}CoNiCu$ (%): C, 38.92; H, 4.79; N, 9.08; Co, 6.3; Ni, 6.34; Cu, 6.86. Found: C, 38.61; H, 4.70; N, 8.60; Co, 6.59; Ni, 6.44; Cu, 7.04.

Complex (**18**), {[(L)$_2$Ni · 2H$_2$O][Cu(OAc)$_2$ · H$_2$O]$_2$}, dark-green. *Anal.* Calcd. for $C_{30}H_{44}N_6O_{16}NiCu_2$ (%): C, 38.72; H, 4.77; N, 9.03; Ni, 6.31; Cu, 13.66. Found: C, 38.41; H, 4.63; N, 9.06; Ni, 6.05; Cu, 13.90.

Complex (**19**), {[(L)$_2$Ni · 2H$_2$O][Zn(OAc)$_2$ · 2H$_2$O]}, green. *Anal.* Calcd. for $C_{26}H_{38}N_6O_{12}NiZn$ (%): C, 41.60; H, 5.10; N, 11.20; Ni, 7.82; Zn, 8.71. Found: C, 41.16; H, 5.29; N, 11.20; Ni, 7.69; Zn, 8.82.

RESULTS AND DISCUSSION

The reactions that lead to formation of the ligand and the metal complexes are schematically represented in Figures 4–6. The metal complexes are stable at room temperature and decompose above 200°C. The non-ionic nature of the complexes is shown by the low molar conductance values in chloroform ($< 2.0\,\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$). The presence of the lattice component and coordinated water molecule in the metal complexes are confirmed by T.G.A. The suggested structures of the metal complexes are based on vibrational spectra (Table I), electronic spectra (Table II) and magnetic moment evidence (Table III) in addition to the analytical data described in the Experimental Section. The 2 : 2 : 1 molar ratio reaction of the ligand (Hisopphen) with sodium hydroxide and nickel(II) acetate in ethanol led to formation of two types of nickel(II) complexes which have the same analytical data. These complexes are the green complex (**2**) and the dark brown complex (**3**). Complex (**2**) is characterized by vibrational bands at 1680 and 1670 cm^{-1} (ν(C=O)) as well as a ν(N–O) band at 1148 cm^{-1} associated with the five-membered chelate ring of the N-coordinated oximato group in the nickel(II) complexes of vicinal oxime–imine ligands.[2–5] This evidence is also applicable to complexes (**3**)–(**19**). The electronic spectra of complex (**2**) had absorption peaks at 680 and 600 nm which indicated[9] the octahedral structure of nickel(II). The magnetic moment of this complex was found to be 2.67 B.M. as expected from the high-spin nickel(II) ion of the d^8 system. The suggested structure of complex (**2**) is shown in Figure 7.

The dark brown complex (**3**) had the same analytical data and magnetic moment as complex (**2**). However, the ν(C=O) vibration is broad (combination bands) and the ν(N–O) vibration is split to two bands (separated by 15 cm^{-1}) as compared with complex (**2**). It is suggested, therefore, that complex (**3**) is the associated form of complex (**2**). Possible associated structures are illustrated in Figures 8–11. All are based on the intermolecular hydrogen bonding of the hydrogen atoms of the amino group of a molecule with both the oximato-oxygen and the carbonyl-oxygen (the oxygen sites) of another molecule. In Figure 8, this interaction involves only one chelate ring of a molecule with another chelate ring of an adjacent molecule. Both chelate rings are involved in Figure 9 through either both amino groups or the oxygen sites of a molecule. In Figure 10, both amino groups and the oxygen sites of the molecules are involved. The layer structure is represented in Figure 11, but ruled out since our earlier reports[2–5] have shown that these interactions occur along the equatorial (x–y) axis. The suggested structure of Figure 10 requires a single vibration for either ν(C=O) or ν(N–O) and therefore is not applicable to complex (**3**) since combination bands were observed for the former vibration and the latter was split to two bands. These observations are consistent with the formulations in either Figure 8 or Figure 9 which have two types of ν(C=O), ν(N–O) and

