

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

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ABSTRACT

Heterobinuclear complexes of transition metal ions with bis(2-aminobenzaldehyde)malonyl- dihydrazone in the presence of 5-nitroindazole Cu(II) / Ni(II)- chloride of the type $[ML_1M'L_2Cl_2]$ or $[ML_1FeL_2Cl_2]Cl$, where $M = Mn(II), Co(II), Ni(II), Cu(II)$ 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 $[ML_1FeL_2Cl_2]Cl$ 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 cross over since both of the metal 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.

Key words: Heterobinuclear complexes, malonyldihydrazone, 5-nitroindazole, biological activity.

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INTRODUCTION

Many of the divalent metal ion are widely presented in vivo as trace elements and essential for the living organism to maintain and regulate biological activities[7,14]. There has been a great interest in the synthesis of heterobinuclear complexes for their relevance as metal for interesting magnetic properties[10,15] and active sites of biomolecules[13]. Heterobinuclear bridged complexes can be formed in step wise fashion from a mononuclear compound which contains a dangling ligand. The first spin cross over complex were reported by Brewer[4]. These complexes are also of interest of bioinorganic chemistry due to the importance of the structurally similar porphyrin complexes with unsymmetrical axial ligation[2,11,16]. 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 ions[1,12,17,21].

MATERIALS AND METHODS

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, 2-aminobenzaldehyde and ethanol. Double distilled water was used. The transition metal complexes of 5-nitroindazole and bis(2-aminobenzaldehyde)malonyl hydrazone were prepared the method reported earlier[3,18].

Preparation of $[MnL_1NiL_2Cl_2]$

A solution of MnL_1Cl_2 (0.462gm, 1mmol) in DMF (15 ml) was added to the solution of NiL_2Cl_2 (0.456gm, 1mmol) and refluxed for 15hr 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 $[MnL_1CuL_2Cl_2]$

This compound was prepared by using same procedure as above.

Preparation of $[CoL_1NiL_2Cl_2]$

A solution of CoL_1Cl_2 (0.466gm, 1mmol) in dry DMF (15ml) was refluxed with a methanolic solution (15 ml) of NiL_2Cl_2 (0.456gm, 1mmol). The purple colour solution of CoL_1Cl_2 turned blue on addition of the solution of

NiL₂Cl₂. A light yellow coloured product was precipitated on refluxing for 6 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

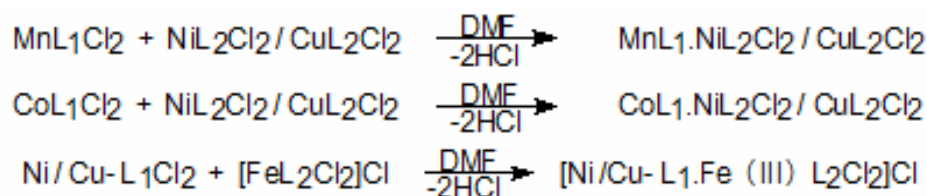
A solution of NiL₂Cl₂ (0.456gm, 1mmol) in methanol (15 ml) was treated with a solution of [FeL₁Cl₂]Cl (0.488gm, 1mmol) in dry DMF (15 ml). The resultant solution was refluxed for 20 h. A brown product precipitated. The complex was filtered, washed with ethanol, ether and dried in vacuo.

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(2-aminobenzaldehyde)malonyl hydrazone, L₂ = 5-nitroindazole.

Analytical data are given in Table 1. All the complexes are soluble in DMF and DMSO. (Fig. 1.)

IR Spectra of the Heterobinuclear Complexes

The relevant IR bands and their assignments are cited in Table 2. The IR spectra of the binuclear complexes under investigation show several bands belonging to ligands L₁ and L₂. They are considerably changed compared with the relevant bands of the ligands and monometallic complexes[22]. Results given in table are consistent with the some previous results[5,8,9,20].

Electronic Spectra and Magnetic Moments

Electronic spectra (UV-vis.) 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 [NiL₁FeL₂Cl₂]Cl and [CuL₁FeL₂Cl₂]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 antiferromagnetic properties at room temperature by intramolecular spin exchange interaction between M and M' metal ions. Results given in table are consistent with the heterobinuclear complexes[19].

