

Synthesis and spectral studies on Co (II), Ni(II) and Cu(II) complexes with 1,2- bis(N-methylbenzimidazolyl)benzene

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Abstract: Reactions of hydrated halides/perchlorate of cobalt(II), nickel(II) and copper(II) with 1,2-bis(N-methylbenzimidazolyl)benzene (L) in stoichiometric amounts in ethanol-tetrahydrofuran/acetone produced complexes of the formulae $MX_2L.nH_2O$ ($n = 1, M = Co, X = Cl$; $n = 0, M = Co, X = Br$ or I ; $n = 0, M = Ni, X = I$; $n = 0, M = Cu, X = Br$), $[MX_2L(H_2O)]$ ($M = Ni, X = Cl$ or Br ; $M = Cu, X = Cl$), $[Co(OCIO_3)_2(L)_{1.5}]_2.2H_2O$, $[Ni(L)_2](ClO_4)_2.H_2O$ and $[Cu(L)_2(OCIO_3)]ClO_4.2H_2O$. The complexes were characterised by elemental analyses, thermogravimetric analysis, magnetic moment measurements, IR, electronic, NMR, ESR, mass spectral techniques. Probable structures have been proposed for the complexes.

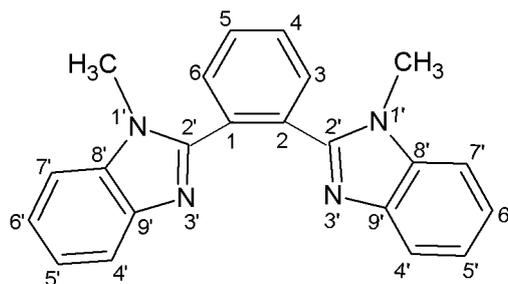
Keywords: 1,2-bis(N-methylbenzimidazolyl)benzene, cobalt, nickel and copper complexes.

I. Introduction:

Benzimidazole is biologically an important scaffold and its functionalization and cyclisation reactions lead to novel derivatives which exhibit selected bioactivity such as anti-infective, anti-inflammatory, antitumour and receptor against/antagonist activities.¹ Cobalt is present in vitamin B₁₂ and linked to 5,6-dimethylbenzimidazole. The binding of imidazole ring of histidine to nickel(II) in various biological centres is known earlier.² Nickel is an essential trace element present in many hydrogenases.³ Metal complexes of multidentate N-heterocycles containing imidazole moiety are of current interest as potential models for metalloenzymes and metalloproteins.⁴ Nickel(II) complexes containing chelating benzimidazolyl ligands are also of importance as they display interesting spectral and magnetic behaviours.⁵ The reactivity of several multidentate N-heterocycles with nickel(II) and the spectral and magnetic properties of the resultant complexes are studied earlier.^{6,7}

Copper is a biologically important element. It is found in hemocyanin, a copper protein which takes up dioxygen. Hemocyanin is responsible for the transport of molecular oxygen in the hemolymph of many species of molluscs and arthropods. In hemocyanin each copper is coordinated to imidazole groups of three histidine molecules. The imidazole groups are also ligated to copper in several blue copper proteins, such as plastocyanin, stellamycin, and azurin.⁸

The metalloenzyme superoxide dismutase contains copper and zinc. Benzimidazole derivatives and their metal complexes exhibit biological and catalytic activities. Synthesis and characterization of transition metal complexes of 1,3-bis(benzimidazolyl/N-methylbenzimidazolyl)benzene have been reported from these laboratories.⁹ In addition, halo and perchlorate complexes of palladium containing cyclooctenyl group and 1,2-bis(N-methylbenzimidazolyl)benzene have also been reported^{10,11}. Herein we describe the synthesis and characterization of halo and perchlorate complexes of divalent cobalt, nickel and copper containing 1,2- bis(N-methylbenzimidazolyl)benzene(L ; I)



