## Synthesis and Enzymatic Behaviour of Mono- and Dinuclear Complexes of Bivalent Transition Metal Ions with Schiff Base Derived from 2,6-Dibenzoyl-4-methylphenol and 2,6-Diaminopyridine

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The synthesis of Schiff base ligand 13,27-dimethyl-2,10,16,24-tetraphenyl-3,9,17,23,31,32-hexaazapentacyclo[26.3.1.1$^{4,8}$.1$^{11,15}$.1$^{18,22}$]-dotriaconta-1(28),2,4(31),5,7, 9,11,13,15(30),16,18,20,22(32),23,25(29),26-hexadecaen-29,30-diol (H$_2$L) and its mono- and dinuclear complexes with VO(IV), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) has been accomplished by both direct as well as template methods. The compounds have been characterized by elemental analyses, molecular weight determinations, molar conductance, room temperature magnetic moments, infrared, electronic and $^1$H NMR spectral data. The macrocyclic ligand complexes have been proposed to have distorted octahedral geometries around the metal ions. The mono- and dinuclear complexes have been evaluated for peroxidase-like activity.

**Keywords: Schiff base, Macrocyclic ligand, Peroxidase-like activity.**

### INTRODUCTION

The multifarious roles of transition metals in biological processes suggest that there is considerable potential for the development of new entities, in which these metals are complexed to ligand systems. Consequently, a number of novel macrocyclic ligands have been synthesized mainly because of their similarity with those found in biological systems and greater stability and inertness of their complexes. The interest in the fundamental chemistry of synthetic macrocyclic systems continues to grow because of their utility as model compounds that can mimic some of the properties of biological processes[1,2]. If a metalloprotein is regarded as a highly elaborated coordination compound, then it is very much possible to contemplate simulating the immediate coordination environment of the metallobiosite by use of synthetic analogue derived from small molecules[3,4], which generally are macrocyclic ligand complexes.

The design and synthesis of macropolycyclic Schiff bases have the potential to act as metal specific ligands and allow simultaneous incorporation of two or more metals in well defined homo- or heterodinuclear arrays[5-7]. In continuation of our earlier work on the activity of macrocyclic compounds to mimic peroxidase-like activity[8], we report herein the synthesis and enzymatic behaviour of another class of Schiff bases.

### EXPERIMENTAL

**Physico-chemical measurements:** The $^1$H NMR spectra of the ligands were recorded in CDCl$_3$ or TFA on a Bruker AC-300F (300 MHz) nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as internal standard. The infrared spectra (4000-350 cm$^{-1}$) of the ligands, their precursors and the complexes were recorded on a Perkin Elmer FTIR spectrophotometer in KBr pellets and frequencies are expressed in cm$^{-1}$. The electronic spectra of the complexes were recorded in dimethylformamide (DMF) and tetrahydrofuran (THF), at room temperature on a UV-visible spectrophotometer (model Elico SL 159). The magnetic susceptibility measurements of powdered complexes were carried out at room temperature with a Sherwood Scientific (England) magnetic balance. The molar conductance ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) values of $1 \times 10^{-3}$ to $1 \times 10^{-5}$ M solution of the complexes in DMF were measured at room temperature ($25 \pm 1$ °C) using a digital conductivity meter (model NDC-732) with a glass-walled cell having a cell constant of one. The C, H, N elemental analysis was performed on elemental analyzer, model 1106. The metals, *viz.*, manganese, cobalt, nickel, copper and zinc were estimated by using an atomic absorption spectrophotometer (Varian Techtron, Model AA120 with appropriate cathode lamp. Vanadium was estimated gravimetrically[9] as V$_2$O$_5$. The molecular mass was determined cryoscopically.

The ligand precursor 2,6-dibenzoyl-4-methylphenol was prepared by the method of Mandal and Nag[10].

