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Synthesis and Characterization of Transition Metal Complexes of 12- and 14-Membered Tetraaza Macrocycles

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Template synthesis of transition metal complexes with macrocyclic tetraaza (N_4) ligands L' and L" [L' = 1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone and L" = 1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone have been described. The complexes were characterized by elemental analyses, molar conductance, magnetic susceptibility measurements, CV and electronic, IR, EPR spectral studies. On the basis of these studies Cu(II) complex has been assigned tetragonal geometry while other complexes are assigned octahedral geometry.

Key Words: Synthesis, Characterization, Transition metal complexes, 12- and 14-Membered tetraaza macrocycles.

INTRODUCTION

In recent years, more attention is being paid for the preparation of macrocyclic ligand and its complexes, since macrocyclic ligands serve as anion/cation receptors[1,2], while the complexes are used as MRI[3,4] and chemotherapeutic agents[5]. Besides it has been shown recently that macrocyclic oxamide complex by virtue of its exogenous oxygen atoms aids in the preparation of multimetallic complexes[6-12] that were shown to serve as molecular magnetic materials[13], catalysts[14] and biomodels of enzymes[15].

The synthesis of macrocycles bearing multiple metal binding sites either requires multi step process[16] or it becomes difficult due to the competitive formation of acyclic/cyclic oligomers. Hence synthetic techniques such as template synthesis or high dilution have been adopted for the preparation of macrocyclic complexes. Herein, the template synthesis of transition metal complexes is reported with a new aza macrocycle L' and L"* (*Non-template synthesis of complexes with ligand L" have been reported[17]).

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.

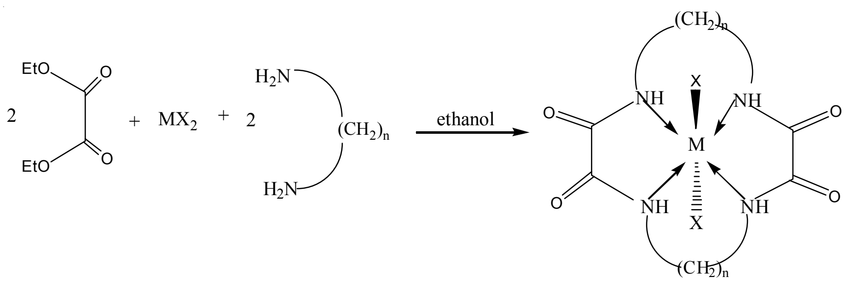
Preparation of ML'X_2 complexes: Diethyl oxalate (0.79 mL, 5.8 mmol) was dissolved in ethanol. Then ethanolic solution of copper(II) chloride dihydrate (0.500 g, 2.9 mmol) was added to it and the mixture was stirred for 15 min. To the mixture ethylenediamine (0.39 mL, 5.8 mmol) was added dropwise and stirring continued for 0.5 h. Then the solution was concentrated nearly to its one tenth of its volume on a water bath to get the complex. The formed complex was filtered and dried in vacuum over anhydrous $CaCl_2$. Similarly other metal complexes of the type ML'X_2 (M = Co^{2+}, Mn^{2+}, Ni^{2+} or Zn^{2+})were prepared using corresponding metal salts.

Preparation of ML"X_2 complexes: Adopting the above procedure but using 1,3-diaminopropane instead of ethylenediamine, the complexes ML"X_2 were prepared.

Physical measurements: 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 FTIR-410 spectrometer. The electronic spectra of the samples were recorded using Analytik-Jena specord diode array photometer (specord S 100). Nujol was used as a reference. Cyclic voltammetric measurements were made in DMSO medium using Bio-Analytical system (BAS) model CV-50W electrochemical analyzer. The three-electrode cell comprised of reference Ag/AgCl, auxiliary platinum and working Pt electrode was used for the measurement; tetra-*n*-butylammoniumtetrafluoroborate (TBAB) was used as a supporting electrolyte. EPR spectra were recorded in solid state at room temperature for Cu(II) complex on an E4-EPR spectrometer using DPPH as a g marker.

