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Template Syntheses and Chracterization of 14-Membered Tetraazamacrocyclic Complexes

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A new series of 14-membered tetraazamacrocyclic complexes $[CuL]X_2$, [X = Cl or NO_3] and $[MLX_2]$ [M = Co^{2+}, Ni^{2+} and Zn^{2+}, X = Cl or NO_3] have been synthesized by template condensation of *o*-bromoaniline, phthalaldehyde and diaminoethane in ethanol and were characterized by elemental analysis, IR, ^1H NMR, electronic spectral, conductivity as well as magnetic susceptibility measurements. An octahedral geometry is proposed for all the complexes except for copper complexes which were found to be square-planar.

Key Words: Template syntheses, 14-Membered tetraazamacrocyclic complexes.

INTRODUCTION

Macrocyclic ligands capable of binding metal ions are of interest. They impose a high degree of pre-organization on metal complex formation[1]. They also constitute an excellent basis for the study of the molecular recognition phenomena since the cavity size, shape and components can be readily varied[2]. In addition to their catalytic properties[3], theyare relevant important biological processes such as photosynthesis and dioxygen transport[4].

Macrocyclic complexes are best prepared with the aid of metal ions as templates to direct the steric course of the condensation reaction which ultimately results in ring closure[5]. In most cases, high dilution techniques are employed for the cyclization process when template reaction is not operative. We have previously reported a wide variety of tetraaza[6], pentaaza[7], hexaaza[8], octaaza[9] and mixed thioazamacrocyclic complexes[10]. Here we report the synthesis and physico-chemical studies of a new series of tetraazamacrocyclic complexes by template condensation which is an easy synthesis and may be utilized for the preparation of other related complexes.

EXPERIMENTAL

The metal salts MX_2 (M = Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, X = Cl^- or NO_3^-) (all Aldrich) were commercially available pure samples. Diaminoethane (Merck) and phthalaldehyde (Fluka) were used. Solvents were dried before use.

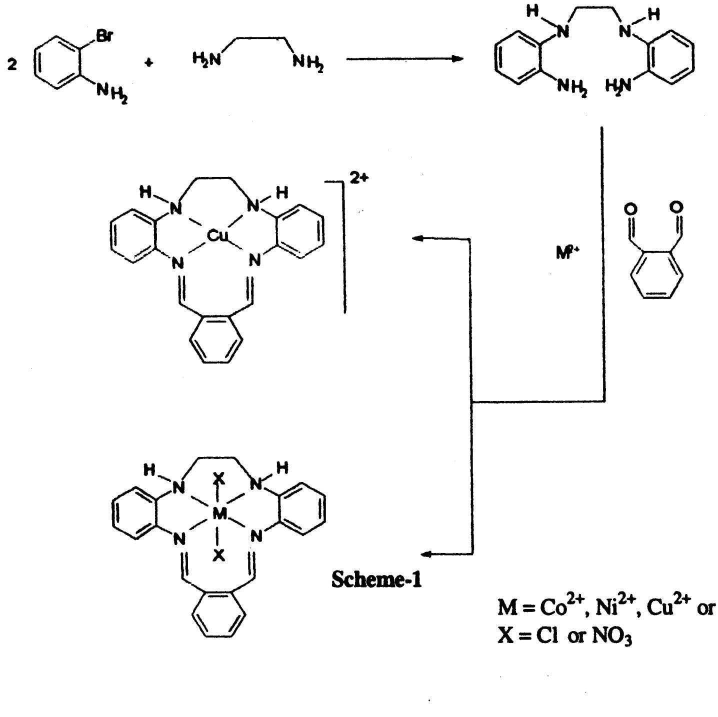
Synthesis of dichloro/nitro (2,3;8,9;12,13-tribenzo-1,4,7,10-tetraaza-cyclotetradeca-1,10-diene) metal(II) [MLX_2] (M=Co, Ni and Zn; X = Cl or NO_3), and (2,3;8,9;12,13-tribenzo-1,4,7,10-tetraazacyclotetradeca-1,10-diene) metal(II) chloride/nitrate [CuL]X_2 (X = Cl or NO_3).