TABLE I Infrared features (cm^{-1}) of the ligand and its metal complexes

Ref. no.	$\nu(OH)$	$\nu(NH)$	$\nu(C{=}O)$	$\nu(C{=}N)$		ν_{as}(*carboxylate*)	$\nu(N{-}O)$
				imine	*oxime*		
(1)	2750–2500 (br)	3470 (m) 3370 (m)	1672 (m)	1628 (m)	1605 (s)	—	1020 (s) 1010 (s)
(2)	3500–3400 (br)	3300 (s) 3200 (s)	1680 (m) 1670 (s)	1605 (m)	1575 (s)	—	1148 (s)
(3)	3450–3400 (br)	3300 (s) 3200 (s)	1680 (m,br) 1670 (s)	1605 (m)	1580 (s)		1165 (s) 1150 (s)
(4)	3500–3300 (br)	3250–3100 (br)	1680 (s) 1670 (s)	1605 (m)	1580 (m)	1560 (s) 1550 (s)	1150 (s)
(5)	3500–3300 (br)	3200–3100 (br)	1680 (s) 1670 (s)	1600 (m)	1580 (m)	1570 (s) 1560 (s)	1150 (s)
(6)	3500–3300 (br)	3250 (s) 3200 (s)	1680 (s) 1670 (s)	1605 (m)	1580 (m)	1570 (s) 1560 (s)	1150 (s)
(7)	3500–3300 (br)	3250–3100 (br)	1680 (s) 1670 (s)	1600 (m)	1580 (m)	1570 (s) 1560 (s)	1150 (s)
(8)	3500–3300 (br)	3250–3100 (br)	1685 (s) 1675 (s)	1605 (m)	1580 (m)	—	1148 (s)
(9)	3500–3300 (br)	3250–3100 (br)	1680 (s)	1605 (m)	1580 (m)	1560 (s)	1170 (m)
(10)	3500–3300 (br)	3250–3100 (br)	1680 (s) 1670 (s)	1600 (m)	1580 (m)	1560 (s)	1150 (m)
(11)	3500–3300 (br)	3250–3100 (br)	1670 (s)	1600 (m)	1580 (m)	1560 (s)	1170 (m) 1150 (m)
(12)	3500–3300 (br)	3250–3100 (br)	1670 (s)	1600 (m)	1580 (m)	1560 (s)	1170 (m) 1150 (m)
(13)	3500–3300 (br)	3250–3150 (br)	1670 (s)	1600 (m)	1580 (s)	1560 (s)	1170 (m) 1150 (m)
(14)	3500–3300 (br)	3250–3100 (br)	1670 (s)	1600 (m)	1580 (m)	1560 (s)	1170 (m) 1150 (m)
(15)	3500–3300 (br)	3250–3100 (br)	1680 (s) 1670 (s)	1600 (m)	1580 (m)	1560 (s)	1150 (s)

TABLE I (*Continued*)

Ref. no.	$\nu(OH)$	$\nu(NH)$	$\nu(C{=}O)$	$\nu(C{=}N)$		ν_{as}(*carboxylate*)	$\nu(N{-}O)$
				imine	*oxime*		
(16)	3500–3300 (br)	3250–3100 (br)	1680 (s) 1670 (s)	1600 (m)	1580 (m)	1560 (s)	1150 (s)
(17)	3500–3300 (br)	3250–3100 (br)	1680 (s)	1600 (m)	1580 (s)	1560 (s)	1150 (s)
(18)	3500–3300 (br)	3250–3100 (br)	1680 (s)	1600 (m)	1580 (m)	1560 (s)	1155 (s)
(19)	3500–3300 (br)	3250–3100 (br)	1680 (s)	1600 (m)	1580 (m)	1570 (s)	1140 (s)

br = broad, s = strong, and m = medium.

TABLE II Electronic spectra of the ligand and its metal complexes

Ref. no.	*Solvent*	λ_{max} (nm)[a]
(1)	EtOH	318(3940), 280(7290)[b]
(2)	N.M.	680, 600
	$CHCl_3$	680, 600, 350, 300
(3)	N.M.	700 (br), 600 (br)
	$CHCl_3$	740, 690, 595, 350, 300
(4)	N.M.	680 (br), 600 (br)
	$CHCl_3$	680 (br), 600 (br), 360, 310
(5)	N.M.	680 (br), 570 (br)
	$CHCl_3$	700 (br), 600 (br), 400 (br), 310
(6)	N.M.	690, 600
	$CHCl_3$	700 (br), 600 (br), 400 (sh), 310
(7)	N.M.	690 (br), 620 (br)
	$CHCl_3$	650 (br), 365, 310
(8)	N.M.	690 (br), 600 (br)
	$CHCl_3$	695, 600, 400 (br)
(9)	N.M.	690 (br), 600 (br)
	$CHCl_3$	690 (br), 600 (br), 400, 270
(10)	N.M.	670 (br), 600 (br)
	$CHCl_3$	680 (br), 600 (br), 400, 300
(11)	N.M.	650 (br), 500 (br)
	$CHCl_3$	650 (br), 500 (br), 410, 340, 270
(12)	N.M.	690 (br), 600 (br), 500 (br)
	$CHCl_3$	685 (br), 620 (br), 410, 340, 270
(13)	N.M.	650 (br)
	$CHCl_3$	650 (br), 400, 340, 270
(14)	N.M.	650 (br)
	$CHCl_3$	600 (br), 420, 340, 270
(15)	N.M.	625 (br)
	$CHCl_3$	650 (br), 390, 305, 270
(16)	N.M.	670 (br), 600 (br)
	$CHCl_3$	680 (br), 600 (br), 400, 300
(17)	N.M.	650 (br)
	$CHCl_3$	650 (br), 400, 350, 270
(18)	N.M.	650 (br)
	$CHCl_3$	650 (br), 380, 310
(19)	N.M.	690 (br), 590 (br)
	$CHCl_3$	690 (br), 590 (br), 350, 300

N.M. = Nujol Mull.

