International Journal of
Chemical, Environmental and Pharmaceutical Research

ijCEPr

Vol. 1, No.1, 27-31
May-August, 2010

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

Netra Pal Singh* and Abhay Nanda Srivastava
Depatrment of Chemistry,Meerurt College Meerut, U.P.(India).
E-mail: netrapal_chem@yahoo.com

Article history:
Received: 15 July 2010
Accepted: 23 August 2010

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.

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-aminobenzaldehydeand ethanol. Double distilled water was used. The transition metal complexesof 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

NiL_2Cl_2. 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 [$CoL_1CuL_2Cl_2$]

This compound was prepared by using same procedure as above.

Preparation of [$NiL_1FeL_2Cl_2$]Cl

A solution of NiL_2Cl_2 (0.456gm, 1mmol) in methanol (15 ml)was treated with a solution of [FeL_1Cl_2]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 [$CuL_1FeL_2Cl_2$].Cl

This complex was prepared by using same procedure as above.

RESULTS AND DISCUSSION

The complexes were prepared according to the following chemical equations-

$$MnL_1Cl_2 + NiL_2Cl_2 / CuL_2Cl_2 \xrightarrow[-2HCl]{DMF} MnL_1.NiL_2Cl_2 / CuL_2Cl_2$$

$$CoL_1Cl_2 + NiL_2Cl_2 / CuL_2Cl_2 \xrightarrow[-2HCl]{DMF} CoL_1.NiL_2Cl_2 / CuL_2Cl_2$$

$$Ni / Cu\text{-}L_1Cl_2 + [FeL_2Cl_2]Cl \xrightarrow[-2HCl]{DMF} [Ni / Cu\text{-}L_1.Fe\ (III)\ L_2Cl_2]Cl$$

Where, L_1 = bis(2-aminobenzaldehyde)malonyl hydrazone, L_2 = 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 L_1 and L_2. 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 [$NiL_1FeL_2Cl_2$]Cl and [$CuL_1FeL_2Cl_2$]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 Tabkle 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 *Aspirgillus niger* and *Aspirgillus 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
$[MnL_1NiL_2Cl_2]$	$C_{31}H_{26}Cl_2MnN_{12}O_6Ni$ (846.8)	Light pink	324	30	44.00 (43.92)	3.09 (3.04)	19.85 (19.65)
$[MnL_1CuL_2Cl_2]$	$C_{31}H_{26}Cl_2MnN_{12}O_6Cu$ (852.07)	Pink	328	35	43.70 (43.66)	3.07 (3.01)	19.73 (19.65)
$[CoL_1NiL_2Cl_2]$	$C_{31}H_{26}Cl_2CoN_{12}O_6Ni$ (851.23)	Light Yellow	336	39	43.74 (43.68)	3.08 (3.03)	19.75 (19.71)
$[CoL_1CuL_2Cl_2]$	$C_{31}H_{26}Cl_2CoN_{12}O_6Cu$ (856.06)	Dirty Yellow	318	42	43.49 (43.42)	3.06 (3.02)	19.63 (19.54)
$[NiL_1FeL_2Cl_2]Cl$	$C_{31}H_{24}Cl_3FeN_{12}O_6Ni$ (883.65)	Brown	342	28	42.13 (42.08)	3.00 (2.88)	19.02 (18.84)
$[CuL_1FeL_2Cl_2]Cl$	$C_{31}H_{24}Cl_3FeN_{12}O_6Cu$ (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	*v* (C=O)	*v* (N-H)	*Ring Stretching*	*v* (NO_2) (Asym / Sym)	*v* (C=N)	*v* (M-N)	*v* (M-N)	*v* (M-Cl)
$[MnL_1NiL_2Cl_2]$	1725	3318	1615	1528/1382	1615	482	475	322
$[MnL_1CuL_2Cl_2]$	1718	3322	1612	1530/1385	1610	478	470	318
$[CoL_1NiL_2Cl_2]$	1738	3328	1618	1538/1395	1628	460	466	320
$[CoL_1CuL_2Cl_2]$	1735	3330	1622	1536/1392	1624	468	468	324
$[NiL_1FeL_2Cl_2]Cl$	1726	3324	1632	1564/1344	1570	466	472	322
$[CuL_1FeL_2Cl_2]Cl$	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	
				$g_{\parallel}$	$g_{\perp}$
$[MnL_1NiL_2Cl_2]$	20,020(302) 18,178(260) 12,502(45)	$^4A_2g \rightarrow {}^4T_1g(P)$ $^4A_2g \rightarrow {}^4T_1g$ $^4A_2g \rightarrow {}^4T_2g$	3.90		
$[MnL_1CuL_2Cl_2]$	38,320(56) 25,448(428) 20,408 16588(406)	C.T. $^4A_{1g}(G) \leftarrow {}^6A_{1g}$ $^4T_{2g}(G) \leftarrow {}^6A_{1g}$ $^2E_g(G) \leftarrow {}^6B_{1g}$ $^4T_{1g}(G) \rightarrow {}^6A_{1g}$	5.10	1.91	1.82
$[CoL_1NiL_2Cl_2]$	6,565(3.1) 14,415(5.3)	$^4T_{2g}(F) \leftarrow {}^6T_{1g}(F)$ $^4A_g(F) \rightarrow {}^4T_{1g}(F)$	1.93		

