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Template Synthesis of Transition Metal Complexes with Octaamide Macrocyclic Ligand†

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The 'one-pot' template synthesis of metal complexes with a new [2+2] macrocycle bearing four oxamide units is reported. The metal complexes MLX_2, where M = Cu(II), Co(II), Ni(II), Mn(II) and Zn(II), L = 1,4,7,10,13,16,19,22-octaazacyclotetracosane-2,3,8,9,14,15,20,21-octaones and X = Cl^-/ OAc^- have been characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, electronic, IR and EPR spectral studies. On the basis of these studies Cu(II) complex has been assigned tetragonal geometry while other complexes are assigned octahedral geometry and are found to be high spin.

Key Words: Cyclic polyamide, Macrocycle, Transition metals.

INTRODUCTION

In recent years, the preparation of multimetallic complexes gains great importance for it aids in understanding the functional role of metalloenzymes[1], the magnetic interaction between paramagnetic centers[2-8] and for the construction of metallosupramolecular architectures[9]. Polynuclear complexes bearing macrocyclic ligands are of special interest for macrocycle, besides possessing greater kinetic and thermodynamic stability over acyclic analogues, offers special structure and properties. For instance cyclic polyamides have been extensively studied as anion receptors[10] and recently shown[11,12] to bind DNA and inhibit HIV replication. Robertson *et al.*[13], using 'complex as ligand' approach, prepared trinuclear complex with a cyclam based macrocyclic oxamide wherein the enforced exo-*cis* oxygens of oxamide group act as bidentate linkers of mononuclear macrocyclic complex. Adopting this strategy many homo/hetero polymetallic complexes have been subsequently prepared[14-20]. Generally, syntheses of

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macrocycles comprising multiple metal binding sites may either require a multi step process[21] or lead to a mixture of [1+1], [2+2] and higher adducts. In the present study, it is shown for the first time that by template method, a mononuclear complex with an exclusive [2+2] macrocycle *i.e.*, 1,4,7,10,13,16,19,22-octaazacyclotetracosane-2,3,8,9,14,15,20,21-octaones can be prepared in one-pot.

EXPERIMENTAL

All the fine chemicals used were of AnalaR grade. Metal salts procured from E. Merck were used as received. All solvents used were of HPLC/ Spectroscopic grade.

The C, H and N were analyzed on Carlo Erba 1106 elemental analyzer. The metals were estimated by standard methods. Taking $Hg[Co(SCN)_4]$ as a calibrant magnetic susceptibility was measured at room temperature using Gouy balance. IR spectra (KBr) were recorded using Jasco FT IR-410 spectrometer. The electronic spectra were recorded in nujol on Shimazdu UV 460 spectrophotometer. EPR spectra were recorded in solid at room temperature for Cu(II) on an E4-EPR spectrometer using DPPH as a g marker.

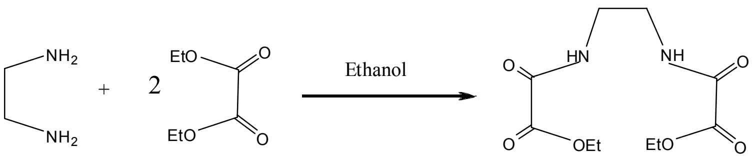
Preparation of the precursor ethyl 2-({2-[(2-ethoxy-2-oxoacetyl)-amino]ethyl}amino)-2-oxoacetate [P]: Diethyl oxalate (10 mL, 0.074 mol) was dissolved in minimum amount of ethanol in a beaker. When ethylenediamine (1 mL, 0.015 mol) was added drop wise to the diethyl oxalate solution the precursor [**P**] (white precipitate) was formed. The solution was stirred for *ca.* 0.5 h to ensure the completion of the reaction. Then the formed precursor was filtered, washed with dichloromethane and then subsequently dried in vacuum over anhydrous $CaCl_2$. Yield = 84 %. m.p. = 268 ºC.

