

Full Paper

## Synthesis and Spectral Investigations of Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of New Polydentate Ligands Containing a 1,8-Naphthyridine Moiety

Sreedasyam Jagannatha Swamy\*, Erra Ram Reddy, Devunuri Naga Raju and Sunkari Jyothi

Department of Chemistry, Kakatiya University, Warangal – 506 009, India; e-mails: errku2006@yahoo.co.in, naag1977@yahoo.com, jyothisri97@yahoo.co.in

\* Author to whom correspondence should be addressed; E-mail: sj\_swamy@yahoo.com; Phone: +91 870 243 8866, Fax: +91 870 243 8800

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**Abstract:** 2-(*o*-Hydroxyphenyl)-1,8-naphthyridine (**HN**), 2-(4-hydroxy-6-methylpyran-2-one-3-yl)-1,8-naphthyridine (**HMPN**) and 2-(benzimidazol-2-yl)-1,8-naphthyridine (**BN**) react with acetates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) to yield metal ion complexes of definite composition. These compounds were characterized by elemental analyses, molar conductivity, magnetic susceptibility measurements, thermal studies, IR, UV-visible, NMR and mass spectral investigations. The complexes are found to have the formulae  $[M(\mathbf{HN})_2(\text{H}_2\text{O})_2]$ ,  $[M(\mathbf{HMPN})_2(\text{H}_2\text{O})_2]$  and  $[M(\mathbf{BN})_2(\text{OAc})_2]$ , respectively.

**Keywords:** 1,8-Naphthyridine, polydentate ligands, transition metal complexes, spectral investigations of metal complexes

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### Introduction

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups [1-3] and it is multiplied manyfold when the ligands have biological importance [4,5]. As part of our research, we have developed a number of polydentate ligands containing amide groups [6-11]. 1,8-Naphthyridines constitute a group of very important

biodynamic agents whose coordination chemistry is investigated very little [12-14]. We report herein the results of our studies on chelating properties of substituted 1,8-naphthyridines, i.e., 2-(*o*-hydroxyphenyl)-1,8-naphthyridine (**HN**), 2-(4-hydroxy-6-methylpyran-2-one-3-yl)-1,8-naphthyridine (**HMPN**) and 2-(benzimidazol-2-yl)-1,8-naphthyridine (**BN**) and the characterization of their corresponding Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes.

## Results and Discussion

The complexes were prepared by heating together methanol solutions of the appropriate ligand and metal acetate. All the complexes prepared are non-hygroscopic and stable at room temperature. The complexes of **HN** and **HMPN** are insoluble in methanol, ethanol, benzene and THF, but soluble in DMSO and DMF. The characterization data are presented in Table 1. The molar conductance values of the complexes of **HN** and **HMPN** ( $10^{-3}$  M solution in DMF) are found to be in the range  $8\text{--}15\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ . These low values indicate that the complexes are non-ionic [15]. The complexes of **BN** are insoluble in common solvents and hence molar conductance could not be measured, but this very insolubility indicates that the complexes are neutral [15].

### Mass Spectra

The ligands **HN**, **HMPN** and **BN** exhibit their highest mass peaks at  $m/z$  223, 254 and 246, respectively, corresponding to the  $[M+1]^+$  ions. The conspicuous fragments in the mass spectra of all the **HN**, **HMPN**, and **BN** complexes correspond to the ions  $[M(L)_2(H_2O)_2]^{2+}$  ( $L = \text{HN}$  and **HMPN**) and  $[M(\text{BN})_2(\text{OAc})_2]^{1+}$ , respectively. Further, the interaction of the ligands with the metal ions is confirmed by the appearance of the fragments corresponding to  $[M(L)_2]^{2+}$  and  $[M(\text{BN})_2]^{1+}$ . The presence of lower mass fragments that also appeared in the spectra of the ligands substantiates the presence and coordination of the ligands to the metal ions. The analytical data presented in Table 1 confirm the formulae of the complexes of the three ligands as  $[M(\text{HN})_2(H_2O)_2]$ ,  $[M(\text{HMPN})_2(H_2O)_2]$  and  $[M(\text{BN})_2(\text{OAc})_2]$ , where  $M = \text{Mn(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$  or  $\text{Zn(II)}$  [16,17].

