Tetraamide Macrocyclic Complexes Of Some Transition Metal Ions

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Abistract: *A new family of 15 – membered tetraamide macrocyclic complexes (ML1CL2) and (ML2CL2) (M = Fe ,Co, Ni, Cu, and Zn) have been synthesized by template condensation reaction of o-aminobenzoic acid with aliphatic or aromatic diamines and diethyl malonate in 2:1:1 molar ratio. The stoichiometries and coordination modes of these complexes were deduced from physicochemical and spectroscopic measurements. An octahedral geometry has been assigned for all complexes.*

Key words: *Template synthesis, O-amino benzoic acid, aliphatic and aromatic diamines, diethyl malonate, iron, cobalt, nickel, copper, zinc, physico chemical and spectroscopic studies.*

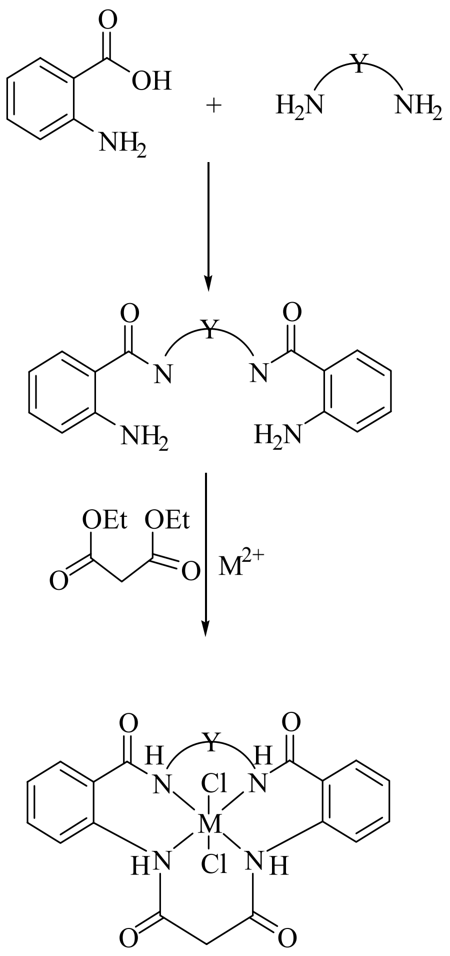
Introduction

The chemistry of macrocyclic ligands has been known for several decades [1]. Among them, tetraazamacrocycles have been studied thoroughly. Such ligands often lead to complexes with enhanced thermodynamic and kinetic stability with respect to metal ion dissociation, compared to their open-chain analogues [2]**.** The amide macrocyclic complexes are of particular interest in view of their application as catalysts [3,4]. Generally, macrocyclic polyamides are prepared by reaction of polyamine with either the diester salt of a dicarboxylic acid or the dicarboxylic acid dichloride [5-7].

An amide group offers two potential binding atoms, the oxygen and nitrogen for complexation with metal ions. Many macrocyclic ligand complexes have been reported with several amid groups which exhibit diverse coordination behaviour with different metal ions [8-13]. I have previously reported a wide variety of tetraaza [13-15], pentaaza [16-17], hexaaza [18-20], octaaza [21,22], dithiadiaza [23] and dithiatetraazamacrocyclic complexes [24]. Here is reported the synthesis and physicochemical studies of a new series of tetraazamacrocyclic complexes bearing tetraamide groups derived from o-aminobenzoic acid, with ethylene diamine or o-phenylene diamine and diethyl malonate in the presence of transition metal ions as templates.

Results And Discussion

The reaction of anthranilic acid with aliphatic or aromatic diamine and diethyl malonate in ethanol in the presence of transition metal ions as templates, yielded in each case a novel series of tetraazamacrocyclic complexes as shown in scheme1.



M^{2+} = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}

Y = C_2H_4 or C_6H_4

SCHEME 1

The purity of the compounds has been checked by established TLC technique by dissolving the compounds in DMF using ethylacetate (85), methanol (10) and acetic acid (5) as eluents. Only one spot was observed in each case after developing in iodine chamber, indicating that the compounds were pure. The yields are moderate. However, the yields in case of (ML_2Cl_2) were found to be comparatively low which may be due to the more stiric hindrance of the aromatic than that of the aliphatic diamine. The elemental analysis is consistent with the proposed formulations (Table 1). The color and crystalline habits of the complexes under study indicate that they are of the same family. Attempts to prepare the macrocyclic metal-free ligands could not prove successful. The low molar conductivity values observed in DMSO of all compounds indicate [25] that they are non-electrolytes (Table I). The overall geometries were inferred from the various spectroscopic studies discussed below.

