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Non-template synthesis and Characterization of 17-Membered Schiff Base Macrocycle Containing Oxygen and Nitrogen Heteroatoms and Its Metal Complexes

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A new ligand 1,7-bis(2′-formylphenyl)-4-benzyl-1,7-dioxa-4-azaheptane (L′) has been synthesized by the direct reaction of $PhCH_2N(CH_2CH_2Cl)_2$ with salicylaldehyde. The condensation of L′ with ethylenediamine in methanol gave a new type of oxa-aza Schiff base macrocycle 3,4:12,13-dibenzo-8-benzyl-1,8,15-triaza-5,11- dioxacycloheptadeca-1,14-diene (L), and its complexes with Cu^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} and UO_2^{2+} are synthesized and characterized by elemental analysis UV-Vis, IR, ^1H NMR and MS spectral techniques as well as molar conductance. An octahedral geometry around the metal ion is inferred for (ML]Xn ($M = Cu^{2+}$, Ni^{2+}, Fe^{3+} and Co^{2+}; $X = ClO_4^-$, Cl^- or NO_3^-; n = 2 or 3). The molar conductivity for all complexes suggests them to be 1 : 2 electrolytic nature. In the complexes, the metal ions are coordinated by N and O atoms of the ligand.

Key words: Non-template synthesis, 17-Membered Schiff base, Metal complexes.

INTRODUCTION

Oxa-aza Schiff base macrocycles are of great interest in the field of coordination chemistry and have been studied intensively in recent years, because they possess cavities capable of providing a favorable environment for transition metal ions[1–4]. These macrocycles have both the structure moieties of crown ether and polyaza Schiff base macrocycles. The strength of the ion binding is determined by ion size, macrocyclic cavity size and conformation of the donor atoms. Their specific complexation behavior is clearly of interest in many areas such as the design of potential transition ion selective reagents and the treatment of metal poisoning intoxications[5–14].

We are especially interested in getting a better understanding of the coordination properties of these macrocyclic ligands. By the direct reaction of salicyl-

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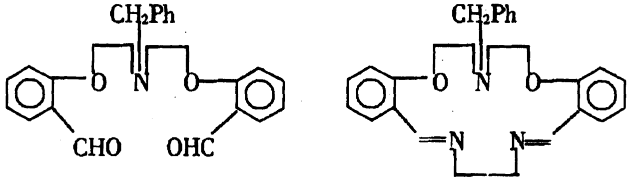


L′ L

Fig 1. Structure formulae of L′ and L.

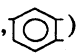
adehyde with $PhCH_2N(CH_2CH_2Cl)_2$, a novel dialdehyde 1,7-bis(2′-formylphenyl)-4-benzyl-1,7-dioxa-4-azaheptane (L′, Fig. 1) has been synthesized. Then the condensation of L′ with ethylendiamine gave a new type of Schiff base macrocycle containing oxygen and nitrogen heteroatoms 3,4:12,13-dibenzo-8-benzyl-1,8,15-triaza-5,11-dioxacycloheptadeca-1,14-diene (L, Fig. 1). The complexes of L with transition and rare-earth metal ions have been synthesized.

EXPERIMENTAL

All chemicals used were of analytical grade. The solvents were purified by conventional methods. $PhCH_2N(CH_2CH_2Cl)_2$ was prepared by the literature procedure[15] and characterized by infrared spectra and elemental analysis.

Elemental analyses were determined by Perkin-Elmer 240 C elemental analyser. IR spectra were recorded as KBr discs on a Nicole Model FT 170 SX spectrometer. ^{1}HNMR spectra were recorded in $CDCl_3$ using a FX-90 Q spectrometer with TMS as an internal standard. Mass spectra were measured on a VG ZAB-HS chromatography-mass instrumentation. Electronic spectra of the compounds in DMF were recorded on Shimadzu 240 spectrometer at room temperature. The electrical conductivities of 10^{-3} M solutions in DMF were obtained on a DDS-11A conductometer at 25°C.