	21,268(3.4) 16,378(2.2)	$^2A_{1g}\rightarrow{}^1B_{1g}$ $^1A_{1g}\rightarrow{}^1B_{2g}$			
[$CoL_1CuL_2Cl_2$]	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	
[$NiL_1FeL_2Cl_2$]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. $^4E_{1g}(G) \leftarrow {}^6A_{1g}$ $^4T_{2g}(G) \leftarrow {}^6A_{1g}$ $^2T_1(G)\leftarrow{}^6A_{1g}$ $^1A_{1g}\rightarrow{}^1B_{1g}$ $^1A_{1g}\rightarrow{}^1A_{2g}$	5.87		
[$CuL_1FeL_2Cl_2$]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. $^4A_{1g}(G) \leftarrow {}^6A_{1g}$ $^4T_{1g}(G) \leftarrow {}^6A_{1g}$ $^4T_2(G) \leftarrow {}^6A_{1g}$ $^1B_{1g}(G)\rightarrow{}^2A_{1g}$ $^2B_{1g}\leftarrow{}^2E_g$	5.82		

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

Compounds	*Conc.	Bacterial Inhibition (%)		Antifungal Inhibition (%)	
		B. subtilis	*E. coli*	*A. niger*	*A.flavus*
[$MnL_1.NiL_2Cl_2$]	100 500	40 48	51 58	62 74	65 78
[$MnL_1.CuL_2Cl_2$]	100 500	48 53	51 55	71 83	72 85
[$CoL_1.NiL_2Cl_2$]	100 500	52 61	73 82	82 91	80 86
[$CoL_1.CuL_2Cl_2$]	100 500	42 58	62 74	68 77	70 79
[$NiL_1.FeL_2Cl_2$].Cl	100 500	46 52	59 64	69 72	75 79
[$CuL_1.FeL_2Cl_2$].Cl	100 500	48 55	54 68	65 81	78 84

* = (μ*g moL*$^{-1}$), *B. subtilis =Bacillus subtilis , E. coli = Escherichia coli, A. niger = Aspirgillus niger , A. flavus = Aspirgillus flavus.*

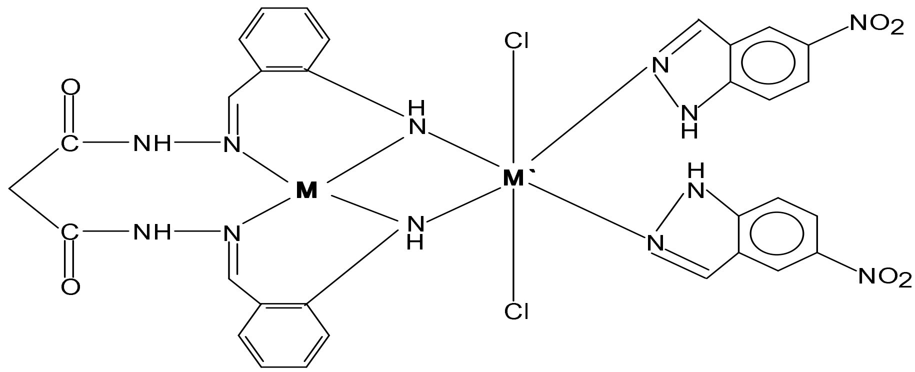

Fig.-1:Heterobinuclear complexes of the type [$ML_1.M`L_2Cl_2$].

ACKNOWLEDGEMENTS

The authors are thankful to ACBR, Delhi for providing spectral data and SAIF, CDRI, Lucknow for providing elemental analysis data. Authors are also thankful to SARC, Meerut for providing antimicrobial activity.

REFERENCES

1. Arjmand Farukh et al., European Journal of Medicinal Chemistry,(2010), 1.
2. Bag, N. et al., Inorganic Chemistry, **34**, (1995), 753.
3. Bandini, A. L. et al., Canadian Journal of Chemistry, **57**, (1979), 3237.
4. Brewer, C. T. et al., Journal of Chemical Society, Dalton Trans., **1**, (1993), 1513.
5. Campell, M.J.M. et al., Journal of Inorganic Nuclear Chemistry, **36**, (1974), 2485.
6. Dharmaraj, N. et al., Transition Metal Chemistry, **26**, (2002), 105.
7. Fenton, D. E. ,1995, Biocoordination Chemistry, First Ed., Oxford University .
8. Ferraro, J.R. ,1971, Plenum Press, New York.
9. Folgado, J.V. et al., Journal of Chemical Science. Dalton Trans, (1986), 1061.
10. Gatteschi, D. et al.,1991, Magnetic Molecular Materials, Kluwev Academic Dordrecht.
11. Kadish , K. M. et al., Inorganic Chemistry, **37**, (1998), 2693.
12. Kalam, A. et al., Turkish Journal of Chemistry, **34**, (2010), 147.
13. Karlin, K. D. , Tyeklav, Z.,1993, Bioinorganic Chemistry of Copper, Chapmanand Hall, London.
14. Karlin, K. D., Zubieta, J.,1996, Biological and Inorganic Copper Chemistry, Academic Press, New York.
15. Khan, O. ,1993, Molecular Magnetism, Wiley-VCH, New York.
16. Kobayashi, K. et al., Journal of Biological Chemistry¸**255**, (1980), 2239.
17. Lashanizadegan, M. and Seraj, S., Turkish Journal of Chemistry, **34**, (2010), 263.
18. Rajavel, R. et al., E-Journal of Chemistry, **5(3)**, (2008), 620.
19. Sakamoto, M., Synthesis Reactivity of Inorganic Metal Organic Chemistry, **27(4)**,(1997), 567.
20. Shah, N. , Kar, S.K. , Journal of Inorganic Nuclear Chemistry, **39**, (1997), 1236.
21. Travnicek Zdenek et al., Inorganica Chemica Acta, **363**, (2010), 2071.
22. Woo, L.K., Maurya, M.R. , Inorganic Chemistry, **30**, (1991), 4671.