Nickel(II), Copper(II) and Zinc(II) Complexes of 14- and 15-Membered N₂O₂ Macrocycles: Synthesis and Characterization

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A new class of 14- and 15 - membered diazadioxa - macrocyclic complexes, [ML$^{1-3}$X$_2$] [M = Ni(II), Cu(II) or Zn(II); X = Cl⁻ or NO$_3$⁻], has been synthesized via the template condensation reaction of salicylaldehyde with 1,2-diamino ethane, 1,3-diamino propane or o-phenylene diamine and 1,2-dibromoethane in 2:1:1 molar ratio. The stoichiometry and coordination modes of the complexes were characterized by elemental analysis, IR, ^{1}H-NMR, EPR, UV-vis spectral studies as well as the molar conductivity and magnetic susceptibility measurements.

Introduction

The chemistry of macrocyclic complexes has been known since the beginning of the last century, but this field has seen an enormous expansion only during the last decades. The interest is still growing due to the possible relevance of these compounds as metal-ion selective ligands[1-3] for metal enzymes and metal proteins. The design and synthesis of macrocyclic ligand complexes has been the subject of recent interest[4,5] and was mostly related to transition metal ions. In these complexes, both the metal ion and the size of the ring play an important role[6]. The fact that some macrocyclic ligands can be made only in poor yields, or even not at all, in the absence of metal ions has lead to the concept of "template effect", i.e., that the metal coordinates and properly arranges the ligand precursor fragments in its coordination sphere, thereby assisting the linking process that produces the macrocyclic ligand. One of the earliest examples of a templated reaction involves the reaction of ethylenediamine with acetone in the presence of nickel(II) ion[7].

The aza-crowns have complexation properties that are intermediate between those of all oxygen crowns and all of nitrogen cyclams. Lindoy[8,9] and co-workers have reported the synthesis and characterization of certain mixed nitrogen, oxygen and/or sulfur donor atom macrocycles. Recently, we have reported the synthesis and characterization of octaaza-[10,11], hexaaza-[12,13], pentaaza-[14,15], tetraaza-[16-20], dithiatetraaza-[21], tetrathia-[22], dithiadiaza-[23] and dioxadiaza macrocyclic complexes[24]. Dealing with our program for the development of macrocycles, herein we present the template synthesis and physicochemical studies of mixed macrocyclic complexes containing nitrogen and oxygen as donor atoms in the ring system, derived from the condensation of salicylaldehyde, with aliphatic or aromatic diamines and 1,2-dibromoethane.

Results and Discussion

The template condensation reaction of salicylaldehyde with aliphatic or aromatic diamines and a suitable functional alkylating agent such as 1,2- dibromoethane in 2:1:1 molar ratio resulted in the formation of a new series of 14- and 15-membered macrocyclic complexes as shown in (Scheme 1). Attempts to prepare the macrocyclic metal – free ligands did not prove successful. The complexes are stable in the atmosphere and freely soluble in DMSO and DMF. The color and crystalline habits of the solid complexes indicate that they are of the same family. The molar conductance values indicate that they are non-electrolytes[25]. The analytical data (Table 1) are in consistence with the proposed mononuclear macrocyclic framework.

IR Spectra

The nature of the macrocyclic ligand in the complexes was inferred from their IR spectra, (Table 2). The absence of $\nu(NH_2)$, $\nu(OH)$ and $\nu(C=O)$ bands and the appearance of a new weak absorption band in the 1590-1630 cm^{-1} region, assignable to the $\nu(C=N)$ comparable with that reported[26-28] for coordinated –C=N, provide evidence for the skeleton of the macrocyclic moiety, which was further supported by the negatively shifted band near 1070 cm^{-1} in all complexes corresponding to $\nu(C-O-C)$ stretching vibrations, also indicate coordination through oxygen atoms. This was confirmed by

the appearance of a strong intensity band in the 400–450 cm^{-1} region and the broad band in the 480–530 cm^{-1} in all complexes assignable to ν(M–N) and ν(M–O) stretching vibrations, respectively, consistent with those reported for complexes derived from nitrogen and oxygen ligands[29,30]. The chloro- complexes display bands around 300 cm^{-1}, attributable[31] to the ν(M-Cl) vibrations. The spectra of the nitrato complexes gave additional bands around 1220, 1010 and 880 cm^{-1}, consistent[17] with the nitrate group. Bands around 260 cm^{-1} may be due to the [ν(M-O) of the NO_3^- group], whereas the bands occurring in 1470–1430, 1110–1090 and 780–750 cm^{-1} regions are assigned to benzene ring vibration.

