IARJSET
ISSN (O) 2393-8021, ISSN (P) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified ⋇ Impact Factor 7.12 ⋇ Vol. 9, Issue 10, October 2022
DOI: 10.17148/IARJSET.2022.91007

Microwave Assisted Synthesis Characterization and Biological Evolution of 3d- series Metal Complexes with Amide Ligands

Raja Ram

Green Chemistry Research Centre (GCRC), Department of Chemistry, Govt. Dungar (NAAC GRADE- 'A'),

Bikaner – 334001, M.G.S. University, Bikaner-India

Abstract: This study discussion the microwave synthesis, spectral, Characterization and anti microbial study of the complexes of Mn, Co, Ni and Cu with amide ligands. The complexes have been characterized on the basis of elemental analysis, IR, UV and magnetic susceptibility studies. Antibacterial activities of these ligands and complexes have also been reported on *S. aureus* and *E.coli* microorganisms. Antibacterial activities have carried out by disc diffusion method. The diffuse reflectance spectrums of the transition metal Mn(II) complexes show bands in the region 17636 cm^{-1} to 26881cm^{-1}, assignable to $^6A_{1g}\rightarrow{}^4T_{2g}$, $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (4G) transitions. These are also typical of tetrahedral environment around the Manganese. The magnetic moment (5.79-5.92 BM) of the complex indicates high tetrahedral environment and Co, Ni and Cu metal complexes are in distorted Octahedralin environment. The green method of synthesis of these complexes carried out by green microwave bioreactor (GMBR). This method is easily, appropriate and eco-friendly.

Keywords: Microwave, pyrimidine derivatives, Mn(II), Antibacterial, Tetrahedral

I. INTRODUCTION

Manganese transition metal is more necessary for production iron and steel by virtue of its sulfur-fixing, deoxidizing alloying properties (1). This metal has been broadly uses in alloys of aluminium metal and key component of low-cost stainless steel formation. MnO_2 is used in dry cells and as a catalyst. $KMnO_4$ is generally used as a potent oxidizer and as a typical medicine (disinfectant). Manganese oxide is a brown pigment that can be used to make paint and is a component of natural umber. Manganese phosphate is used for rust and corrosion prevention on steel. Manganese will be mostly replaced with lithium battery technology in manufacture of disposable battery, standard and alkaline cells (2-3). Manganese particles usually settle to earth within some days. Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese that derives from human sources can also enter on surface water, ground water and sewage water. Through the application of manganese pesticides, manganese enters in soil (4-5). Manganese plays an important role for plants growth. Deficiency of manganese ions causes disturbances in plant mechanism. Many herbs also contain manganese, burdock root, fennel dandelion, fenugreek, ginseng, horsetail, lemongrass, seed,parsley, peppermint, chamomile, wild yam and raspberry (6). In mammalian cells, manganese causes DNA damages and chromosome aberrations. Large amount of manganese affect fertility in mammals and are toxic to the embryo and foetus (7-8). Manganese has been shown to cross the blood brain barrier and a limited amount of manganese is also able to cross the placenta during pregnancy, enabling it to reach a developing fetus (9-10). Manganese deficiency in the foetus may also causes malformation of the inner ear, ataxia and bone malformation. Lack of co-ordination head retraction, tremor, loss of righting reflexes, hyper irritability, faulty cartilage and bone matrix formation, heart problems and learning difficulties also occur (11). Metal or metalloid of amide are compounds which contain one or more (–$CONH_2$) ligand groups or a simple derivative [such as –CONHR, -$CONR_2$, where R = methyl, phenyl, acetyl etc.) attached to metal. (12-18).

II. EXPERIMETAL

Apparatus

(i) EC Double Beam UV-VIS Spectrophotometer (UV 5704SS), with quartz cell of 10 mm light path was used for Electronic spectral measurement at GCRC (Green Chemistry Research Center) Govt. Dungar College (NAAC A-Grade) Bikaner, (Raj.).

(ii) IR spectra were recorded on Bruker Optic Model Alpha (FT-IR) (Zn-Se Optics, ATR) (4000-500 cm-1) using KBr disc at SIL, P.G. Dept. of chemistry, Govt. Dungar College (NAAC-A- Grade) Bikaner, Rajasthan.

