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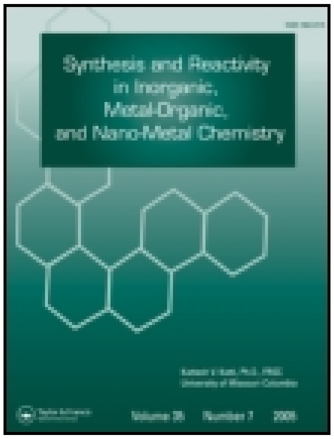

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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Synthesis, Magnetic, and Spectral Studies of Mixed-Ligand Complexes of Nickel(II) Involving Some Chelating 4-Oximino-2-pyrazoline-5-one Derivatives

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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Synthesis, Magnetic, and Spectral Studies of Mixed-Ligand Complexes of Nickel(II) Involving Some Chelating 4-Oximino-2-pyrazoline-5-one Derivatives

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ABSTRACT

The synthesis, magnetic and spectral studies of mixed-ligand complexes of nickel(II) derived from chelating 4-oximino-2-pyrazoline-5-one derivatives, *viz.*, 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazoline-5-one (bomppH), 4-acetyloxime-3-methyl-1-phenyl-2-pyrazoline-5-one (aomppH) and 3-methyl-1-phenyl-4-propionyloxime-2-pyrazoline-5-one (mppopH), and certain heterocyclic ligands , viz., 3-methyl-1-phenyl-2-pyrazoline-5-one (mpp), 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (adpp), 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (dpp), 2,3-dimethyl-4-methylaminomethanesulfonate sodium-1-phenyl-3-pyrazoline-5-one (dmspp), benzimidazole (bzl) and benzothiazole (bzt) are

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described. The complexes, which have been characterized by conductance measurements, electron spin resonance, magnetic measurements, thermogravimetric analyses, electronic and infrared spectral studies have the general formulas $[Ni(A-A)_2(L)_2]$ and $[Ni(A-A)_2(L-L)]$ where, $(A-A)H$ = bomppH, aomppH, or mppopH, L = mpp, dpp, bzl or bzt and L–L = adpp or dmspp. All the complexes were found to be non-electrolytes and octahedral structures have been proposed for them.

Key Words: Mixed-ligand Ni(II) chelates; Spin free octahedral symmetry; 4-Oximino-2-pyrazoline-5-one derivatives; Nuclear hyperfine coupling; *trans*-Octahedral structure; *cis*-Octahedral structure.

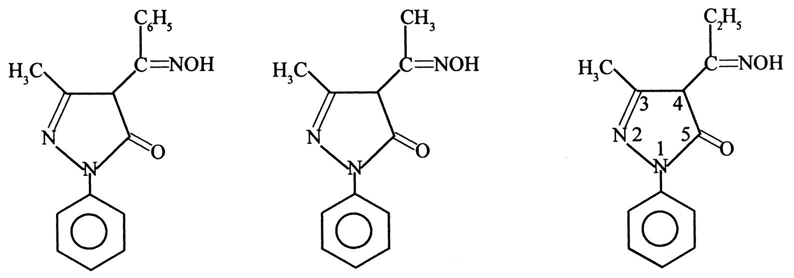
INTRODUCTION

In continuation of our interest to synthesize and characterize novel metal complexes involving chelating molecules,[1] our studies have been extended so as to observe the ligational behaviour of chelating 4-oximino-2-pyrazoline-5-one derivatives in the presence of some 5-pyrazolones, benzothiazole or benzimidazole, towards nickel(II).

The chelating behaviour of 4-oximino-2-pyrazoline-5-ones,[2–4] viz., 4-oximino-1-phenyl-3-methyl-2-pyrazoline-5-one, 4-oximino-3-methyl-2-pyrazoline-5-one, 4-oximino-3-phenyl-2-pyrazoline-5-one, 4-oximino-1,3-diphenyl-3-methyl-2-pyrazoline-5-one is well established. They coordinate through the cyclic carbonyl oxygen and oximino nitrogen, thus behaving as bidentate O, N donors.

