

Cobalt(II), Nickel(II) and Copper(II) Complexes with 3,8-Diphenyl, 4-7-diaza-2, 9-dihydroxyimino-5-methyl-3,7-decadiene

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A series of complexes having the formula $[M(H_2L)X_2]$ [$M = Co(II), Ni(II), X = Cl^-, Br^-, I^-, NO_3^-$ and ClO_4^-] and $[ML]$ [$M = Co(II), Ni(II)$ and $Cu(II), L = 3,8$ -diphenyl-4,7-diaza-2,9-dihydroxyimino-5-methyl-3,7-decadiene] have been isolated from ethanolic medium. Yet another series of binuclear clusters of the type $Cu_2(L)X_2$ was obtained by reacting CuL complexes with copper(II) salts in ethanolic medium. Characterisation of the complexes has been made on the basis of elemental analysis, infrared spectra, electronic spectra, magnetic moment value, conductivity measurements and 1H NMR spectra.

INTRODUCTION

Metal complexes of dioximes and their derivatives have been extensively studied in recent years¹⁻⁸ due to their capacities to form organometallic and encapsulation compounds. This prompted us to synthesize metal complexes with the ligand obtained by the condensation of 1-methyl-1,2-diamino ethane and 1-phenyl-1,2-propanedione-2-oxime. The promising ligand (Fig. 1) acts in a tetradentate manner to form two series of complexes having the formula $[M(H_2L)X_2]$ and ML [$M = Co(II), Ni(II)$ and $Cu(II), X = Cl^-, Br^-, I^-, NO_3^-$ and ClO_4^-] when it is allowed to react with metal salts in the molar ratio 1 : 1 in ethanolic and aqueous (basic) media respectively. The complex CuL further reacts in an ethanolic medium with CuX_2 salts to give yet another series of binuclear complexes of the type $(CuLX)_n$ where $X = Cl^-, Br^-, I^-, NO_3^-$ and ClO_4^- .

EXPERIMENTAL

All the chemicals used were BDH or E. Merck reagents except 1-phenyl-1,2-propanedione-2-oxime which was an Aldrich reagent. Bromide salts of cobalt(II), nickel(II) and copper(II) were prepared by dissolving the respective metal carbonate in the minimum volume of hydrobromic acid followed by crystallisation.

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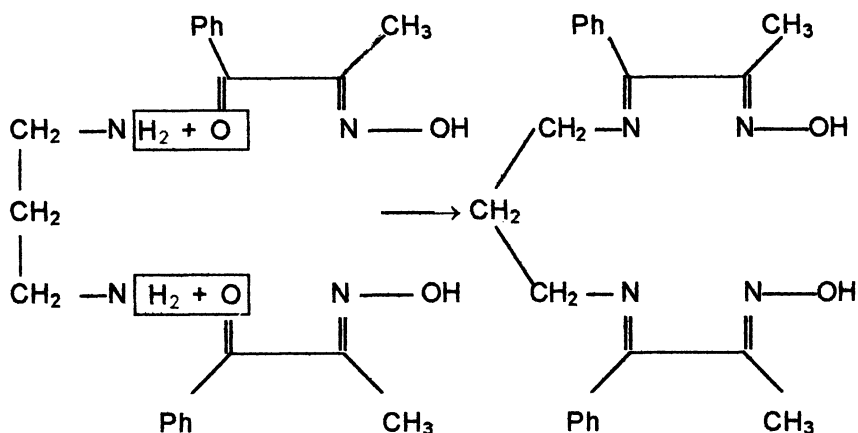


Fig. 1

Preparation of the Ligand H_2L

The ligand 3,8-diphenyl-4,7-diaza-2,9-dihydroxyimino-5-methyl-3,7-decadiene was synthesized by the method reported⁷ earlier [m.p. = $170 \pm 2^\circ\text{C}$, yield = 57%]

Preparation of the complexes

A similar procedure was used for the preparation of all the complexes. The preparation of one typical complex of Co(II), Ni(II) and Cu(II) is described below for each of the series of complexes.

(1) 3,8-Diphenyl-4,7-diaza-2,9-dihydroxyimino-5-methyl-3,7-decadienato copper(II) complex, CuL

An ethanolic solution of Cu(II) bromide hexahydrate (0.01 mole) was treated with ligand H_2L , dissolved in minimum amount of ethanol. The mixture was heated on water bath for 3 h. A brown precipitate was obtained which was filtered and washed thoroughly with ethanol. The complex was insoluble in various solvents which was indicative of its polymeric nature.