$[MLX_2]$

M = Cu, Ni & Zn; X = Cl$^-$ or NO_3^-

L^1 L^2 L^3

$[MLX_2]$

L^1: m = $(CH_2)_2$; L^2: m = $(CH_2)_3$; L^3: m = C_6H_4
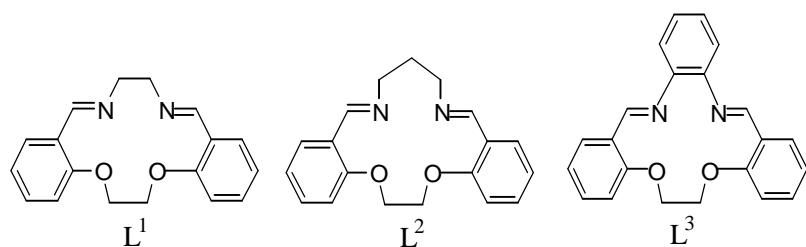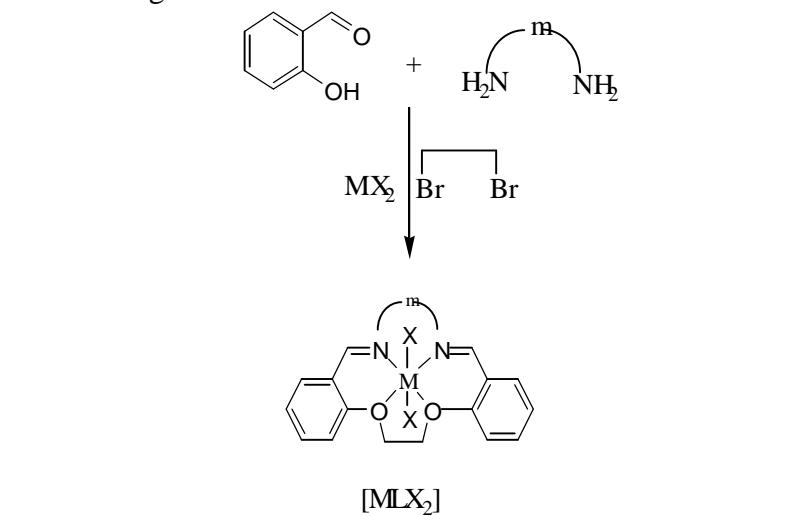
Table 1: Colours, m.p., yields elemental analyses, and molar conductance values of the complexes.