Template synthesis of complexes from precursor: The precursor (ethyl-2-({2-[(2-ethoxy-2-oxoacetyl)amino]ethyl}amino)-2-oxoacetate) (1.526 g, 0.006 mol) and cupric chloride (0.5 g, 0.003 mol), dissolved individually in ethanol, were mixed. After stirring this mixture for 0.5 h, ethylene diamine (0.40 mL, 0.006 mol) was added to it. Stirring was further continued for 1 h to get the copper complex. Then the formed copper complex was filtered, washed with aqueous ethanol and then subsequently dried in vacuum over anhydrous $CaCl_2$. Co(II), Ni(II), Mn(II) and Zn(II) complexes were similarly prepared by taking corresponding metal salts.

RESULTS AND DISCUSSION

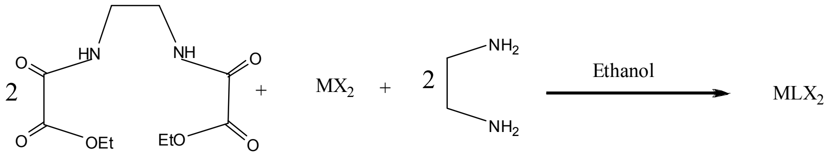
The given scheme explains the formation of the precursor [**P**] and template synthesis of complexes from the precursor [**P**].

Preparation of Precursor[P]



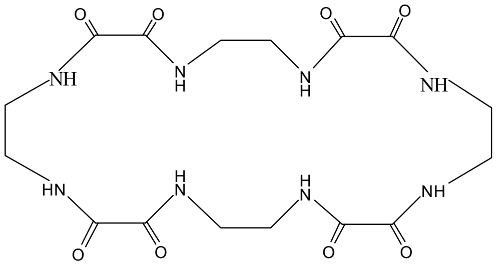
Precursor[P]

Template synthesis of complexes from precursor



Where, M=Cu(II),Co(II),Ni(II),Mn(II)and Zn(II), X=Cl^- / oAc^-

L=1,4,7,10,13,16,19,22-octaazacyclotetracosane-2,3,8,9,14,15,20,21-octaones



Scheme

In the preparation of precursor, cyclization is avoided by taking excess ester (diethyl oxalate) relative to ethylene diamine. The acyclic nature of the precursor is evident from the band at 1740 cm^{-1} corresponding to ester carbonyl group in the IR[22] spectrum of the precursor. The appearance of the bands at 1668 cm^{-1} [amide I (C = O stretching)] and 1536 cm^{-1} [amide II (NH deformation)][23] confirms the presence of amide moiety in the precursor. Nevertheless the disappearance of band at 1740 cm^{-1} in the IR spectrum of the complexes indicate that cyclization occurs by the further condensation of the ester groups with amine during the template synthesis of complexes from precursor and amine.

Further to ascertain the mode of coordination of amide in complexes, a cyclic polyamide (PA_{cy}) was prepared from precursor [**P**] and ethylenediamine in the absence of metal. IR spectrum of the amide (PA_{cy}) shows amide I and amide II bands at 1652 and 1533 cm^{-1}, respectively. On comparison of the amide (PA_{cy}) with complexes indicates that upon complexation amide I band shifts by 15-20 cm^{-1} towards the higher side. This in turn predicts the amide nitrogen involves in coordination with the metal. On the basis of C, H and N analysis and metal estimation the complexes were assigned the composition as shown in Table-1.

TABLE-1
ELEMENTAL DATA OF METAL COMPLEXES

Complexes (Colour)	m.p. (°C) / [Yield (%)]	Elemental Analysis: Calcd. (Found) %			
		M	C	H	N
$Cu(L)Cl_2$	217	10.76	32.50	4.06	18.90
(Blue)	[84]	(10.74)	(32.48)	(4.05)	(18.87)
$Co(L)Cl_2$	249	10.06	32.76	4.09	19.11
(Pale pink)	[82]	(10.06)	(32.74)	(4.08)	(19.12)
$Mn(L)Cl_2$	222	9.44	32.88	4.10	19.10
(Brown)	[79]	(9.43)	(32.90)	(4.09)	(19.09)
$Ni(L)(OAc)_2$	280	9.27	30.34	3.79	17.70
(Pale blue)	[80]	(9.26)	(30.33)	(3.78)	(17.71)
$Zn(L)Cl_2$	210	11.04	32.49	4.05	18.90
(White)	[81]	(11.03)	(32.50)	(4.05)	(18.87)