A methanol solution (25 mL) of 1,2-diaminoethane (0.01 mol) was added to a methanolic solution (25 mL) of *o*-bromoaniline (0.02 mol) and the mixture was stirred with gentle heating for 30–45 min. A methanol solution (25 mL) of the metal salt (0.01 mol) was then added dropwise followed by the addition of phthalaldehyde (0.01 mol) in 25 mL of methanol. The mixture was refluxed for 8–10 h, which resulted in the formation of a solid mass. It was collected, washed several times with methanol and then storred in vacuo.

Elemental analysis were obtained from the Microanalytical Laboratory of Al Azhar University, Gaza. Metals were determined by atomic absorption spectrometer. Chloride was determined gravimetrically[11]. Infrared spectra were recorded as Nujol mulls using CsI KBr disc in the region 4000–200 cm^{-1} on a FTIR-8201 pc spectrophotometer. ^1H NMR spectra were recorded in DMSO-d_6 by a Jeol JNM-LA 300-NMR spectrometer using Me_4Si as an internal standard. UV-Vis spectrophotometer (model UV-1601) was used for measuring the electronic spectra of the compounds in DMSO at room temperature. Magnetic susceptibility measurements were made using a Faraday balance at room temperature. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained using AC 13CM-30V conductivity meter at 25°C.

RESULTS AND DISCUSSIONS

A new series of tetraazamacrocyclic complexes were prepared by the template reactions of *o*-bromoaniline and 1,2-diaminoethane with phthalaldehyde (**Scheme-1**). The yields in all cases were moderate. The analytical results (Table-1) suggest



Scheme-1

M = Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}
X = Cl or NO_3

that the macrocycolic complexes have 1 : 1 metal-to-ligand ratio. The non-electrolytic nature for all complexes except for those of copper in DMSO was indicated by the low molar conductance values while the copper complexes were found to be 1 : 2 electrolytes[12]. Attempts to synthesize the corresponding metal-free ligands were unsuccessful and the evidences obtained agree well with the proposed structure.

Selected infrared frequencies of the complexes are given in Table-2. The IR spectra for all the complexes have given a strong evidence for the proposed structure being formed. Bands characteristic of free amine or free carbonyl were absent. Instead, a single sharp band was observed in all cases in the region 1620–1590 cm^{-1} assignable to coordinated ν(C=N) and another single sharp band was found in the region 3220–3190 cm^{-1} assignable to ν(N—H) vibration[6, 13]. These results were also supported by a sharp band which appears in 430–390 cm^{-1} region assignable to (M—N) stretching vibration[13]. Also, the bands occur in the 1430–1410, 1090–1070 and 740–720 cm^{-1} regions assignable to the disubstituted benzene ring vibrations. The complexes of the type [MLX_2] show bands at 310–290 and 245–230 cm^{-1} in the chloro and nitro complexes which may be assigned to ν(M—Cl) and ν(M—O) stretching vibrations respectively.

The ^1H NMR spectrum of the zinc(II) complexes recorded in DMSO-d_6 showed a singlet in the δ 8.40–8.45 ppm region, assignable[8, 14] to the two equivalent imine protons (—CH=N, 2H). The multiplet at 3.10–3.14 ppm in both the zinc complexes correspond to methylene (—CH_2—N; 4H) protons[6]. Both the spectra show multiplets in the region 7.18–7.44 ppm corresponding[9] to ring (12 H) protons. A multiplet at 6.42–6.48 ppm corresponding[6] to (—C—NH, 2H) protons was also found.

TABLE -1
COLOUR, m.p., ELEMENTAL ANALYSIS AND MOLAR CONDUCTANCE VALUES OF THE COMPOUNDS

Complex	Colour	m.p. (°C)	Yield (%)	Found (Calcd.) (%)					Ω_M ($cm^2\ \Omega^{-1}\ mol^{-1}$)
				M	C	H	N	Cl	
[$CoLCl_2$]	Olive green	222	42	12.4 (12.6)	56.0 (56.2)	4.2 (4.2)	11.8 (11.9)	15.0 (15.1)	22
[$CoL(NO_3)_2$]	Olive green	213	40	11.2 (11.3)	50.4 (50.5)	3.8 (3.8)	15.9 (16.1)	—	17
[$NiLCl_2$]	Light yellow	228	45	12.3 (12.5)	56.1 (56.2)	4.2 (4.2)	11.7 (11.9)	15.0 (15.1)	13
[$NiL(NO_3)_2$]	Light yellow	216	40	11.2 (11.3)	50.3 (50.5)	3.8 (3.8)	16.0 (16.1)	—	12
[CuL]Cl_2	Blue	241	55	13.2 (13.4)	55.4 (55.6)	4.2 (4.2)	11.7 (11.8)	14.8 (15.0)	98
[CuL]$(NO_3)_2$	Blue	225	53	11.9 (12.0)	49.8 (50.0)	3.8 (3.8)	15.7 (15.9)	—	102
[$ZnLCl_2$]	Colourless	254	45	13.5 (13.7)	55.2 (55.4)	4.2 (4.2)	11.6 (11.7)	14.9 (15.0)	21
[$ZnL(NO_3)_2$]	Colourless	237	43	12.2 (12.3)	49.7 (49.9)	3.8 (3.8)	15.8 (15.9)	—	16