**Synthesis of metal complexes:** The metal complexes (mono- and dinuclear) of the ligand $H_2L$ with VO(IV), Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) were prepared by template methods (**Scheme-I**). A mixture of the ligand precursors and metal salt in the ratio of 2:2:1 (for mononuclear) and 1:1:1 (for dinuclear) in ethanol was refluxed for 3-6 h to afford the macrocyclic complexes. The detailed procedure is described with the example of Co(II).
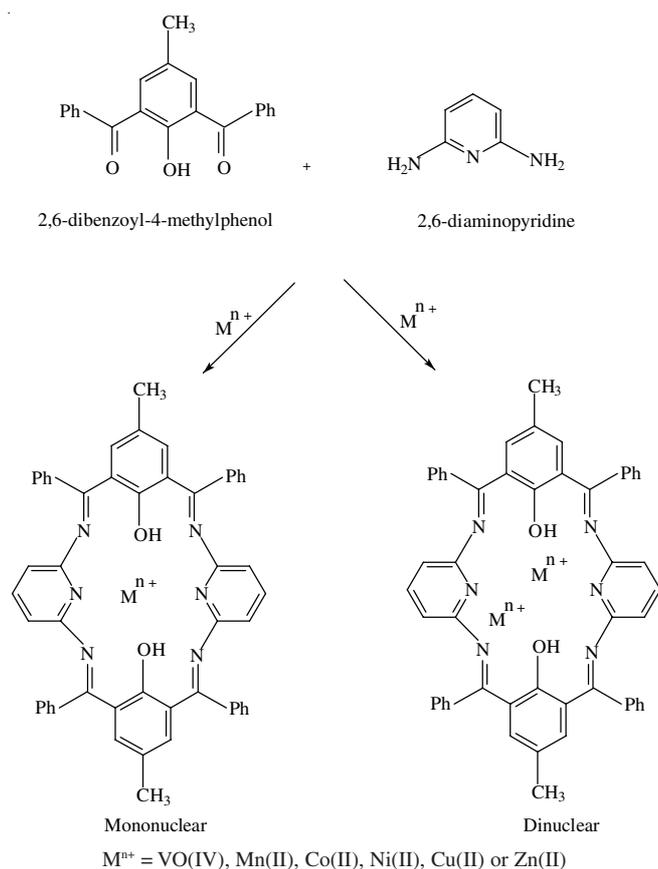


**Scheme-I**

**[Co(HL)NO$_3$]:** To a solution of 2,6-dibenzoyl-4-methyl-phenol (0.316 g, 0.001 mol) in anhydrous ethanol (25 mL) were added 2,6-diaminopyridine (0.11 g, 0.001 mol) and cobalt nitrate hexahydrate (0.145 g, 0.0005 mol). The reaction mixture was heated, under reflux for 6 h during which the solid started separating out. The solid thus obtained, on cooling was filtered, washed well with ethanol, recrystallization from DMF-EtOH (4:1) and dried, yield 0.29 g, 32 %; m.p. above 300 °C.

**[Co$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$]:** The dicobalt(II) complex of the ligand $H_2L$ was prepared from 2,6-dibenzoyl-4-methylphenol, 2,6-diaminopyridine and cobalt(II) ion in 1:1:1 stoichiometry by following the same procedure as employed for mononuclear complex, yield 0.27 g, 26 %; m.p. above 300 °C.

Different molar stoichiometries of the metal salts led to the synthesis of mono- and dinuclear compounds. The following table details the quantities of the compounds used and their yields. All the compounds had m.p. above 300 °C.

**Mononuclear compounds:** [VO(L)] – VOSO$_4$·H$_2$O; (0.091 g, 0.0005 mol), yield 0.25 g, 30 %; [Mn(HL)Cl] – MnCl$_2$·4H$_2$O; (0.099 g, 0.0005 mol), yield 0.29 g, 33 %; [Ni(HL)Cl] – NiCl$_2$·6H$_2$O; (0.119 g, 0.0005 mol), yield 0.33 g, 38 %; [Cu(HL)Cl] – CuCl$_2$.2H$_2$O; (0.085 g, 0.0005 mol), yield 0.32 g, 36 %; [Zn(HL)(CH$_3$COO)] – Zn(CH$_3$COO)$_2$·2H$_2$O; (0.109 g, 0.0005 mol), yield 0.26 g, 29 %.