[a] Saturated solution of the sparingly soluble complexes.

[b] Values in parenthesis are molar absorptivities in $l \cdot mol^{-1} cm^{-1}$.

ν(NH). The latter vibration was partially mixed with the broad ν(OH) of the water molecules.

Molecular association through intermolecular hydrogen bonding involving peripheral electron donor–acceptor groups appears to be responsible for chelate isomerism (Figure 3) within the same molecule provided that they have the proper strength and steric orientations in the associated molecule. This process increases the crystal field stabilization energy within the chelate rings to the extent that the molecules with chelate isomerism had

TABLE III Magnetic moment of the metal complexes at 293 K

Ref. no.	*Metal ion in chelate ring* (M_1)	*Second metal ion* (M_1)–M_2	*Third metal ion* (M_1)–M_2–M_3	μ_{eff} (B.M.) Exp.	μ_{eff}[a] (B.M.) Cal.
(1)	Hisopphen	Ligand	—	Diamagnetic	
(2)	Ni	—	—	2.67	2.83
(3)	Ni	—	—	2.68	2.83
(4)	Ni	(Ni)–Ni	—	4.27	4.00
(5)	Ni	(Ni)–Ni	(Ni)–Ni–Ni	5.42	4.90
(6)	Ni	(Ni)–Ni	—	4.04	4.00
(7)	Ni	(Ni)–Ni	(Ni)–Ni–Ni	4.72	4.90
(8)	Ni	(Ni)–Ni	(Ni)–Ni–Ni	4.83	4.90
(9)	Ni	(Ni)–Ni	(Ni)–Ni–Co	6.62	5.57
(10)	Ni	(Ni)–Ni	(Ni)–Ni–Cu	4.32	4.36
(11)	Ni	(Ni)–Co	—	4.87	4.80
(12)	Ni	(Ni)–Co	(Ni)–Co–Ni	6.60	5.57
(13)	Ni	(Ni)–Co	(Ni)–Co–Co	7.61	6.17
(14)	Ni	(Ni)–Co	(Ni)–Co–Cu	5.80	5.11
(15)	Ni	(Ni)–Cu	—	3.14	3.32
(16)	Ni	(Ni)–Cu	(Ni)–Cu–Ni	4.32	4.36
(17)	Ni	(Ni)–Cu	(Ni)–Cu–Co	5.20	5.11
(18)	Ni	(Ni)–Cu	(Ni)–Cu–Cu	3.37	3.74
(19)	Ni	(Ni)–Zn	—	3.00	2.83

[a] Calculated by adding the paramagnetic susceptibilities corresponding to the spin-only magnetic moment[12,13] of the metal ions (high-spin states for divalent nickel and cobalt ions of the d^8 and d^7 systems, respectively) and calculating the magnetic moment from $\mu_{eff} = 2.84\sqrt{\chi_M T}$.

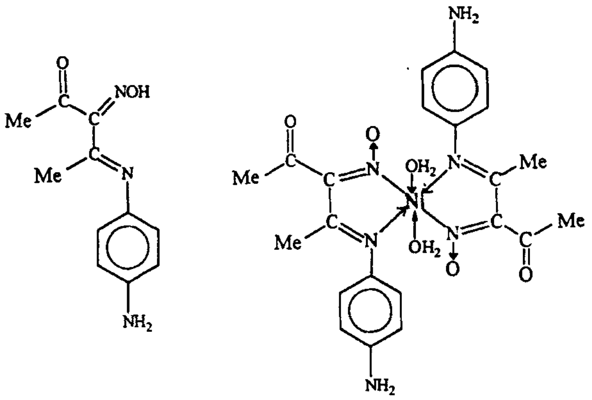

FIGURE 7 Suggested structure of the half unit ligand and the green octahedral nickel(II) complex (2).

one chelate ring with a (NO) chromophore and the molecule is square planar (low-spin) whereas the (N_2) chromophore of a comparable ligand produced the octahedral (high-spin) structure[2] (Figures 3 and 7).

The data of Table IV indicate that the coordinated chromophore (NO–NN) of the ligands (square-planar structure) exerts a higher crystal field

