



Synthesis, Characterization and Spectral Studies of Noble Heterobinuclear Complexes of Transition Metal Ions and their Biological Activity

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Abstract: Some noble heterobinuclear complexes of transition metal ions with bis(salicylaldehyde)malonyl-dihydrazone in the presence of 5-nitroindazole Cu(II) / Ni(II)- chloride of the type $[ML_1 M' L_2 Cl_2]$ or $[ML_1 Fe L_2 Cl_2]Cl$, where $M = Ni(II), Cu(II)$ and $M' = Mn(II), Co(II)$, have been prepared. All the complexes have been characterized by IR, UV vis and EPR spectroscopy, elemental analysis, magnetic moment and molar conductance measurement. Spectral studies and magnetic moment measurement in DMF suggest the covalent nature of the complexes, except the $[ML_1 Fe L_2 Cl_2]Cl$ complex which is 1:1 electrolyte. An octahedral geometry is proposed for M' and square planer for M for the heterobinuclear complexes. The low value of magnetic moment and overlapping EPR signals are due to spin crossover since both of the metals have unpaired electrons with same molecular symmetry. The lowering of the magnetic moment has been discussed. The biological activity (antifungal and antibacterial) of the represented compounds has been studied.

Keywords: Heterobinuclear complexes, Malonyldihydrazone, 5-Nitroindazole, Biological activity.

Introduction

Many of the divalent metal ions are widely presented *in vivo* as trace elements and essential for the living organism to maintain and regulate biological activities¹⁻². There has been a great interest in the synthesis of heterobinuclear complexes for their interesting magnetic properties³⁻⁴ and active sites of biomolecules⁵. Heterobinuclear bridged complexes can be formed in stepwise fashion from a mononuclear compound which contains a dangling ligand. The first spin crossover complexes were reported by Tabassum *et al.*⁶. These complexes are also of interest of bioinorganic chemistry due to the importance of the structurally similar porphyrin complexes with unsymmetrical axial ligation⁷⁻⁹. The aim of this work is preparation

and characterization of heterobinuclear complexes of Fe(III),Co(II), Mn(II), Cu(II) and Ni(II). Many other works have been done earlier by various chemists which show current importance and interest of coordination chemistry of transition metal ions¹⁰⁻¹³.

Experimental

All the chemicals used in this work were analytical grade. Hydrated Mn(II), Co(II), Ni(II), Cu(II) and Fe(III) chloride (BDH), 5-nitroindazole (Fluka), DMSO, DMF, acetonitrile, malonyl dihydrazone, salicylaldehyde and ethanol. Double distilled water was used throughout the experiment. The transition metal complexes of 5-nitroindazole and bis(salicylaldehyde)malonyl hydrazone were prepared as per the method reported earlier¹⁴⁻¹⁵.

Preparation of [MnL₁NiL₂Cl₂]

A solution of MnL₁ (0.393 g, 1 mmol) in DMF (15 mL) was added to the solution of NiL₂Cl₂ (0.455 g, 1 mmol) and refluxed for 10 h and then kept in refrigerator overnight. A light pink colour product was formed which was filtered and washed with ethanol, ether and dried *in vacuo*.

Preparation of [MnL₁CuL₂Cl₂]

This compound was prepared by using same procedure as above.

Preparation of [CoL₁NiL₂Cl₂]

A solution of CoL₁ (0.397 g, 1 mmol) in dry DMF (15 mL) was refluxed with a methanolic solution (15 mL) of NiL₂Cl₂ (0.455 g, 1 mmol). The purple colour solution of CoL₁ turned blue on addition of the solution of NiL₂Cl₂. A light yellow coloured product was precipitated on refluxing for 8 h. The compound was filtered, washed with ethanol, ether and dried *in vacuo*.

Preparation of [CoL₁CuL₂Cl₂]

This compound was prepared by using same procedure as above.