Compound	Color	M.p. (°C)	Yield (%)	Found (Calc.)(%)					WM cm² W⁻¹mol⁻¹
				M	C	H	N	Cl	
[NiL^{1}Cl$_2$]	orange	255	43	13.72 (13.85)	50.74 (50.95)	4.27 (4.29)	6.59 (6.61)	16.61 (16.75	17
[NiL^1(NO$_3$)$_2$]	orange	852	43	18.21 1)3.2(1	0245. (45.29	3.80 (3.81)	11.66 (11.74)	-	14
[NiL^2 CL$_2$]	orange	482	40	.2631 (13.40)	51.88 (52.06)	4.60 (4.61)	6.37 (6.39)	16.07 (16.21)	21
[NiL^2 (NO$_3$)$_2$]	orange	244	42	11.83 (11.96)	46.26 (46.44)	4.10 (4.11)	11.28 (11.40)	-	17
[NiL^3 CL$_2$]	orange	242	26	12.31 (12.44)	55.74 (55.94)	4.03 (4.06)	5.90 (5.93)	14.92 (15.04)	20
[NiL^3(NO$_3$)$_2$]	orange	246	25	13.67 (13..81)	61.91 (62.13)	4.50 (4.57)	13.06 (13.18)	-	17
[CuL^{1}Cl$_2$]	green	246	48	14.67 (14.82)	50.12 (50.38)	4.22 (4.24)	6.50 (6.53)	16.44 (16.56)	20
[CuL^1(NO$_3$)$_2$]	green	248	48	13.11 (13.19)	44.65 (44.84)	3.76 (3.77)	11.54 (11.62)	-	18
[CuL^2 CL$_2$]	green	245	45	14.26 (14.35)	51.28 (51.50)	4.55 (4.56)	6.27 (6.32)	15.88 (16.03)	22
[CuL^2(NO$_3$)$_2$]	green	248	45	12.73 (12.81)	45.83 (45.99)	4.02 (4.07)	11.18 (11.30)	-	21
[CuL^3 CL$_2$]	green	244	28	13.18 (13.33)	55.17 (55.37)	4.00 (4.02)	5.81 (5.87)	14.80 (14.89)	16
[CuL$_3$(NO$_3$)$_2$]	green	246	26	11.91 (11..99)	49.64 (49.83)	3.62 (3.62)	10.50 (10.57)	-	22
[ZnL^{1}Cl$_2$]	off white	182	46	15.07 (15.18)	49.93 (50.16)	4.19 (4.22)	6.44 (6.50)	16.36 (16.49)	12
[ZnL^1(NO$_3$)$_2$]	off white	188	46	13.43 (13.51)	44.48 (44.67)	3.72 (3.76)	11.51 (11.58)	-	11
[ZnL^2 CL$_2$]	off white	167	48	14.63 (14.70)	51.06 (51.28)	4.52 (4.54)	6.24 (6.30)	15.88 (15.97)	16
[ZnL^2(NO$_3$)$_2$]	off white	172	46	13.01 (13.13)	45.60 (45.82)	4.01 (4.06)	11.18 (11.25	-	17
[ZnL^3 CL$_2$]	off white	185	25	13.52 (13.66)	55.00 (55.16)	4.00 (4.00)	5.82 (5.85)	14.72 (14.83)	18
[ZnL^3(NO$_3$)$_2$]	off white	190	26	12.20 (12.29)	49.43 (49.66)	3.60 (3.61)	10.44 (10.53)	-	17

^{1}H NMR Spectra

The ^{1}H NMR spectra of the [ZnL^{2}Cl$_2$] complexe recorded in DMSO–d$_6$, agree well with its proposed macrocyclic framework. It showed a singlet at 8.74 ppm region, assignable[16,30] to the two equivalent imine protons (−CH=N, 2H), and multiplets at *ca*.3.85 ppm, assignable to (−CH$_2$−O; 4H) protons adjacent to oxygen[24], whereas the multiplet at 7.32 ppm region, corresponds[11,16] to phenyl

ring protons. The multiplet at 3.18 ppm, corresponds[16,17] to ethylene (N-CH2-;(4H) protons. In addition to the above, the complexe showed a multiplet at 2.50 ppm, assignable[32] to the middle methylene protons of the propane chain. All the above results, along with the absence of any signal corresponding to free amine or alcoholic protons, strongly suggest that the proposed macrocyclic frameworks have been formed.

Table 2: IR frequencies (cm^{-1}) of the complexes.

Compound	n(C=N)	n (C- O- C)	n (M- O)	n (M- N)	n (M- Cl)	ring	vibration	
[NiL^{1}Cl$_2$]	1595	1065	500	425	315	1440	1100	760
[NiL^1(NO$_3$)$_2$]	1605	1080	520	415		1460	1095	775
[NiL^{2}Cl$_2$]	1600	1060	505	440	295	1465	1110	750
[NiL^2(NO$_3$)$_2$]	1620	1070	505	430		1470	1090	780
[NiL^{3}Cl$_2$]	1595	1065	495	450	320	1455	1100	760
[NiL^3(NO$_3$)$_2$]	1630	1075	500	435		1460	1095	770
[CuL^{1}Cl$_2$]	1600	1060	515	440	300	1440	1105	765
[CuL^1(NO$_3$)$_2$]	1605	1080	520	425		1455	1100	780
[CuL^{2}Cl$_2$]	1615	1065	505	450	305	1465	1095	765
[CuL^2(NO$_3$)$_2$]	1630	1070	510	430		1460	1090	775
[CuL^{3}Cl$_2$]	1595	1060	490	415	320	1450	1100	755
[CuL^3(NO$_3$)$_2$]	1605	1075	515	440		1470	1090	775
[ZnL^{1}Cl$_2$]	1610	1080	530	420	315	1440	1100	770
[ZnL^1(NO$_3$)$_2$]	1620	1070	525	445	-	1460	1090	755
[ZnL^{2}Cl$_2$]	1615	1080	530	435	295	1465	1100	750
[ZnL^2(NO$_3$)$_2$]	1605	1065	495	450	-	1470	1090	780
[ZnL^{3}Cl$_2$]	1595	1060	480	440	310	1455	1110	760
[ZnL^3(NO$_3$)$_2$]	1600	1075	520	445	-	1460	1095	770