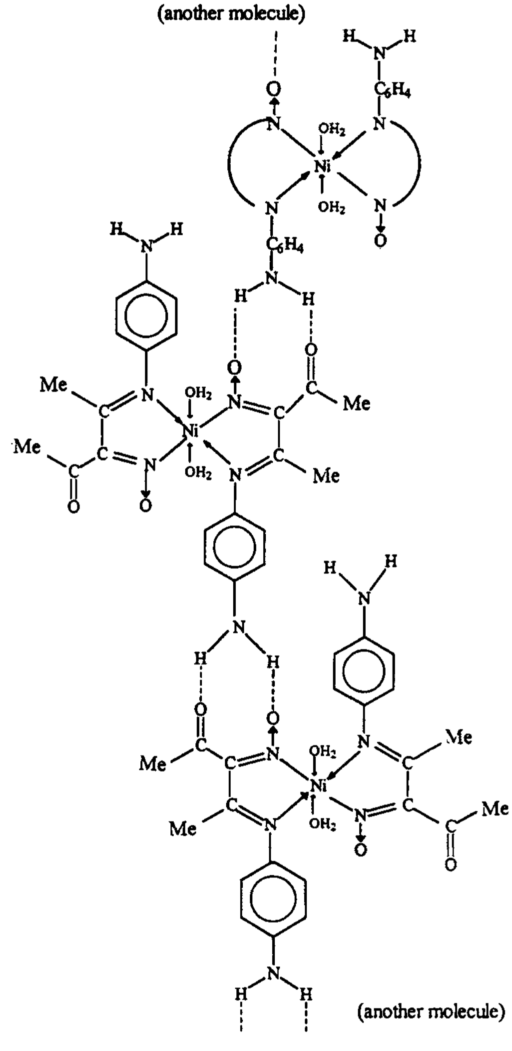

FIGURE 8 A suggested molecular association of the dark brown complex (3).

stabilization energy than the (NN–NN) chromophore. This is at variance with the known higher field of the latter chromophore over the chelate ring of the (NO) chromophore (six-membered chelate ring) as result of the peripheral bridges. This finding is compatible with the differences in the *d–d* transition bands of the associated complex (**3**) between the solid state and solution spectra (Table II). Furthermore, the spectrum of the latter complex was noticeably different from that of the molecular complex (**2**). Therefore

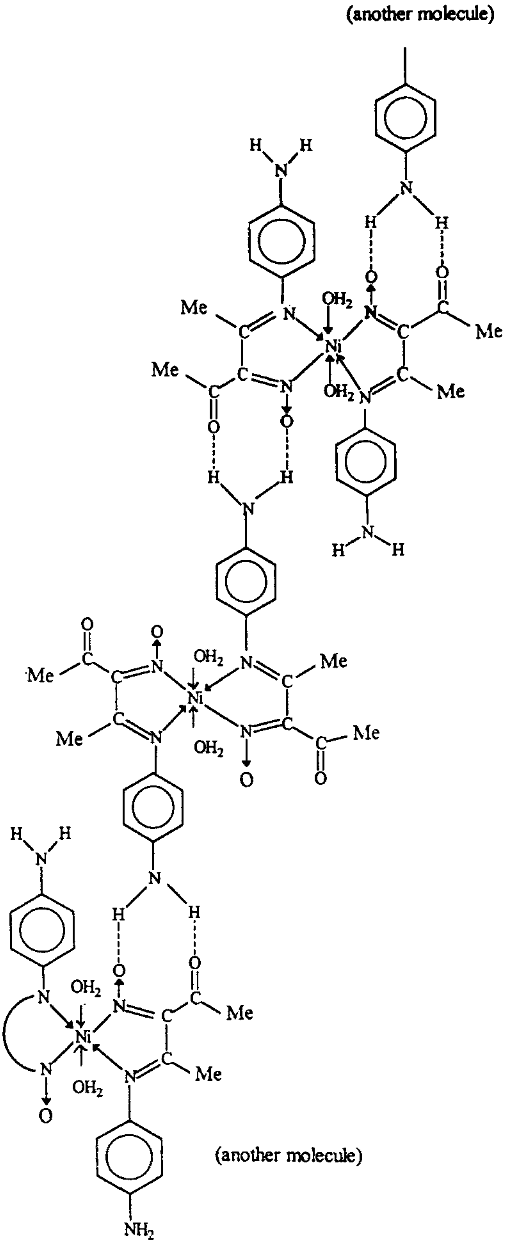

FIGURE 9 Another suggested structure of the dark brown complex (**3**).

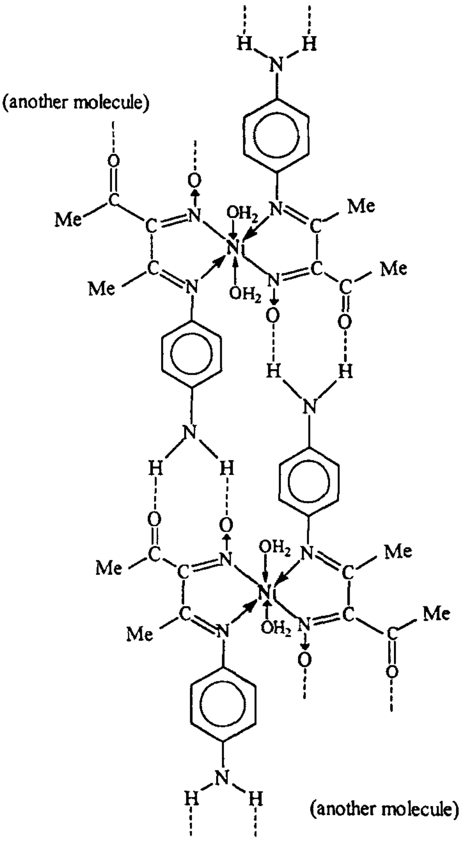

FIGURE 10 Ruled out structure for complex (3).

the supramolecular structure of complex (3) takes place *via* bridging the intermolecular hydrogen bonding and the metal ion by the aromatic Schiff-base moiety.