TABLE-2
MAGNETIC MOMENT AND SPECTRAL DATA OF THE COMPLEXES

Complexes	λ_{max} (cm^{-1})	ν(C=O) (cm^{-1})	μ_{eff} (BM)
$Cu(L)Cl_2$	15714	1666	1.7
$Co(L)Cl_2$	16177	1670	4.8
$Mn(L)Cl_2$	18644	1668	5.6
$Ni(L)(OAc)_2$	11957	1671	2.8
$Zn(L)Cl_2$	–	1670	Diamagnetic

The complexes were found to be insoluble in common solvents thereby indicating that these complexes may be non electrolytes. Thus the complexes may be formulated as $[M(L)X_2]$.

The magnetic moment for the copper complex lies in 1.7 BM corresponding to one unpaired electron. The electronic spectrum shows one broad band at 15714 cm^{-1}. The studies on electronic spectrum of Cu(II) complexes indicate that the band may be arising due to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$ expected for tetragonally distorted octahedron.

EPR spectrum of the Cu(II) complex (Fig. 1) was recorded at room temperature in solid state. The analysis of spectrum gives $g_{11} = 2.05$ and $g_\perp = 1.9$. The trend $g_{11} > g_\perp$ indicates that the unpaired electron is localized in

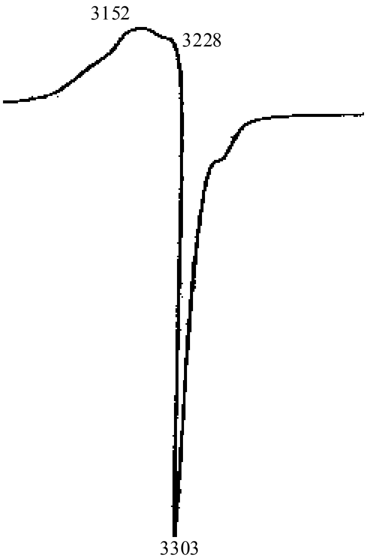


Fig. 1. ESR Spectra for Cu(II) complex in solid state at room temperature

$d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral features are characteristic for the axial symmetry[24,25]. It is obvious the complex has tetragonal geometry.

According to Hathaway *et al.*[26,27] and Reddy *et al.*[28] if $G > 4$ the exchange interaction is negligible but $G < 4$ indicates the considerable exchange interaction in the solid complex. The complex reported here has $G < 4$ indicating exchange interaction in the solid complex.

Manganese(II) complex: Mn(II) complex has magnetic moment of 5.6 BM corresponding to five unpaired electrons. The electronic spectrum of Mn(II) complex shows a band at 18644 cm^{-1}. This agrees with the transition $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ [ν_2][29] of an octahedral Mn(II) complex.

Cobalt(II) complex: The magnetic moment of the cobalt complex at room temperature lies in 4.8 BM. The electronic spectrum of the complex shows a band at 16177 cm^{-1} corresponding to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ [ν_3][30] characteristic of an octahedral Co(II) complex.

Nickel(II) complex: Ni(II) complex has magnetic moment at 2.8 BM. The band at 11956 cm^{-1} in its electronic spectrum may be assigned to the transition $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ [ν_2][31] of an octahedral Ni(II) complex.

Conclusion

Metal complexes with an exclusive [2+2] macrocycle, *i.e.*, 1,4,7,10,13,16,19,22-octaazacyclotetracosane-2,3,8,9,14,15,20,21-octaones have been prepared in one-pot from a suitable precursor by template fashion, characterized by magnetic and spectral techniques. Further studies on utility of these complexes as cation/anion receptors, as precursors for new polynuclear magnetic materials are in progress.

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