II. Experimental

Reagents

Hydrated metal chlorides and metal bromides were procured from BDH. Metal iodide and hydrated perchlorates were prepared by dissolving metal carbonate in 1:1 or 1:2 aqueous hydroiodic acid and perchloric

acid respectively and evaporating the resulting solution to almost dryness under reduced pressure. The N-heterocycle(I) was prepared following the procedure reported for related N-heterocycles.⁹⁻¹¹

Measurements

C, H and N analyses of the complexes were carried out on a Heracus Carlo Erba 1108 microanalyser. Metal content was determined using a Spectra AA-30 spectrophotometer equipped with a Varian DS-15 computer. IR (nujol mull) and Far-IR (polyethylene powder) spectra of the complexes were recorded on Shimadzu IR-435 and Bruker IFS 113V spectrometers respectively. Magnetic moment measurements at room temperature were made using a Gouy balance with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the calibrant. ESR powder spectra (at room temperature and 77 K) were recorded on a Bruker ESP-300 spectrometer at X-band frequency. Conductivity data were obtained using a Systronics – 304 conductivity bridge. NMR spectra were recorded in $\text{DMSO}-d_6$ on AMX 400 MHz spectrometer using TMS as the internal standard at NMR Research centre I.I.Sc., Bangalore. TGA was carried out on a Mettler TAHE – 20 thermal analyzer with a scan rate of $5^\circ \text{C min}^{-1}$ in air. The FAB-mass spectra were recorded on a JEOL SX NO₂ / DA – 6000 mass spectrometer at room temperature using argon (6 KV, 100 mA) as the FAB gas at CDRI Lucknow, India.

Preparation of the complexes

$\text{CoX}_2\text{L} \cdot n\text{H}_2\text{O}$ (X = Cl, n = 1; X = Br or I, n = 0, L = $\text{bbzIme}_2\text{bzH}$)

To a solution of hydrated cobalt(II) halide (1 mmol) in absolute alcohol/acetone-triethylorthoformate(teof) mixture (10:5 cm^3), $\text{bbzIme}_2\text{bzH}$ (1 mmol) in absolute alcohol/acetone (10 cm^3) was added. The solution was refluxed for 4 hrs when a blue solid separated. The solid was washed with absolute alcohol/acetone and dried in vacuo. Yield: 60-80%.

$[\text{Co}(\text{OCIO}_3)_2(\text{L})_{1.5}]_2 \cdot 2\text{H}_2\text{O}$

To a solution of hydrated cobalt(II) perchlorate (2 mmol) in absolute alcohol-teof mixture (10:5 cm^3), $\text{bbzIme}_2\text{bzH}$ (3 mmol) in absolute alcohol (10 cm^3) was added. The solution was refluxed for 4 hrs when a pink solid separated. The solid was washed with absolute alcohol and dried in vacuo. Yield: 85%.

$\text{NiX}_2\text{L} \cdot (\text{H}_2\text{O})$ (X = Cl or Br) and NiL_2L

To a solution of hydrated nickel(II) halide (1 mmol) in absolute alcohol/thf-teof mixture (10:5 cm^3), $\text{bbzIme}_2\text{bzH}$ (1 mmol) in absolute alcohol/thf (10 cm^3) was added. The solution was refluxed for 5 hrs when a purple/blue solid separated. The solid was washed with absolute alcohol/thf and dried in vacuo. Yield: 90%.

$[\text{Ni}(\text{L})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

To a solution of hydrated nickel(II) perchlorate (1 mmol) in absolute alcohol-teof mixture (10:5 cm^3), $\text{bbzIme}_2\text{bzH}$ (2 mmol) in absolute alcohol (10 cm^3) was added. The solution was refluxed for 4 hrs when a cream solid separated. The solid was washed with absolute alcohol and dried in vacuo. Yield: 90%.

$\text{CuCl}_2\text{L}(\text{H}_2\text{O})$ and CuBr_2L

To a solution of copper(II) halide (1 mmol) in ethanol-teof mixture (10:5 cm^3) was added slowly with stirring to 20 cm^3 of an ethanolic solution of the $\text{bbzIme}_2\text{bzH}$ (1 mmol) when a green coloured precipitate separated out. The mixture was allowed to stand at room temperature for about 1 hr and subsequently the precipitate was washed with ethanol and dried in vacuo. Yield: 75%.

