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# Synthesis, Characterization, Spectroscopic Studies and Toxicity analysis of Bis-(4-Amino-n-Butyric acid) Complexes with 5-Nitro Indazole Complexes Heterobinuclear Complexes of Mn(II), Ni(II) and Cu(II) ions

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**Abstract:** Heterobinuclear complexes of transition metal ions with 5-nitroindazole in the presence of bis-(4 amino n butyric acid)malonyldihydrazone Cu(II)/Ni(II) chloride of the type  $[M_1L_1M_2(L_2)_2]$  where  $M_1=Cu(II),Ni(II), M_2=Cu(II),Mn(II) L_1=$  bis-(4 amino n butyric acid)malonyldihydrazone  $L_2=5$ -nitroindazole, have been prepared and characterized by IR, UV-Vis and EPR spectroscopy, elemental analysis, magnetic moments and molar conductance measurements.

Key Words: Heterobinuclear complexes, bis-(4 amino n butyric acid)malonyldihydrazone, 5-nitroindazole and spectroscopy.

# **INTRODUCTION**

Metal centers coordinated to appropriately designed binucleating ligands may confer much more different structural, magnetic, optical or catalytically features and unique chemical behaviour than do their analogous mononuclear complexes. There has been considerable interest in the synthesis of polyazabis(macrocyclic)ligands and their transition metal complexes<sup>2-17</sup>. Such compounds often generate interesting chemical properties which are not observed in monomeric macrocyclic compounds. Dinuclear complexes

with two metal ions in close proximity show interesting magnetic, catalytic and electron transfer properties. The electro catalytic properties of (tetraazacyclotetra decane)  $M^{++}$  ions and (biscyclam)  $M_2^{++++}$  ions with respect to carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) reduction. The bimetallic complex is a better eletrocatalyst than its mononuclear analog for evolving hydrogen from H<sub>2</sub>O<sup>18</sup>. These molecules play an important role in the processes of molecular recognition of organic compounds<sup>19,20</sup>. In this view we have started a systematic study involving the synthesis and characterization of heterobinuclear complexes.

# **EXPERIMENTAL**

## **Material and Methods**

Hydrated Mn(II), Co(II), Ni(II), Cu(II) chlorides (BDH), 5-nitroindazole (Fluka), diethyl malonate, hydrazine, 4 amino n butyric acid (Merck) were used. The transition metal complexes of 5nitroindazole was synthesized by the method reported earlier and bis-(4 amino n butyric acid)malonyldihydrazone was prepared by refluxing of methanolic solution of diethyl malonate(1mole), hydrazine(2mole) and 4-amino n butyric acid(2mole) for 10 hrs.

## Preparation of [NiL<sub>1</sub>Cu(L<sub>2</sub>)<sub>2</sub>]

The solution of  $[Cu(L_2)_2]$  in dry DMF (25 ml) was treated with a methanolic solution (20ml) of

 $[NiL_1]$ . The pale-green solution of  $[Cu(L_2)_2]$  changed to blue after addition of the solution of  $[NiL_1]$ . The mixture was refluxed for *ca.* 8h. The crystalline solid which was separated out on cooling the mixture was filtered, washed with alcohol ether and dried *in vacuo*.

## Preparation of [NiL<sub>1</sub>Mn(L<sub>2</sub>)<sub>2</sub>]

The solution of  $[Mn(L_2)_2]$  in dry DMF (20 ml) was treated with a methanolic solution (20ml) of  $[NiL_1]$  and refluxed for 10h and then kept in a refrigerator over night. A cream coloured product was formed. It was filtered, washed with ethanol, ether and dried *in vacuo*.

## **Preparation of** [CuL<sub>1</sub>Mn(L<sub>2</sub>)<sub>2</sub>]

This complex was prepared by the same procedure as above.

	Emprical Formula		<b>m.p.</b> ( <sup>0</sup> C) Vield –		Calcd (Founds) %			
Complexes	(Formula Weights)	Colour	$\pm 2$	(%)	С	н	Ν	
	C25H30NiN12O8Cu	Light			40.09	4.03	22.44	
$[NiL_1Cu(L_2)_2]$	(748.819)	Green	300	30	(40.11)	(4.81)	(22.61)	
	C <sub>25</sub> H <sub>30</sub> NiN <sub>10</sub> O <sub>8</sub> Mn				40.56	4.08	22.70	
$[NiL_1Mn(L_2)_2]$	(740.179)	Cream	320	28	(41.01)	(4.20)	(22.81)	
	$C_{25}H_{30}CuN_{12}O_8Mn$				40.30	4.05	22.55	
$[CuL_1Mn(L_2)_2]$	(745.039)	Brown	335	35	(41.11)	(4.10)	(22.71)	

## Table I. Analytical Data, Melting Points and % Yields of Heterobinuclear Complexes.



Figure 1. Heterobinuclear complex of the type [M<sub>1</sub>L<sub>1</sub>M<sub>2</sub>(L<sub>2</sub>)<sub>2</sub>]

Complexes	v(N-H)	Ring Stretching	v(NOc)(Asym/Sym)	v(C=N)	v(M-N)	v(M'-N)
Complexes	V(11-11)	Stretting	v(1vO <sub>2</sub> )(1xSym/Sym)		•(1•1-1•)	<b>V</b> (1 <b>1</b> -1 <b>1</b> )
$[NiL_1Cu(L_2)_2]$	3338	1518	1550s/1356	1432	486	525
$[NiL_1Mn(L_2)_2]$	3344	1632	1532s/1392	1457	469	514
$[CuL_1Mn(L_2)_2]$	3327	1624	1533s/1395	1475	480	530

# Table II. Important IR Spectral Data (cm<sup>-1</sup>) of the Heterobinuclear Complexes

# **RESULTS AND DISCUSSIONS**

Analytical data of heterobinuclear complexes are given in Table I.