Substituted pyrazolones have been well established as mono-, bi and tridentate ligands.[5] The ligational behaviours of benzothiazole, benzimidazole and their derivatives have been reported earlier from our Coordination Chemistry Laboratory[6–8] by Maurya et al. and also by others.[9–11]

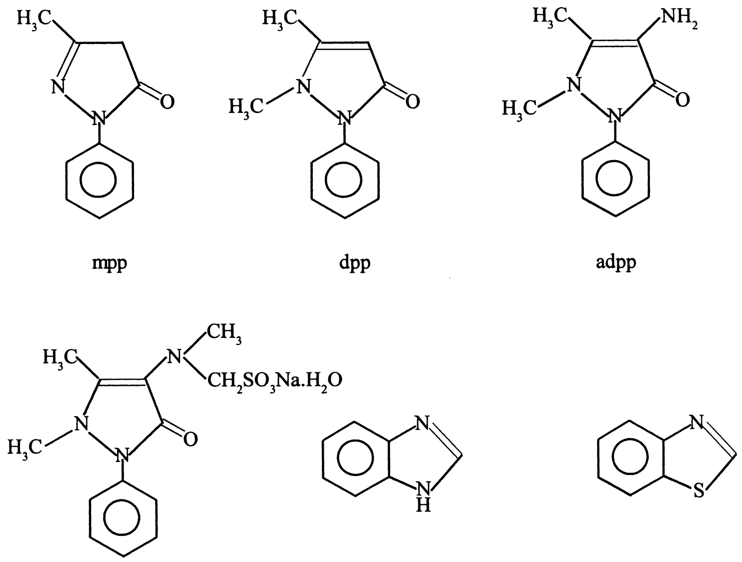
Monomeric complexes of nickel(II) cobalt(II) and chromium(III) with 4-oximino-1-phenyl-3-methyl-2-pyrazoline-5-one, 4-oximino-3-methyl-2-pyrazoline-5-one, 4-oximino-3-phenyl-2-pyrazoline-5-one and 4-oximino-1,3-diphenyl-2-pyrazoline-5-one have been prepared and characterized by Shah et al.[2] The same group of workers has carried out structural studies on oxovanadium(IV), chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) chelates of 4-formyloxime-3-methyl-1-phenyl-2-pyrazoline-5-one.[12] The chelates have been isolated in the solid state and characterized as monomers by different physico-chemical studies. Structural studies[3] on Fe(II), Mn(II), Zn(II), VO(IV) and UO_2(VI) complexes of some 4-oximino-2-pyrazoline-5-ones have also been carried out by the same group of workers. Pyridine and 3-picoline adducts of Ni(II) and Zn(II) chelates with some 4-oximino-2-pyrazoline-5-ones (mixed-ligand complexes) have been



bomppH aomppH mppopH

Figure 1. Structures of oximes.

synthesized and characterized by the same group of workers,[4] and they are suggested to have *trans*-octahedral structures with axial pyridine/3-picoline. However, there is no report on the synthesis and characterization fo mixed-ligand complexes of Ni(II) involving the chelating molecules 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazoline-5-one (bomppH), 4-acetyloxime-3-methyl-1-phenyl-2-pyrazoline-5-one (aomppH) and 3-methyl-1-phenyl-4-



mpp dpp adpp

dmspp bzl bzt

Figure 2. Structures of ligands.

propionyloxime-2-pyrazoline-5-one (mppopH). It was, therefore, thought of interest to synthesize mixed-ligand complexes of Ni(II) with the aforementioned oxime derivatives along with 3-methyl-1-phenyl-2-pyrazoline-5-one (mpp), 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (adpp), 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (dpp),2,3-dimethyl-4-methylamino-methanesulphonate sodium monohydrate 1-phenyl-3-pyrazoline-5-one (dmspp), benzimidazole (bzl) and benzothiazole (bzt). The structures of the oxime derivatives and other ligands used in the present study are shown in Figures 1 and 2, respectively.

EXPERIMENTAL

Materials

Nickel(II) chloride hexahydrate (Polypharm Pvt. Ltd., Bombay), acetyl chloride (B. D. H. Chemicals, Bombay), benzoyl chloride (Robert Johnson, India), propionyl chloride, 3-methyl-1-phenyl-2-pyrazoline-5-one (Kemphasol, Bombay), hydroxylamine hydrochloride (Loba Chemie, Bombay), 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (B. D. H. Chemicals, England), 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (Aldrich Chemicals Company, U. S. A.), 2,3-dimethylaminomethanesulphonate sodium monohydrate-1-phenyl-3-pyrazoline-5-one (Indian Drugs and Pharmaceuticals Ltd., Hyderabad), benzimidazole (Wilson Laboratories, Bombay), benzothiazole (E. Merck, Germany) were used as such. All other chemicals were of A. R. grade. 4-Benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one (bmpp), 4-acetyl-3-methyl-1-phenyl-2-pyrazoline-5-one (ampp) and 3-methyl-1-phenyl-4-propionyl-2-pyrazoline-5-one (mppp) were prepared by the method reported by Jensen.[13]