$[\text{Cu}(\text{OCIO}_3)(\text{L})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$

To a solution of hydrated copper(II) perchlorate (1 mmol) in ethanol (25 cm^3) was added slowly with stirring an ethanolic solution (25 cm^3) of $\text{bbzIme}_2\text{bzH}$ (2 mmol) when a green colored complex precipitated out instantaneously. The mixture was allowed to stand at room temperature for about 1 hr and then the precipitate was washed with ethanol and dried in vacuo. Yield: 60%.

III. Results and discussion

The halides and perchlorates of cobalt, nickel and copper react with $\text{bbzIme}_2\text{bzH}$ (L) to produce blue/pink/purple/cream/green complexes of the compositions MX_2L (M = Co, X = Br or I; M = Ni, X = I; M = Cu, X = Br), $\text{CoCl}_2\text{L} \cdot \text{H}_2\text{O}$, $[\text{MX}_2\text{L}(\text{H}_2\text{O})]$ (M = Ni, X = Cl or Br; M = Cu, X = Cl) $[\text{Co}(\text{OCIO}_3)_2(\text{L})_{1.5}]_2 \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{L})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{OCIO}_3)(\text{L})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$. The halo and perchlorate complexes of cobalt and copper are insoluble in common organic solvents but are soluble in DMF, in which they behave as non-electrolytes excepting that of copper perchlorate complex which exhibits uni-univalent electrolyte behaviour.⁸ The complexes of nickel decompose in dmf as evidenced by the colour change in solution and also the conductivity data.⁵ Physical properties and analytical data of the complexes are listed in Table 1.

The solid state i.r. spectra of the complexes are comparable with those of the uncoordinated N-heterocycle barring minor shifts in the positions of the peaks. The spectra of the complexes displayed peaks around 1545 and 1631 cm^{-1} due to $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ respectively and a peak at 1403 cm^{-1} due to the N-CH₃ deformation vibration. The perchlorate complexes, in addition to the heterocycle peaks, showed additional peaks due to the perchlorate group. The complex $[\text{Co}(\text{OCIO}_3)_2(\text{L})_{1.5}]_2 \cdot 2\text{H}_2\text{O}$ displayed split peaks around 1114 and 622

cm^{-1} which are characteristic of coordinated perchlorate group.⁹ The $[\text{Ni}(\text{L})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ complex exhibited peaks at 1098 and 622 cm^{-1} due to ionic perchlorate groups.¹² The $[\text{Cu}(\text{OCIO}_3)(\text{L})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ complex revealed intense peaks at 1103, 1098 and 622 cm^{-1} due to the presence of both coordinated and ionic perchlorates.¹³ The spectral features are characteristic of coordination of one of the perchlorate groups to Cu(II), the other being outside the coordination sphere.⁵ The far-IR spectra of the chloro complexes displayed peaks due to terminal $\nu_{\text{M-Cl}}$ and $\nu_{\text{M-N}}$ ($\text{M} = \text{Co}, \text{Ni}$ or Cu) around 315 and 278 cm^{-1} respectively.¹⁴

The room temperature magnetic moments of the complexes indicate the paramagnetic nature of the metal ions except for $[\text{Ni}(\text{L})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ which behaved as diamagnetic.⁵ The magnetic moments of the halo complexes of Co(II) are in the range 4.0 – 4.7 BM. The values are typical of tetrahedral geometry for the complexes. The $[\text{Co}(\text{OCIO}_3)_2(\text{L})_{1.5}]_2 \cdot 2\text{H}_2\text{O}$ complex has a magnetic moment of 4.9 BM and this is expected for a trigonal bipyramidal geometry. The μ_{eff} values of nickel(II) halo complexes are in the range 3.1 – 3.5 BM. The values are in the range expected for tetrahedral/square pyramidal geometry.¹⁵⁻¹⁷ The magnetic moments of the copper(II) complexes are in the range 1.9 – 2.0 BM observed for tetrahedral/square pyramidal geometry. However the values are slightly higher than spin only moment 1.7 BM and the higher values arise presumably due to orbital contribution to the magnetic moment.