The reactions, of complex (2) with nickel(II) acetate are compared with those of complex (3) using the 1 : 1 or 1 : 2 molar ratios. The reaction of complex (2) with nickel(II) acetate (1 : 1 molar ratio) led to formation of complex (4) with a self-assembly structure (Figure 12). A similar structure is suggested for complexes (11), (15) and (19) of the cobalt(II), copper(II) and zinc(II) acetates, respectively. Coordination of the amino group to the metal ion[10] in the self-assembly structure is shown by a shift of the ν(NH) in complex (2) to lower frequency. This evidence also pertains to complexes (5)–(19). The ν_{as} vibration of the carboxylate was detected at the expected

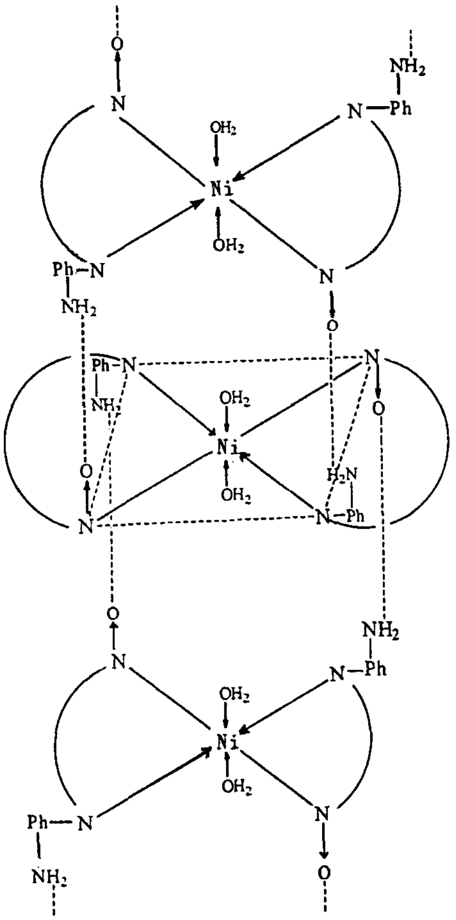

FIGURE 11 Ruled out layer structure for complex (3).

TABLE IV The effect of the peripheral moiety (R) of the equatorial plane of the ligand on the exerted ligand field for the nickel(II) complexes of vicinal oxime–imine ligands (Figure 3)

(R) *Moiety* (*Figure* 3)	*Coordinated chromophore of ligands*	*Chelate isomerism*	μ_{eff} (B.M.)	*Suggested structure*
-NH	(NO–NN)	Operative	Diamagnetic	Square-planar
Ethanolamine	(NO–NN)	Operative	Diamagnetic	Square-planar
o-Hydroxy aniline	(NN–NN)	Not operative	3.12	Octahedral
p-Hydroxy aniline	(NN–NN)	Not operative	3.08	Octahedral
Aniline	(NN–NN)	Not operative	2.81	Tetrahedral
One chelate ring aniline, the other -NH	(NO–NN)	Operative	Diamagnetic	Square-planar
p-Amino aniline	(NN–NN)	Not operative	2.67	Octahedral

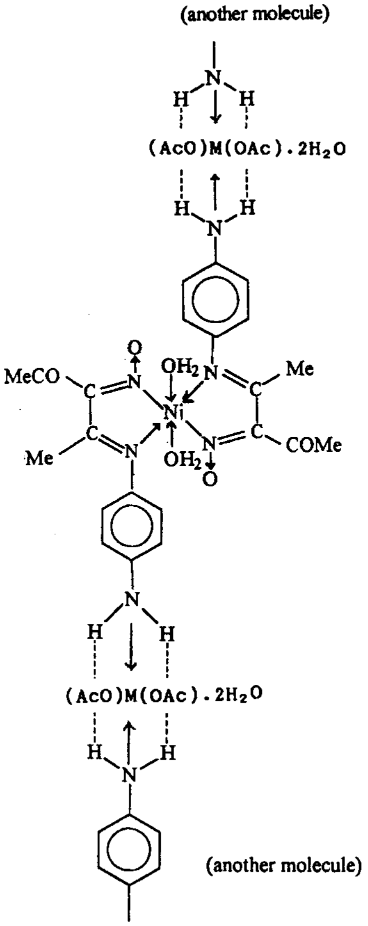

FIGURE 12 Self-assembly structure of complexes (**4**), (**11**), (**15**) and (**19**) with M = divalent nickel, cobalt, copper and zinc, respectively.