Preparation of Oxime Derivatives of bmpp, ampp, and mppp

These oximes were prepared by following the general method[14] given below: A solution of hydroxylamine hydrochloride (5 mmol, 0.347 g) and sodium hydroxide (5 mmol, 0.200 g) in 60 mL aqueous/ ethanol (1:1) were added to a solution of bmpp, ampp or mppp (5 mmol) in 40 mL ethanol. The mixture was refluxed for two hours. On cooling, a crystalline product was obtained which was filtered by suction, washed several times with water and finally with ethanol. The oxime of bmpp was precipitated by pouring the reaction mixture in excess (150 mL) of distilled water. Melting point (colour): bmppoxime 155 °C (brown), amppoxime 170 °C (yellowish brown) and mpppoxime 160 °C (light brown)), and yields are 70–75%.

Preparation of Mixed-Ligand Complexes

The complexes were prepared by refluxing the combined solutions of aqueous (5 mL) nickel(II) chloride hexahydrate (10 mmol, 2.377 g), ethanolic (~ 25 mL) bomppH (20 mmol, 5.860 g), aomppH (20 mmol, 4.620 g) or mppopH (20 mmol, 4.900 g), and ethanolic (~ 20 mL) mpp (20 mmol, 3.480 g), dpp (20 mmol, 3.76 g), adpp (10 mmol, 2.030 g), dmspp (10 mmol, 3.510), bzl (20 mmol, 2.360 g) or bzt (20 mmol, 2.700 g) for 30–60 minutes. During this time coloured crystals were precipitated. They were filtered by suction, washed several times with ethanol and dried in vacuo.

Analyses

Carbon, hydrogen and nitrogen were determined microanalytically at the Central Salt and Marine Chemicals Research Institute, Bhavnagar, India. The nickel content in each of the complexes was determined gravimetrically as nickel dimethylglyoximate.[15]

Physical Methods

Solid state IR spectra were recorded in Nujol mulls on a Perkin-Elmer model 1620 FI-IR spectrophotometer at the National Chemical Laboratory, Pune, India. ESR spectra were recorded on an EPR-112 spectrometer using powdered samples at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras. Electronic spectra of the complexes were recorded on a Shimadzu model UV-160 spectrophotometer. Magnetic measurements were performed by Gouy's method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant at the Central Salt and Marine Chemicals Research Institute, Bhavnagar. Conductance measurements were performed at room temperature in dimethylformamide using a Toshniwal conductivity bridge and dip-type cell with a smooth platinum electrode of cell constant 1.3. Thermogravimetric cruves were recorded by heating the sample at the rate of 15 °C min^{-1}, up to 740 °C on a thermal analyzer at the Regional Sophisticated Instrumentation Centre, Nagpur.

RESULTS AND DISCUSSION

The Ni(II) chelates were synthesized according to the following equations:

$$\text{NiCl}_2\cdot 6\text{H}_2\text{O} + 2(\text{bomppH}) + 2\text{L} \rightarrow [\text{Ni}(\text{bompp})_2(\text{L})_2] + 2\text{HCl} + 6\text{H}_2\text{O}$$

Table 1. Analytical data and important IR spectral bands (cm^{-1}) of the synthesized complexes.

