Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1231-1238

Synthesis and Spectral Studies of 15 and 16-Membered Diamidediimine Tetraazamacrocyclic Metal Complexes

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The template condensation reaction of *o*-aminobenzoic acid with 2,4-pentanedione in the presence of primary aliphatic diamines gave a new type of 15 and 16-membered diamide tetraazamacrocyclic complexes. The mode of bonding and overall geometry of these complexes has been inferred through UV-vis, IR, ^{1}H NMR spectral techniques as well as molar conductance and magnetic moment data. An octahedral geometry is suggested for all complexes except those of copper which were found to be square planar.

Key Words: Synthesis, Spectral studies, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Macrocyclic complexes.

INTRODUCTION

Much of the current interest in macrocyclic chemistry arises from the hope that unusual geometrical relationship imposed on the metal ions by the macrocyclic donor set. Among polyaza macrocyclic complexes, the tetraazacyclalkanes have growing interest to coordination chemistry, followed by the work on the metal controlled template synthesis of macrocyclic species[1-3]. Many diamide macrocycles have been reported in the literature[4-6] by convenient synthetic techniques and most of them were isolated as metal-free macrocyclic lignads. The amide macrocyclic ligands are of particular interest in view of the applications of their metal complexes in catalyzing[7,8] organic oxidation reactions similar to the porphyrin analogues. An amide group offers two potential binding atoms, *i.e.* amide oxygen and amide nitrogen. However, in most of amide macrocyclic complexes, amide nitrogen is engaged in coordination and not the oxygen[9-18]. Generally, the macrocyclic polyamides are prepared[19] by the reaction of polyamine with either the dicarboxylic acid dichloride or the diester salt of a dicarbocyclic acid. A wide variety of macrocyclic complexes[14-18] bearing amide groups is reported earlier. In view of this, a new series of diamide diimine macrocyclic metal complexes by template condensation of *o*-aminobenzoic acid with 2,4-pentanedione and the aliphatic diamines is reported.

EXPERIMENTAL

2,4-Pentanedione (Ubichem), 1,2-diaminoethane and 1,3-diaminopropane (both E. Merck), *o*-aminobenzoic acid (S.D. Fine chemical) and the metal salts $FeX_2·4H_2O$; $CoX_2·6H_2O$; $NiX_2·6H_2O$; $CuX_2·2H_2O$ and $ZnX_2·6H_2O$ (X = Cl or NO_3) (all BDH) were commercially available pure samples. All the solvents were dried before used.

Synthesis of dichloro/nitro-(2,3;10,11-dibenzo-4,9-dioxo-13,15-dimeth-yl-1,5,8,12-tetraazacyclopentadeca-1,12-diene)metal(II) [ML_1X_2] (M = Fe, Co, Ni and Zn; X = Cl or NO_3) and (2,3;10,11-dibenzo-4,9-dioxo-13,15-dimethyl,1,5,8,12-tetraazacyclopentadeca-1,12-diene)copper(II) dichloride/nitrate:

A mixture of *o*-aminobenzoic acid (0.02 mol) and 1,2-diaminoethane (0.01 mol) in 25 cm^3 methanol was heated with constant stirring for 45-60 min a methanolic solution (25 cm^3) of the metal salt (0.01 mol) was then added followed by the addition of 2,4-pentanedione (0.01 mol) in methanol. The resultant mixture was refluxed for 12-15 h. The solid mass thus formed was washed several times with methanol and stored *in vaccuo*.