Preparation of [NiL₁FeL₂Cl₂]Cl

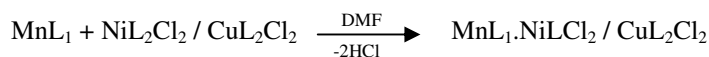
A solution of NiL₁ (0.397g, 1 mmol) in methanol (15 mL) was treated with a solution of [FeL₂Cl₂]Cl (0.488 g, 1 mmol) in dry DMF (15 mL). The resultant solution was refluxed for 20 h. A brown product precipitated. The complex was filtered, washed with ethanol, ether and dried *in vacuo*.

Preparation of [CuL₁FeL₂Cl₂].Cl

This complex was prepared by using same procedure as above.

Results and Discussion

The complexes were prepared according to the following chemical equations-



Where, L₁ = bis(salicylaldehyde)malonyl hydrazone, L₂ = 5-nitroindazole.

Analytical data are given in Table 1. All the complexes are soluble in DMF and DMSO. Molar conductance values are measured in DMF solvent and show non-electrolyte nature of complexes, except $[\text{NiL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$ and $[\text{CuL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$ which are 1:1 electrolyte. (Figure 1.)

Table 1. Analytical data of heterobinuclear complexes

Complexes	Molecular Formula (Formula weight)	Colour	M.P., °C	Yield, %	Calcd. found%		
					C	H	N
$[\text{MnL}_1\text{NiL}_2\text{Cl}_2]$	$\text{C}_{31}\text{H}_{24}\text{Cl}_2\text{MnN}_{10}\text{O}_8\text{Ni}$ (849.15)	Light pink	326	32	43.85 (43.88)	2.85 (2.88)	16.50 (16.54)
$[\text{MnL}_1\text{CuL}_2\text{Cl}_2]$	$\text{C}_{31}\text{H}_{24}\text{Cl}_2\text{MnN}_{10}\text{O}_8\text{Cu}$ (853.97)	Pink	330	38	43.60 (43.65)	2.83 (2.86)	16.40 (16.45)
$[\text{CoL}_1\text{NiL}_2\text{Cl}_2]$	$\text{C}_{31}\text{H}_{24}\text{Cl}_2\text{CoN}_{10}\text{O}_8\text{Ni}$ (853.14)	Light Yellow	338	40	43.63 (43.68)	2.84 (2.88)	16.42 (16.44)
$[\text{CoL}_1\text{CuL}_2\text{Cl}_2]$	$\text{C}_{31}\text{H}_{24}\text{Cl}_2\text{CoN}_{10}\text{O}_8\text{Cu}$ (857.96)	Dirty Yellow	320	41	43.40 (43.44)	2.82 (2.85)	16.33 (16.38)
$[\text{NiL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$	$\text{C}_{31}\text{H}_{24}\text{Cl}_3\text{FeN}_{10}\text{O}_8\text{Ni}$ (885.60)	Brown	340	29	42.04 (42.08)	2.73 (2.76)	15.82 (15.86)
$[\text{CuL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$	$\text{C}_{31}\text{H}_{24}\text{Cl}_3\text{FeN}_{10}\text{O}_8\text{Cu}$ (890.40)	Reddish Brown	348	35	41.81 (41.84)	2.72 (2.76)	15.73 (15.76)

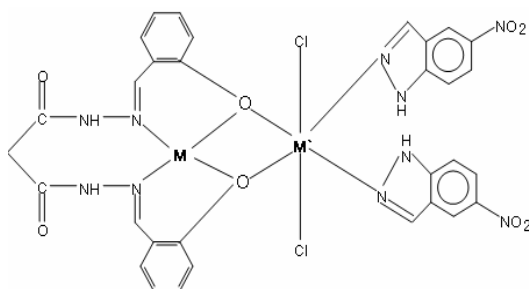


Figure 1. Heterobinuclear complexes of the type $[\text{ML}_1.\text{M}'\text{L}_2\text{Cl}_2]$

IR spectra of the heterobinuclear complexes

The relevant IR bands and their assignments are shown in Table 2. The IR spectra of the binuclear complexes under investigation show several bands belonging to ligands L_1 and L_2 . They are considerably changed compared with the relevant bands of the ligands and monometallic complexes¹⁶. Results given in table are consistent with the some previous results¹⁷⁻²².