### Thermal analysis

The thermograms of the complexes of **HN** and **HMPN** exhibit weight losses in two different temperature regions, one in the region of  $150\text{--}250\text{ }^\circ\text{C}$  and the other between  $260$  and  $800\text{ }^\circ\text{C}$ . Endothermic peaks were observed in the low temperature region of  $150\text{--}250\text{ }^\circ\text{C}$  in the DTA thermograms of all complexes, indicating that there are water molecules in the complexes. The loss of matter in this temperature region corresponds to two water molecules and the loss in this temperature region confirms that the water molecules are coordinated to the metal ion [18]. In the high temperature region, the DTA curves show exothermic peaks which indicate the loss of organic matter [19], and in all the cases the residue left corresponds to the respective metal oxides [11]. These results confirm that the formula of the complexes is  $[M(L)_2(H_2O)_2]$  ( $L = \text{HN}$  and **HMPN**). Thus **HN** and **HMPN** are expected to act as bidentate uninegative ions and the coordination number of the metal ions is six.

**Table 1:** Characterization data of the complexes of **HN**, **HMPN** and **BN**.

S. No.	Complex	m/z	Yield %	Found (Calculated) %				$\mu_{\text{eff}}$ B. M.	$\Lambda_{\text{M}}$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
				C	H	N	M		
1	[Mn( <b>HN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	533, 497, 223, 154, 91	56	62.38 (63.04)	3.88 (4.16)	10.41 (10.50)	10.03 (10.30)	5.89	11.2
2	[Co( <b>HN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	537, 501, 223, 154, 107, 91	76	62.10 (62.58)	3.88 (4.13)	10.24 (10.42)	10.50 (10.91)	4.92	12.8
3	[Ni( <b>HN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	536.7, 500, 223, 154, 91, 69	68	62.14 (62.60)	3.95 (4.13)	10.34 (10.43)	10.47 (10.93)	2.94	15.1
4	[Cu( <b>HN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	542, 506, 223, 154, 107, 91, 69	64	61.63 (62.04)	3.89 (4.09)	10.14 (10.34)	11.49 (11.72)	1.94	10.3
5	[Zn( <b>HN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	543.8, 507, 223, 91	76	61.65 (61.83)	4.01 (4.08)	10.13 (10.30)	11.60 (12.02)	---	8.4
6	[Mn( <b>HMPN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	603, 567, 258, 209, 105, 87	65	57.02 (57.15)	5.96 (5.82)	9.14 (9.52)	10.31 (10.02)	5.91	12.4
7	[Co( <b>HMPN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	608, 571, 258, 162, 105, 69	62	56.95 (57.17)	5.92 (5.83)	9.68 (9.53)	10.42 (9.98)	4.83	11.6
8	[Ni( <b>HMPN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	606.7, 570, 258, 162, 105, 87	67	56.42 (56.71)	5.81 (5.78)	9.26 (9.45)	10.51 (10.72)	3.05	10.1
9	[Cu( <b>HMPN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	611.5, 575.5, 258, 209, 162, 87, 69	61	63.13 (63.42)	6.18 (5.99)	9.10 (9.24)	10.96 (10.74)	1.92	10.9
10	[Zn( <b>HMPN</b> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	613, 577, 258, 209, 162, 87, 41	68	64.12 (64.87)	5.89 (5.7)	7.98 (7.56)	7.52 (7.96)	---	11.1
11	[Mn( <b>BN</b> ) <sub>2</sub> (OAc) <sub>2</sub> ]	666, 607, 548, 356, 246, 225, 196, 88	65	60.94 (61.36)	3.68 (3.94)	16.66 (16.84)	7.84 (8.25)	5.96	---
12	[Co( <b>BN</b> ) <sub>2</sub> (OAc) <sub>2</sub> ]	669, 610, 551, 246, 223, 196	62	60.72 (60.99)	3.56 (3.91)	16.58 (16.94)	8.54 (8.80)	4.96	---
13	[Ni( <b>BN</b> ) <sub>2</sub> (OAc) <sub>2</sub> ]	668.7, 609, 550, 246, 196, 175, 105	67	60.77 (61.01)	3.55 (3.92)	16.36 (16.74)	8.39 (8.77)	2.98	---
14	[Cu( <b>BN</b> ) <sub>2</sub> (OAc) <sub>2</sub> ]	673.5, 614, 555, 246, 223, 196, 105,	61	60.57 (60.03)	3.61 (3.89)	16.20 (16.62)	9.01 (9.43)	1.90	---
15	[Zn( <b>BN</b> ) <sub>2</sub> (OAc) <sub>2</sub> ]	676, 616, 557, 246, 223, 196, 175, 105	68	60.12 (60.41)	3.48 (3.88)	16.24 (16.58)	9.41 (9.67)	---	---