location of 1560 and 1550 cm^{-1} of the probably monodentate acetate.[11] The electronic spectrum of complex (**4**) is identical with that of the octahedral complex (**2**) (Table II) indicating that both metal ions are octahedral high-spin (d^8). The magnetic moment of the complex was 4.27 B.M., slightly higher than the calculated[12] value of 4.00 B.M. (Table III) obtained by adding the paramagnetic susceptibilities corresponding to the spin-only value of two high-spin nickel(II) ions. The higher value is ascribed to the orbital contribution to the magnetic moment.[12,13]

The 1 : 2 reaction of complex (**2**) with nickel(II) acetate produced the trinuclear complex (**5**). The same trinuclear nickel(II) complex was also

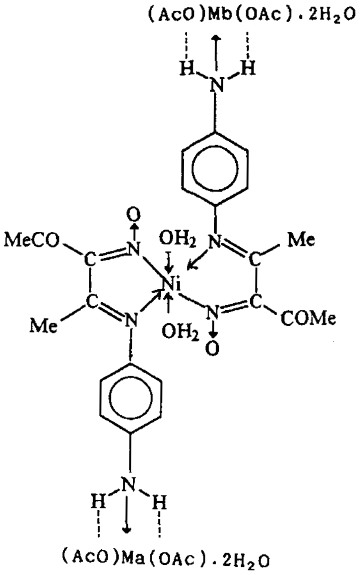

FIGURE 13 Terminated structure of complexes (**5**), (**9**), (**10**), (**12**)–(**14**) and (**16**)–(**18**); for Ma = Ni and Mb = Ni, Co or Cu, complexes (**5**), (**9**) and (**10**), respectively; for Ma = Co and Mb = Ni, Co or Cu, complexes (**12**), (**13**) and (**14**), respectively; and for Ma = Cu and Mb = Ni, Co or Cu, complexes (**16**), (**17**) and (**18**), respectively.

obtained from the 1 : 1 reaction of the dinuclear complex (**4**) with nickel(II) acetate. It is of interest to compare the dinuclear complex (**4**) and the trinuclear complex (**5**) with the comparable complexes (**6**) and (**7**) obtained from the dark brown complex (**3**). The vibrational spectra of the green complexes (**4**) and (**5**) and the dark brown complexes (**6**) and (**7**) are identical for ν(OH), ν(NH), split ν(C=O) and single ν(N–O) vibrations (Table II; see Figure 12 for complex (**4**), Figure 13 for complex (**5**), Figures 14 and 15 for complex (**6**) and Figure 16 for complex (**7**)). It is assumed that the trinuclear complex (**7**) is derived from dinuclear complex (**6**) by rotation around the single bond of the Schiff-base bridge$=N-C_6H_4-NH_2$ (Figure 8 anticlockwise; Figure 9 clockwise) or by intermolecular association after coordination of the second nickel(II) acetate. The magnetic moments of the trinuclear complexes (**5**) and (**7**) are 5.42 and 4.72 B.M., respectively (compared with the calculated value of 4.90 B.M., Table III) whereas those of the dinuclear complexes (**4**) and (**6**) are 4.27 and 4.04 B.M., respectively (compared with the calculated value of 4.00 B.M.). It is concluded, therefore, that the exchange pathway and the extent of the overlap of the magnetic orbitals are not identical in these green and dark brown complexes.

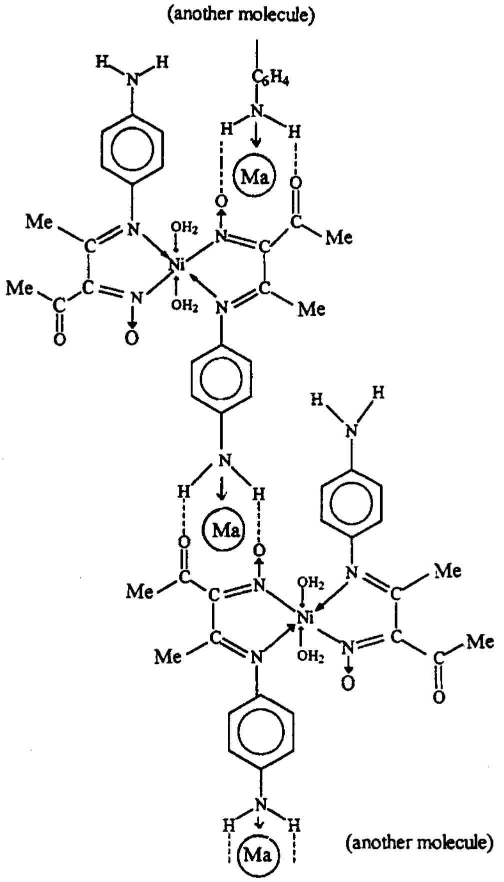

FIGURE 14 A suggested structure of complex (6), Ma = $Ni(OAc)_2 \cdot 2H_2O$.

This observation is compatible with the suggested structure of both complexes (**5**) (Figure 13) and (**7**) (Figure 16) whereby the continuous array structure of complex (**7**) allows for more significant magnetic exchange than for the terminated structure of complex (**5**). The latter structure is also suggested for the trinuclear complexes (**9**), (**10**), (**12**)–(**14**) and (**16**)–(**18**).