(2) 3,8-Diphenyl-4,7-diaza-2,9-dihydroxyimino-5-methyl-3,7-decadienato Ni(II) complex, NiL

An ethanolic solution of Ni(II) bromide hexahydrate (0.01 mole) dissolved in minimum amount of ethanol was treated with ligand (0.01 mole) dissolved in minimum volume of ethanol. The mixture was treated on water bath for 3 h. A green crystalline precipitate was obtained which was filtered and washed thoroughly with ethanol. The complex was insoluble in various solvents which was indicative of its polymeric nature.

(3) 3,8-Diphenyl-4,7-diaza-2,9-dihydroxyimino-5-methyl-3,7-decadienato cobalt(II) complex, CoL

Cobalt bromide hexahydrate (0.01 mole) was dissolved in minimum amount

of ethanol. This solution was treated with ligand (0.01 mole) in *minimum amount* of ethanol. The mixture was heated on water bath for 3 h. A yellowish green precipitate was obtained which was filtered and washed thoroughly with ethanol. The complex was insoluble in various solvents which was indicative of its polymeric nature.

Elemental analyses were done using standard procedure⁹. The infrared spectra of the complexes were recorded on a Beckman IR-20 spectrophotometer. Magnetic moments are measured by the Gouy method using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as the calibrant. Conductivity measurements were made on a Systronic conductometer model 303 using dimethyl sulphoxide as a solvent. NMR spectra were carried out at room temperature on a Varian 400 spectrophotometer and samples were dissolved in DMSO-d_6 and chemical shifts were expressed in ppm using TMS as the internal standard.

RESULTS AND DISCUSSION

The vibrational spectra of the complex have been recorded in frequency region $4000\text{--}600\text{ cm}^{-1}$. Structurally important vibrational bands for O—H stretch (3300 cm^{-1}) C \equiv N (Stretch $1620\text{--}1450\text{ cm}^{-1}$) and N—O stretch ($1130\text{--}1030\text{ cm}^{-1}$) have been clearly distinguished and provide unequivocal evidence relating to the structure of the complexes.

The infrared spectra of all the metal complexes of the type $\text{M}(\text{H}_2\text{L})\text{X}_2$ show a broad and strong band near 3300 cm^{-1} which can be assigned to $\nu(\text{O—H})$ of the oxime group. The width of this band manifests intramolecular hydrogen bonding. It is striking to note that this band disappears from the spectra of the inner complex salts $\text{M}(\text{L})$ and binuclear copper(II) complexes $\text{Cu}_2(\text{L})\text{X}_2$ where O—H bands of the N—OH groups have been broken down in the process of coordination. The spectra of all the metal complexes show two sharp and strong bands in the vicinity of 1600 cm^{-1} and 1500 cm^{-1} which have been attributed to $\nu(\text{C}\equiv\text{N})$ stretching vibration of azomethine and oxime groups respectively. The characteristic behaviour of this band that is the shift of the azomethine and oxime $\nu(\text{C—N})$ bands respectively towards a red and blue region of the spectra as compared with the free ligand leads us to suggest that in the inner complex the oxime ligand acts as an endo-quadridentate ligand through its nitrogen atoms and the structure may be represented in Fig. 2.

The shift of the $\nu(\text{C}\equiv\text{N})$ band and the existence of a hydrogen bonded OH group as evidenced by the infrared spectra for the series of metal complexes of the types $\text{M}(\text{H}_2\text{L})\text{X}_2$ with uncharged ligand clearly manifests a hydrogen bonded cyclic ring structure as shown in Fig. 3.

The particular significance of the vibrational spectra of the binuclear copper(II) complexes is shift of the N—O bands to a lower frequency region. This shift unequivocally suggests further coordination of the oxime groups of the inner complex salts to a neighbouring copper(II) ion (Fig. 4). Infrared spectra of nitrate and perchlorate ions indicate them to be coordinated to the copper(II) ion through one of their oxygen atoms in a unidentate manner.

The possibility of the complexes $\text{Cu}_2(\text{L})\text{X}_2$ having dimeric structure as shown in