(iii) Microwave synthesis was carried out in domestic microwave oven and GMBR (Green Microwave Biochemical Reactor) at GCRC, P.G. Dept. of Chemistry, Govt. Dungar College (NAAC-A- Grade) Bikaner, Rajasthan.
(iv) All biological activities have been carried out with horizontal laminar, BIFR, Bikaner.

2.2 Materials and method

For the synthesis of Mn(II) complexes with amide group containing ligands, a solution of $MnCl_2$ (1mmole in 30 mL ethyl alcohol) has been taken in a 250 ml round bottom flask, in this solution respective amide ligand (i.e. $(N6H2MC4PB)_2Cl_2$, $(N6H2MC4PB)_2Cl_2$, $(N26DH4PB)_2Cl_2$, $(N26DH4PA)_2Cl_2$ (0.003 mole) was added slowly with constant stirring. The reaction mixture was placed on a magnetic stirrer with constant stirring for more than 6-7 hrs at room temperature.

In the microwave synthesis, the reaction mixture was irradiated in a microwave reactor (GMBR) for 2-5 minutes. The solid precipitate obtained in both the methods was separated and crystallized. Crystals were purified and recrystalized with ethyl alcohol and dried under vacuum.

III. RESULTS AND DISCUSSION

The complexes of Mn (II) with all the amide group containing ligands are stable at room temperatures over a long period of time. The manganese complexes under investigations were white (brown) coloured powder; these complexes were, partially soluble in DMSO and insoluble in all other solvents. The elemental and metal estimations give satisfactory results. The physical and analytical data of complexes are given in Table 1

(i). Vibrational Spectra

Vibrational spectra were recorded in KBr pellets and polyethylene film in mid and far IR regions and some diagnostic bands are presented in Table 3.
The IR bands due to amide ν (N-H) mode observed at 3163-3382 cm-1 for the free amide group containing ligands are shifted to higher frequencies indicating non-participation of nitrogen atom of amide group in coordination. Amide 1 bands due to ν (C=O) shift negatively opposite to that of ν (N-H) in the complexes suggesting carbonyl oxygen coordination (19). In complexes it is represented that pyrimidinyl nitrogen participates in bonding, which has been confirmed by the 16-100 cm^{-1} negative shifting of pyrimidinyl ring peak in complexes to the comparison of ligands. (Figure 5 to 8). These observations have ambiguous and support the final structural conclusions of the complexes and the mode of bonding in them.(Fig. 9-12)

(ii). Magnetic Susceptibility Measurements

Complexes of bivalent manganese are known in both high spin (S=5/2) and low spin (S = 1/2) states. Because of the additional stability of the half filled d-orbitals Mn (II) generally forms high spin complexes which have an orbitally degenerate 6S ground state term and the spin only magnetic moment of 5.9 ± 0.1 BM is expected which will be independent of the temperature and of stereochemistry (20). The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are given in Table 2. All the manganese (II) complexes have magnetic moment values in the range 5.70-5.92 BM indicating the presence of five unpaired electrons and hence these are high spin complexes with tetrahedral coordinate manganese (21).

(iii). Electronic Spectra

The electronic spectra of the manganese complexes with amide group containing ligands show weak absorption in the visible region. This is presented in Table 2 and in Fig.1 to 4.

The observed spectra of the manganese (II) complexes with the ligands exhibit bands in the region 17636 cm-1 and 28011 cm-1 assignable to
$^6A_{1g}\rightarrow{}^4T_{2G}$ and $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (4G)
The electronic spectral transitions of Mn complexes with the pyrimidine derivative ligands are typical of tetrahedral (Td) environment around the Mn (22).

Thermal Studies.

The complexes of Mn (II) with the amide group containing ligands show first order kinetics in their thermal decomposition reaction. This is based on a straight line plot of Coats and Redfern (for n = 1). Activation energy has been carried out by the linearization method of Goats and Redfern. The thermal studies give the description about the thermal stability of the complexes. It has been observed that no decomposition takes place at room temperature and complexes are fairly stable well above the room temperature. The initial decomposition started above 500K.