EPR Spectra

The EPR spectra of [CuL^{2}X$_2$] recorded at 25°C, each gave only a single signal - with no hyperfine splitting - for which g_{II} and $g_{\perp}$ values appeared at ca. 2.25 and 2.14 respectively, characteristic[33] of axially distorted octahedral copper (II) complexes in which the unpaired electron is present in the dx^2–y^2 orbital. In an axial symmetry, the g values are related by the expression $G = \dfrac{(g_{II} - 2)}{(g_{\perp} - 2)}$. If G>4, exchange interaction between copper centers in the solid is negligible, whereas, if G<4, indicates considerable exchange interaction in the complexes. The G values are calculated using the relation $g_{av} = \dfrac{1}{3}(g_{II} + g_{\perp})$, gave the values in the range 2.23 ± 0.07,

which are in agreement with an orbitally non-degenerate ground state[34].

Table 3: Magnetic moments and UV spectral data of the complexes**.**

Compound	m_{eff} (BM)	Band Position (cm^{-1})	Assignments		
[NiL^{1}Cl$_2$]	3.15	20500	$^3A_2g(F)$	⟶	$^3T_1g(F)$
		11200	$^3A_2g(F)$	⟶	$^3T_2g(F)$
[NiL^1(NO$_3$)$_2$]	3.12	19800	$^3A_2g(F)$	⟶	$^3T_1g(F)$
		11100	$^3A_2g(F)$	⟶	$^3T_2g(F)$
[NiL^{2}Cl$_2$]	3.12	20300	$^3A_2g(F)$	⟶	$^3T_1g(F)$
		11300	$^3A_2g(F)$	⟶	$^3T_2g(F)$
[NiL^2(NO$_3$)$_2$]	3.14	20400	$^3A_2g(F)$	⟶	$^3T_1g(F)$
		11250	$^3A_2g(F)$	⟶	$^3T_2g(F)$
[NiL^{3}Cl$_2$]	3.10	20200	$^3A_2g(F)$	⟶	$^3T_1g(F)$
		11300	$^3A_2g(F)$	⟶	$^3T_2g(F)$
[NiL^3(NO$_3$)$_2$]	3.12	20100	$^3A_2g(F)$	⟶	$^3T_1g(F)$
		11150	$^3A_2g(F)$	⟶	$^3T_2g(F)$
[CuL^{1}Cl$_2$]	1.73	20100	^2B_1g	⟶	^2Eg
		16300	^2B_1g	⟶	^2B_2g
[CuL^1(NO$_3$)$_2$]	1.70	20300	^2B_1g	⟶	^2Eg
		16400	^2B_1g	⟶	^2B_2g
[CuL^{2}Cl$_2$]	1.72	20200	^2B_1g	⟶	^2Eg
		16200	^2B_1g	⟶	^2B_2g
[CuL^2(NO$_3$)$_2$]	1.74	20350	^2B_1g	⟶	^2Eg
		16350	^2B_1g	⟶	$^2 B_2g$
[CuL^{3}Cl$_2$]	1.72	20350	^2B_1g	⟶	^2Eg
		16300	^2B_1g	⟶	^2B_2g
[CuL^3(NO$_3$)$_2$]	1.72	20200	^2B_1g	⟶	^2Eg
		16250	^2B_1g	⟶	^2B_2g