TABLE 1 . Color, M.P(°C),Yield (%), Elemental Analyses and Molar Conductivity Data of the Complexes

Compound	**Color**	**M.P (°C)**	**Yield**	**M**	**C**	**H**	**N**	**Cl**	**Molar Cond. ($cm^2\Omega^{-1}mol^{-1}$)**
FeL_1Cl_2	Brown	312	55	11.28 (11.31)	46.00 (46.24)	3.67 (3.68)	11.25 (11.36	14.30 (14.4)	24
CoL_1Cl_2	Dull grey	246	50	11.76 (11.87)	45.80 (45.96)	3.65 (3.66)	11.20 (11.28	14.27 (14.31)	16
NiL_1Cl_2	Sky grey	314	65	11.73 (11.88)	45.80 (45.96)	3.63 (365)	11.21 (11.28	14.25 (14.31)	12
CuL_1Cl_2	Dull green	238	70	12.61 (12.69)	45.37 (45.53)	3.61 (3.63)	11.09 (11.18	14.07 (14.17	14
ZnL_1Cl_2	Off white	166	58	12.94 (13.01)	45.17 (45.36	3.60 (3.61)	11.02 (11.14	14.00 (14.12)	18
FeL_2Cl_2	Brown	328	35	10.27 (10.80)	50.83 (51.02)	3.32 (3.36)	10.27 (10.35	13.00 (13.12)	15
CoL_2Cl_2	Dull grey	253	35	10.80 (10.82)	50.60 (50.72)	3.30 (3.34)	10.20 (10.29	13.00 (13.04)	20
NiL_2Cl_2	Sky grey	322	40	10.78 (10.82)	50.57 (50.72)	3.30 (3.34)	10.22 (10.29	12.93 (13.04)	20
CuL_2Cl_2	Dull green	245	42	11.39 (11.48	50.06 (50.29)	3.30 (3.31)	1011 (1020	12.86 (12.93	18
ZnL_2Cl_2	Off white	185	37	11.80 (11.87)	49.96 (50.12)	3.30 (3.30)	10.09 (10.17	12.80 (12.89)	16

IR Spectra

The IR spectra of the macrocyclic complexes under study (Table 2), show no bands characteristic of NH_2, OH, or OET. Instead, four amide bands appeared in the 1670-1710, 1520-1550, 1240-1280 and 640-660 cm^{-1} regions, assignable to amide I ν (C=O), amide II ν (C-N) + δ (N-H), amide III δ (N-H) and amide IV ϕ (C=O) bands, respectively, along with a negatively shifted[11,26] amide N-H stretching vibration in the 3195-3240 cm^{-1} region, provide evidence for the skeleton of the macrocyclic moiety. This was further supported by the appearance of a new medium intensity band in the 430-470 cm^{-1} region, assignable[11,26,27] to M-N stretching vibration, confirming the involvement of nitrogen in coordination. However the amide I band is found to be unaffected on coordination when compared to that reported[11] for analogous metal-free ligand and thus rules out the coordination through amide oxygen. This has been further supported by the absence of any band attributable to M-O stretching vibration. The medium bands in the 300-320 cm^{-1} regions may be assigned to M-Cl stretching vibrations[27] . Bands observed in the 1230-1240, 1025-1125 and 850-870 cm^{-1} regions are the usual modes of disubstituted benzene.

TABLE 2 . IR Spectral Data (cm^{-1}) of the Compounds

Compound	ν (N–H)	Amide Bands				ν (M–N)	ν (M–Cl)	Ring Vibrations		
	amide	I	II	III	IV					
FeL_1Cl_2	3230	1680	1520	1240	645	470	320	1230	1100	870
CoL_1Cl_2	3240	1710	1525	1265	650	450	300	1240	1025	855
NiL_1Cl_2	3200	1700	1550	1260	645	430	305	1230	1110	860
CuL_1Cl_2	3215	1690	1530	1265	640	445	315	1235	1105	850
FeL_2Cl_2	3220	1670	1525	1250	650	460	315	1240	1115	850
CoL_2Cl_2	3220	1700	1520	1260	660	450	310	1235	1110	865
NiL_2Cl_2	3195	1685	1540	1280	650	435	320	1240	1120	850
CuL_2Cl_2	3210	1710	1540	1255	650	440	305	1230	1125	855

The ^{1}HNMR Spectra

The ^{1}HNMR spectra of both the zinc (II) complexes (Table 3), recorded in d_6 DMSO showed a multiplet in the 2.16-2.18 ppm regions which may be ascribed[17] to CO- CH_2-CO (2H) protons, along with a broad signal in the 8.38, 8.40 ppm regions, assignable to the amide C-NH-CO (4H) protons. In addition, the ^{1}HNMR spectra of [ZnL_1CL_2] complex showed a multiplet in the 2.56 ppm region which may be assigned[17] to N-CH_2-CH_2-N (4H) protons. The ZnL_1CL_2 complexes showed a broad muliplet in the 7.30 ppm region and the ZnL_2CL_2 complex in the 7.45 ppm region assignable[17] to phenyl ring C_6H_4 (8H) and C_6H_4 (12H) protons, respectively. All the above along with the absence of any band characteristic of NH_2, or OH protons, support the proposed macrocyclic framework.

Table 3. ^{1}H NMR Spectral data* of the complexes**.**

Compound	CO-CH_2-CO	N-CH_2-CH_2-N	CO-NH	Ring vibration
ZnL_1Cl_2	2.18 s	2.56m	8.40m	7.45m
ZnL_2Cl_2	2.16s	----	8.38m	7.30m

*chemical shift (ppm) with multiplicities in paranthesis.
S = Singlet, m = multiplet.