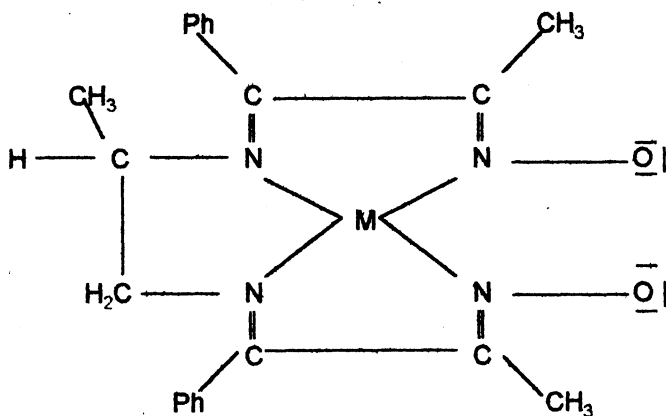


Fig. 2

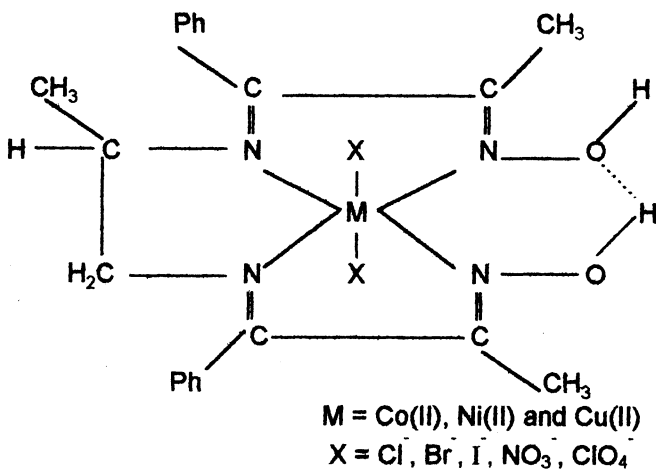


Fig. 3

Fig. 5 cannot be ruled out. Attempts were made to prepare similar binuclear metal complexes of the type $M_2(L)X_2$ where $M = \text{Co(II)}$ or Ni(II) but were unsuccessful. The infrared spectral data are recorded in Table-1.

Magnetic moment data and electronic spectra

During the course of the present investigation, it has been found that a single broad band in the electronic spectra of inner complex salt of copper(II), Cu(L) , the centre of gravity of which lies at 14000 cm^{-1} , has been attributed to the ligand field band due to the chromophore CuN_4 . The broad band which shows considerable structures represents two or three superposed absorptions. The band is comparable both in position and width with earlier reported planar copper(II) complexes and leads us to believe that the inner complex Cu(L) is essentially planar.

TABLE-1
SALIENT FEATURES OF IR SPECTRA IN cm^{-1} OF THE COMPLEXES OF THE TYPE
[M(H₂L)X₂]

Sl. No.	Complexes	$\nu(\text{O—H})$	$\delta(\text{O—H})$	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{C}=\text{N})$ oxime	$\nu(\text{N—O})$
1.	[Ni(H ₂ L)Cl ₂]	3385ms	1680m	1595m	1480m	1090(S)
2.	[Ni(H ₂ L)Br ₂]	3380ms	1685m	1600s	1475m	1095(S)
3.	[Ni(H ₂ L)I ₂]	3385ms	1680m	1505s	1485m	1095(S)
4.	[Ni(H ₂ L)(NO ₃) ₂]	3375ms	1675m	1600s	1480s	1100(S)
5.	[Ni(H ₂ L)(ClO ₄) ₂]	3380ms	1680(S)	1505s	1475m	1105(S)
6.	[Co(H ₂ L)Cl ₂]	3370ms	1685m	1600s	1480m	1110(S)
7.	[Co(H ₂ L)Br ₂]	3375ms	1680m	1605s	1485m	1005(S)
8.	[Co(H ₂ L)I ₂]	3380ms	1675m	1600s	1475m	1105(S)
9.	[Co(H ₂ L)(NO ₃) ₂]	3385ms	1685m	1595m	1480m	1115(S)
10.	[Co(H ₂ L)(Py) ₂]	3380ms	1680(S)	1600s	1475m	1110(S)

INFRARED SPECTRA OF THE LIGAND H₂L AND ITS METAL CHELATES

Sl. No.	Complexes	$\nu(\text{O—H})$	$\delta(\text{O—H})$	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{C}=\text{N})$ oxime	$\nu(\text{N—O})$
1.	H ₂ L ligand	3380ss	1680ms	1660s	1400s	1110s
2.	Cu(L)	—	—	1600s	1480m	1095s
3.	Ni(L)	—	—	1595s	1475m	1105s
4.	Co(L)	—	—	1605s	1485m	1090s

IR SPECTRA OF THE COPPER(II) COMPLEXES OF THE TYPE [Cu₂(L)X₂]