The electronic spectra of the complexes have been recorded in nujol mull (Table 2). The spectra of cobalt(II) complexes exhibited three multiple absorption bands around 4000, 7000 and 15000 cm^{-1} . The positions of the bands and their intensities suggest a tetrahedral geometry for the complexes. The bands are assigned to the transitions ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2(\text{F})(\nu_1)$, ${}^4\text{T}_1(\text{F})(\nu_2)$ and ${}^4\text{T}_1(\text{P})(\nu_3)$ respectively. The bands are split and the nature of splitting indicates that the tetrahedral structure is distorted. The ligand field (10 Dq), the Racah (B', interelectronic repulsion) and nephelauxetic (β) parameters have been calculated for the complexes. The 10 Dq values for the halo complexes follow the known spectrochemical series order $\text{I} < \text{Br} < \text{Cl}$. The magnitude of B' in the complexes is considerably reduced relative to the free ion value (971 cm^{-1}) indicating appreciable covalent character for the metal–ligand bonds. The spectrum of $[\text{Co}(\text{OCIO}_3)_2(\text{L})_{1.5}]_2 \cdot 2\text{H}_2\text{O}$ complex displayed four absorption bands around 7000, 10000, 18000 and 27000 cm^{-1} (Table 2) due to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{E}''(\text{F})$, ${}^4\text{E}'(\text{F})$, ${}^4\text{A}_2(\text{P})$ and ${}^4\text{E}''(\text{P})$ transitions respectively of trigonal bipyramidal geometry around the metal ion.^{18,19} The $\text{NiX}_2\text{L} \cdot (\text{H}_2\text{O})$ ($\text{X} = \text{Cl}$ or Br) complexes have displayed weak and broad bands around 10000 and 18000 cm^{-1} and a shoulder around 25000 cm^{-1} due to ${}^3\text{B}(\text{F}) \rightarrow {}^3\text{E}(\text{P})$, ${}^3\text{A}_2(\text{P})$ and ${}^3\text{E}(\text{P})$ transitions respectively arising from a square pyramidal geometry.²⁰ The spectrum of $[\text{Ni}(\text{L})_2]$ complex exhibited absorption bands at 4462, 8741 and 15239 cm^{-1} . The positions of the bands and their intensities are characteristic of tetrahedral geometry.²¹ The bands may be assigned to the transitions ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$, ${}^3\text{A}_2(\text{F})$ and ${}^3\text{T}_1(\text{P})$ and the Racah parameter (B') has reduced as compared to the free ion value (1041 cm^{-1}) indicating the covalent character for the metal–ligand bonds. The spectrum of $[\text{Ni}(\text{L})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ has displayed weak and broad bands at 16181 and 25773 cm^{-1} and they are assigned respectively to the transitions ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ arising out of the square planar geometry. The spectra of $\text{CuCl}_2\text{L} \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{OCIO}_3)(\text{L})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ have displayed bands at 16233 and 17256 cm^{-1} respectively and are assigned to ${}^4\text{A}_2 \rightarrow {}^4\text{A}_1(\text{P})$ transition of tetrahedral geometry (Table 3). CuBr_2L has displayed a band at 15974 cm^{-1} and this is assigned to ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$ transition of square pyramidal geometry. A shoulder observed in the region 33000 cm^{-1} for all the copper complexes may be due to charge-transfer transition from the halogen/perchlorate to copper.²²