UV- Vis Spectra

The overall geometries of the macrocyclic complexes under study have been deduced on the basis of the observed magnetic moment values and the band positions in the electronic spectra (Table 3). The observed magnetic moments for the nickel (II) complexes (Table 3) are typical for high–spin species establishing the triplet ground state. Their electronic spectra show two main bands in the 11100, 11300 and 19800, 20600 cm^{-1} assignable to $^3A_2g \rightarrow {}^3T_1g(F)$ and $^3A_2g \rightarrow {}^4T_1g(P)$ transitions, respectively, suggesting an octahedral geometry around the nickel (II) ions[35].

The magnetic moment values observed for the copper (II) complexes agree well with the proposed geometry. Their electronic

spectra show a broad band in the 16200, 16400 and 20100, 20500 cm^{-1} regions, may be ascribed to $^2B_1g \rightarrow ^2Eg$ and $^2B_1g \rightarrow ^2B_2g$ transitions, respectively, corresponding[35] to a distored octahedral geometry around the copper (II) ions.

All the above complexes exhibit a high intensity band around 36500 cm^{-1} may be related to the intra ligand charge transfer.

Experimental
The commercially available pure samples, $NiX_2.6H_2O$, ; BDH). The NO_3^- or Cl^- $CuX_2.2H_2O$, $ZnCl_2$ and $Zn(NO_3)_2$ $6H_2O$, (X = chemicals: 1,2-diaminoethane, 1,3-diaminopropane, *o*-phenylene diamine, 1,2-dibromoethane, (Merck) and salicylaldehyde (Riedel-de Haen) were used as supplied. The solvent-ethanol-was dried before used.

Synthesis of dichloro/nitrato-(1,2;9,10-dibenzo-4,7-diaza-11,14-dioxacyclotetradeca 3,7-diene)M(II); [ML¹X₂]; [M = Ni, Cu or Zn; X = Cl⁻ or NO₃⁻]:
A mixture of salicylaldehyde (0.5g, 4mmol) and <u>1,2-diaminoethane</u> (0.12g, 2mmol) dissolved in 20 ml ethanol was stirred with gentle heating for about 45 min. An ethanolic solution (20 ml) of nickel chloride hexahydrate (0.5g, 2 mmol) was then added followed by the dropwise addition of 1,2–dibromoethane (0.36g, 2 mmol) in 5 ml ethanol. The resulted mixture was refluxed for 7-10 h, resulting in the formation of a solid mass which was washed several times with ethanol and then stored in vacuo.

Synthesis of dichloro/nitrato-(1,2;10,11-dibenzo-4,8-diaza-12,15-dioxacyclopentadeca-3,7-diene)M(II); [ML²X₂]; [ML¹X₂]; [M = Ni, Cu or Zn; X= Cl⁻ or NO₃⁻]:
The procedure adupted here was exactly similar to that described above except that here 1,3-diaminopropane is used instead of 1,2-diaminoethane.

Synthesis of dichloro/nitrato-(1,2;9,10-dibenzo-4,7-diaza-11,14-dioxacyclotetradeca-3,7-diene)M(II); [ML³X₂]; [M = Ni, Cu or Zn; X = Cl⁻ or NO₃⁻]:

The procedure adupted here was exactly similar to that described above except that here o-phenylene diamine is used instead of 1,2-diaminoethane.

Elemental analyses were obtained from the Micro-Analytical Laboratory of Al Azhar University, Gaza. Metals were determined by Atomic absorption spectrometer. Chlorides were determined gravimetrically[36]. IR spectra (4000–200 cm^{-1}) were recorded as KBr discs on Shimadzo FTIR–8201 PC spectrophotometer. NMR spectra were recorded in DMSO-d_6 using a JEOL–JNM–LA300NMR spectrometer with tetramethyl silane as an internal standard. Electronic spectra of the compounds in DMSO were recorded on UV–1601 UV–Vis spectrophotometer at room temperature. Magnetic susceptibility measurements were made using a farady balance at room temperature. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained using AC13CM–30V conductivity meter at 25°C.

Acknowledgements

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