IV. CONCLUSIONS

On the basis of vibration spectra, the amide group containing ligands show bidentate behavior in respect of Mn(II) complexes by coordinating through carbonyl oxygen of amide groups and nitrogen of pyrimidine ring. Thus, Mn (II) adopts tetrahedral geometry in the complexes with bioactive amide ligands. On the basis of these studies the tentative structures have been proposed for the complexes and which are given in Fig. 9 to 12 for Mn(II) complexes. The complexes synthesized by novel green method are at par with conventional synthesis and in many cases yield was found to be better than conventional synthesis.

V. ACKNOWLEDGEMENTS

Author **(RR)** is thankful to all members of GCRC.

REFERENCES

[1] Burns RE, Helgoland Marine Research, 33 (1-4) (1980) 433.
[2] Sistrunk Shannon C, Ross Matthew K & Filipov Nikolay, Environ. Toxicol Pharmacol., 23 (3) (2007) 286.
[3] Faglin Zhang, Xu Zhaofa, Gao Jian Xu Bin & Deng Yu, Environ. Toxicol Pharmacol., 26 (2) (2008) 232.
[4] Vandenabeele J, Vande Woestyne M, Houwen F, Germonpre R, Vandesande D & Verstraete W, Microbial Ecology, 29(1) (1995)83.
[5] Granina LZ & Callender E, Hydrobiologia, 568 (2006) 41.
[6] Pae Chi-Un, Yoon Su-Jung, Patkar Ashwin, Kim Jung- Lin, Jun Tae- Youn, Lee Chul & Paik In-Ho, Progress in Neuro- Psychopharmacology and Biological Psychiatry 30(7) (2006) 1326.
[7] Poranen Minna M, Salgado Paula S, Koivunen Minni RL,Wright Sam, Bamford Dennis H, Satuart David I & Grimes Jonathan M, Nucleic Acids Research, 36 (20) (2008) 6633.
[8] Papp-Wallace Kristztina M, Moomaw Andrea S & Maguire Michael E, Microbiology Monograph, 6 (2007) 235.
[9] Gerber GB, Leonard A & Hantson P, Critical Review in Oncology/Hematology, 42 (1) (2002) 25.
[10] Komura J & Sakamoto M, Environ. Res; 57 (1) (1992) 34.
[11] Kitao Mitsutoshi, Lei Thomas T & Koite Takayoshi, Physiologia Platarum, 101 (2) (2006) 249.
[12] Garg B.S. , Bhojak N., Sharma R.K., Bist J.S. and Mittal S., 1999. Separation and preconcentration of metal ions and their estimation in vitamin, steel and milk sample using o-vanillin-immobilized silica gel. Talanta.48, 1, 49 55.
[13] Bhojak N., Gudasaria D. D., Khiwani N. & Jain R., (2007). “Microwave Assisted Synthesis Spectral and Antibacterial Investigations on Complexes of Mn (II) With Amide Containing Ligands.” E-Journal of Chemistry, 4(2), 232-237.
[14] Garg B. S., Bhojak N., Nandan D. (2005). “Micellar spectrofluorimetric determination of lead (II) in natural water, waste water and egg samples with N-(2′-pyridyl)- 2- hydroxybenzamide”.Ind. J. Chem., 44A, 1504.
[15] Raja Ram, Verma K.K., Solanki K.and Bhojak N. (2015). Microwave assisted synthesis, spectral and antibacterial investigations on complexes of Co (II) with amide containing ligands. International Journal of New Technologies in Science and Engineering. 2(6), 92-100.
[16] Verma K. K., Soni Gupta P., Solanki K.and Bhojak N. (2015). “Microwave Assisted Synthesis, Characterisation and Anti microbial activities of few Cobalt (II) Thiosemicarbazones Complexes. World Journal of pharmacy and pharmaceutical sciences.” 4(11), 1673-1683.
[17] Raja Ram, Verma K. K., Bhandari H. S. and Bhojak N. (2015). “Microwave assisted synthesis, spectral and antibacterial investigations on complexes of Ni (II) with amide group containing ligands.” IARJSET, 2(11), 40-43.
[18] Singh B. and Bhojak N. (2008). “Microwave assisted synthesis, spectral and antibacterial investigations on complexes of Mn (II) with amide containing ligands.” RJC,1(1), 105-109,
[19] Garg BS, Kumar V & Reddy MJ, Transition Met. Chem., 18 (1993) 364.
[20] 38Figgis BN & Lewis J, Progress in Inorganic Chemistry, (1964) 37.
[21] 39Singh R, Sharma K & Fahmi N, Transition Met. Chem., 24 (1999)562.
[22] 40Paul RC, Chopra RS, Bhambri RK & Singh G, J. Inorg. Nucl. Chem., 36 (1974) 3703.