Sr. no.	Compound (empirical formula) (mol. wt.)	Found (calc., %) C	H	N	Ni	ν(C=O) (cyclic) oxime	ν(C=N) cyclic	ν(C=O) pyrazolone	ν(C=N) oxime	ν(N–O) oxime
–	bomppH ($C_{17}H_{15}N_3O_2$) (293)	69.71 (69.62)	5.17 (5.12)	14.28 (14.33)	–	1690 s	1605 s	–	1585 s	1035 m
(**1**)	[Ni(bompp)$_2$(mpp)$_2$] ($C_{54}H_{48}NiN_{10}O_6$) (990.69)	65.69 (65.41)	4.82 (4.84)	14.20 (14.13)	5.85 (5.92)	1633 s	1600 s	1537 s	1516 s	1072 m
–	aomppH ($C_{12}H_{13}N_3O_2$) (231)	62.38 (62.34)	5.52 (5.63)	18.25 (18.18)	–	1710 s	1605 s	–	1590 s	1045 m
(**2**)	[Ni(aompp)$_2$(mpp)$_2$] ($C_{44}H_{44}NiN_{10}O_6$) (886.69)	60.73 (60.92)	5.05 (5.07)	16.85 (16.15)	6.72 (6.77)	1621 s	1592 s	1551 s	1500 s	1092 m
–	mppopH ($C_{13}H_{15}N_3O_2$) (245)	63.58 (63.67)	4.10 (6.12)	17.20 (17.14)	–	1700 s	1608 s	–	1586 s	1030 m
(**3**)	[Ni(mppop)$_2$(mpp)$_2$] ($C_{46}H_{48}NiN_{10}O_6$) (894.69)	61.75 (61.69)	5.30 (5.36)	15.25 (15.64)	6.50 (6.56)	1621 s	1592 s	1551 s	1462 s	1061 m
(**4**)	[Ni(bompp)$_2$(dpp)$_2$] ($C_{56}H_{52}NiN_{10}O_6$) (1018.69)	66.24 (65.96)	5.12 (5.10)	14.12 (13.74)	5.80 (5.76)	1628 s	1598 s	1535 s	1514 s	1089 m
(**5**)	[Ni(bompp)$_2$(bzl)$_2$] ($C_{48}H_{40}NiN_{10}O_4$) (878.69)	65.50 (65.55)	4.50 (4.55)	15.90 (15.93)	6.65 (6.68)	1628 s	1600 s	–	1513 s	1090 m
(**6**)	[Ni(bompp)$_2$(bzt)$_2$] ($C_{48}H_{38}NiN_8O_4S_2$) (912.69)	63.05 (63.11)	4.20 (4.16)	12.75 (12.27)	6.45 (6.43)	1650 s	1616 s (oxime)	–	1514 s	1072 m
(**7**)	[Ni(bompp)$_2$(adpp)] ($C_{45}H_{41}NiN_9O_5$) (845.69)	63.70 (63.85)	4.80 (4.85)	14.85 (14.89)	6.90 (6.94)	1628 s	1598 s (oxime)	1538 s	1514 s	1069 m
(**8**)	[Ni(bompp)$_2$(dmspp)] ($C_{47}H_{46}NiN_9O_9NaS$) (993.69)	56.20 (56.75)	4.50 (4.63)	12.65 (12.68)	5.90 (5.91)	1628 s	1599 s (oxime)	1537 s	1514 s	1072 m

Where L = mpp (**1**), dpp (**4**), bzl (**5**) or bzt (**6**).

$$\mathrm{NiCl_2{\cdot}6H_2O + 2(A\text{-}A)H + 2mpp}$$
$$\rightarrow \mathrm{[Ni(A\text{-}A)_2(mpp)_2] + 2HCl + 6H_2O}$$

Where (A-A)H = aomppH (**2**) or mppopH (**3**)

$$\mathrm{NiCl_2{\cdot}6H_2O + 2bomppH + L\text{-}L}$$
$$\rightarrow \mathrm{[Ni(bompp)_2(L\text{-}L)] + 2HCl + 6H_2O}$$

Where L–L = adpp (**7**) or dmspp (**8**).

The resulting products are non-hygroscopic, coloured solids. The elemental analyses of these complexes are given in Table 1, while the colours, decomposition temperatures and percent yields are given in Table 2. These compounds were characterized on the basis of conductance and magnetic measurements, thermogravimetric analysis, electron spin resonance, infrared and electronic spectral studies as described below in detail.

Conductance Measurements

The observed molar conductances of these complexes in 10^{-3} molar dimethylformamide solutions are found in the range 5–39 $\mathrm{ohm^{-1}}$ $\mathrm{cm^2mol^{-1}}$. These data, which are comparable to our previous results,[16] indicate the non-electrolytic nature of these complexes. Such a non-zero molar conductance value for each of the complex in the present study is most probably due to the strong donor capacity of dimethylformamide which may lead to the displacement of anionic ligands and change of electrolyte[17] type.

Electron Spin Resonance Spectra

Room temperature X-band ESR spectra of two representative compounds, $\mathrm{[Ni(bompp)_2(bzl)_2]}$ (**5**) and $\mathrm{[Ni(bompp)_2(adpp)]}$ (**7**) (Figures 3 and 4), were recorded on powdered samples using a microwave frequency of 9.45–9.47 GHz with the field set at 3300 G and the scan range of 2.0 KG. Both parallel and perpendicular features of ^{61}Ni were resolved in both spectra, which are characteristic of axial symmetry.[18] Nuclear hyperfine coupling is observed in the g perpendicular regions with four components clearly resolved. The observed $g\perp$ and $g\|$ values are given in Table 2. The deviation of g values from the free electron value (2.0036) may be due to angular momentum contributions[19] in the complexes.