Perusal of the thermal analyses data of the metal complexes of **BN** indicates that they decompose in a single stage. This decomposition occurs between 208 – 800 °C with the loss of two acetate ions and two ligand molecules [19]. The experimental data of the thermal analyses are in good agreement with the theoretical values and also with the results of the elemental analyses. These results confirm that the formula of the complexes is [M(**BN**)<sub>2</sub>(OAc)<sub>2</sub>]. Thus, **BN** is expected to act as a bidentate neutral ligand and the coordination number of the metal ions is six. The thermal stability of the complexes of **HN**, **HMPN** and **BN** was found to follow the order Mn(II) < Co(II) ≈ Ni(II) < Cu(II) > Zn(II).

### Infrared spectra

The IR spectra of ligands **HN** and **HMPN** exhibit characteristic absorptions at  $1615\text{ cm}^{-1}$   $\nu_{(\text{C}=\text{N})}$ ,  $3425\text{ cm}^{-1}$   $\nu_{(\text{O}-\text{H})}$  and  $1217\text{ cm}^{-1}$   $\nu_{(\text{C}-\text{O})}$ . The complexes of these ligands exhibit a broad absorption between  $3600$  and  $3100\text{ cm}^{-1}$ , attributable to the  $\nu_{(\text{O}-\text{H})}$  of the coordinated water molecules. Further, the absorption at  $827\text{ cm}^{-1}$  indicates that the water molecules are coordinated [20]. The  $\nu_{(\text{C}=\text{N})}$  and  $\nu_{(\text{C}-\text{O})}$  of the ligands are shifted to the lower frequency region by  $10$  to  $30\text{ cm}^{-1}$  in the spectra of the complexes, confirming the coordination through ring nitrogen atom and the phenolic oxygen atom [21, 22].

The IR spectrum of the **BN** ligand exhibits a characteristic absorption at  $1581\text{ cm}^{-1}$  that may be assigned to the 1,8-naphthyridine ring  $\nu_{(\text{C}=\text{N})}$ . This absorption was shifted to the low frequency side by  $10$  to  $15\text{ cm}^{-1}$  in the spectra of the complexes, confirming the coordination through the nitrogen atoms of the naphthyridine and benzimidazole groups. The  $\nu_{\text{asym}(\text{COO}^-)}$  and  $\nu_{\text{sym}(\text{COO}^-)}$  stretching frequencies of free acetate ions are observed at  $1560$  and  $1416\text{ cm}^{-1}$ , respectively. In the IR spectra of the complexes of **BN**, the acetate ion-stretching frequencies are found to have shifted to  $1535$ – $1555$  and  $1385$ – $1380\text{ cm}^{-1}$ , respectively. The energy separation between  $\nu_{\text{asym}(\text{COO}^-)}$  and  $\nu_{\text{sym}(\text{COO}^-)}$  is found to be  $>144\text{ cm}^{-1}$  ( $150$ – $185\text{ cm}^{-1}$ ), and this indicates the monodentate nature of the acetate ion [22], since in the event of bidentate coordination, the energy separation is reported to be  $<144\text{ cm}^{-1}$ . Further, the IR spectra of the complexes exhibit two new bands in the far-IR region at  $410$ – $475\text{ cm}^{-1}$  and  $500$ – $525\text{ cm}^{-1}$ . These absorptions may be assigned to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  respectively [6,15,23].