Table- 1

Physico-chemical Data of Mn (II) Metal Complexes

(C.M.= Conventional method, M.M.= Microwave method)

S.N.	Complexes	Colour	m.p. (°C)	Reaction period		Yield %		Elemental analysis Calculated(Found)%		
				C.M. hrs.	M.M. min.	C.M.	M.M.	C	H	N
1	[Mn-(N6H2MC4PB)$_2$]Cl$_2$,	Off white	304	6.5	2.00	45	55	42.58 (42.50)	2.90 (2.85)	13.54 (13.50)
2	[Mn-(N6H2MC4PB)$_2$]Cl$_2$,	Light buff	310	6.5	2.30	40	45	33.88 (33.80)	3.29 (3.24)	19.76 (1968)
3	[Mn-(N26DH4PB)$_2$]Cl$_2$,	Orange	288	7	2.00	45	55	44.89 (44.80)	3.06 (3.00)	14.28 (14.20)
4	[Mn-(N26DH4PA)$_2$]Cl$_2$	Orange	295	6.5	2.00	45	55	31.03 (30.95)	3.01 (2.96)	18.10 (18.00)

Table-2

Magnetic moments and electronic Spectral data of ligand and Mn(II) metal complex

SN	Ligand and Complex	R_f value	μ_{eff} (BM)	Electronic Spectral Bands λ_{max} (cm^{-1})	Tentative assignments	Expected Geometry
1	[Mn-(N6H2MC4PB)2]Cl2	(0.711)h	5.88	18903,20120,21691, 24038,24570,27322,	$^6A_{1g}\rightarrow{}^4T_{2G}$ $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (4G)	Tetrahedral
2	[Mn-(N6H2MC4PA)2]Cl2	(0.818)g	5.78	18939,20161,21621, 22624,24570,26917,	$^6A_{1g}\rightarrow{}^4T_{2G}$ $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (4G)	Tetrahedral
3	[Mn-(N26DH4PB)2]Cl2	(0.792)h	5.70	18832,19230,24691, 26990	$^6A_{1g}\rightarrow{}^4T_{2G}$ $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (4G)	Tetrahedral
4	[Mn-(N26DH4PA)2]Cl2	(0.875)g	5.82	19083,21645,23952, 24630,26075	$^6A_{1g}\rightarrow{}^4T_{2G}$ $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (4G)	Tetrahedral

a = ethyl acetate: carbon tetrachloride (2:8), b = ethyl acetate: carbon tetrachloride (4:6), d = ethyl acetate: carbon tetrachloride (6:4), e= ethyl acetate: acetone (5:5), f = acetone: carbon tetrachloride (5:5), g= acetone: carbon tetrachloride (6:4)