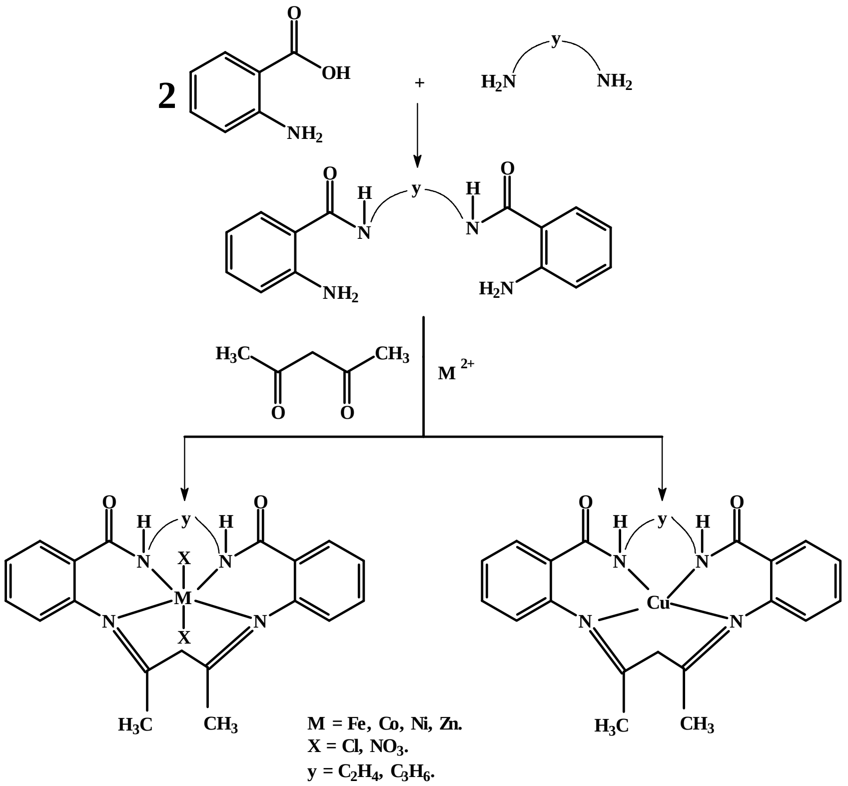
Synthesis of dichloro/nitro-(2,3:11,12-dibenzo-4,10-dioxo-14,16-dimethyl-1,5,9,13-tetraazacyclopentadeca-1,13-dien)metal(II) [ML_2X_2] (M = Fe, Co, Ni and Zn; X = Cl or NO_3) and (2,3;11,12-dibenzo-4,10-dioxo-14,16,dimethyl-1,5,9,13-tetraazacyclopentadeca-1,13-diene)copper(II) dichloride/nitrate:

The procedure adopted for these syntheses was exactly the same as described above except that, 1,3-diaminopropare was used here instead of 1,2-diaminoethane.

Elemental analysis was obtained for the microanalytical laboratory of Al-Azhar University, Gaza. Metals were determined by atomic absorption spectrophotometer. IR spectra 4000-400 cm^{-1} were recorded as KBr discs on Shimadzu FTIR-8201 PC spectrophotometer. ^1H NMR spectra were recorded in d_6-DMSO using a Jeol JNM-LA 300-NMR spectometer with tetramethyl silane as an internal standard. The electronic spectra in DMSO were recorded on UV-1601 UV-vis spectrophotometer at room temperature. Magnetic susceptibility measurements were carried out using Faraday balance at room temperature. The electrical conductivity values of 10^{-3} M solutions in DMSO were obtained on AC13CM-30V conductivity meter at 25ºC and chlorides were determined gravimetically[20].

RESULTS AND DISCUSSION

The template condensation reaction of *o*-aminobenzoic acid with aliphatic primary diamines in the presence of 2,4-pentanedione yielded a new series of diamide tetrazamacrocyclic complexes as shown in **Scheme-1**. However, the ligand corresponding to *o*-phenylenediamine could not be formed. Most of the complexes were obtained in moderate yields (Table-1). All the complexes are stable in the atmosphere and are polycrystalline, slightly soluble in DMF and freely soluble in DMSO. The synthesis was remarkably facile and proceded smothly. All the complexes prepared here have 1:1 metal-to-liquid stoichiometry and all the complexes are non-electrolytes except copper which show 1:2 electrolytic nature in DMSO[21]. The elemental analysis agreed well with the proposed structures (Table-1).



Scheme-1

The derivation of the infrared spectra gave a strong inference for the strucutre of the compounds which showed bands mainly in the regions 1730-1680, 1530-1500, 1270-1240 and 680-650 cm^{-1}, assignable[13,22] to amide I [ν(C=O)], amide II [ν(C-O) + δ(N-H)], amide III [δ(N-H)] and amide IV [Φ(C=O)] vibrations, respectively. A single sharp absorption band for all the complexes was observed in the region 3270-3240 cm^{-1} possibly arising from the secondary amine ν(NH), although, its position is found to be lower by 30-60 cm^{-1} than the analogous metal free ligands[23-25] (Table-2). This suggests that the amide nitrogens take part in coordination to the metal