### <sup>1</sup>H-NMR spectra

The <sup>1</sup>H-NMR spectra of the ligands **HN** and **HMPN** and the diamagnetic Zn(II) complexes were recorded in *d*<sub>6</sub>-DMSO. The characteristic proton resonance signals of **HN** and **HMPN** are the phenolic H's at  $\delta$  15.08<sub>s</sub> and 14.36<sub>s</sub> ppm, the phenyl and naphthyridine ring H's at 9.11 – 6.99<sub>m</sub> and the methyl H's, in the case of **HMPN**, at 2.3<sub>s</sub> ppm. In the spectra of their Zn(II) complexes, the signals at  $\delta$  15.08<sub>s</sub> in **5** and 14.36<sub>s</sub> ppm in **10** disappeared, indicating the deprotonation of the phenolic proton and complex formation [24]. A new signal at 5.55 ppm is observed in the spectra of the Zn(II) complexes of **HN** and **HMPN**. This may be assigned to the proton resonance signal of coordinated water molecules. The complexes of **BN** are insoluble in common organic solvents and hence <sup>1</sup>H-NMR spectra could not be recorded.

### Magnetic moment and UV-Vis spectra

The evaluated magnetic moment values of the complexes are presented in the Table 1. The electronic spectra of the complexes of **HN** and **HMPN** in DMF solution and the reflectance spectra of the complexes of **BN** in solid state (the solubility of these complexes is very poor in common solvents) were recorded and are presented in Table 2. The high spin *d*<sup>5</sup> Mn(II) octahedral complexes ( $\mu_{\text{eff}}$  5.9 B.M.) exhibit complex spin forbidden transitions from the <sup>6</sup>A<sub>1g</sub> ground state. The Mn(II) complexes of all the ligands shows five absorptions characteristic of electronic transitions to the excited states <sup>4</sup>T<sub>1g</sub>, <sup>4</sup>T<sub>2g</sub>, <sup>4</sup>A<sub>2g</sub>(D), <sup>4</sup>E<sub>1g</sub>(D) and <sup>4</sup>T<sub>1g</sub>(P). The high spin octahedral Co(II) and Ni(II) complexes exhibit magnetic moment values around 4.9 and 2.9 B. M. respectively and three transitions each in the

electronic spectra. The Co(II) complex exhibits three electronic transitions from ground state  $^4T_{1g}(F)$  to the excited states  $^4T_{2g}(F)$ ,  $^4A_{2g}(F)$  and  $^4T_{2g}(P)$  respectively. In the case of Ni(II) complexes, the three observed absorptions can be attributed to the transitions [25],  $^3A_{2g} \rightarrow ^3T_{2g}(P)$ ,  $^3A_{2g} \rightarrow ^3T_{1g}(F)$  and  $^3A_{2g} \rightarrow ^3T_{1g}(P)$ . The parameters like  $\beta$ ,  $B$  and  $Dq$  have been evaluated from the electronic spectral absorptions of Co(II) and Ni(II) complexes. The  $\beta$  values are found to be less than 1.0, indicating that the M-L bond is covalent [26]. The magnetic moment values evaluated from the spectra [27] are in good agreement with the experimentally determined values (Table 1). The Cu(II) complexes of the ligands **HN**, **HMPN**, and **BN**, with  $\mu_{\text{eff}} = 1.94$ , exhibit a broad absorption centered at  $15149 \text{ cm}^{-1}$ ,  $14405 \text{ cm}^{-1}$  and  $15375 \text{ cm}^{-1}$  respectively suggesting a distorted octahedral geometry [28]. The diamagnetic Zn(II) ( $d^{10}$ ) complexes do not exhibit any characteristic  $d-d$  transitions. However, the ligand absorptions in the UV region have shifted in the spectra of the complexes confirming the coordination of the ligands, **HN**, **HMPN** and **BN** to Zn(II) ions.