Table- 3

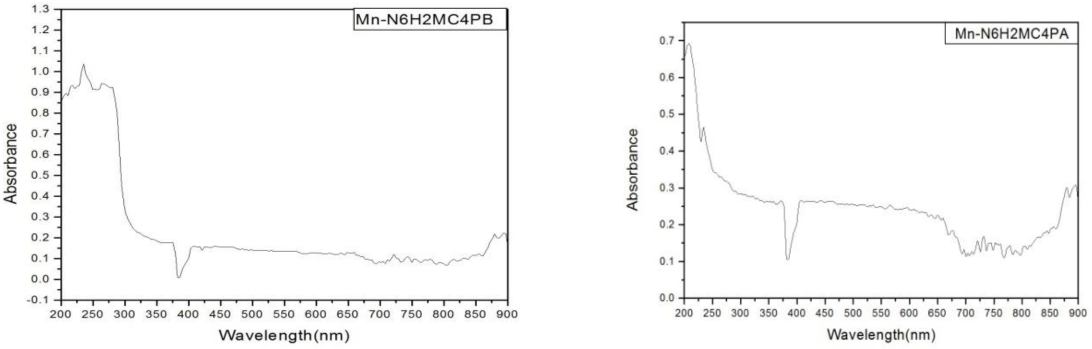
IR Vibrational frequencies of Mn(II) transition metal complexes

S. N.	Complexes	ν_{N-H} (amide)	$(\nu_{C=O})^a$	$(\nu_{C-N}+\delta_{N-H})^b$	$(\nu_{N-H}+\delta_{C-N})^c$	Pyrimidinyl	ν_{M-N}	ν_{M-O}	ν_{M-cl}
1	N6H2MC4PB	3163	1706	1421	1284	1685			
	[Mn-(N6H2MC4PB)2Cl2]	3172	1685	1532	1404	1624	504	538	----
2	N6H2MC4PA	3175	1715	1340	1242	1683			
	[Mn-(N6H2MC4PA)2Cl2]	3186	1648	1442	1382	1604	472	535	----
3	N26DH4PB	3353	1714	1422	1282	1582			
	[Mn-(N26DH4PB)2Cl2	3445	1623	1457	1362	1558	434	476	----
4	N26DH4PA	3196	1716	1284	1249	1416			
	[Mn-(N26DH4PA)2Cl2	3420	1702	1354	1292	1400	468	543	----

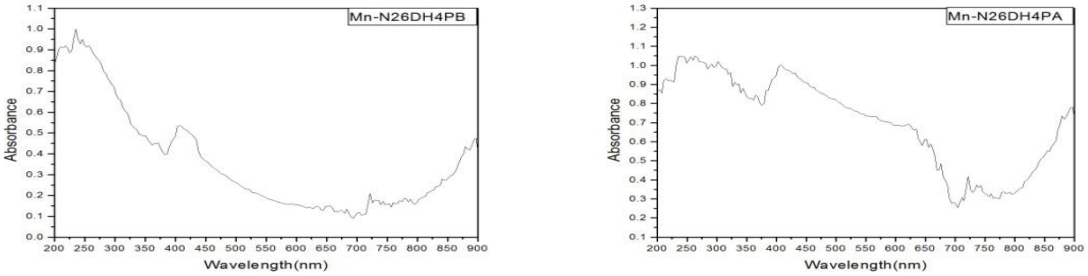
DOI: 10.17148/IARJSET.2022.91007

Fig. 1-4

Transition Spectra of Mn(II) Complexes



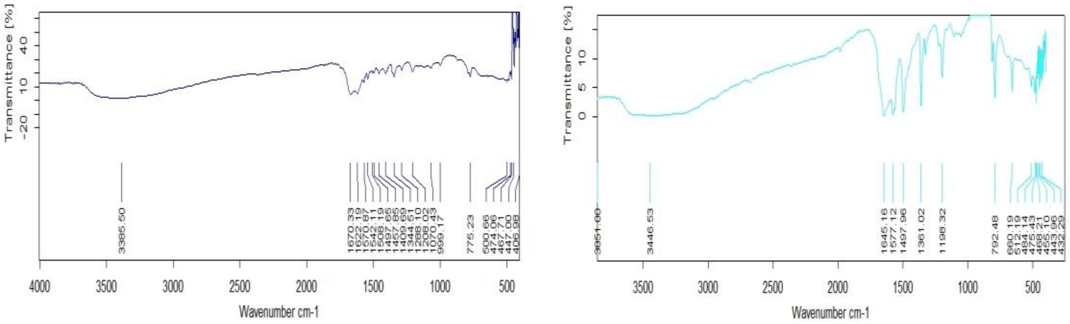
$[Mn-(N6H2MC4PB)_2]Cl_2$ **$[Mn-(N6H2MC4PA)2]Cl_2$**