RESULTS AND DISCUSSION

Scheme for the preparation of ML'X_2 and ML"X_2 complexes



[M = Cu(II), Co(II), Ni(II), Mn(II) and Zn(II)]
X = Cl^-/CH_3COO^-, for ML′X_2, n = 2,
for ML″X_2, n = 3

TABLE-1
ANALYTICAL DATA OF ML'X$_2$ AND ML"X$_2$ COMPLEXES

Complexes (colour)	m.p. (ºC) / Yield (%)	Elemental analysis %: Calcd. (Found)				Molar cond. (Ω^{-1} cm^2 mol^{-1})
		M	C	H	N	
Cu(L')Cl$_2$	217 /	17.90	26.40	3.30	15.45	12
(Green)	84	(17.55)	(26.48)	(3.29)	(15.60)	
Co(L')Cl$_2$	249 /	16.40	23.76	3.30	13.81	11
(Pink)	82	(16.46)	(23.84)	(3.35)	(13.62)	
Mn(L')Cl$_2$	222 /	15.30	27.08	3.33	15.80	14
(Brown)	79	(15.25)	(27.10)	(3.06)	(15.84)	
Ni(L')Cl$_2$	280 /	16.21	26. 08	3.38	15.56	11
(Pale blue)	80	(16.34)	(26.33)	(3.88)	(15.54)	
Zn(L')Cl$_2$	210 /	17.50	26.36	3.29	15.37	9
(White)	81	(17.10)	(26.50)	(3.28)	(15.67)	
Cu(L")Cl$_2$	217 /	16.30	30.33	4.09	14.30	11
(Green)	84	(16.26)	(30.35)	(4.08)	(14.32)	
Co(L")(OAc)$_2$	249 /	13.41	27.72	3.79	12.93	13
(Pink)	82	(13.37)	(27.74)	(3.76)	(12.93)	
Mn(L")Cl$_2$	222 /	14.52	31.51	4.19	14.67	14
(Brown)	79	(14.53)	(31.54)	(4.16)	(14.65)	
Ni(L")Cl$_2$	280 /	15.20	31.10	4.15	14.52	12
(Pale blue)	80	(15.19)	(31.12)	(4.13)	(14.57)	
Zn(L")Cl$_2$	210 /	16.71	30.58	4.07	14.27	11
(White)	81	(16.68)	(30.57)	(4.02)	(14.24)	

TABLE-2
MAGNETIC MOMENT AND SPECTRAL DATA OF
THE COMPLEXES ML'X$_2$

Complexes	λ_{max} (cm^{-1})	Amide I ν(C=O) (cm^{-1})	Amide II δ(NH) (cm^{-1})	μ_{eff} (BM)
Cu(L')Cl$_2$	25440, 23419	1654	1514	2.2
Co(L')Cl$_2$	23872, 20794	1612	1511	4.3
Mn(L')Cl$_2$	25870, 23139	1670	1525	6.1
Ni(L')Cl$_2$	25670	1677	1523	2.7
Zn(L')Cl$_2$	–	1660	1515	Diamag.

TABLE-3
MAGNETIC MOMENT AND SPECTRAL DATA OF
THE COMPLEXES ML"X$_2$

Complexes	λ_{max} (cm^{-1})	ν(OH) *str.* (cm^{-1})	ν(C=N) (cm^{-1})	δ(OH) def. (cm^{-1})	μ_{eff} (BM)
Cu(L")Cl$_2$	25773, 23529	3446	1623	1457	2.2
Co(L")(oAc)$_2$	23866, 20080, 18416	3428	1610	1455	4.6
Mn(L")Cl$_2$	23866, 20080	3436	1648	1458	5.9
Ni(L")Cl$_2$	24449	3446	1621	1460	3.5
Zn(L")Cl$_2$	–	3442	1623	1452	Diamag.

The elemental analysis of the complexes are presented in Table-1. The low molar conductance values of the complexes indicate the non-electrolytic nature of the complexes (Table-1).

IR spectra of complexes-ML'X_2 and ML"X_2: The cyclic product[18] formed by the reaction between ethylenediamine and diethyloxalate show the bands amide I at 1652 cm^{-1} and amide II at 1533 cm^{-1}. For the ML'X_2 complexes the amide I band shifts by 15-20 cm^{-1} towards higher side and amide II shifts towards lower side indicating the amide nitrogen was involved in the coordination.

The ligand L"[17] shows the (Table-2) amide I at 1651 cm^{-1} and amide II at 1518 cm^{-1}. The disappearance of the peaks around 1518 cm^{-1} in the complexes reveal that the ligand L" coordinates with metal in enolic form using azomethine nitrogen. Further the presence of enolic form is evident[19] from the peaks at around 3400 cm^{-1} and at 1450 cm^{-1} corresponding to OH streching and deformation, respectively. The peaks observed in the range 1648-1610 cm^{-1} correspond to the coordinated azomethine group (Table-3).