Syntheses of the ligands

1,7-Bis-(2′-formylphenyl)-4-benzyl-1,7-dioxa-4-azaheptane (L′) 56.6 g salicyl aldehyde in 500 mL butanol, 20 g NaOH was added. The mixture was refluxed for 0.5 h, then 50 g $PhCH_2N(CH_2CH_2Cl)_2$ in 100 mL butanol was added slowly and refluxed under a nitrogen atmosphere for 48 h, cooled slowly, and then the precipitate (NaCl) was filtered off. The solution standing in the refrigerator over night, then the L′ precipitated. Product was filtered, washed two times with butanol and dried in vacuum at room temperature. The colourless crystals were obtained by recrystallization with alcohol. Yield 47.8 g (55%). Anal. Found: C, 74.38; H, 6.45; N, 3.40. Calc. for $C_{25}H_{25}NO_4$ (m.w. 403.46): C, 74.42; H, 6.25; N, 3.47. IR(cm^{-1}): 1680 ν(C═O); 1598, 1485, 1456, 1406 ν(Ar); 1397 ν(C—N)). ^{1}HNMR(ppm): δ 3.20 (6H, NCH_2), 3.82 (2H, $ArCH_2$), 4.20 (4H, OCH_2), 7.31 (5H, —Ar), 6.86–7.76 (8H, ).

3,4:12,13-dibenzo-8-benzyl-1,8,15-triaza-5,11-dioxacycloheptadeca-1,14-diene (L) 25.2 g L′ in 200 mL dry methanol, 4.2 g ethylenediamine in 200 mL dry methanol was slowly added, refluxing for 45 min, cooled and filtered, then the white macrocyclic Schiff base crystals were obtained by recrystallization with butanol. Yield 24.8 g (94.1%). Anal. Found: C, 72.50; H, 6.94; N, 9.62. Calc. for $C_{27}H_{29}N_3O_2 \cdot H_2O$ (m.w. 445.54): C, 72.78; H, 7.01; N, 9.43. IR (cm^{-1}): 3415 ν(H_2O), 1626 ν(C═N), 1599, 1487, 1452 ν(Ar), 1246, 1110 ν(C—O—C), 1159 ν(C—N). ^{1}HNMR (ppm): δ 3.20(4H, NCH_2), 3.90(4H, $=NCH_2$), 3.80(2H, $ArCH_2$), 4.18(4H, OCH_2), 7.31(5H, —Ar), 6.88–7.82(8H, ); 8.64(2H, N═CH—). Ms(m/z): 427(M^+), 329, 251, 149, 91, 65, 44, 40.

Synthesis of the complexes

A solution of compound L (1 mmol) in 15 ml butanol was added to the required metal salt (1 mmol) in 15 mL butanol. The mixture was stirred and heated for 1 h, the corresponding metal complex crystal was obtained upon standing in the refrigerator over night. The precipitate was filtered off, washed with hot butanol and diethyl ether, then dried to constant weight in a vacuum dryer at room temperature. Yield 70–90%.

RESULTS AND DISCUSSION

The new macrocyclic compound L has been synthesized in good yield by the non-template condensation reaction of the parent L′ with ethylenediamine in methanol. In the IR spectra of L, there are no bands at 1680 cm^{-1} due to ν(C═O) of L′) and 3300 cm^{-1} due to ν(N—H of ethylenediamine). A new strong absorption band at 1626 cm^{-1} ν(C = N) is attributable to the characteristic imono-linkage. The IR, ^{1}H NMR and MS spectra indicate that the reaction of L′ with ethylenediamine gives a new macrocyclic Schiff base L.