Stronger hydrogen bonding of complex (**7**) constrains the bridging group. The strong antiferromagnetic interaction is ascribed to the relative orientation of the magnetic orbital and the delocalization required to produce an effective bridge. In this case both the orientation and delocalization of the magnetic orbitals favor overlap and consequently the antiferromagnetic interaction. Both the σ and π orbitals of the bridging moiety contribute to

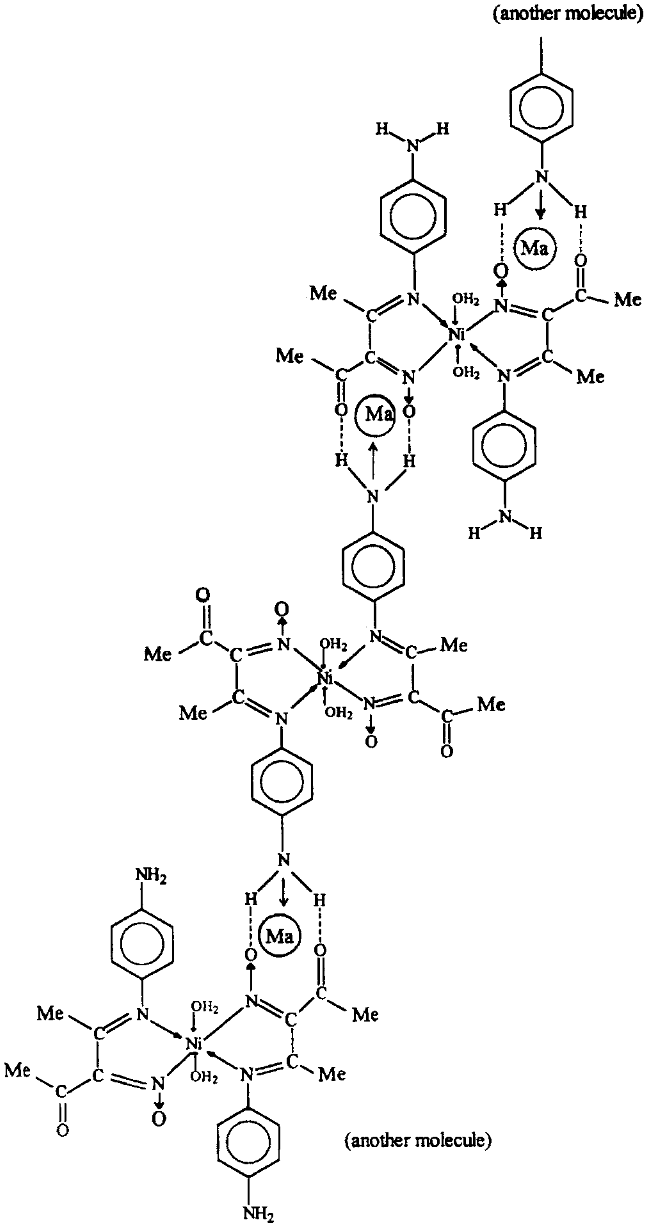

FIGURE 15 Another suggested structure of complex (6), Ma = $Ni(OAc)_2 \cdot 2H_2O$.

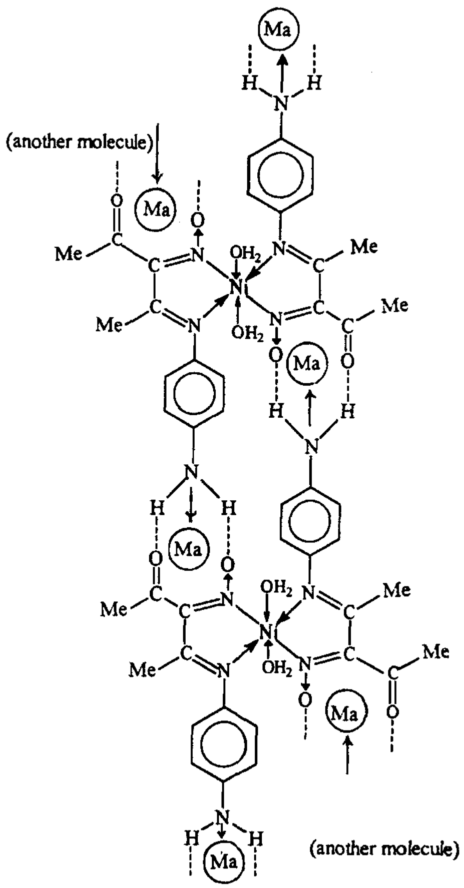

FIGURE 16 Suggested structure of complex (**7**), Ma = $Ni(OAc)_2 \cdot 2H_2O$.

the efficiency of the exchange interaction which is influenced by the strength of the hydrogen bonding of the amino group with the anion of the peripheral metal ion. This is shown by the magnetic moment of the nickel(II) chloride analogue (complex (**8**); 4.83 B.M.) compared with complex (**5**) (5.42 B.M.). The former complex has a significantly lower magnetic moment apparently as a result of the strength of hydrogen bonding involving the chloride ion (Figure 17) compared with the acetate anion of complex (**5**).