Table 2. Some physical properties and yields (%) of the synthesized complexes.

Sr. no.	Compound	Decomp. temp. (°C)	Λ_M ($\mathrm{Ohm^{-1}\ cm^2 mol^{-1}}$)	μ_{eff} (B. M.)	Yield (%)	g	Color
(**1**)	$[\mathrm{Ni(bompp)_2(mpp)_2}]$	155	15	3.08	50	–	Pale buff
(**2**)	$[\mathrm{Ni(aompp)_2(mpp)_2}]$	170	6	3.23	55	–	Mustard
(**3**)	$[\mathrm{Ni(mppop)_2(mpp)_2}]$	160	5	3.18	52	–	Mustard
(**4**)	$[\mathrm{Ni(bompp)_2(dpp)_2}]$	130	21	3.15	50	–	Yellowish green
(**5**)	$[\mathrm{Ni(bompp)_2(bzl)_2}]$	150	36	3.16	55	–	Shiny pale green
(**6**)	$[\mathrm{Ni(bompp)_2(bzt)_2}]$	150	33	3.05	52	$g_\perp = 2.089$, $g_\parallel = 2.0012$, $g_{av} = 2.030$	Shiny yellowish green
(**7**)	$[\mathrm{Ni(bompp)_2(adpp)}]$	250	24	3.10	58	$g_\perp = 2.13$, $g_\parallel = 2.0047$, $g_{av} = 2.04$	Mist grey
(**8**)	$[\mathrm{Ni(bompp)_2(dmspp)}]$	275	39	3.21	56	–	Shiny yellowish green

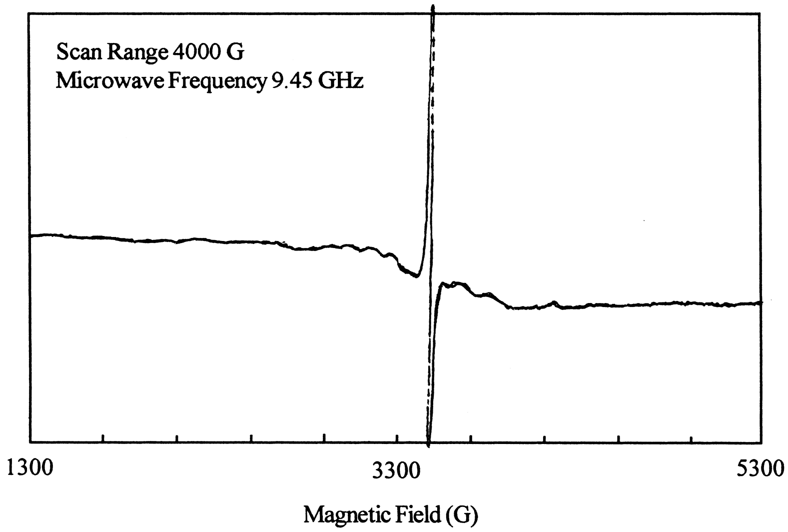


Figure 3. ESR spectrum of [Ni(bompp)$_2$(bzl)$_2$] (**5**).

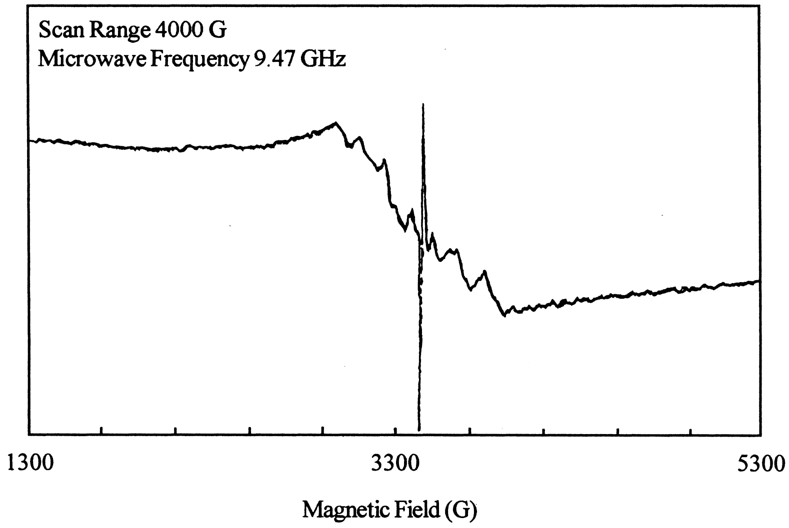


Figure 4. ESR spectrum of [Ni(bompp)$_2$(adpp)] (**7**).