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

Compound	Colour	m.p. (°C)	Yield (%)	Found (Calcd.) %					ΔM (cm^2 Ω^{-1}mol^{-1})
				M	C	H	N	Cl	
[FeL_1Cl_2]	Bright red	168	50	11.4 (11.5)	51.3 (51.5)	4.5 (4.5)	11.4 (11.5)	14.4 (14.5)	20
[$FeL_1(NO_3)_2$]	Bright red	174	52	10.1 (10.3)	46.4 (46.6)	4.0 (4.1)	15.4 (15.5)	-	17
[FeL_2Cl_2]	Bright red	162	58	11.0 (11.1)	52.3 (52.5)	4.8 (4.8)	11.0 (11.1)	14.0 (14.1)	22
[$FeL_2(NO_3)_2$]	Bright red	170	55	10.0 (10.1)	47.3 (47.5)	4.3 (4.3)	15.0 (15.1)	-	11
[CoL_1Cl_2]	Pink	155	54	11.8 (12.0)	51.0 (51.2)	4.5 (4.5)	11.3 (11.4)	14.3 (14.4)	20
[$CoL_1(NO_3)_2$]	Pink	152	55	10.7 (10.8)	46.0 (46.2)	4.0 (4.0)	15.3 (15.4)	-	18
[CoL_2Cl_2]	Pink	160	52	11.6 (11.7)	52.0 (52.2)	4.7 (4.8)	11.0 (11.0)	13.9 (14.0)	20
[$CoL_2(NO_3)_2$]	Pink	156	56	10.5 (10.6)	47.0 (47.2)	4.3 (4.3)	14.9 (15.0)	-	16
[NiL_1Cl_2]	Light Yellow	180	62	11.8 (12.0)	51.0 (51.2)	4.5 (4.5)	11.3 (11.4)	14.3 (14.4)	13
[$NiL_1(NO_3)_2$]	Light Yellow	185	58	10.7 (10.8)	46.0 (46.2)	4.0 (4.1)	15.3 (15.4)	-	18
[NiL_2Cl_2]	Light Yellow	178	65	11.6 (11.7)	52.0 (52.2)	4.7 (4.8)	11.0 (11.0)	13.9 (14.0)	14
[$NiL_2(NO_3)_2$]	Light Yellow	182	60	10.5 (10.6)	47.0 (47.2)	4.3 (4.3)	15.0 (15.0)	-	16
[CuL_1Cl_2]	Blue	196	64	12.6 (12.8)	50.6 (50.8)	4.4 (4.4)	11.2 (11.3)	14.2 (14.3)	98
[$CuL_1(NO_3)_2$]	Blue	188	65	11.5 (11.6)	45.7 (45.9)	4.0 (4.0)	15.2 (15.3)	-	106
[CuL_2Cl_2]	Blue	204	60	12.2 (12.4)	51.5 (51.7)	4.7 (4.7)	10.9 (10.9)	13.8 (13.9)	94
[$CuL_2(NO_3)_2$]	Blue	192	65	11.2 (11.3)	46.7 (46.9)	4.3 (4.3)	14.8 (14.9)	-	102
[ZnL_1Cl_2]	Off White	164	48	13.0 (13.1)	50.6 (50.8)	4.4 (4.4)	11.2 (11.2)	14.1 (14.2)	16
[$ZnL_1(NO_3)_2$]	Off White	160	52	11.7 (11.8)	45.5 (45.7)	4.0 (4.0)	15.1 (15.2)	-	20
[ZnL_2Cl_2]	Off White	168	50	12.6 (12.7)	51.3 (51.5)	4.7 (4.7)	10.9 (10.9)	13.8 (13.9)	16
[$ZnL_2(NO_3)_2$]	Off White	162	55	11.5 (11.6)	46.5 (46.7)	4.3 (4.3)	14.7 (14.8)	-	22

ions. This was further confirmed by the appearance of bands in the 450-410 cm^{-1} region in all the complexes corresponding to ν(M-N) vibrations[9,25]. An important strong intensity band observed in all the complexes in the 1640-1590 cm^{-1} region, assignable[26] to the imine function ν(C=N) of the macrocyclic system. Its position is however, negatively shifted when compared with that reported for the uncoordinated imine function in polyazamacrocyclic moities, indicating the coordination *via* the nitrogen atoms of the ligand[27]. The absorption bands in the 2930-2880 and 1450-1410 cm^{-1} regions observed in all the complexes may reasonably corresponding to CH stretching and CH bending vibrations, respectively. Bands appearing in the region 1470-1430, 1100-1075 and 750-720 cm^{-1} are the usual modes of disubstituted benzene. However, the amide I band was found to be unaffected on coordination when compared to those reported[23] for metal-free amide ligands and thus ruling out the coordination through amide oxygen which was further supported by the absence of any band attributable to ν(M-O) vibration. All the above data along with the absence of the uncondensed functional groups (NH_2,OH), stretching modes of starting materials suggest that the proposed macrocyclic framework has been formed.