Sl. No.	Complexes	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{C}=\text{N})$ oxime	$\nu(\text{N—O})$	$\nu(\text{Cu—X})$
1.	[Cu ₂ (L)Cl ₂]	1600sb	1475m	1055(S)	615(S)
2.	[Cu ₂ (L)Br ₂]	1605m	1470m	1050(S)	610(S)
3.	[Cu ₂ (L)(NO ₃) ₂]	1595m	1475m	1045(S)	620(S)
4.	[Cu ₂ (L)(ClO ₄) ₂]	1600m	1480m	1050(S)	615(S)

Binuclear copper(II) complexes have magnetic moments in the region 1.7–1.9 B.M. and show two ligand field bands: one in the region 18,000–17,000 cm^{-1} and another in the region 13,000–12,000 cm^{-1} . It would be reasonable to say that while the high frequency band arises due to d-d transition for the chromophore CuN₄, the low frequency band originated due to the chromophore CuO₂X₂.

The inner complex salt of cobalt(II) ion of the type Co(L) is of low spin value having magnetic moment 2.0 B.M. The low magnetic moment is characteristic of square planar complexes. It shows a broad band in the region 22,000–20,000 cm^{-1} which suggests cobalt(II) ion to be in a square planar environment and the band presumably arises due to the transition ${}^2A_{1g} \rightarrow {}^1b_{1g}(d_x^2 - y^2)$ where ${}^2A_{1g}$ is probably the ground state for low spin cobalt(II) ion in a square planar environment and b_{1g} is the empty antibonding orbital. The cobalt(II) complexes

$[\text{Co}(\text{H}_2\text{L})\text{X}_2]$ exhibit a multiplet band structure in the region $20,500\text{--}18,500\text{ cm}^{-1}$ and possess magnetic moment value 5.2 B.M. which corresponds to an octahedral stereochemistry about the metal ion. The band can be assigned to the transition ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ and the structure manifests a tetragonal distortion of the complexes. The electronic spectra of Ni(II) complexes are recorded in Table-2. The spectrum consists of three bands, one in the region $14,500\text{--}13,000\text{ cm}^{-1}$, the next one in the vicinity of $18,000\text{ cm}^{-1}$ followed by a strong intense band near $24,000\text{ cm}^{-1}$ and suggests the complexes to be octahedral with certain amount of tetragonal distortion. The band in the lower frequency region can be assigned to transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ whereas the band at $18,000\text{ cm}^{-1}$ can be assigned to the transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$. The band at $24,000\text{ cm}^{-1}$ can be assigned to the transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$.

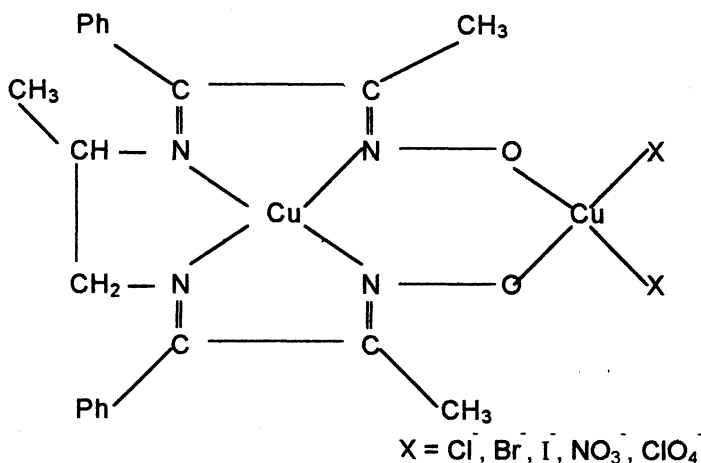


Fig. 4

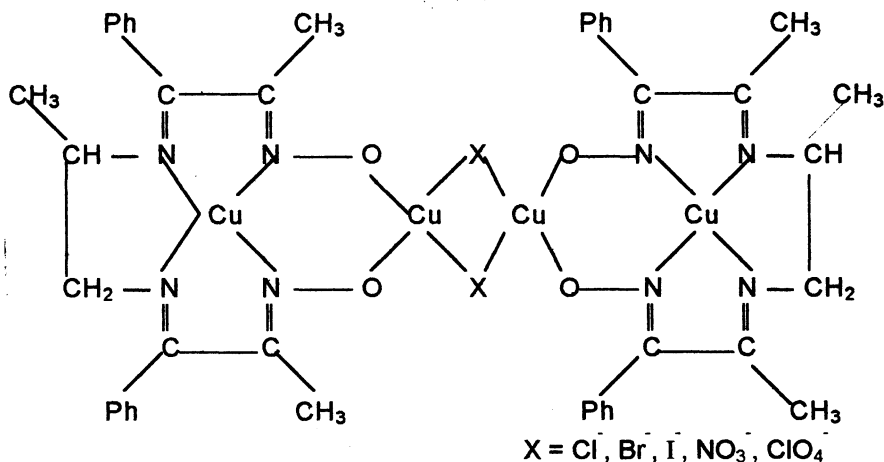


Fig. 5

Conductivity measurements: Conductivities of the complexes were measured in the solvent DMSO and all the complexes were found to be non-electrolytic in nature giving conductivity values in the range 10 to 30 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. The conductivity data also support the structural assignment on the basis of magnetic and spectral studies.