**Dinuclear compounds:** [(VO)$_2$(L)SO$_4$] – VOSO$_4$·H$_2$O; (0.181 g, 0.001 mol), yield 0.29 g, 29 %; [Mn$_2$(L)Cl$_2$(H$_2$O)$_2$] – MnCl$_2$·4H$_2$O; (0.198 g, 0.001 mol), yield 0.27 g, 27 %; [Ni$_2$(L)Cl$_2$(H$_2$O)$_2$] – NiCl$_2$·6H$_2$O; (0.238 g, 0.001 mol), yield 0.31 g, 31 %; [Cu$_2$(L)Cl$_2$(H$_2$O)$_2$] – CuCl$_2$·2H$_2$O; (0.171 g, 0.001 mol), yield 0.2 g, 20 %; [Zn$_2$(L)(CH$_3$COO)$_2$(H$_2$O)$_2$] – Zn(CH$_3$COO)$_2$·2H$_2$O; (0.219 g, 0.001 mol), yield 0.23 g, 22 %.

**Evaluation of peroxidase activity:** The synthesized compounds were evaluated for their peroxidase activity by the reported procedure[11]. Peroxidase (EC 1.11.1.7) activity was measured by following spectrophotometrically the change in absorbance at 460 nm due to oxidation of *o*-dianisidine in the presence of H$_2$O$_2$ and metal complexes (1000 and 500 ppm solutions). The reaction mixture was incubated at 30 °C and contained 0.05 mL of 0.5 % *o*-dianisidine, 0.1 mL of 0.1 M H$_2$O$_2$, 0.1 mL of metal complexes and 2.75 mL of 0.05 M acetate buffer, pH 5.4. The activity was measured at 0, 2, 4, 8 and 40 min intervals. The enzyme extract obtained from Arhar (*Cajanus cajan*) nodules and diluted to 500 times was used as control to compare the peroxidase-like activity of mono- and dinuclear complexes.

## RESULTS AND DISCUSSION

The structures of the metal complexes having the general formulas [VO(L)], [(VO)$_2$(L)SO$_4$], [M(HL)X] and [M$_2$(L)X$_2$(H$_2$O)$_2$] where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and X = NO$_3^-$, Cl$^-$ or CH$_3$COO$^-$ have been proposed on the basis of elemental analyses, molecular weight determinations, conductance measurements, magnetic susceptibility and electronic and infrared spectral data. All the complexes have melting point above 300 °C and are quite stable in air.

Owing to the poor solubility of the complexes in common organic solvents, the molar conductance ($\Lambda_M$) was measured in dimethylformamide (DMF). These values were found to be below 5.0 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ which indicate the non-electrolytic nature of the compounds and the absence of any anion outside the coordination sphere[12]. The results of the elemental analyses (Table-1) are well within the experimental error limits.

**[VO(L)]:** In the infrared spectrum (Table-2) of [VO(L)], the appearance of new absorption band $\nu$(C=N) at 1660 cm$^{-1}$ and the disappearance of the carbonyl (1700 cm$^{-1}$) and amine (3345 and 3260 cm$^{-1}$) stretching frequencies present in 2,6-dibenzoyl-4-methylphenol and 2,6-diaminopyridine lend support to the fact that the condensation reaction had indeed taken place between the ligand precursors. The absence of $\nu$(O-H, phenolic, at 3400 cm$^{-1}$ in the ligand precursor) suggested the involvement of this group in coordination after the deprotonation[13,14]. This is further supported by negative shift of $\nu$(C-O) from 1350 in the ligand precursor to 1340 cm$^{-1}$ in the complex. The absorption bands at 1575 and 605 cm$^{-1}$ are assigned to pyridine ring vibrations[15,16]. A strong band at 945 cm$^{-1}$ has been attributed to $\nu$(V=O) stretching[17-19].