Table 2. IR Spectral data, cm^{-1} of the heterobinuclear complexes

Complexes	ν (C=O)	ν (N-H)	Ring Stretching	ν (NO_2) (Asym/Sym)	ν (C=N)	N (M-N)	N (M-O)	N (M-Cl)
$[\text{MnL}_1\text{NiL}_2\text{Cl}_2]$	1722	3320	1616	1532/1388	1618	485	478	322
$[\text{MnL}_1\text{CuL}_2\text{Cl}_2]$	1714	3324	1618	1526/1382	1614	474	472	318
$[\text{CoL}_1\text{NiL}_2\text{Cl}_2]$	1742	3332	1612	1532/1398	1632	472	472	324
$[\text{CoL}_1\text{CuL}_2\text{Cl}_2]$	1745	3328	1624	1538/1388	1626	465	468	326
$[\text{NiL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$	1718	3322	1638	1570/1348	1572	468	472	320
$[\text{CuL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$	1738	3337	1630	1564/1352	1576	475	464	324

Electronic spectra and magnetic moments

Electronic spectra and magnetic moment value of heterobinuclear complexes are given in Table 3. Magnetic moment values are measured in DMF solvent and show non-electrolyte nature of complexes, except $[\text{NiL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$ and $[\text{CuL}_1\text{FeL}_2\text{Cl}_2]\text{Cl}$ which are 1:1 electrolyte.

The electronic spectra of metal complexes were recorded in DMF solvent and contain mixed transitions due to two different metal ions. The binuclear complexes possess anti-ferromagnetic properties at room temperature by intra-molecular spin exchange interaction between M and M' metal ions. Results given in Table 3 are consistent with the heterobinuclear complexes²³.

Table 3. Electronic spectra, magnetic moment and EPR data of heterobinuclear complexes

Complexes	Transition, cm ⁻¹ (values, cm ⁻¹ M ⁻¹)	Assignments	μ_{eff} (B.M.)	EPR Value	
				$g_{ }$	g_{\perp}
[MnL ₁ NiL ₂ Cl ₂]	20,018(304) 18,182(264) 12,508(46)	⁴ A _{2g} → ⁴ T _{1g} (P) ⁴ A _{2g} → ⁴ T _{1g} ⁴ A _{2g} → ⁴ T _{2g}	3.88		
[MnL ₁ CuL ₂ Cl ₂]	38,322(58) 25,444(426) 20,410 16592(410)	C.T. ⁴ A _{1g} (G) ← ⁶ A _{1g} ⁴ T _{2g} (G) ← ⁶ A _{1g} ² E _g (G) ← ⁶ B _{1g} ⁴ T _{1g} (G) → ⁶ A _{1g}	5.14	1.9 1	1.8 6
[CoL ₁ NiL ₂ Cl ₂]	6,568(3.1) 14,418(5.4) 21,268(3.4) 16,376(2.1)	⁴ T _{2g} (F) ← ⁶ T _{1g} (F) ⁴ A _g (F) → ⁴ T _{1g} (F) ² A _{1g} → ¹ B _{1g} ¹ A _{1g} → ¹ B _{2g}	1.92		
[CoL ₁ CuL ₂ Cl ₂]	6,562(3.3) 14,416(5.2) 18,234(5.3) 15,510(6.3) 20,304(2.8)	⁴ T _{2g} (F) ← ⁴ T _{1g} (F) ⁴ A _{2g} (F) ← ⁴ T _{1g} (F) ⁴ T _{1g} (P) ← ⁴ T _{1g} (F) ² A _{1g} ← ¹ B _{1g} ² E _{1g} → ² B _{1g}	1.91	1.8 4	
[NiL ₁ FeL ₂ Cl ₂]Cl	40,466 29,116(28,414) 19,540(26,455) 15,512(24,270) 21,266(3.4) 18,784(2.4)	C.T. ⁴ E _{1g} (G) ← ⁶ A _{1g} ⁴ T _{2g} (G) ← ⁶ A _{1g} ² T ₁ (G) ← ⁶ A _{1g} ¹ A _{1g} → ¹ B _{1g} ¹ A _{1g} → ¹ A _{2g}	5.86		
[CuL ₁ FeL ₂ Cl ₂]Cl	40,466 29,113(28,411) 15,510(24,241) 19,544(26,460) 15,508(6.04) 18,308(8.4)	C.T. ⁴ A _{1g} (G) ← ⁶ A _{1g} ⁴ T _{1g} (G) ← ⁶ A _{1g} ⁴ T ₂ (G) ← ⁶ A _{1g} ¹ B _{1g} (G) → ² A _{1g} ² B _{1g} ← ² E _g	5.88		