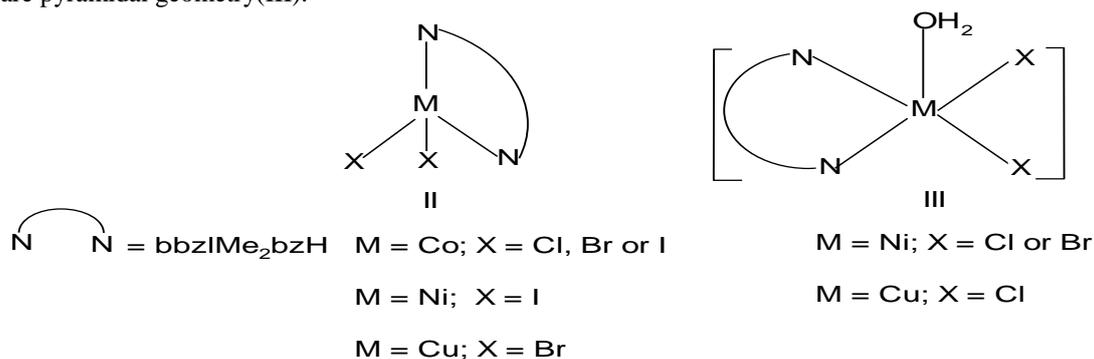
The X-band ESR spectra of powdered samples of the copper complexes have been recorded at ambient temperature. The ESR signals corresponding to g_{\parallel} and g_{\perp} are centred around 2.23 and 1.99 respectively (Table 3). The spectral profiles are typical of axial type ($g_{\parallel} > g_{\perp}$) implying a $d_{x^2-y^2}$ ground state. The spectral features bear a striking resemblance to those reported for five coordinate square-pyramidal copper(II) complexes.^{23,24} The g_{\parallel} value is < 2.3 for the complexes, suggesting considerable covalent character in the metal–ligand bond. The ESR spectrum of $[\text{Cu}(\text{OCIO}_3)(\text{L})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ has shown g_{\parallel} hyperfine structure with four line splitting arising due to the interaction of electron with the nuclear spin of copper atom ($I = 3/2$).^{25,26}

The FAB-mass spectrum of $[\text{Co}(\text{OCIO}_3)_2(\text{L})_{1.5}]_2 \cdot 2\text{H}_2\text{O}$ suggests binuclear nature of the complex.^{18,27} Although the molecular ion peak corresponding to the dimer $\text{Co}_2\text{L}_3(\text{ClO}_4)_4$ (m/z , 1567) is absent, peaks due to fragmentation products $\text{Co}_2\text{L}_3(\text{ClO}_4)_2$ (m/z , 1531), CoL_3 (m/z , 1074), $\text{Co}_2\text{L}_{1.5}\text{-4H}$ (m/z , 621) have been observed. In addition, peaks due to association of fragments are observed at 1284, 1177, 1115 and 564 and these are due to $\text{Co}_4\text{L}_2 \cdot 2\text{H}_2\text{O}$ (L-3H), $\text{CoL}_3(\text{ClO}_4) + 3\text{H}$, $\text{Co}_4\text{L}(\text{ClO}_4)_2$ (L-4H) and $\text{CoL}_{1.5}\text{-2H}$ respectively.

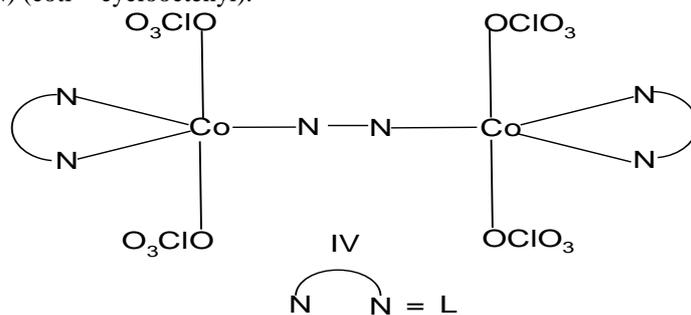
The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of $[\text{Ni}(\text{bbzlMe}_2\text{bzH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ have been recorded in dmsO-d_6 . The spectra indicated that the corresponding protons of the two benzimidazole moieties are equivalent. The ${}^1\text{H}$ NMR spectrum exhibited a multiplet at 7.80 δ due to benzene ring and a singlet due to of N-Me group at 3.48 δ . Benzimidazole ring protons 4', 5', 6' and 7' displayed peaks at 7.48d, 7.19t, & 7.13t and 7.45d δ respectively. ${}^{13}\text{C}$ NMR spectrum of the complex exhibited a peak at 152.04 δ due to most deshielded carbon C-2'. Other quaternary carbons 1 and 2, 8' and 9' showed resonances at 130.55, 135.42 and 142.13 δ respectively. The resonance signal due to N-Me group is observed at 30.49 δ . The peaks due to benzimidazole ring carbons 4', 5', 6' and 7' are detected at 118.78, 122.16, 121.60 and 110.15 δ respectively and phenyl ring carbons C-3,6 and C-