The results of elemental analysis (Table-1) support the proposed macrocyclic structure. All complexes have crystal water. The contents of the metal ions in the complexes were determined by EDTA titration. Since the complexes are not soluble in water and cannot be titrated directly, they were heated and dissolved in mixture of HNO_3 and H_2O_2, then titrated by EDTA. The contents of chlorine in the complexes were determined by $AgNO_3$ titrations. The molar conductive values for all the complexes in DMF solution are between 150 and 170 S cm^2 mol^{-1}, and suggest them to be 1 : 2 electrolytic nature[16].

The electronic spectra of all copper complexes exhibit absorption in the region 580 and 610(nm) which may be assigned to the $^2Eg \rightarrow {}^2T_2g$ transition, respectively, suggesting an octahedral environment around the copper ions. The electronic spectra of $CoLCl_2 \cdot 2H_2O$ shows two distinct bands at 610 and 670 (nm) which are assigned as $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \rightarrow {}^4A_{2g}$ transitions respectively, suggesting an octahedral environment around the cobalt ion. The electronic spectra of $NiL(NO_3)_2 \cdot 3H_2O$ shows a band in the region 540(nm) which can be assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions, respectively, suggesting an octahedral environment around the nickel ion. Therefore, it may be concluded that the transition metal complexes are distorted octahedral[17, 18].

The IR data of the complexes and their assignments are given in Table-2. The C—N absorption peaks decrease from 1159 cm^{-1} in the free ligand L to 1146–

1130 cm^{-1} in the complexes, and the C—O—C absorption has also shifted. The C═N absorption peak (1626 cm^{-1}) of the L has shifted in metal ion complexes. An important feature is the appearance of a new medium intensity band at 460–450 cm^{-1} attributable to ν(M—N) that provides strong evidence for the involvement of nitrogen (C—N) in coordination[19].

In all the complexes, except $FeLCl_3 \cdot 3H_2O$ and $CoLCl_2 \cdot 2H_2O$, there are both coordinated and crystal H_2O, because of the existence of 3400 and 540 cm^{-1} absorption peaks.

TABLE-1
ELEMENTAL ANALYSIS AND UV-SPECTRAL DATA OF THE COMPLEXES

Complex	Colour	% Analysis: Found (Calcd.)					
		C	H	N	M	Cl	UV(nm)
$CuL(ClO_4)_2 \cdot 2H_2O$	green	44.30 (44.66)	4.80 (4.58)	6.03 (5.79)	7.80 (8.71)	—	580
$NiL(ClO_4)_2 \cdot 3H_2O$	blue	43.53 (43.87)	4.91 (4.77)	6.00 (5.69)	8.00 (7.94)	—	
$FeLCl_3 \cdot 3H_2O$	dark brown	49.98 (50.37)	5.43 (5.48)	6.78 (6.53)	9.23 (8.68)	14.98 (16.53)	
$CoLCl_2 \cdot 2H_2O$	blue	54.23 (54.65)	5.91 (5.60)	7.11 (7.08)	9.43 (9.93)	12.03 (11.95)	610,670
$NiL(NO_3)_2 \cdot 3H_2O$	deep green	48.53 (48.81)	5.30 (5.31)	10.23 (10.57)	8.56 (8.84)	—	540
$CoL(NO_3)_2 \cdot 3H_2O$	pink	48.71 (48.80)	5.67 (5.31)	10.79 (10.54)	8.46 (8.87)	—	
$CuL(NO_3)_2 \cdot 3H_2O$	dark green	48.05 (48.01)	5.31 (5.29)	10.19 (10.50)	9.00 (9.52)	—	610
$LaL(NO_3)_3 \cdot 2.5H_2O$	faint yellow	41.03 (40.66)	4.71 (4.30)	10.39 (10.54)	17.92 (17.42)	—	
$PrL(NO_3)_3 \cdot 3H_2O$	faint yellow	40.03 (40.12)	4.30 (4.36)	10.47 (10.40)	16.50 (17.43)	—	310,260
$NdL(NO_3)_3 \cdot 3H_2O$	faint yellow	40.14 (39.94)	4.57 (4.35)	9.97 (10.35)	19.00 (19.96)	—	
$SmL(NO_3)_3 \cdot 3H_2O$	light yellow	39.23 (39.64)	4.09 (4.31)	10.54 (10.28)	17.56 (18.39)	—	
$GdL(NO_3)_3 \cdot 3H_2O$	light yellow	39.71 (39.31)	4.00 (4.28)	10.53 (10.19)	20.00 (19.06)	—	
$UO_2L(NO_3)_2 \cdot 4H_2O$	light yellow	36.70 (36.24)	4.33 (4.17)	7.59 (7.83)	25.90 (26.60)	—	