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Magnetic Measurements

The observed magnetic moments of these mixed-ligand complexes are given in Table 2. The effective magnetic moments, 3.05–3.23 B.M., support the presence of two unpaired electrons. These results suggest a spin-free octahedral[20] symmetry for Ni(II) ion. The possibility of spin-paired octahedral complexes is ruled out as the d^8 arrangement in a very strong octahedral fields may result in tetragonal[21] distortion, making the complexes diamagnetic. The square-planar geometry may be viewed as resulting from the strong tetragonal elongation of an octahedral geometry. Again, this geometry leads to diamagnetism. In the tetrahedral geometry, the ground state term has a built-in orbital contribution and the van Vleck equation[22] predicts $\mu \sim 4.0$ B. M. In reality, regular tetrahedron complexes exhibit $\mu \sim$ 3.6–4.0 B. M. This again rules out the possibility of tetrahedral complexes.

Thermogravimetric Analysis

The thermogravimetric analysis of a representative complex [Ni(bompp)$_2$(dpp)$_2$] (Figure 5) was carried out in the temperature range

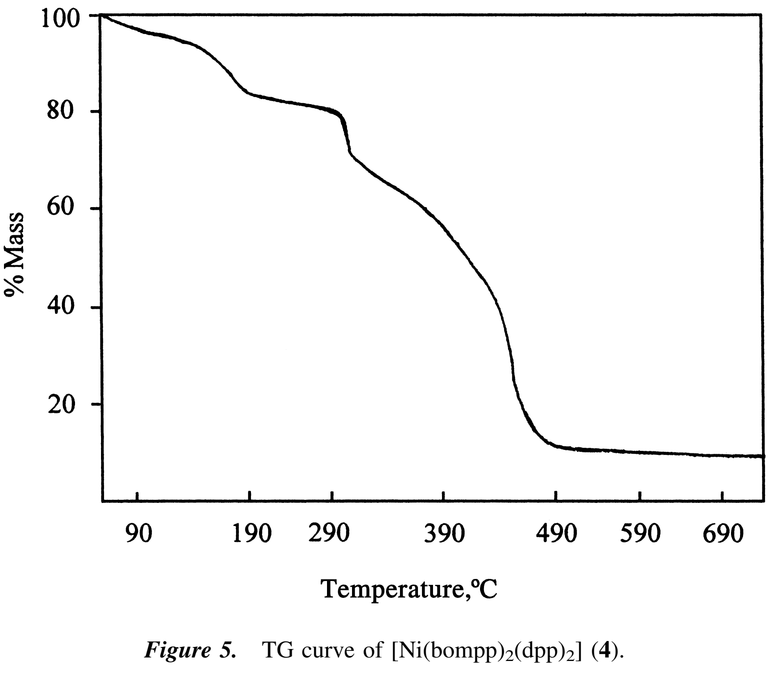

Figure 5. TG curve of [Ni(bompp)$_2$(dpp)$_2$] (**4**).

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from room temperature to 700 °C. It shows a mass loss (observed 37%, theoretical 36.95%) at 340 °C corresponding to the loss of two molecules of dpp. The mass losses observed before this temperature could not be correlated. The second weight loss in the temperature range 340–500 °C (observed 51.4%, theoretical 53%) corresponds to the elimination of two molecules of bompp. The final residue to be NiO. Thus, the overall thermogravimetric results support the conclusion derived from the infrared spectral studies given below.