Electronic spectra and magnetic moment for ML'X_2 and ML"X_2 complexes (Tables 2 and 3)

Copper(II) complex: The magnetic moments for both CuL'X_2 and CuL"X_2 lie in 2.2 BM corresponding to one unpaired electron. The electronic spectrum of each complex shows two bands. The studies on electronic spectrum[20] of Cu(II) complexes indicate that the bands in each complex may be arising due to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_2) and $^2B_{1g} \rightarrow {}^2E_g$ (ν_3) expected for tetragonally distorted octahedron.

Nickel(II) complex: The complexes NiL'X_2 and NiL"X_2 have magnetic moment, respectively at 2.7 and 3.5 BM. Electronic spectra of these complexes, respectively display bands at 25670 and 24449 cm^{-1} attributable to the transition $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) of an octahedral Ni(II) complex.

Manganese(II) complex: The MnL'X_2 and MnL"X_2 complexes are found to have magnetic moment of 5.9 and 6.1 BM, respectively corresponding to five unpaired electrons. The electronic spectrum of the octahedral Mn(II) complex usually shows bands corresponding to the transitions $^6A_{1g} \rightarrow {}^4E_g({}^4D)$, $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}({}^4G)$ and $^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$. Two bands observed at 23139 and 25870 cm^{-1} for MnL'X_2 can be assigned to $^6A_{1g} \rightarrow {}^4E_g({}^4D)$ and $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}({}^4G)$. Further MnL"$X_2$ shows two bands at 20080 and 23866 cm^{-1}, corresponding to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$ and $^6A_{1g} \rightarrow {}^4E_g({}^4D)$.

Cobalt(II) complex: The magnetic moment of the CoL'X_2 and CoL"X_2 complexes at room temperature are found to have magnetic moment of 4.3 and 4.6 BM, respectively. The electronic spectrum of the octahedral Co(II) complex usually shows bands corresponding to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3). Two bands observed at 20794 and 23872 cm^{-1} for CoL'X$_2$ can be assigned to ν_2 and ν_3. Further CoL"X$_2$ shows three bands at 18416, 20080 and 23866 cm^{-1} corresponding to the transition ν_1, ν_2 and ν_3, respectively.

TABLE-4
CYCLIC VOLTAMMETRIC MEASUREMENTS FOR ML'X$_2$ COMPLEXES

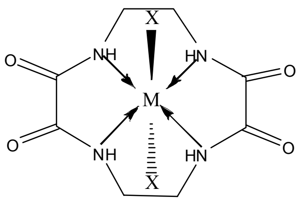
Complex	Ep_c	Ep_a	ΔEp	$E_{½}$
Cu(L')Cl$_2$	-1056	-780	-276	-918
Co(L')Cl$_2$	-1084	-542	-542	-813
Mn(L')Cl$_2$	-988	-675	-313	-832

Electrochemical behaviour: The cyclic voltamogram of Cu(II), Co(II) and Mn(II) complexes were recorded at room temperature, using Pt as the working electrode. It is found that ΔE_p varies with varying scan rate. It is obvious that for all the complexes, ΔE_p is very much different from 60 mV. Further ΔE_p values suggest that copper(II) and cobalt(II) complexes behave as quasi-reversible whereas manganese(II) behaves as irreversible.

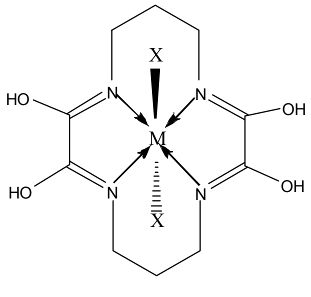
ESR spectra of copper complex for ML'X$_2$: EPR spectrum of the Cu(II) complex was recorded at room temperature in solid state. The analysis of spectrum gives $g_{\|} = 2.05$ and $g_{\perp} = 1.9$. The trend $g_{\|} > g_{\perp}$ indicates that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral features are characteristic of the axial symmetry. It is obvious the complex has tetragonal geometry.

According to Hathway and Billing[21,22] and Reddy *et al.*[23] 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.

From these studies, it is found that the complexes possess octahedral geometry with high spin, while copper(II) complexes have tetragonal geometry. It is further inferred that L' coordinates with metal in amide form whereas L" coordinates with metal in enolic form.



ML'X$_2$



ML"X$_2$

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