EPR Spectra

EPR spectra value of all metal complexes were given in Table 3. the EPR spectra of hetrobinuclear complexes were recorded at room temperature. The spectra of [MnL₁NiL₂Cl₂] show g = 1.91, g = 1.82 which show square planer Mn(II) complexes. The signals for two different metals are merdged 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 *Aspurgillus niger* and *Aspurgillus flavus* and are summerised 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 enhance 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 microorganism [6].

Table-1: Analytical Data of Heterobinuclear Complexes

Complexes	Molecular Formula (Formula weight)	Colour	M.P. (°C)	Yield (%)	Calcd. (found%)		
					C	H	N
[MnL ₁ NiL ₂ Cl ₂]	C ₃₁ H ₂₆ Cl ₂ MnN ₁₂ O ₆ Ni (846.8)	Light pink	324	30	44.00 (43.92)	3.09 (3.04)	19.85 (19.65)
[MnL ₁ CuL ₂ Cl ₂]	C ₃₁ H ₂₆ Cl ₂ MnN ₁₂ O ₆ Cu (852.07)	Pink	328	35	43.70 (43.66)	3.07 (3.01)	19.73 (19.65)
[CoL ₁ NiL ₂ Cl ₂]	C ₃₁ H ₂₆ Cl ₂ CoN ₁₂ O ₆ Ni (851.23)	Light Yellow	336	39	43.74 (43.68)	3.08 (3.03)	19.75 (19.71)
[CoL ₁ CuL ₂ Cl ₂]	C ₃₁ H ₂₆ Cl ₂ CoN ₁₂ O ₆ Cu (856.06)	Dirty Yellow	318	42	43.49 (43.42)	3.06 (3.02)	19.63 (19.54)
[NiL ₁ FeL ₂ Cl ₂]Cl	C ₃₁ H ₂₄ Cl ₃ FeN ₁₂ O ₆ Ni (883.65)	Brown	342	28	42.13 (42.08)	3.00 (2.88)	19.02 (18.84)
[CuL ₁ FeL ₂ Cl ₂]Cl	C ₃₁ H ₂₄ Cl ₃ FeN ₁₂ O ₆ Cu (888.48)	Reddish Brown	346	32	41.90 (41.84)	2.95 (2.91)	18.91 (18.87)

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)	ν (M-N)	ν (M-N)	ν (M-Cl)
[MnL ₁ NiL ₂ Cl ₂]	1725	3318	1615	1528/1382	1615	482	475	322
[MnL ₁ CuL ₂ Cl ₂]	1718	3322	1612	1530/1385	1610	478	470	318
[CoL ₁ NiL ₂ Cl ₂]	1738	3328	1618	1538/1395	1628	460	466	320
[CoL ₁ CuL ₂ Cl ₂]	1735	3330	1622	1536/1392	1624	468	468	324
[NiL ₁ FeL ₂ Cl ₂]Cl	1726	3324	1632	1564/1344	1570	466	472	322
[CuL ₁ FeL ₂ Cl ₂]Cl	1730	3327	1634	1558/1348	1578	470	464	320

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 _⊥
[MnL ₁ NiL ₂ Cl ₂]	20,020(302) 18,178(260) 12,502(45)	⁴ A _{2g} → ⁴ T _{1g} (P) ⁴ A _{2g} → ⁴ T _{1g} ⁴ A _{2g} → ⁴ T _{2g}	3.90		
[MnL ₁ CuL ₂ Cl ₂]	38,320(56) 25,448(428) 20,408 16588(406)	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}	5.10	1.91	1.82
[CoL ₁ NiL ₂ Cl ₂]	6,565(3.1) 14,415(5.3)	⁴ T _{2g} (F) ← ⁶ T _{1g} (F) ⁴ A _g (F) → ⁴ T _{1g} (F)	1.93		