**TABLE-1**
**PHYSICAL AND ANALYTICAL DATA OF MACROCYCLIC COMPLEXES OF H$_2$L**

| Compound | m.f, | m.w. Found (calc.) | Analytical data (%): Found (calc.) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | N | M |
| Mononuclear complexes | | | | | | |
| [VO(L)] | C$_{52}$H$_{36}$N$_6$O$_3$.V | 840 (843) | 73.9 (74.0) | 4.1 (4.2) | 9.7 (9.9) | 5.8 (6.0) |
| [Mn(HL)Cl] | C$_{52}$H$_{37}$N$_6$O$_2$Cl.Mn | 865 (867) | 71.6 (71.9) | 4.2 (4.3) | 9.5 (9.7) | 5.9 (6.3) |
| [Co(HL)NO$_3$] | C$_{52}$H$_{37}$N$_7$O$_5$.Co | 897 (898) | 69.3 (69.5) | 3.9 (4.1) | 10.7 (10.9) | 6.3 (6.5) |
| [Ni(HL)Cl] | C$_{52}$H$_{37}$N$_6$O$_2$Cl.Ni | 870 (871) | 71.5 (71.6) | 4.2 (4.2) | 9.4 (9.6) | 6.4 (6.7) |
| [Cu(HL)Cl] | C$_{52}$H$_{37}$N$_6$O$_2$Cl.Cu | 874 (876) | 70.9 (71.2) | 4.1 (4.2) | 9.5 (9.6) | 7.1 (7.2) |
| [Zn(HL)(CH$_3$COO)] | C$_{54}$H$_{40}$N$_6$O$_4$.Zn | 899 (901) | 71.7 (71.9) | 4.3 (4.4) | 9.1 (9.3) | 7.1 (7.3) |
| Dinuclear complexes | | | | | | |
| [(VO)$_2$(L)SO$_4$] | C$_{52}$H$_{36}$N$_6$O$_8$S.V$_2$ | 1004 (1006) | 61.7 (62.0) | 3.4 (3.6) | 8.1 (8.4) | 9.8 (10.1) |
| [Mn$_2$(L)Cl$_2$(H$_2$O)$_2$] | C$_{52}$H$_{40}$N$_6$O$_4$Cl$_2$.Mn$_2$ | 991 (993) | 62.7 (62.8) | 3.9 (4.0) | 8.4 (8.5) | 10.9 (11.1) |
| [Co$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$] | C$_{52}$H$_{40}$N$_8$O$_{10}$.Co$_2$ | 1053 (1054) | 59.0 (59.2) | 3.7 (3.8) | 10.5 (10.6) | 11.0 (11.2) |
| [Ni$_2$(L)Cl$_2$(H$_2$O)$_2$] | C$_{52}$H$_{40}$N$_6$O$_4$Cl$_2$.Ni$_2$ | 997 (997) | 62.1 (62.4) | 3.8 (4.0) | 8.1 (8.4) | 11.5 (11.7) |
| [Cu$_2$(L)Cl$_2$(H$_2$O)$_2$] | C$_{52}$H$_{40}$N$_6$O$_4$Cl$_2$.Cu$_2$ | 1006 (1010) | 61.6 (61.8) | 3.8 (4.0) | 8.0 (8.3) | 12.5 (12.6) |
| [Zn$_2$(L)(CH$_3$COO)$_2$(H$_2$O)$_2$] | C$_{56}$H$_{46}$N$_6$O$_8$.Zn$_2$ | 1059 (1061) | 63.2 (63.3) | 4.0 (4.3) | 7.7 (7.9) | 12.0 (12.3) |