TABLE-2
IR SPECTRAL DATA (cm^{-1}) OF THE METAL COMPLEXES

Compound				Amide bands						
	ν(N-H)	ν(C-H)	ν(C=N)	I	II	III	IV	δ(C-H)	ν(C-N)	ν(M-N)
$[FeL_1Cl_2]$	3265	2930	1600	1710	1525	1260	670	1430	1190	420
$[FeL_1(NO_3)_2]$	3240	2910	1590	1680	1500	1245	680	1450	1175	450
$[FeL_2Cl_2]$	3270	2880	1640	1730	1530	1270	650	1415	1200	420
$[FeL_2(NO_3)_2]$	3250	2890	1610	1690	1510	1240	665	1425	1160	430
$[CoL_1Cl_2]$	3260	2920	1600	1720	1520	1250	660	1410	1180	450
$[CoL_1(NO_3)_2]$	3260	2900	1630	1710	1530	1240	655	1420	1170	410
$[CoL_2Cl_2]$	3270	2910	1615	1730	1520	1270	670	1440	1180	420
$[CoL_2(NO_3)_2]$	3255	2890	1620	1715	1515	1260	650	1420	1190	430
$[NiL_1Cl_2]$	3260	2885	1629	1700	1520	1250	670	1430	1180	440
$[NiL_1(NO_3)_2]$	3270	2920	1640	1725	1530	1260	650	1430	1185	440
$[NiL_2Cl_2]$	3260	2910	1600	1710	1530	1250	670	1410	1200	450
$[NiL_2(NO_3)_2]$	3250	2920	1610	1730	1515	1270	660	1440	1200	430
$[CuL_1Cl_2]$	3260	2930	1620	1710	1510	1240	670	1420	1180	430
$[CuL_1(NO_3)_2]$	3260	2920	1640	1715	1530	1250	650	1450	1170	440
$[CuL_2Cl_2]$	3250	2900	1600	1730	1520	1270	670	1430	1190	415
$[CuL_2(NO_3)_2]$	3270	2890	1590	1720	1520	1260	660	1440	1185	450
$[ZnL_1Cl_2]$	3250	2910	1600	1690	1530	1250	670	1410	1170	450
$[ZnL_1(NO_3)_2]$	3260	2930	1630	1715	1520	1270	650	1420	1190	420
$[ZnL_2Cl_2]$	3270	2900	1620	1700	1535	1240	670	1450	1180	450
$[ZnL_2(NO_3)_2]$	3260	2920	1630	1720	1540	1260	680	1430	1170	430

^1H NMR spectra of all the zinc complexes show a broad signal at δ 8.12-8.34, which may be assigned[18,22] to amide CO-NH(2H) protons. all the complexes show a multiplet in the region δ 3.45-3.60, corresponding[18] to CO-N-CH_2(4H) protons. A sharp signal at δ 2.48-2.55 may be assigned[26] to CH_3-C=N(6H) protons. A singlet observed in the δ 2.26-2.34 region may reasonably be assigned to methylene (C-CH$_2$-C)2H) protons[26] of the 2,4-pentanedione. The multiplets at δ 7.45-7.68 corresponds to phenyl ring vibrations[9,26]. The complexes of the type [ZnL$_2$X$_2$] show a multiplet at δ 2.12-2.18 corresponds to the middle (-CH$_2$-;2H) protons of the propane chain[18,22]. All the above, along with the absence of bands assigned either for primary amine or alcoholic protons suggests the formation of the macrocyclic framwork.