**Table 2:** Electronic spectral data of transition metal complexes of ligands **HN**, **HMPN** and **BN**.

Complex No.	Absorptions, $\text{cm}^{-1}$
1	19011, 18518, 18350, 19231, 23795
2	9090, 18725, 21367
3	8450, 14050, 24910,
4	15649
6	19008, 19754, 20715, 21967, 23809
7	12135, 14725, 21967
8	11848, 15976, 24242
9	14405
11	18867, 20833, 23923
12	14814, 21739
13	25316, 17064, 14880
14	15375

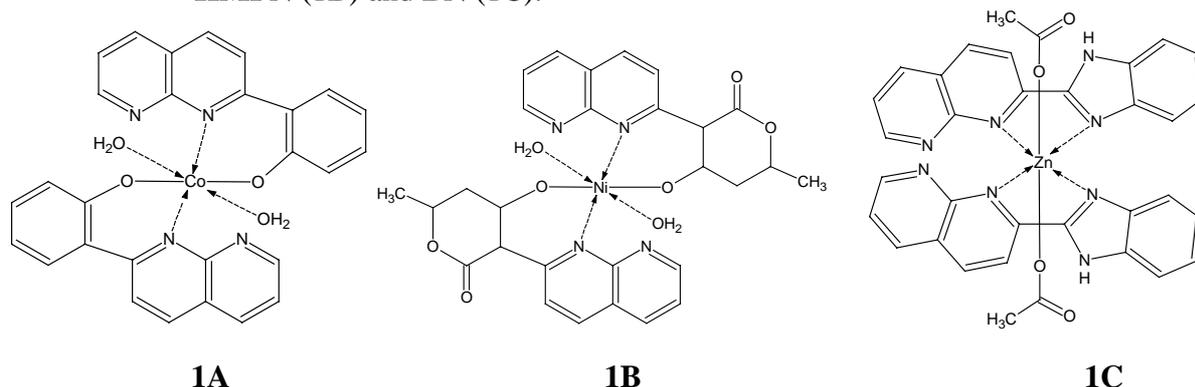
### Electron Spin Resonance Spectra

The ESR spectra of the Cu(II) complexes were recorded at liquid nitrogen temperature and the bonding parameters have been evaluated using Kneubuhl's approximation. The  $g_{\parallel}$ ,  $g_{\perp}$  and  $g_{\text{ave}}$  values are found to be: **[Cu(HN)(H<sub>2</sub>O)<sub>2</sub>]** – 2.212, 2.087, 2.125; **[Cu(HMPN)(H<sub>2</sub>O)<sub>2</sub>]** – 2.30, 2.18, 2.22; **[Cu(BN)(H<sub>2</sub>O)<sub>2</sub>]** – 2.198, 2.085, 2.123, respectively. The  $\lambda$  values of the complexes are found to be less than that of the free ion value ( $829 \text{ cm}^{-1}$ ), suggesting a considerable mixing of ground and excited state terms [29]. The same is evident from slightly higher magnetic moment values for Cu(II) complexes of **HN**, **HMPN** and **BN** (1.92, 1.94 and 1.88 B.M. respectively), as compared to the spin-only value of 1.73 B.M.