4,5 resonances are located at 131.15 and 129.75 δ respectively. An upfield shift of the resonances relative to those of the uncoordinated heterocycle has been noticed. This is attributed to metal-to-ligand π -back donation in the complex.

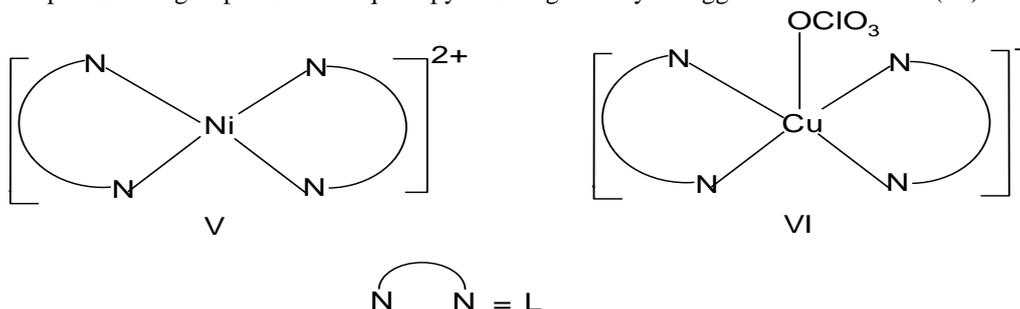
Thermogravimetric analyses of the halo and perchlorate complexes have been carried out at a heating rate of 5°C in air. The presence of lattice and coordinated water molecules in the complexes is revealed by the data (Table 4). While the lattice water is lost below 100°C, the coordinated water is lost above 100°C. The ultimate product of thermal decomposition in all the complexes is metal oxide. In the case of $[\text{NiBr}_2\text{L}\cdot\text{H}_2\text{O}]$, a sharp exotherm is observed at 483°C and this corresponds to the loss of one bromide and water molecule.^{8, 28, 29} The analytical data, IR and electronic spectral results have indicated that the N-heterocycle is coordinated to the metal ion. The N-heterocycle is planar and can serve as chelating or bridging bidentate ligand. In the case of MX_2L ($\text{M} = \text{Co}$, $\text{X} = \text{Cl}$, Br or I ; $\text{M} = \text{Ni}$, $\text{X} = \text{I}$ and $\text{M} = \text{Cu}$, $\text{X} = \text{Br}$) complexes, the tertiary nitrogen of each benzimidazole unit and the halides are coordinated to the metal. Hence the complexes are proposed to have a tetrahedral geometry (II) in which the N-heterocycle acts as a chelating bidentate ligand. In the case of $\text{MX}_2\text{L}\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Ni}$, $\text{X} = \text{Cl}$ or Br ; $\text{M} = \text{Cu}$, $\text{X} = \text{Cl}$) complexes, the tertiary nitrogen of each N-heterocycle unit, and a water molecule and the halides are coordinated to the metal ions and the complexes are suggested to have a square pyramidal geometry(III).^{5,8,9}