EPR spectra

EPR spectra value of all the metal complexes was given in Table 3. The EPR spectra of heterobinuclear complexes were recorded at room temperature. The spectra of $[\text{MnL}_1\text{NiL}_2\text{Cl}_2]$ show $g_{\parallel} = 1.91$, $g_{\perp} = 1.86$ which show square planer Mn(II) complexes. The signals for the two different metals are merged together and new signals are obtained.

Antimicrobial activity

In vitro antimicrobial activity of heterobinuclear metal complexes have been tested against the bacteria *Bacillus subtilis* and *Escherichia coli* and fungi *Aspiggillus niger* and *Aspiggillus flavus* and are summarized in Table 4. The values indicate that all complexes have higher antimicrobial activity than the free ligand. Such increased activity of the metal chelates can be explained on the basis of chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in enzymes of microorganism. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of microorganism²⁴.

Table 4. Antibacterial and antifungal activity of heterobinuclear metal complexes

Compounds	*Conc., $\mu\text{g mol}^{-1}$	Bacterial Inhibition, %		Antifungal Inhibition, %	
		<i>B. subtilis</i>	<i>E. coli</i>	<i>A. niger</i>	<i>A. flavus</i>
$[\text{MnL}_1.\text{NiL}_2\text{Cl}_2]$	100	42	55	66	59
	500	46	60	72	72
$[\text{MnL}_1.\text{CuL}_2\text{Cl}_2]$	100	44	48	74	68
	500	55	52	86	81
$[\text{CoL}_1.\text{NiL}_2\text{Cl}_2]$	100	50	70	73	76
	500	58	78	82	85
$[\text{CoL}_1.\text{CuL}_2\text{Cl}_2]$	100	44	58	65	72
	500	62	70	74	81
$[\text{NiL}_1.\text{FeL}_2\text{Cl}_2].\text{Cl}$	100	44	60	71	73
	500	50	62	78	76
$[\text{CuL}_1.\text{FeL}_2\text{Cl}_2].\text{Cl}$	100	47	58	61	76
	500	56	64	83	82

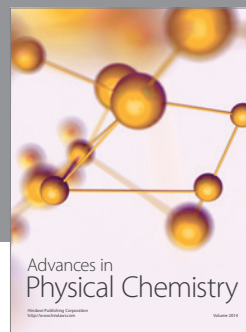
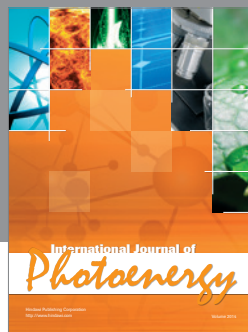
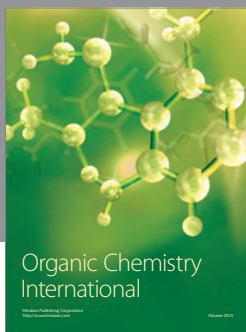
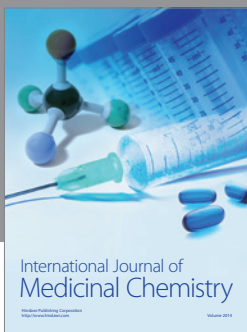
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