TABLE-3

LIGAND FIELD BANDS (cm^{-1}) AND MAGNETIC MOMENTS OBSERVED IN THE ELECTRONIC SPECTRA FOR THE COMPLEXES

Compound	μ_{eff} (B.M.)	Band position	Assignment
[FeL$_1$Cl$_2$]	5.42	11,500	$^5T_{2g} \rightarrow {}^5E_g$
[FeL$_1$(NO$_3$)$_2$]	5.39	11,300	$^5T_{2g} \rightarrow {}^5E_g$
[FeL$_2$Cl$_2$]	5.40	11,700	$^5T_{2g} \rightarrow {}^5E_g$
[FeL$_2$(NO$_3$)$_2$]	5.43	11,450	$^5T_{2g} \rightarrow {}^5E_g$
[CoL$_1$Cl$_2$]	4.08	16,300	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		21,400	$^4T_{1g}(F) \rightarrow {}^4A_{1g}(P)$
[CoL$_1$(NO$_3$)$_2$]	4.14	16,450	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		21,550	$^4T_{1g}(F) \rightarrow {}^4A_{1g}(P)$
[CoL$_2$Cl$_2$]	4.26	16,200	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		21,650	$^4T_{1g}(F) \rightarrow {}^4A_{1g}(P)$
[CoL$_2$(NO$_3$)$_2$]	4.20	16,400	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		21,600	$^4T_{1g}(F) \rightarrow {}^4A_{1g}(P)$
[NiL$_1$Cl$_2$]	3.15	11,400	$^3A_{2g}(F) \rightarrow {}^3T_g(F)$
		17,500	$^3A_{2g}(F) \rightarrow {}^3T_g(P)$
[NiL$_1$(NO$_3$)$_2$]	3.12	11,350	$^3A_{2g}(F) \rightarrow {}^3T_g(F)$
		17,300	$^3A_{2g}(F) \rightarrow {}^3T_g(P)$
[NiL$_2$Cl$_2$]	3.14	11,500	$^3A_{2g}(F) \rightarrow {}^3T_g(F)$
		17,450	$^3A_{2g}(F) \rightarrow {}^3T_g(P)$
[NiL$_2$(NO$_3$)$_2$]	3.09	11,300	$^3A_{2g}(F) \rightarrow {}^3T_g(F)$
		17,400	$^3A_{2g}(F) \rightarrow {}^3T_g(P)$
[CuL$_1$Cl$_2$]	1.74	11,750	$^2B_{1g}(F) \rightarrow {}^2B_{2g}$
		16,150	$^2B_{1g}(F) \rightarrow {}^2A_{1g}$
		22,000	$^2B_{1g}(F) \rightarrow {}^2E_g$
[CuL$_1$(NO$_3$)$_2$]	1.73	12,000	$^2B_{1g}(F) \rightarrow {}^2B_{2g}$
		15,950	$^2B_{1g}(F) \rightarrow {}^2A_{1g}$
		21,800	$^2B_{1g}(F) \rightarrow {}^2E_g$
[CuL$_2$Cl$_2$]	1.75	11,500	$^2B_{1g}(F) \rightarrow {}^2B_{2g}$
		16,000	$^2B_{1g}(F) \rightarrow {}^2A_{1g}$
		21,900	$^2B_{1g}(F) \rightarrow {}^2E_g$
[CuL$_2$(NO$_3$)$_2$]	1.73	11,850	$^2B_{1g}(F) \rightarrow {}^2B_{2g}$
		16,100	$^2B_{1g}(F) \rightarrow {}^2A_{1g}$
		21,850	$^2B_{1g}(F) \rightarrow {}^2E_g$

The electronic spectra (Table-3) of the iron(II) complexes exhibit a weak intensity band in the 11700-11300 cm^{-1} regions assignable to $^5T_{2g} \rightarrow {}^5E_g$ transition consistent with an octahedral environment around the iron(II) ion[28]. The magnetic susceptibility measurements confirm the above geometry. However, the electronic spectra of the cobalt(II) complexes gave two ligand field bands in the region 16450-16200 and 21650-21400 cm^{-1} which may be assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, corresponding to the octahedral gemetry around the cobalt(II) ion[28], which was furthure supported by their magnetic moment values[18] (Table-3). The macrocyclic complexes of the nickel(II) exhibit two bands in the regions 11500-11300 and 17500-17300 cm^{-1} in their electronic spectra which may be assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3A_{1g}(P)$, transitions, respectively suggesting an octahedral geametry around nickel(II) ion. Their magnetic moment values (Table-3) furthure support the above geometry, whereas, the copper(II) complexes gave three bands in their electronic spectra at 12000-11500, 16150-15950 and 22000-21800 cm^{-1} regions, attributable to the $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively which are consistant with the square planner geometry of the copper(II) ions[28]. The observed magnetic moment values (Table-3) are in close agreement with their electronic spectral data.

ACKNOWLEDGEMENTS

The Department of Chemistry, Al-Azher University of Gaza is highly acknowledged for providing necessary facilities.

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(*Received*: 15 December 2005; *Accepted*: 8 September 2006) AJC-5081