**TABLE-2**
**INFRARED SPECTRAL DATA (cm$^{-1}$) OF LIGAND H$_2$L AND ITS METAL COMPLEXES**

| Compound | v(O-H) | v(C=N) | v(C=C) | v(C-O) | Pyridine ring | SO$_4^{2-}$/NO$_3^-$/ CH$_3$COO$^-$ | v(M-O) | v(M-N) |
|---|---|---|---|---|---|---|---|---|
| Mononuclear complexes | | | | | | | | |
| [VO(L)] | - | 1660 | 1615 | 1340 | 1575, 605 | - | 455 | 430 |
| [Mn(HL)Cl] | 3320 | 1663 | 1625 | 1325 | 1565, 610 | - | 470 | 410 |
| [Co(HL)NO$_3$] | 3325 | 1660 | 1620 | 1330 | 1570, 620 | 1455, 1295, 930 | 460 | 415 |
| [Ni(HL)Cl] | 3315 | 1655 | 1625 | 1325 | 1570, 615 | - | 445 | 405 |
| [Cu(HL)Cl] | 3325 | 1665 | 1605 | 1345 | 1565, 625 | - | 470 | 415 |
| [Zn(HL)(CH$_3$COO)] | 3320 | 1655 | 1615 | 1325 | 1580, 600 | 1570 | 440 | 425 |
| Dinuclear complexes | | | | | | | | |
| [(VO)$_2$(L)SO$_4$] | - | 1650 | 1620 | 1335 | 1565, 605 | 1125, 620 | 450 | 405 |
| [Mn$_2$(L)Cl$_2$(H$_2$O)$_2$] | 3210 | 1645 | 1625 | 1330 | 1580, 625 | - | 445 | 420 |
| [Co$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$] | 3220 | 1665 | 1620 | 1325 | 1560, 620 | 1465, 1300, 935 | 465 | 405 |
| [Ni$_2$(L)Cl$_2$(H$_2$O)$_2$] | 3215 | 1650 | 1635 | 1335 | 1560, 610 | - | 435 | 430 |
| [Cu$_2$(L)Cl$_2$(H$_2$O)$_2$] | 3225 | 1655 | 1615 | 1325 | 1585, 625 | - | 460 | 410 |
| [Zn$_2$(L)(CH$_3$COO)$_2$(H$_2$O)$_2$] | 3220 | 1665 | 1626 | 1340 | 1580, 605 | 1555 | 455 | 417 |

The electronic spectrum (Table-3) of [VO(L)] exhibited two absorption bands at 12450 and 18700 cm$^{-1}$. For the vanadyl complexes, these bands are assigned to $^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2B_1$ transitions[20], respectively, which are characteristic of distorted octahedral geometry around VO(II). The room temperature magnetic moment ($\mu_{eff.}$ = 1.84 BM) rules out the possibility of any antiferromagnetic spin exchange[21].

**[(VO)$_2$(L)SO$_4$]:** The infrared spectrum of dioxovanadyl complex of H$_2$L is almost similar to that of its monoanalogue. The dinuclear compound exhibited v(C=N) at 1650 cm$^{-1}$ which is a new band indicating that the condensation reaction has taken place. The two phenolic hydroxyl groups are also involved in coordination, after deprotonation[13,14], as evidenced by the absence of v(O-H) at 3400 cm$^{-1}$ (present in the ligand precursor). This was further confirmed by v(C-O of C-OH) at 1335 which was at 1350 cm$^{-1}$ in the spectrum of the ligand precursor. In addition to these, an absorption band observed at 835 cm$^{-1}$ was assigned to V-O-V bridge[22]. The absorption bands at 1565 and 605 cm$^{-1}$ are assigned to pyridine ring vibrations[15,16]. Sulphate anion acting as bridging[23,24] ligand is present at 1125 and 620 cm$^{-1}$. Major infrared absorption bands of the dioxovanadyl complex are given in Table-2.