UV Vis Spectra

The observed magnetic moments and the positions of the absorption bands (Table 4) in the electronic spectra of the iron (II) macrocyclic complexes recorded in DMSO showed a weak intensity band at 11550,11700 cm^{-1} corresponding to high spin d^6 system which may be assigned[28] to $^5T_2g \rightarrow {}^5Eg$, consistent with an octahedral environment around the iron (II) ion. However, the cobalt (II) complexes (Table 4) exhibit two bands in the

21950, 22150 and 13800, 14000 cm^{-1} regions which may correspond to high spin d^7 system assignable[11,28] to $^4T_1g(F) \rightarrow {}^4A_2g$ (F) and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transitions, respectively, consistent with an octahedral geometry around the cobalt(II) ions. The nickel (II) complexes, each showed a magnetic moment corresponding to a spin – free complex. Their electronic spectra (Table 4) showed three distinct bands arising from the octahedral geometry of the nickel (II) complexes. Two bands around 27300, 27450 and 20250, 20350 cm^{-1} and one broad band around 11150 and 11250 cm^{-1} assignable[11,28] to ^3A_2g (F) $\rightarrow {}^3T_1g$ (P), and ^3A_2g (F) $\rightarrow {}^3T_2g$ (F) transitions, respectively. The electronic spectra of the copper (II) complexes (Table 4) each showed a main broad band in the 20250, 20400 cm^{-1} region along with a shoulder in the 16450, 16550 cm^{-1} region (Table 4) which may unambiguously be assigned to $^2B_1g \rightarrow {}^2Fg$ and $^2B_1g \rightarrow {}^2B_2g$ transitions, respectively, corresponding[17,28] to a distorted octahedral geometry. Their magnetic moment values further support the above proposed geometry.

The high intensity bands observed around 33000 cm^{-1}for all the complexes in the u.v. region may be assigned as a metal-to-ligand charge transfer excitation[11,19] .

TABLE 4. Band Position and Their Assignments .

Compound	μ_{eff}(BM)	Band Position X10^3,cm^{-1}	Assignments
FeL_1Cl_2	5.43	11.700	$^5T_2g \rightarrow {}^5Eg$
FeL_2Cl_2	5.42	11.550	$^5T_2g \rightarrow {}^5Eg$
CoL_1Cl_2	4.53	22.150	^4T_1g (F) $\rightarrow {}^4T_2g$ (p)
		14.000	^4T_1g (F) $\rightarrow {}^4A_2g$ (F)
CoL_2Cl_2	4.51	21.950	^4T_1g (F) $\rightarrow {}^4T_1g$ (p)
		13.800	^4T_1g (F) $\rightarrow {}^4A_2g$ (F)
NiL_1Cl_2	3.12	27.300	^3A_2g (F) $\rightarrow {}^3T_1g$(P)
		20.250	^3A_2g (F) $\rightarrow {}^3T_1g$(F)
		11.150	^3A_2g (F) $\rightarrow {}^3T_2g$(F)
NiL_2Cl_2	3.18	27.450	^3A_2g (F) $\rightarrow {}^3T_1g$(P)
		20.350	^3A_2g (F) $\rightarrow {}^3T_1g$(F)
		11.250	^3A_2g (F) $\rightarrow {}^3T_2g$(F)
CuL_1Cl_2	1.76	20.400	$^2B_1g \rightarrow {}^2Eg$
		16.550	$^2B_1g \rightarrow {}^2E_2g$
CuL_2Cl_2	1.73	20.250	$^2B_1g \rightarrow {}^2Eg$
		16.450	$^2B_1g \rightarrow {}^2E_2g$

Experimental

The metal salts $FeCL_2$, $CoCL_2.6H_2O$, $NiCL_2.6H_2O$, $CuCL_2$. $2H_2O$ and $ZnCL_2$ (BDH) were commercially available pure samples. Anthanilic acid, ethylene diamine, o-phenylene diamine(E.Merk) and diethyl malonate (BDH) were used as recieved.

Synthesis of dichloro-(1,2;8,9 – dibenzo- 4,6,10,15- tetraoxo – 3,7,11,14 – tetraazacyclopentadecane metal(II) ; [M L_1 Cl_2]

A mixture of anthranilic acid (0.8 g, 5 mmol) and ethylene diamine (0.15 g, 2.5 mmol) dissolved in 50 ml ethanol was stirred for about one hour. A hot ethanolic solution of the appropriate metal chloride (0.35 g, 2.5 mmol) was then added, followed by addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol and dried in vacuo.

Synthesis of dichloro –(1,2; 8,9;12,13- tribenzo -4,6,10,15- tetraoxa - 3,7,11,14- tetraazacyclopentadecane metal (II) ; [M L_2 Cl_2]

These complexes were prepared by the same procedure ,substituting o-phenylene diamine for 1,2-diaminoethane.

Conclusion

The above procedures outlined for the preparation of the resultant macrocyclic complexes are facile and appear to proceed smoothly. These complexes may have wider applicability. It should prove useful for investigation of metal containing – biological molecules such as metallo-enzymes, and their catalytic activity for industry.

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