	21,268(3.4) 16,378(2.2)	$^2A_{1g} \rightarrow ^1B_{1g}$ $^1A_{1g} \rightarrow ^1B_{2g}$			
[CoL ₁ CuL ₂ Cl ₂]	6,565(3.4) 14,412(5.1) 18,230(5.2) 15,508(6.2) 20,302(2.7)	$^4T_{2g}(F) \leftarrow ^4T_{1g}(F)$ $^4A_{2g}(F) \leftarrow ^4T_{1g}(F)$ $^4T_{1g}(P) \leftarrow ^4T_{1g}(F)$ $^2A_{1g} \leftarrow ^1B_{1g}$ $^2E_{1g} \rightarrow ^2B_{1g}$	1.93	1.86	
[NiL ₁ FeL ₂ Cl ₂].Cl	40,462 29,112(28,410) 19,542(26,457) 15,508(24,268) 21,266(3.4) 18,788(2.6)	C.T. $^4E_{1g}(G) \leftarrow ^6A_{1g}$ $^4T_{2g}(G) \leftarrow ^6A_{1g}$ $^2T_{1g}(G) \leftarrow ^6A_{1g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ $^1A_{1g} \rightarrow ^1A_{2g}$	5.87		
[CuL ₁ FeL ₂ Cl ₂].Cl	40,460 29,111(28,409) 15,512(24,242) 19,541(26,458) 15,506(6.03) 18,305(8.2)	C.T. $^4A_{1g}(G) \leftarrow ^6A_{1g}$ $^4T_{1g}(G) \leftarrow ^6A_{1g}$ $^4T_{2g}(G) \leftarrow ^6A_{1g}$ $^1B_{1g}(G) \rightarrow ^2A_{1g}$ $^2B_{1g} \leftarrow ^2E_g$	5.82		

Table-4: Antibacterial and Antifungal Activity of Heterobinuclear Metal Complexes.

Compounds	*Conc.	Bacterial Inhibition (%)		Antifungal Inhibition (%)	
		<i>B. subtilis</i>	<i>E. coli</i>	<i>A. niger</i>	<i>A.flavus</i>
[MnL ₁ .NiL ₂ Cl ₂]	100	40	51	62	65
	500	48	58	74	78
[MnL ₁ .CuL ₂ Cl ₂]	100	48	51	71	72
	500	53	55	83	85
[CoL ₁ .NiL ₂ Cl ₂]	100	52	73	82	80
	500	61	82	91	86
[CoL ₁ .CuL ₂ Cl ₂]	100	42	62	68	70
	500	58	74	77	79
[NiL ₁ .FeL ₂ Cl ₂].Cl	100	46	59	69	75
	500	52	64	72	79
[CuL ₁ .FeL ₂ Cl ₂].Cl	100	48	54	65	78
	500	55	68	81	84

* = ($\mu\text{g mol}^{-1}$), *B. subtilis* = *Bacillus subtilis*, *E. coli* = *Escherichia coli*, *A. niger* = *Aspurgillus niger*, *A. flavus* = *Aspurgillus flavus*.

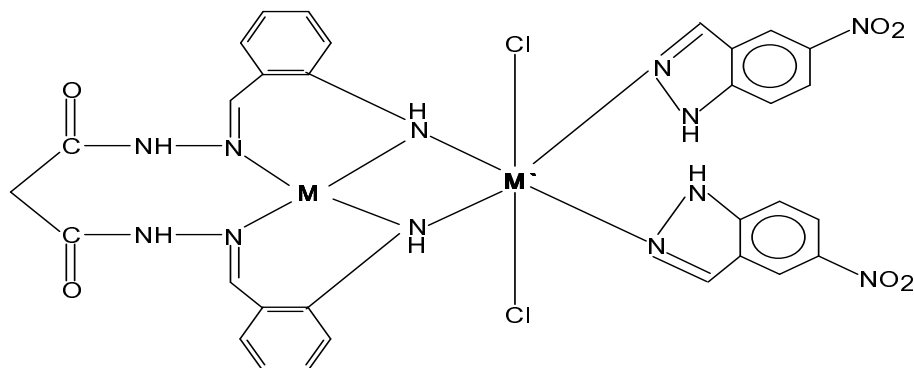


Fig.-1:Heterobinuclear complexes of the type $[ML_1.M'L_2Cl_2]$.

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