The FAB-mass spectrum of $[\text{Co}(\text{OCIO}_3)_2(\text{L})_{1.5}]_2 \cdot 2\text{H}_2\text{O}$ has supported the binuclear nature of the complex. Based on molar conductivity, IR and electronic spectral data, the complex may be assigned, dinuclear structure (IV) with each cobalt having trigonal bipyramidal environment involving coordinated perchlorate ions and N-heterocycle bridge. A similar bidentate bridging behaviour of the N-heterocycle has been proposed in the case of $[\text{Pd}(\text{cotl})\text{Br}]_2 (\mu\text{-N-N})$ (cotl = cyclooctenyl).¹¹



Based on conductivity data, together with IR, NMR spectral studies, for the nickel perchlorate complex cation, a mononuclear structure with square planar geometry (V) around the metal ion has been proposed. Copper perchlorate complex behaved as 1:1 electrolyte and IR spectral data indicated the presence of both ionic and coordinated perchlorate groups. Hence a square pyramidal geometry is suggested for the cation(VI).



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Table 1. Analytical data and i.r spectral data of the cobalt (II), nickel(II) and copper (II) complexes

Compound	Color	M.p (°C)	μ_{eff} (BM)	χ^2 ($\Omega^2 \text{ cm}^2 \text{ mol}^{-1}$)	Analytical data				I.r. Spectral data (cm^{-1})		
					Found (calcd,%)				$\delta_{\text{Co-Cu}}$	$\nu_{\text{Co-C}} \& \nu_{\text{Co-N}}$	$\nu_{\text{Co-O}}$
					Co/Ni/Cu	C	H	N			
L	White	250	-	-	-	78.08(78.14)	5.36(5.37)	16.56(16.11)	1403	1545,1616	
[CoCl ₂ L].H ₂ O	Blue	>290	4.7	26	12.33(12.12)	54.30(54.34)	4.17(4.14)	11.64(11.52)	1403	1550,1621	
[CoBr ₂ L]	Blue	> 250	4.1	7	9.98(9.96)	44.59(44.69)	3.00(3.06)	9.57(9.47)	1403	1550,1610	
[Co ₂ L]	Blue	> 270	4.2	23	9.04(9.00)	40.65(40.57)	2.75(2.78)	8.63(8.60)	1403	1550,1616	
[Co(OClO ₂) ₂ L ₂].2H ₂ O	Pink	>270	4.9	15	10.67(10.80)	48.79(48.63)	3.67(3.71)	10.40(10.30)	1403	1522,1621	1114,1041 (ν_2), 645 (ν_4)
[NiClL(H ₂ O)]	purple	>260	3.5	-	11.40(11.46)	54.29(54.30)	3.99(4.10)	10.75(11.52)	1403	1548,1610	
[NiBr ₂ L(H ₂ O)]	Blue	>270	3.1	-	10.37(10.20)	46.01(45.95)	3.19(3.15)	9.67(9.74)	1403	1547,1616	
[Ni ₂ L]	Blue	>270	3.4	-	9.10(9.00)	40.63(40.59)	2.74(2.78)	8.50(8.60)	1398	1547,1621	
[Ni ₂](ClO ₄) ₂ .H ₂ O	Cream	>290	Diamagn etic	7	6.29(6.16)	55.44(55.48)	4.02(4.02)	11.63(11.76)	1403	1548,1621	1098 (ν_2), 628 (ν_4)
[CuCl ₂ L(H ₂ O)]	Green	>270	1.8	32	12.86(12.94)	54.83(53.83)	4.14(4.12)	11.30(11.46)	1398	1545,1626	
[CuBr ₂ L]	Green	>260	1.8	36	11.28(11.31)	47.24(47.03)	3.17(3.22)	9.68(9.97)	1403	1545,1616	
[Cu(OClO ₂) ₂ L ₂].ClO ₄ .2H ₂ O	Green	>270	1.9	72	6.52(6.51)	54.25(54.18)	4.16(4.13)	11.40(11.48)	1403	1545,1636	1103 (ν_2), 622 (ν_4)