^1H NMR spectra: The ^1H NMR spectra of the coordination compounds have been recorded with Varian EM 400 spectrometer (DMSO-d_6). Four signals are observed in the PMR spectra of the ligand. The first peak is observed at 4.85 in the form of multiplet which can be assigned to methylene protons. The second peak is a sharp singlet at 6.25 and has been assigned to phenyl protons. The methyl protons appear at still higher field 5.65. All these peaks remain almost unperturbed in metal complexes indicating their non-involvement.

TABLE-2
MAGNETIC MOMENT DATA AND SALIENT FEATURES OF ELECTRONIC ABSORPTION SPECTRA, ELECTRONIC SPECTRA OF Co(II) COMPLEXES OF THE TYPE $[\text{Co}(\text{H}_2\text{L})\text{X}_2]$ AND MAGNETIC MOMENT DATA

Sl. No.	Complexes	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$	μ_{eff} (B.M.)
1.	$[\text{Co}(\text{H}_2\text{L})\text{Cl}_2]$	18,500	5.11
2.	$[\text{Co}(\text{H}_2\text{L})\text{Br}_2]$	19,400	5.15
3.	$[\text{Co}(\text{H}_2\text{L})\text{I}_2]$	19,700	5.21
4.	$[\text{Co}(\text{H}_2\text{L})(\text{NO}_3)_2]$	19,300	5.15
5.	$[\text{Co}(\text{H}_2\text{L})(\text{ClO}_4)_2]$	20,500	5.21

ELECTRONIC SPECTRA AND MAGNETIC MOMENT DATA OF Ni(II) COMPLEXES OF THE TYPE $[\text{Ni}(\text{H}_2\text{L})\text{X}_2]$

Sl. No.	Complexes	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$	μ_{eff} (B.M.)
1.	$[\text{Ni}(\text{H}_2\text{L})\text{Cl}_2]$	13,700	17,800	24,000	2.82
2.	$[\text{Ni}(\text{H}_2\text{L})\text{Br}_2]$	14,000	18,000	24,000	3.00
3.	$[\text{Ni}(\text{H}_2\text{L})\text{I}_2]$	13,700	18,700	24,300	2.95
4.	$[\text{Ni}(\text{H}_2\text{L})(\text{NO}_3)_2]$	14,100	18,300	24,700	2.90
5.	$[\text{Ni}(\text{H}_2\text{L})(\text{ClO}_4)_2]$	13,600	17,900	24,800	2.80

ELECTRONIC SPECTRA OF TRINUCLEAR COPPER(II) COMPLEX WITH IMINE-OXIME LIGAND H_2L AND MAGNETIC MOMENT DATA

Sl. No	Complexes	Chromophore CuO_2X_2	Chromophore CuN_4	μ_{eff} (B.M.)
1.	$[\text{Cu}_2(\text{L})\text{Cl}_2]$	12,300	17,000	1.80
2.	$[\text{Cu}_2(\text{L})\text{Br}_2]$	12,000	17,500	1.90
3.	$[\text{Cu}_2(\text{L})(\text{NO}_3)_2]$	12,700	17,400	1.75
4.	$[\text{Cu}_2(\text{L})(\text{ClO}_4)_2]$	12,500	17,000	1.80

The signal for oxime proton in the ligand is expected to appear at a low field compared to other protons. Thus, the singlet 8.82 due to oxime proton in the ligand spectrum shifted down field at 9.00 in the spectra of the co-ordination compounds of the type $[M(H_2L)X_2]$. Disappearance of this signal from the spectra of the complexes of the type $M(L)$ and $Cu_2(L)X_2$ is an evidence of its deprotonation and having taken part in the coordination compound formation.

Thus 1H NMR and spectral observations are supplements to each other.

The spectral features so far discussed strongly supported the complexes as shown in Fig. 2 to 5 assigned as on the basis of infrared spectra.

The results of the investigation reveal that the oxygen atom of the oxime group in a mononuclear metal oxime complex can further coordinate to the neighbouring metal complexes specially in case of copper(II) with strikingly different magnetic and spectral properties.

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