## Conclusions

Based on the reported results, it may be concluded that **HN** and **HMPN** act as bidentate uninegative ligands, coordinating through one of the naphthyridine nitrogen atom and the deprotonated phenolic oxygen. **BN** acts as bidentate neutral ligand coordinating through the naphthyridine and benzimidazole nitrogen atoms. In a majority of unsubstituted 1,8-naphthyridine complexes, the ligand is found to act as a bridging group coordinating to the two metal ions through two nitrogen atoms of the two rings [30], but the presence of an electron pair donating atom on the phenyl rings at the second position, as reported in the present work, which facilitates formation of six member rings, shifts the nitrogen atom of the other ring away from the coordination site. In the present investigations, all the complexes are found to be mononuclear, based on the mass spectral data. The coordination number six is attained by coordination with the two bidentate ligand ions/molecules and to two water molecules in the case of **HN** and **HMPN** ions and to two acetate ions in the case of **BN**. Based on the physicochemical and the spectral studies the tentative structures proposed for the complexes are shown in Figures 1A-1C.

**Figure 1:** Tentative structures of the transition metal complexes of ligands **HN** (1A), **HMPN** (1B) and **BN** (1C).



## Experimental

### General

All the chemicals, the hydrated metal acetates and solvents used were purchased from E-Merck India Ltd. The chemicals and solvents were of AR grade and were purified before use wherever required by standard methods. The metal ion contents in the complexes were determined by complexometric titrations [31] using EDTA. Carbon, hydrogen and nitrogen were determined using Perkin-Elmer-2401 CHN analyzer. Magnetic susceptibility measurements were made on Gouy balance at room temperature. Molar conductance measurements were made in DMF using Digisun Digital DI-909 instrument. IR spectra were recorded on Perkin-Elmer BX series spectrometer using KBr pellets in the range of 4000-600 cm<sup>-1</sup> and as Nujol mulls between CsI plates in the far-IR region. The electronic spectra were recorded on Shimadzu UV-2401PC Spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on JEOL 200 MHz spectrometer. Mass spectra (FAB) were recorded on a Jeol JMS D-300 spectrometer. TGA, DTA and DSC thermograms of the complexes were obtained in the temperature

range of 50 – 1000°C with a heating rate of 20 °C min<sup>-1</sup> in nitrogen atmosphere using Mettler TGA 851 and Mettler DSC 822E instruments.

### Preparation of complexes

The ligands **HN**, **HMPN** and **BN** were prepared by the methods reported elsewhere [32]. These compounds were recrystallized from ethanol and the spectral properties were compared with the reported data. The ligands **HN**, **HMPN** and **BN** (2 mmol, 444, 508 and 492 mg, respectively) were dissolved in methanol (20 mL) and to this the metal acetate (1.0 mmol) dissolved in methanol (20 mL) was added slowly with constant stirring over a period of 10 min. The reaction mixture was refluxed for 4-5 hours. The solid complexes obtained were collected on a fine frit filter and washed with cold methanol and then with acetone. The complexes were dried over fused calcium chloride in a vacuum desiccator. The yields of the complexes were in the range 60-80%.