Infrared Spectral Studies

The important IR spectral bands and their tentative assignments are presented in Table 1. The IR spectra of the three oximino derivatives (bomppH, aomppH and mppopH) have a strong band at 1690–1710 cm^{-1} which is assigned to ν(C=O) (cyclic). In the spectra of all the complexes, this band is shifted to the lower frequency side and is observed at 1621–1650 cm^{-1}, indicating the coordination of the cyclic carbonyl oxygen of the oxime ligands to the metal ion. This is in agreement with the results reported elsewhere.[2] The ligands mpp, adpp, dpp and dmspp exhibit a strong band for ν(C=O) (cyclic carbonyl) at 1620–1650 cm^{-1}. The coordination of the respective ligand to the metal is inferred by the shifting of this band to lower wave numbers[23] and then appearing in the region 1535–1551 cm^{-1}. All the complexes display a band in the range 1592–1616 cm^{-1}, which is assigned to ν(C=N) (cyclic) of both oximino derivatives as well as of mpp. Based on our previous results[24] on pyrazolone-based ligands, it appears that this mode does not undergo any appreciable change after complexation, suggesting the reluctance of the ν(C=N) (cyclic) nitrogen of the oximino derivatives and mpp to participate in bonding. The coordination of the oximino nitrogen in all the complexes is inferred by the appearance of a strong band due to the ν(C=N) mode in the region 1462–1516 cm^{-1}. This assignment is based on previous reports of such complexes.[2–4] A medium-intensity band at 1061–1092 cm^{-1}, assignable to ν(N–O), suggests bond formation through the nitrogen of the oximino group.[2–4]

In the IR spectrum of $[Ni(bompp)_2(adpp)]$ (compound 7), the appearance of two bands at 3300 and 3200 cm^{-1} are assigned as ν_{as}(N–H) and $_{\nu s}$(N–H) for the coordinated amino nitrogen of adpp. The characteristic ν(C–N) (exocyclic) band in free dmspp is observed at 1300 cm^{-1} which undergoes a shift[25] to lower wave numbers and appears at 1265 cm^{-1} in $[Ni(bompp)_2(dmspp)]$ (compound **8**), indicating bonding of the exocyclic nitrogen of dmspp to nickel(II).

The characteristic band for coordinated tertiary nitrogen of bzl and bzt is the ν(C=N) mode, which should appear above 1600 and 1620 cm^{-1}, respectively. This band seems to be merged with the ν(C=O)(cyclic) mode of the oximino derivatives at 1628 and 1650 cm^{-1}, respectively. The imidazole-NH nitrogen and thiazole-S were found to be reluctant towards coordination.

We have concluded, using the overall IR data, that 1) oximino derivatives in all the complexes behave as mononegative bidentate ligands, 2) mpp, dpp, bzl or bzt behave as monodentate ligands and 3) adpp or dmspp behave as bidentate ligands.

Electronic Spectra

The electronic spectra of these compounds (in 10^{-3} M DMF solutions) recorded in the range 350–800 nm, display two absorption bands at 440–460 and 530–560 nm assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, respectively, in agreement with the results reported elsewhere.[26–28] This suggests an octahedral geometry around Ni(II) ion. Considering the low[29] molar extinction coefficients (10–30 L mol^{-1} cm^{-1}) of the electronic spectral bands, the possibilities of tetrahedral and square-planar geometries are ruled out. An electronic spectral band of a tetrahedral or square-planar complex has a high[29] molar extinction coefficient (~50–600 L mol^{-1} cm^{-1}). The electronic spectrum of one representative compound is shown in the Figure 6.

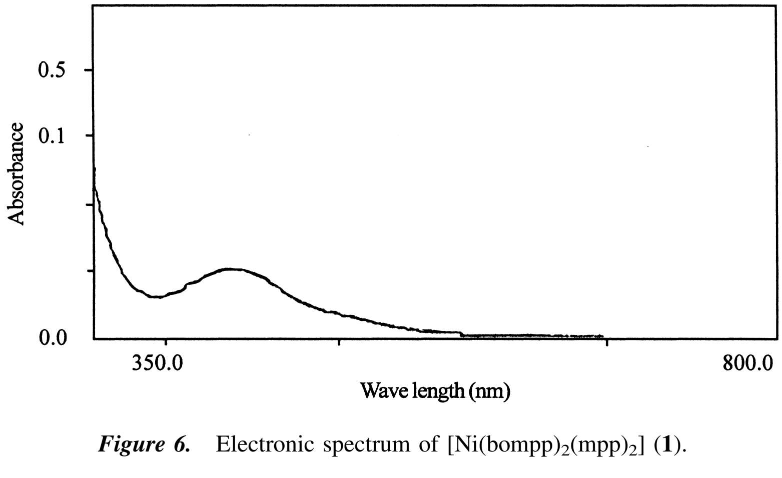
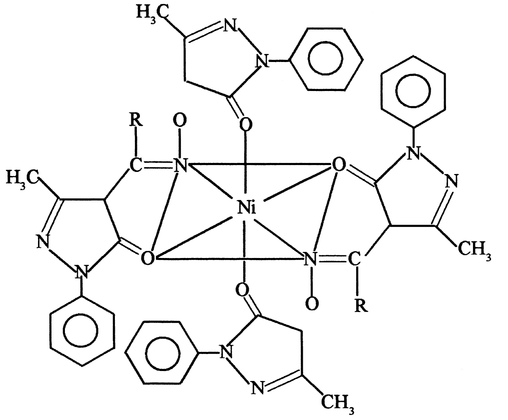