**TABLE-3**
**ELECTRONIC SPECTRA (cm$^{-1}$) AND MAGNETIC MOMENT ($\mu_{eff.}$) OF METAL COMPLEXES OF H$_2$L**

| Compound | $v_1$ | $v_2$ | $v_3$ | $\mu_{eff.}$ (BM) |
|---|---|---|---|---|
| Mononuclear complexes | | | | |
| [VO(L)] | 12450 | 18700 | – | 1.84 |
| [Mn(HL)Cl] | 19000 | 23500 | 32650 | 5.94 |
| [Co(HL)NO$_3$] | 8800 | 17800 | 22550 | 4.95 |
| [Ni(HL)Cl] | 10550 | 16650 | 25000 | 3.1 |
| [Cu(HL)Cl] | 13500 | – | – | 1.78 |
| [Zn(HL)(CH$_3$COO)] | 26900 | 39000 | – | – |
| Dinuclear complexes | | | | |
| [(VO)$_2$(L)SO$_4$] | 13700 | 19050 | – | 1.9 |
| [Mn$_2$(L)Cl$_2$(H$_2$O)$_2$] | 18850 | 21900 | 31500 | 6.18 |
| [Co$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$] | 9800 | 20050 | 24500 | 4.9 |
| [Ni$_2$(L)Cl$_2$(H$_2$O)$_2$] | 9750 | 15350 | 25050 | 3.3 |
| [Cu$_2$(L)Cl$_2$(H$_2$O)$_2$] | 12600 | – | – | 1.98 |
| [Zn$_2$(L)(CH$_3$COO)$_2$(H$_2$O)$_2$] | 29100 | 40450 | – | – |

The electronic spectrum of dioxovanadyl complex exhibited two major absorptions at 13700 and 19050 cm$^{-1}$, for d-d transitions, similar to those observed in case of [VO(L)]. The room temperature magnetic moment ($\mu_{eff.}$) has been found to be 1.9

BM characteristic of distorted octahedral geometry around vanadium[20]. On the basis of elemental analysis and spectral data, the following structures have been proposed for mono- and divanadyl compounds (Fig. 1).
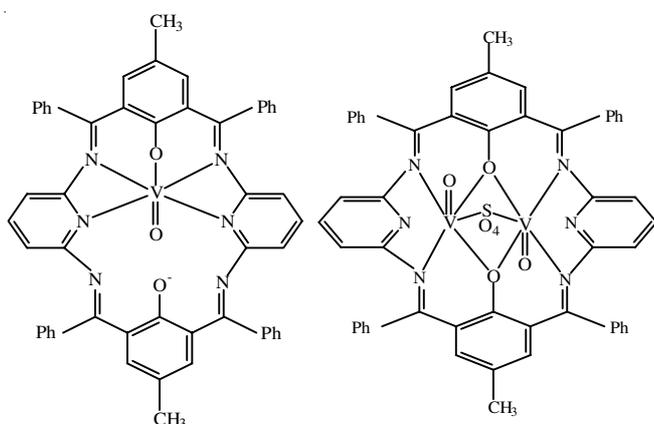


Fig. 1. Structure of [VO(L)] and [(VO)$_2$(L)SO$_4$] complexes

**[Co(HL)NO$_3$]:** The incorporation of cobalt in the macrocyclic cavity of the ligand was achieved by the template action of Co(II) in the condensation reaction of 2,6-dibenzoyl-4-methylphenol and 2,6-diaminopyridine in ethanol. In the infrared spectrum of the Co(II) complex (Table-2), appearance of new absorption band ν(C=N) at 1660 cm$^{-1}$ and disappearance of the carbonyl ν(C=O) at 1700 cm$^{-1}$ and amine ν(NH$_2$) at 3340 and 3270 cm$^{-1}$ stretching frequencies lends support to the fact that the condensation reaction had indeed taken place. Negative shift in ν(O-H) at 3325 cm$^{-1}$ (less intense than 3400 cm$^{-1}$ in the ligand precursor) has been attributed to the involvement of phenolic –OH in coordination after deprotonation[13,14]. Appearance of absorption bands ν(C-O) at 1330, ν(Co-O) at 460 and ν(Co-N) at 415 cm$^{-1}$ confirmed the coordination of Co(II) ion to these donor groups[25,26]. The decrease in absorption frequencies of the order of 10-30 cm$^{-1}$ support the involvement of N$_4$O donor set in coordination and Co(II) ion is found to be hexacoordinated. The absorption bands at 1570 and 620 cm$^{-1}$ are assigned to coordinated pyridine ring vibrations[15,16]. The presence of coordinated[23,24] nitrate ion is indicated by absorption bands at 1455, 1295 and 930 cm$^{-1}$.