TABLE-2
KEY IR FREQUENCIES (cm^{-1}) OF THE METAL-COMPLEXES

Complex	ν(H_2O)	ν(C=N)	ν(C—N)	ν(C—O—C)	ν(ClO_4^-)	ν(NO_3^-)	ν(M—N)
$CuL(ClO_4)_2 \cdot 2H_2O$	3402,531	1645	1130	1210, 1090	1093,923,624		456
$NiL(ClO_4)_2 \cdot 3H_2O$	3422,548	1646	1135	1224,1098	1090,931,624		457
$FeLCl_3 \cdot 3H_2O$	3401	1627	1146	1206,1085			452
$CoLCl_2 \cdot 2H_2O$	3436	1627	1130	1200,1081			451
$NiL(NO_3)_2 \cdot 3H_2O$	3401,540	1646	1135	1221,1095		1385,825	460
$CoL(NO_3)_2 \cdot 3H_2O$	3401,528	1631	1132	1198,1091		1385,811	455
$CuL(NO_3)_2 \cdot 3H_2O$	3401,540	1646	1130	1207,1093		1385,825	458
$LaL(NO_3)_3 \cdot 2.5H_2O$	3524,541	1637	1135	1202,1091		1385,1299,1034,819,720	455
$PrL(NO_3)_3 \cdot 3H_2O$	3401,532	1637	1130	1220,1098		1385,1300,1035,818,719	454
$NdL(NO_3)_3 \cdot 3H_2O$	3401,539	1636	1136	1208,1092		1385,1288,1026,817,721	455
$SmL(NO_3)_3 \cdot 3H_2O$	3436,529	1636	1140	1210,1089		1385,1299,1028,824,721	453
$GdL(NO_3)_3 \cdot 3H_2O$	3401,543	1636	1135	1216,1083		1385,1300,1028,819,719	454
$UO_2L(NO_3)_2 \cdot 4H_2O$	3402,540	1630	1131	1205,1095		1385,821	450

In nitrato complexes, according to bands at 820 and 1380 cm^{-1}, NO_3^- ions are uncoordinated in the complexes of $NiL(NO_3)_2 \cdot 3H_2O$, $CuL(NO_3)_2 \cdot 3H_2O$, $CoL(NO_3)_2 \cdot 3H_2O$ and $UO_2L(NO_3)_2 \cdot 4H_2O$. In the rare-earth metal complexes, NO_3^- ions exist in two forms: coordinated and uncoordinated because of the existence of 1350, 1050, 820 and 720 cm^{-1} absorption peaks[20].

ClO_4^- are present as free ions in $CuL(ClO_4)_2 \cdot 2H_2O$ and $NiL(ClO_4)_2 \cdot 3H_2O$[21].

From the above experimental results and discussion, it can be suggested that: In lanthanide complexes, the Ln^{3+} ions are coordinated by N and O atoms of Ligand L, and NO_3^-. In the transition metal complexes and $UO_2L(NO_3)_2 \cdot 4H_2O$, the metal ions are coordinated by both N and O atoms of ligand L. In $FeLCl_3 \cdot 3H_2O$ and $CoLCl_2 \cdot 2H_2O$, Cl^- are probably coordinated.

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