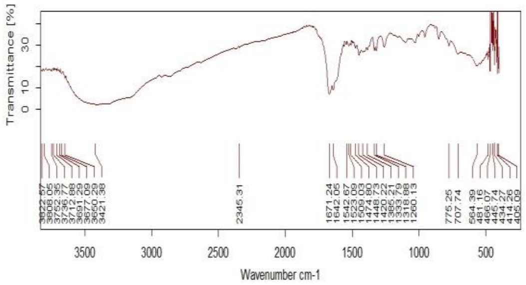
$[Mn-(N26DH4PB)_2]Cl_2$ **$[Mn-(N26DH4PA)_2]Cl_2$**

Fig. 5-8

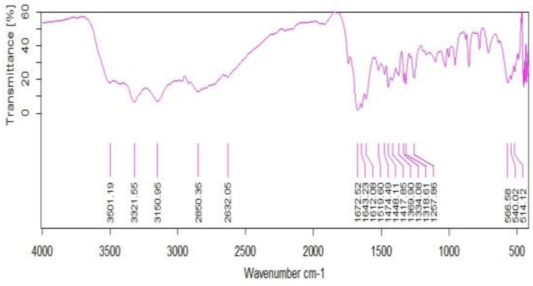
Vibrational Spectra of Mn(II) Complexes



$[Mn-(N6H2MC4PB)_2]Cl_2$ **$[Mn-(N6H2MC4PB)_2]Cl_2$**



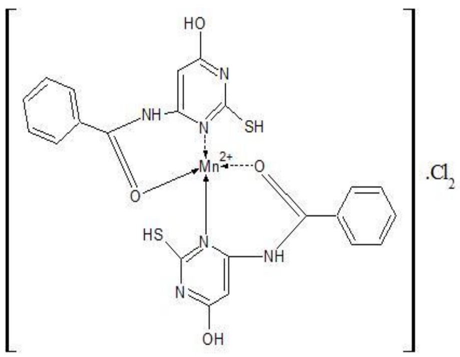
[Mn-(N26DH4PB)$_2$]Cl$_2$



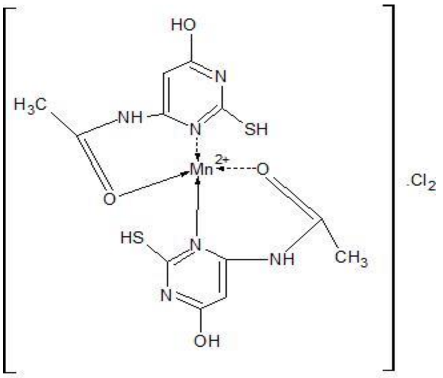
[Mn-(N26DH4PA)$_2$]Cl$_2$

Fig. 9-12

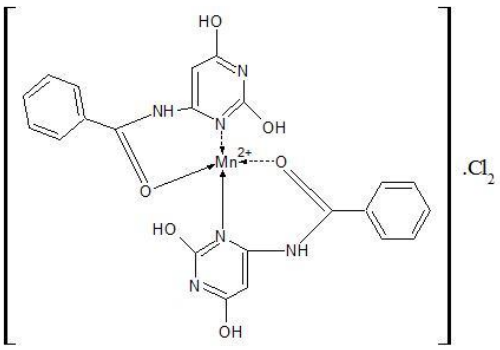