The powdered [Co(L)NO$_3$] complex shows magnetic moment (μ$_{eff.}$) value of 4.95 BM at room temperature, indicative of a spin quartet ground state for distorted octahedral geometry. The electronic spectrum recorded in DMF shows three distinct absorption bands at 8800, 17800, 22550 cm$^{-1}$ which are attributed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions[27,28] and are characteristic of distorted octahedral geometry around cobalt.

**[Co$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$]:** The infrared spectrum of dinuclear complex [Co$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$] shows similar absorption bands as observed for its monoanalogue (Table-2). The appearance of ν(C=N) at 1665 cm$^{-1}$ and the disappearance of the carbonyl ν(C=O) at 1700 cm$^{-1}$ and amine ν(NH$_2$) 3345 and 3260 cm$^{-1}$ stretching frequencies lends support to the fact that the condensation reaction had indeed taken place between the ligand precursors 2,6-dibenzoyl-4-methylphenol and 2,6-diamino-pyridine. The involvement of both phenolic hydroxyl groups

in coordination is supported by the absence of ν(O-H) and shifting of ν(C-O) to 1325 cm$^{-1}$ which in the spectrum of 2,6-dibenzoyl-4-methylphenol is present at 1350 cm$^{-1}$. A broad band at 3220 cm$^{-1}$ was attributed to the presence of coordinated water[29,30]. This was further confirmed by an additional peak at 805 cm$^{-1}$. The coordinated[23,24] nitrate group is observed at 1465, 1300 and 935 cm$^{-1}$. The coordination of two Co(II) ions to oxygen and nitrogen is clear from ν(Co-O) and ν(Co-N) at 465 and 405 cm$^{-1}$. The coordinated pyridine ring vibrations[15,16] are observed at 1560 and 620 cm$^{-1}$. In addition to these, an absorption band observed at 740 cm$^{-1}$ was assigned to Co-O-Co bridge[31].

The electronic spectrum of dicobalt(II) complex has three intense bands at 9800, 20050 and 24500 cm$^{-1}$ which are attributed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions[27,28], which are the characteristic of distorted octahedral geometry around cobalt. The room temperature magnetic moment (μ$_{eff.}$) of the complex is 4.9 BM. In addition to VO(IV) and Co(II), other first row transition metal ions *viz.* Mn(II), Ni(II), Cu(II) and Zn(II) have been also used to prepare their mono- and dinuclear complexes. The synthesis of these complexes involved the same procedures and characterization was achieved by similar techniques as used for above complexes, since all the metal complexes have distorted octahedral geometry. All the complexes have high m.p. (above 300 °C) and are insoluble in common organic solvents. The electrical conductance values indicate the non-ionic nature of the coordination compounds. The elemental analysis is reported in Table-1. Infrared absorption bands are listed in Table-2, while the electronic spectral data and room temperature magnetic moment (μ$_{eff.}$) are given in Table-3.

On the basis of above mentioned results, the mono- and dinuclear complexes of H$_2$L are proposed to have a distorted octahedral geometry around central metal ions. The tentative structures of both mono- dinuclear compounds are shown in Fig. 2.
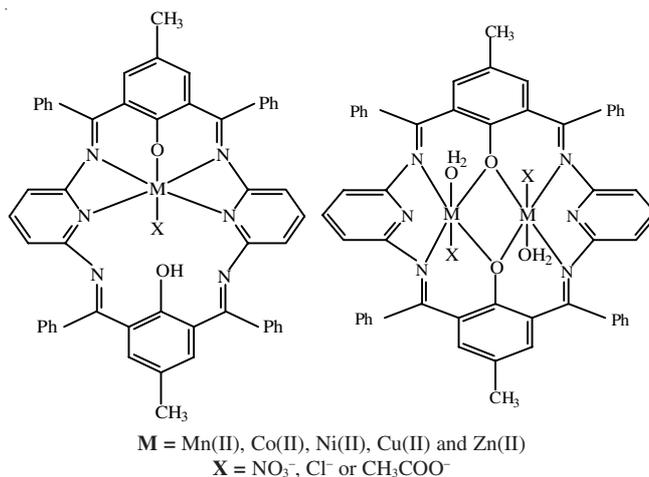