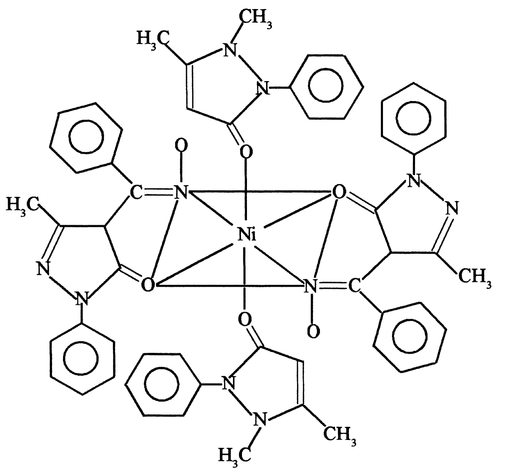
Figure 6. Electronic spectrum of $[Ni(bompp)_2(mpp)_2]$ (**1**).

CONCLUSIONS

Satisfactory analytical data as well as all the studies presented above suggest that the present complexes may be formulated as [Ni(bompp)$_2$(L)$_2$] (where L = mpp, dpp, bzl or bzt, [Ni(A-A)$_2$(mpp)$_2$] {where (A–A)H = aompp



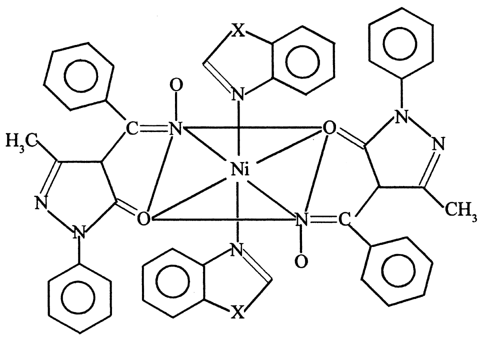
R = C_6H_5, (1)
R = CH_3, (2)
R = C_2H_5, (3)



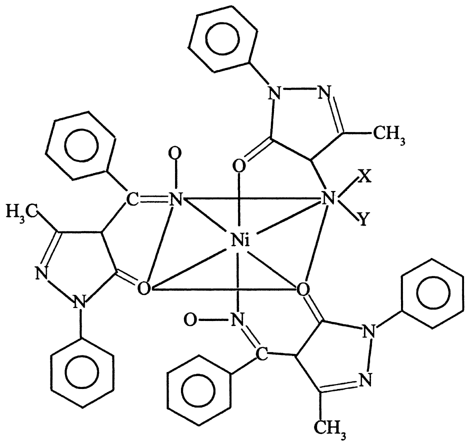
(4)

Figure 7. Proposed octahedral structure of complexes.

(*continued*)



X = NH **(5)**
X = S **(6)**



X = H, Y = H **(7)**
X = CH$_3$, Y = CH$_2$SO$_3$Na **(8)**

Figure 7. Continued.

H or mppopH} and [Ni(bompp)$_2$(L–L)] (where L–L = adpp or dmspp). Considering the well documented square-pyramidal structure of [Cu(4-Menp)$_2$(py)][30] (np = *o*-nitrosophenol, finding a natural place in the family of carbonyl oximes, py = pyridine) having the oxime nitrogen *trans* to the other oxime nitrogen by crystal structure determination, and the monomeric *trans*-octahedral structure of [Ni(4-Menp)$_2$(py)$_2$][30] with axial py, a *trans*-octahedral structure (having oxime nitrogen *trans* to oxime nitrogen) as shown in Figure 7 has been proposed for each of the complexes (**1**)–(**6**). Moreover, following the definitely known *cis*-octahedral structure of Na[Fe(Ynp)$_3$] (Y is H$_2$C=CH–C$_6$H$_4$–COO– attached to the 4-position of the np ring), where the oxime nitrogen is *trans* to carbonyl oxygen, it is reasonable to propose a similar *cis*-octahedral structures for complexes (**7**) and (**8**) as shown in Figure 7.

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