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### References

1. Hancock, R. D.; Martell, A. E. Ligand design for selective complexation of metal ions in aqueous solution. *Chem. Rev.* **1989**, *9*, 1875-1914.
2. Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. Dendrimer-Metalloporphyrins: Synthesis and Catalysis. *J. Am. Chem. Soc.* **1996**, *118*, 5708-5711.
3. Castillo-Blum, S. E.; Barba-Behrens, N. Coordination chemistry of some biologically active ligands. *Coord. Chem. Rev.* **2000**, *196*, 3-30.
4. Mohan, G.; Rajesh, N. Synthesis and anti-inflammatory activity of N-pyridinobenzamide-2-carboxylic acid and its metal chelates. *Indian J. Pharm.* **1992**, *24*, 207-211.
5. Kong, D.; Reibenspies, J.; Mao, J.; Clearfield, A. Novel 30-membered octaazamacrocyclic ligand: synthesis, characterization, thermodynamic stabilities and DNA cleavage activity of homodinuclear copper and nickel complexes. *Inorg. Chim. Acta* **2003**, *342*, 158-170.
6. Ravinder, V.; Swamy, S.J.; SriHari, S.; Lingaiah, P. Synthesis and spectral studies of copper(II) complexes with amide group ligands. *Polyhedron* **1985**, *4*, 1511-1518.
7. Kumar, B. K.; Ravinder, V.; Swamy, G. B.; Swamy, S. J. Synthesis and characterization of iron(III), cobalt(II), nickel(II), copper(II), ruthenium(II, III), rhodium(III) and palladium(II) complexes with N-(2-carboxyphenyl)- and 2-amino-N-(2-carboxyphenyl)-benzamides. *Indian J. Chem.* **1994**, *33A*, 136-142.
8. Swamy, S. J.; Kumar, B. K. Lanthanide complexes of a new tetradentate nitrogen donor and their applications in organic synthesis. *Indian J. Chem.* **1996**, *35B*, 489-493.

9. Swamy, S. J.; Dharma Reddy, A. Synthesis of iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with new quadridentate N, O<sup>-</sup> donor ligands. *J. Indian Chem. Soc.* **2000**, *77*, 336-338.
10. Swamy, S. J.; Veerapratap, B.; Nagaraju, D.; Suresh, K.; Someshwar, P. Non-template synthesis of 'N<sub>4</sub>' di- and tetra-amide macrocyclic ligands with variable ring sizes. *Tetrahedron* **2003**, *59*, 10093-10096.
11. Swamy, S. J.; Veerapratap, B.; Someshwar, P.; Suresh, K.; Nagaraju, D. Synthesis and spectral studies of Iron(III), ruthenium(III) and Rhodium(III) complexes with new tetraaza macrocyclic ligands. *J. Chem. Res.* **2005**, 313-315 and references therein.
12. Koizumi, T. A.; Tomon, T.; Tanaka, K. Synthesis, Structures and Fluxional Behavior of Ruthenium(II) Complexes Bearing a Bidentate 1,8-Naphthyridine Ligand. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1969-1975.
13. He, C.; Lippard, S. J. Design and Synthesis of Multidentate Dinucleating Ligands Based on 1,8-Naphthyridine. *Tetrahedron* **2000**, *56*, 8245-8252.
14. Swamy, S. J.; Raveender Reddy, S. Synthesis and characterization of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of new polydentate ligands containing 1,8-naphthyridine moiety. *Indian J. Chem.* **2001**, *40A*, 1093-1096.
15. Ravinder, V.; Jagannatha Swamy, S.; SriHari, S.; Lingaiah, P. Structural studies of palladium complexes with ligands containing amide group. *Transit. Met. Chem.* **1984**, *9*, 103-106.
16. Zanella, P.; Rossetto, G. Chloride and oxinate mixed complexes of uranium(IV) and thorium(IV). *Inorg. Chim. Acta*, **1984**, *82*, 227-231.
17. Karthikeyan, S.; Rajendran, T. M.; Kannappan, R.; Mahalakshmy, R.; Venkatesan, R.; Sambasiva Rao, P. Synthesis and physicochemical studies on binuclear Cu(II) complexes derived from 2,6-[(N-phenylpiperazin-1-7l)methyl]-4-substituted phenols. *Proc. Indian Acad. Sci. (Chem. Sci.)* **2001**, *113*, 245-256.
18. Swamy, S. J.; Bhaskar, K. Synthesis and characterization of dioxouranium(VI) complexes of polydentate ligands. *Indian J. Chem.*, **1999**, *38A*, 961-965.
19. Patil, P. R.; Krishnan, V. Thiomalates of oxocations of vanadium, zirconium & hafnium. *Indian J. Chem.* **1980**, *19A*, 555-557.
20. Bala Swamy, G.; Ravinder, V.; Swamy, S. J. Synthesis and characterization of cobalt(II), nickel(II), copper(II) and palladium(II) complexes of polydentate ligands. *Indian J. Chem.* **1993**, *32A*, 589-593.
21. Moustafa, M. E. Synthesis and Structural and Biological Activity Studies on Some Lanthanide Chelates with O<sup>-</sup> and N-Containing Ligands. *Spectrosc. Lett.* **2005**, *38*, 23-34.
22. Kumar, D.; Gupta, P. K.; Syamal, A. Syntheses, magnetic and spectral studies on polystyrene supported coordination compounds of bidentate and tetradentate Schiff bases *J. Chem. Sci.*, **2005**, *117*, 247-253.
23. Nakamoto, K. *Infrared and Raman spectra of inorganic and coordination compounds*; Wiley: New York, **1978**.
24. Erdal, C.; Mehmet, K. Studies on mononuclear chelates derived from substituted Schiff-base ligands (part 7): Synthesis and characterization of a new naphthyliden-p-