Effective bridging between two paramagnetic centers occurs *via* m-xylylene,[14] Schiff bases of aromatic diamines[15] and pyridazine heterocycles.[16] Oximato complexes of transition metal ions were also investigated in this connection.[16] Antiferromagnetic exchange interactions between

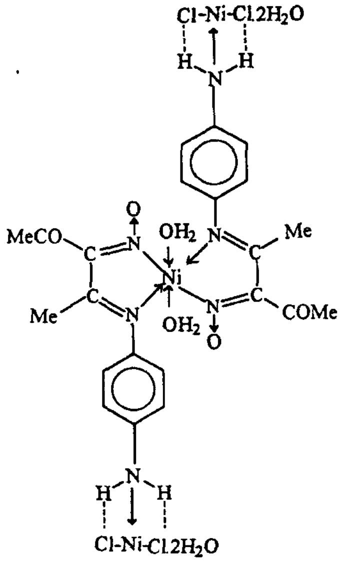

FIGURE 17 Suggested structure of complex (**8**).

the adjacent metal centers have been demonstrated in some of these complexes.[17-23] The best known examples are the dinuclear copper(II) complexes.[17-23] Some points may be made for the studied systems: (a) The net antiferromagnetic interactions decreased[12,24] in some homodinuclear complexes as the metal ion was changed in the order Cu(II), Ni(II), Co(II), Fe(II) and Mn(II). In this case the variation in the antiferromagnetism reflects the changing number of unpaired electrons and the associated pathways from one complex to another.[12,24] (b) Most of the investigated ligands are those of the binucleating type which possess two inequivalent coordination sites[25,26] whereby one metal ion has a N_2O_2 coordination site and the other a O_4 site. Such coordination site inequalities could dominate the overall exchange interaction. (c) Mixed metal complexes of binucleating ligands with two equivalent coordination sites have also been reported.[12] Taking these points into consideration, the following experimental designs were attempted: (i) The dinuclear complex (**4**) was treated with either cobalt(II) acetate or copper(II) acetate (1 : 1 molar ratio) to produce the heteronuclear complexes (**9**) and (**10**) (Figure 4). (ii) The 1 : 1 molar ratio reaction of complex (**2**) with cobalt(II) acetate produced the heterodinuclear complex (**11**) whose reaction with either nickel(II) acetate or copper(II) acetate led to formation of the heterotrinuclear complexes (**12**) and (**14**), respectively. The latter complex contains three different metal ions. The heterotrinuclear complex (**13**) was obtained from the 1 : 2 reaction of complex (**2**) with cobalt(II) acetate (Figure 5). (iii) The 1 : 1 reaction of complex (**2**) with copper(II) acetate produced the heterodinuclear complex (**15**) whose 1 : 1 reaction with either nickel(II) acetate or cobalt(II) acetate led to complexes (**16**) and (**17**), respectively (Figure 6). Complex (**18**) was obtained from the 1 : 2 reaction of complex (**2**) with copper(II) acetate. (iv) Complex (**19**) was obtained from either the 1 : 1 or 1 : 2 reaction of complex (**2**) with zinc(II) acetate (Figure 6).

The vibrational evidence detailed above for complex (**4**) regarding the chelate ring, ν_{as} of the carboxylate and the coordination of the amino group to the peripheral metal ion (Table I) are applicable for all complexes (**5**)–(**19**). A weak band at $1180\,\mathrm{cm}^{-1}$ in the case of the cobalt(II) complexes (**9**), (**12**)–(**14**) and (**17**) (which was ascribed to the ν(N–O) of cobalt(II) complexes of a vicinal oxime–imine ligand) indicates partial transmetallion of added cobalt(II) ion with the chelated nickel(II) ion. The electronic spectra of the metal complexes are a composite of that of the octahedral nickel(II) structure of the precursor complex (**2**) and that of the added metal acetate.[27] The magnetic moments of complexes (**9**), (**12**)–(**14**) and (**17**) are higher than the calculated values (Table III) obtained by adding the paramagnetic susceptibilities corresponding to spin-only magnetic moment of the high-spin metal ions.[12] This arises from either a possible ferromagnetic interaction in those cases similar to those reported[12] for manganese(II) or to an orbital contribution to the magnetic moment[28] by the high-spin cobalt(II). An effective antiferromagnetism was detected for copper(II) acetate addition to complex (**2**) (complexes (**15**) and (**18**)) whereby the observed magnetic moments were noticeably lower than the calculated[12] values (Table III). This observation accords with the reported trend of antiferromagnetism in which copper(II) produced the highest effect.[12] Complex (**19**) was obtained from either the 1 : 1 or 1 : 2 molar ratio reaction of complex (**2**) with zinc(II) acetate. This complex illustrates the stability of the self-assembly product of the 1 : 1 molar ratio reaction (Figure 12) in the presence of zinc(II) ion.

Acknowledgments

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