Tentative structure of complexes



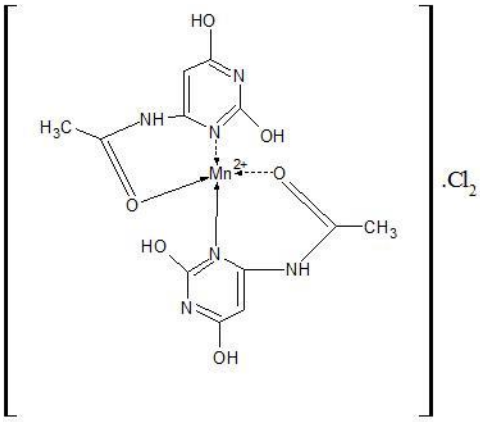
[Mn-(N6H2MC4PB)$_2$]Cl$_2$



[Mn-(N6H2MC4PB)$_2$]Cl$_2$



[Mn-(N26DH4PA)$_2$]Cl$_2$



[Mn-(N26DH4PA)$_2$]Cl$_2$

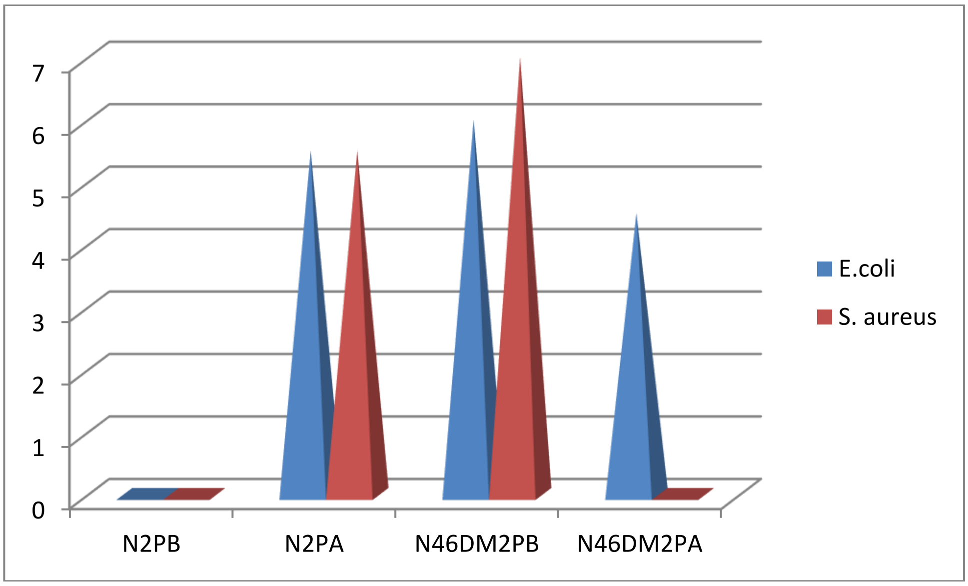


Fig.13. Biological activity of amide Ligands.

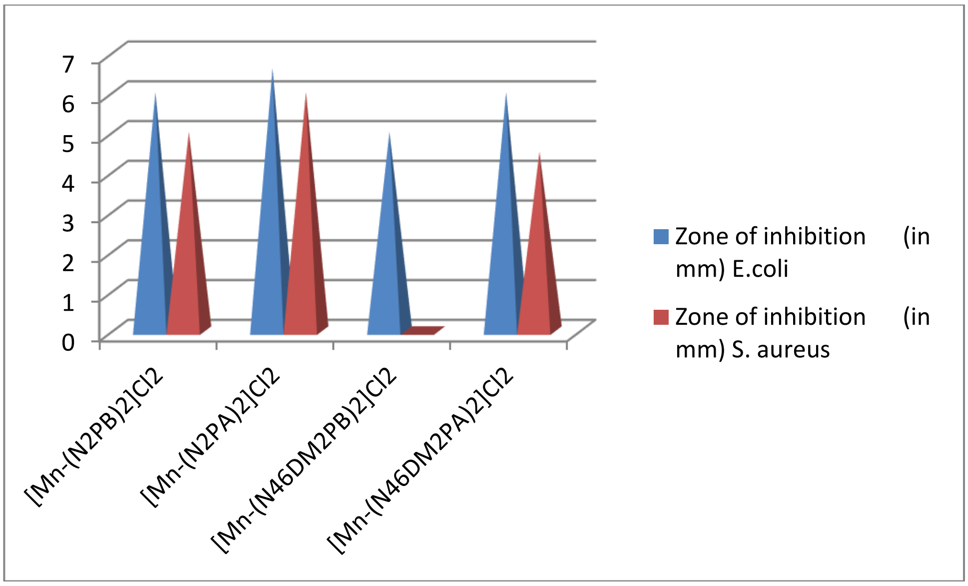


Fig.14. Biological activity of metal complexes containing amide Ligands.