- aminoacetophenoneoxime and its complexes with Co(II), Ni(II) Cu(II) and Zn(II). *J. Coord. Chem.* **2005**, *58*, 1063-1069.
25. Lever, A. B. P. *Inorganic electronic spectroscopy*; Elsevier: Amsterdam, **1984**.
  26. Kamal, M. I.; Sahar, I. M.; Nagwa, N.; Zeinab, A. Y. Synthesis and structure studies of Co(II), Ni(II), Cu(II), Pd(II), Ru(II), Ag(I), Cd(II) and dioxouranium (VI) complexes with 1-acetoacet-*o*-toluidide-4-phenyl-3-thiosemicarbazone. *Ind. J. Chem.* **2004**, *43A*, 2294-2300.
  27. Figgis, B. N. *Introduction to ligand fields*; Wiley Interscience: New York, **1966**.
  28. Rajib, L. D.; Benerjee, I.; Subhadra, G.; Mukherjee, A. K. Synthesis and reactivity of the copper (II) complexes of N- $\alpha$ -acetophenyl-X-salicylaldimines ( $\alpha = 4$  or  $3$ , X = H, 5-Br or 3 COOH). Molecular structure of bis-(N-4-acetophenyl-salicylaldiminato) copper(II). *Indian J. Chem.* **2002**, *41A*, 1380-1384.
  29. Syamal, A.; Kumar, D.; Singh, A. K.; Gupta, P. K.; Jaipal, P.; Sharma, L. K. Synthesis and characterization of a chelating resin containing ONO donor tridentate Schiff base and its coordination compounds with copper(II), nickel(II), cobalt(II), iron(III), zinc(II), cadmium(II), molybdenum(VI), zirconium (IV) and uranium(VI). *Indian J. Chem.* **2002**, *41A*, 1385-1390.
  30. Cristian Saul Campos-Fernández,; Lisa M. Thomson,; José Ramón Galán-Mascarós,; Xiang, Ouyang,; Kim, R. D. Homologous Series of Redox-Active, Dinuclear Cations  $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$  (M = Mo, Ru, Rh) with the Bridging Ligand 2-(2-Pyridyl)-1,8-naphthyridine (pynp). *Inorg. Chem.* **2002**, *41*, 1523-1533.
  31. Vogel, A. I. *Quantitative inorganic analysis*; Longman: London, **1985**; pp. 746, 715, 794, 802, 433.
  32. Mogilaiah, K.; Reddy, N. V.; Rao, R. B. Microwave assisted synthesis of 1,8-naphthyridines. *Indian J. Chem.*, **2001**, *40B*, 837.

*Sample Availability:* Samples of the complexes **1** – **15** and the ligands **HN**, **HMPN** and **BN** are available from the authors.