TABLE-2

IR SPECTRAL FREQUENCIES (cm^{-1}) OF THE COMPLEXES

Complex	ν(C=N)	ν(N—H)	ν(M—N)	ν(M—O)	ν(M—Cl)	Ring vibrations
$[CoLCl_2]$	1620	3200	395	—	310	1420, 1070, 730
$[CoL(NO_3)_2]$	1595	3220	420	245	—	1410, 1090, 720
$[NiLCl_2]$	1600	3195	400	—	295	1430, 1080, 720
$[NiL(NO_3)_2]$	1610	3210	390	230	—	1415, 1070, 740
$[CuL]Cl_2$	1610	3190	410	—	—	1410, 1090, 730
$[CuL](NO_3)_2$	1590	3220	430	—	—	1420, 1075, 740
$[ZnLCl_2]$	1590	3200	410	—	290	1410, 1085, 720
$[ZnL(NO_3)_2]$	1600	3190	390	240	—	1430, 1090, 730

The above results and the absence of signals for free amine protons, strongly support the proposed macrocyclic framework.

The observed magnetic moments (Table-3) for the cobalt(II) complexes are in a range expected for three unpaired electrons. The electronic spectra (Table-3) of cobalt(II) complexes show two bands in the regions 22,100–21,700 and 16,300–15950 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(p)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition respectively[15], consistent with an octahedral geometry around the cobalt(II) ion. The macrocyclic complexes of nickel(II) show magnetic moments (Table-3) corresponding to spin-free complex, and the electronic spectrum shows three distinct bands, consistent with the octahedral nickel(II) complexes[15, 16]. The band around 11,350–11,200 cm^{-1} and two intense bands around 20,100–20,000 and 27,500–27,300 cm^{-1} may reasonably be assigned to $^3A_{2g}(F) \rightarrow {}^2T_{2g}(F)$, $^3T_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(p)$ transitions respectively.

TABLE-3

MAGNETIC MOMENT VALUES AND ELECTRONIC SPECTRAL DATA OF THE COMPLEXES

Complex	μ_{eff} (B.M.)	Band position (cm^{-1})	Assignments
$[CoLCl_2]$	4.56	16.300	$^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$
		22.100	$4T_{1g}(F) \longrightarrow {}^4T_{1g}(p)$
$[CoL(NO_3)_2]$	4.54	15.950	$^4T_{1g}(F) \longrightarrow {}^4A_{1g}(F)$
		21,700	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(p)$
$[NiLCl_2]$	3.9	11.200	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		20.100	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		27.300	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(p)$
$[NiL(NO_3)_2]$	3.11	11,350	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
		20.100	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
		27.500	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(p)$
$[CuL]Cl_2$	1.74	12.300	$^2B_{1g} \longrightarrow {}^2B_{2g}$
		16.500	$^2B_{1g} \longrightarrow {}^2A_{1g}$
		21.800	$^2B_{1g} \longrightarrow {}^2E_g$
$[CuL](NO_3)_2$	1.77	11.850	$^2B_{1g} \longrightarrow {}^2B_{2g}$
		16.200	$^2B_{1g} \longrightarrow {}^2A_{1g}$
		21.550	$^2B_{1g} \longrightarrow {}^2E_g$

The electronic spectra of the copper(II) complexes show three bands in the regions 12,300–11,850, 16,500–16,200 and 21,800–21,550 cm^{-1} assignable[15, 16] as the $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, consistent with a square-planar geometry for copper(II) complexes. The magnetic moment values further confirm the above proposed geometry (Table-3).

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