^a Gouy method

^b Molar conductance of ca. 10⁻³ M solution in DMF

Table 2. Electronic spectral data (cm^{-1}) of cobalt (II) and nickel(II) complexes

Complex*	Transitions and assignments			Crystal field parameters		
Tetrahedral	$^4A_2(F) \rightarrow ^4T_2(F)$	$^4A_2 \rightarrow ^4T_1(F)$	$^4A_2 \rightarrow ^4T_1(P)$	10 Dq	B ¹	β
[CoCl ₂ L]. H ₂ O	4074	7225	15434	4928	647	0.665
[CoBr ₂ L]	4152	9293	15723	4799	630	0.647
[Co ₂ L]	4128	8756	14838	4543	593	0.609
Tetrahedral	$^3T_1(F) \rightarrow ^3T_2(F)$	$^3T_1(F) \rightarrow ^3A_2(F)$	$^3T_1(F) \rightarrow ^3T_1(P)$			
[Ni ₂ L]	4462	8741	16233	4279	773	0.742
Square planar	$^1A_{1g} \rightarrow ^1A_{2g}$	$^1A_{1g} \rightarrow ^1B_{1g}$	---	---	--	--

[NiL ₂](ClO ₄) ₂ .H ₂ O	16181	25773	---	---	--	--
Trigonal bipyramidal	⁴ A ₂ ' (F) → ⁴ E" (F)	⁴ A ₂ ' (F) → ⁴ E ¹ (F)	⁴ A ₂ '(F) → ⁴ A ₂ ' (P)	⁴ A ₂ ' (F) → ⁴ E" (P)		
[Co(OCIO ₃) ₂ L _{1.5}] ₂ .2H ₂ O	7042	10183	18050	27173		
Square pyramidal	³ B(F) → ³ E(P)	³ B(F) → ³ A ₂ (P)	³ B(F) → ³ E(P)			
[NiCl ₂ L(H ₂ O)]	10204	18796	25173 sh			
[NiBr ₂ L(H ₂ O)]	9960	18050	25162 sh			

*Spectra recorded in nujol
B is taken to be 972 cm⁻¹ for Co²⁺ ion and 1041 cm⁻¹ for Ni²⁺ ion

Table 3. Electronic and ESR spectral data of copper(II) complexes.

Complex	Electronic spectral bands (cm ⁻¹) ^a		ESR spectral parameters*	
	d-d band	CT band	g	g _⊥
	² B ₁ → ² B ₂	----		
[CuCl ₂ L.H ₂ O]	16233	32051	2.23	2.05
[CuBr ₂ L]	⁴ A ₂ → ⁴ A ₁ (P)	----	2.22	2.07
	15974	33112		
[Cu(OCIO ₃) ₂ L ₂].ClO ₄ . 2H ₂ O	² B ₁ → ² B ₂	----	2.09, 2.20, 2.32	1.99
	17256	33783		

^aSpectra recorded in nujol *Polycrystalline spectra at room temperature

Table 4. Thermogravimetric data of the complexes.

Complex	Temperature °C	Weight loss (%)*	Species loss
[CoCl ₂ L]. H ₂ O	<100	3.68(3.69)	H ₂ O (lattice)
[Co(OCIO ₃) ₂ L _{1.5}] ₂ . 2H ₂ O	<100	4.56(4.50)	2H ₂ O (lattice)
[NiCl ₂ LH ₂ O]	422	3.80(3.70)	H ₂ O (co-ordinated)
[NiBr ₂ LH ₂ O]	483	16.80(17.02)	(Br+H ₂ O)(co-ordinated)
[NiL ₂](ClO ₄) ₂ H ₂ O	<100	1.50(1.45)	H ₂ O (lattice)
[CuCl ₂ L.H ₂ O]	326	3.57(3.66)	H ₂ O (co-ordinated)
[Cu(OCIO ₃) ₂ L ₂].ClO ₄ . 2H ₂ O	<100	3.80(3.70)	2H ₂ O (lattice)

*Calculated values are in parentheses