All the complexes are soluble in DMSO or DMF in the range<sup>21,22</sup> of non-electrolytes for the heterobinuclear complexes. As a consequence,

bis-(4 amino n butyric acid)malonyldihydrazone Cu(II)/Ni(II) chloride with dichlorobis(5-nitro indazole) $M_2(II)$  form a covalent bond in the inner sphere of the binuclear complexes. (Fig. 1).

# IR SPECTRA OF THE HETEROBINUCLEAR COMPLEXES

The relevant IR bands and their assignments are cited in Table II.

Strong bands at 1457 and 3344 cm<sup>-1</sup> due to v(C=N) and v(N-H), respectively, remain unaltered in the binuclear complexes. New bands due to the NH<sub>2</sub> group of the M<sub>1</sub>L<sub>1</sub> complexes in the range 3320-3348 cm<sup>-1</sup> appear confirming binuclear complexation. The far-IR spectral data with assignments of v(M-N) (450-550 cm<sup>-1</sup>) bands are given in Table II. Our results are consistent with the results reported earlier.<sup>23-25</sup>

## ELECTRONIC SPECTRA ANDS MAGNETIC MOMENTS

In Table III are listed the magnetic moment values, EPR parameter and UV-Vis, spectral data of the heterobinuclear complexes. The  $\mu_{eff}$  values of the binuclear complexes deviate from their calculated values due to change in the environment on the central metal atom. The binuclear complexes possess anti-ferromagnetic properties at room temperature by intramolecular

spin exchange interaction between  $M_1$  and  $M_2$ metal ions. The electronic spectra of the complexes contain mixed transitions due to two different metal ions in different oxidation states and different coordination numbers. Both  $M_1$  &  $M_2$  are associated with square planar geometry.

# **EPR Spectra**

The signals of two different metals are merged together and new signals are obtained. The heterobinuclear compounds exhibit a slightly higher  $g_{\perp}$  values and a higher  $g_{II}$  values than Cu(II) in a square-planar environment. This might be expected if the interaction changes the geometry of the central metal ion.

The EPR spectra of the complex [Cu(II)  $L_1Mn(II)(L_2)_2$ ] at room temperature show a broad signal due to spin crossover of one unpaired electron of the Cu(II) ion in the binuclear complex. The values of  $g_{II}$  and  $g_{\perp}$  for copper are suppressed by Mn(II) spin-spin interaction, which is further supported by the  $\mu_{eff}$  value which is lower than the calculated value.

# **Physical Measurements**

The IR and far-IR spectra (4000-200cm<sup>-1</sup>) were recorded on a Perkin Elmer 621 spectro photometer in KBr and Nujol, respectively. UV-Vis spectra were run on a Systronic 119 spectrophotometer in DMF. Magnetic susceptibility measurements were made on a Gouy balance using Hg[Co(NCS)<sub>4</sub>] as calibrating agent,  $\chi_g = 16.44 \times 10^{-6}$  cgs units. The EPR spectra were recorded on Bruker 500 MHz and Bruker ESP-300X band spectrometers. The conductivity measurements were made in DMF on a type CM-82T Elico conductivity bridge. Elemental analysis done on a model 1106 Carlo Erba microanalyzer. Determinations of chloride ions were done by a standard gravimetric method and metals were

determined by atomic absorption using a portable digital voltmeter (PDV-2000). Chemotronics Ltd., Bentley-6102, Perth, Western Australia.

<b>Fable III. Electroni</b>	c Spectral Data of the He	eterobinuclear Complexes
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Complexes	Transition (cm- <sup>1</sup> ) (values, cm <sup>-1</sup> M <sup>-1</sup> )	Assignments		EPR (Value) µeff(B.M.) g <sub>II</sub>		
$[CuL_2Ni(L_2)_2]$	14,390 (540)	$^{2}B_{1g} \rightarrow ^{2}A_{1g}$	1.78	2.13	2.23	
	17,250	$^{2}E_{g}\rightarrow ^{2}T_{2g}$				
	(broad band) (324)					
	21,270 (2.4)	$^{1}A_{g} \rightarrow ^{1}B_{1g}$				
		$^{1}A_{g} \rightarrow ^{1}B_{2g}$				
$[MnL_2Ni(L_2)_2]$	20,000 (300)	${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)$	3.90			
	18,181 (265)	${}^{4}A_{2g} \rightarrow {}^{3}A_{1g}$				
	12,500 (45)	${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$				
$[MnL_2Cu(L_2)_2]$	38,310 (54)	C.T.	5.10	2.03		
	25,440 (425)	${}^{4}A_{1g}(G) \leftarrow {}^{6}A_{1g}$				
	20,400 (mixed) (8.4)	${}^{4}T_{2g}(G) \leftarrow {}^{6}A_{1g}$				
	6,594 (410)	$^{2}E_{g}\leftarrow ^{2}B_{1g}$				
	· · · ·	${}^{4}T_{1g}(G) \rightarrow {}^{6}A_{1g}$				
	20,300 (9)	$^{2}\mathrm{E}_{1g} \rightarrow ^{2}\mathrm{B}_{1g}$				

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