**M** = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)
**X** = NO$_3^-$, Cl$^-$ or CH$_3$COO$^-$

Fig. 2. Structure of [M(HL)X] and [M$_2$(L)X$_2$(H$_2$O)$_2$] complexes

**Peroxidase-like activity:** To measure the peroxidase-like activity, a control experiment was run with peroxidase enzyme extract obtained from Arhar nodules following the literature procedure[11]. The crude extract (10 mL from 5 g tissue) was diluted 500 times and optical density (OD) measured at 460

nm for 5 min. After 5 min the OD increased from 0.032-0.200. The synthesized mono- and dinuclear compounds were similarly evaluated for peroxidase-like activity at 1000 and 500 ppm.

A perusal of data in Tables 4 and 5 reveals that out of the mono- and dinuclear complexes studied, $[Co(HL)NO_3]$ showed the maximum peroxidase like activity (0.099) followed by $[Cu_2(L)Cl_2(H_2O)_2]$ (0.088), $Mn_2(L)Cl_2(H_2O)_2]$ (0.081), $[Cu_2(L)Cl_2(H_2O)_2]$ (0.058).

TABLE-4
OD VALUES OF PEROXIDASE-LIKE ACTIVITY OF SOME
MONO- AND DINUCLEAR COMPLEXES (500 ppm)

| Compound | 0 min | 2 min | 4 min | 8 min | 40 min |
|---|---|---|---|---|---|
| Mononuclear complexes | | | | | |
| $[Mn(HL)Cl]$ | 0.158 | 0.164 | 0.170 | 0.174 | 0.174 |
| $[Co(HL)NO_3]$ | 0.106 | 0.122 | 0.132 | 0.142 | 0.142 |
| $[Ni(HL)Cl]$ | 0.075 | 0.088 | 0.092 | 0.095 | 0.096 |
| Dinuclear complexes | | | | | |
| $[Mn_2(L)Cl_2(H_2O)_2]$ | 0.191 | 0.199 | 0.205 | 0.209 | 0.209 |
| $[Co_2(L)(NO_3)_2(H_2O)_2]$ | 0.094 | 0.101 | 0.108 | 0.114 | 0.117 |

TABLE-5
OD VALUES OF PEROXIDASE-LIKE ACTIVITY OF SOME
MONO- AND DINUCLEAR COMPLEXES (1000 ppm)

| Compound | 0 min | 2 min | 4 min | 8 min | 40 min |
|---|---|---|---|---|---|
| Mononuclear complexes | | | | | |
| $[Mn(HL)Cl]$ | 0.347 | 0.365 | 0.376 | 0.383 | 0.383 |
| $[Co(HL)NO_3]$ | 0.351 | 0.399 | 0.430 | 0.450 | 0.452 |
| $[Ni(HL)Cl]$ | 0.396 | 0.402 | 0.408 | 0.414 | 0.414 |
| $[Cu(HL)Cl]$ | 0.163 | 0.180 | 0.195 | 0.210 | 0.210 |
| Dinuclear complexes | | | | | |
| $[Mn_2(L)Cl_2(H_2O)_2]$ | 0.361 | 0.401 | 0.426 | 0.442 | 0.444 |
| $[Co_2(L)(NO_3)_2(H_2O)_2]$ | 0.293 | 0.308 | 0.322 | 0.331 | 0.331 |
| $[Ni_2(L)Cl_2(H_2O)_2]$ | 0.161 | 0.168 | 0.174 | 0.179 | 0.179 |
| $[Cu_2(L)Cl_2(H_2O)_2]$ | 0.175 | 0.205 | 0.239 | 0.263 | 0.263 |

The increase in OD which is a measure of peroxidase-like activity reveals that the crude extract exhibited an increase of 0.168 in OD (0.032-0.200) while the best value (0.099) was shown by the $[Co(HL)NO_3$ It can thus be safely concluded that $[Co(HL)NO_3]$ exhibited 59 % activity at 1000 ppm concentration compared to the crude enzyme extract.

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