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NOTE

Zn^{II} complexes of cyclic tetradentate thioethers

Abul Kalam[a], Shekhar Srivastava[a]*, Yogesh Pandey[b], Anil Kumar[b] and Sharat Srivastava[b]

[a]Department of Chemistry, University of Allahabad, Allahabad-211 002, Uttar Pradesh, India

E-mail : shekhsri@rediffmail.com; kalam_abul@rediffmail.com; abul_k33@yahoo.com

[b]Department of Chemistry, Bipin Bihari (P.G.) Science College, Jhansi-284 128, Uttar Pradesh, India

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Abstract : A new series of 14- and 15-membered tetrathia macrocyclic complexes, $[MLX_2]$ [M = Zn^{II}; X = Cl or NO_3; L = L^1 = 1,4,8,11-tetrathiacyclotetradecane; L^2 = 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane; L^3 = 3,6,10,13-tetrathiacyclotetradecane-1-ol; L^4 = 4,5-benzo-3,6,10,13-tetrathiacyclotetradecane-1,8-diol; L^5 = 4,5,11,12-dibenzo-3,6,10,13-tetrathiacylotetradecane-1,8-diol] have been prepared. The complexes have been characterized on the basis of elemental analyses, conductivity, IR and X-ray photoelectron spectra. Octahedral structures have been proposed for all the prepared metal complexes.

Keywords : Metal complexes, X-ray photoelectron spectra.

Introduction

The occurrence of sulphur as a donor atom for transition metals is a well known[1]. It acts as a very good ligating atom when in the form of the sulfide ion (S^{2-}) or as a mercaptide ion (RS^-) but complexes of sulfur as a thioether (RSR) are much less abundant[1,2-5].

Macrocyclic tetrathioethers such as Me_3[16]aneS_4, [16]aneS_4, [14]aneS_4 and [12]aneS_4 have become increasingly important in the recent years since they can in principle provide low-oxidation state metal sulphur sites for model studies of the metal catalyzed processes such as nitrogen fixation.

In the continuation of our earlier work[6,7], this paper deals with synthesis and characterization of zinc(II) metal complexes with some tetradentate ligands having thioether as the exclusive donor i.e. L^1 = 1,4,8,11-tetrathiacyclotetradecane; L^2 = 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane; L^3 = 3,6,10,13-tetrathiacyclotetradecane-1-ol; L^4 = 4, 5-benzo-3,6,10,13-tetrathiacyclotetradecane-1,8-diol; L^5 = 4,5,11,12-dibenzo-3,6,10,13-tetrathiacyclotetradecane-1,8-diol.

Results and discussion

These newly synthesized Zn^{II} complexes were yellowish-white solid and stable at room temperature. The elemental analyses were within ±0.5% from C, H, N, Zn and Cl. The low molar conductance data in DMF (20-30 Ω^{-1} cm^2 mol^{-1}) of these complexes indicates that all these are non-electrolytes[8]. All the prepared ligands show ν_{C-S} band at 1040-1050 cm^{-1}, which shifted towards higher side in all prepared these Zn^{II} metal complexes (1080-1100 cm^{-1})[9,10]. The presence of new bands in metal complexes in the region 420-430 cm^{-1}, attributed due to the ν_{Zn-S} vibration[9,10].

The $Zn2p_{1/2,3/2}$ and $S2p$ binding energies (eV) data of ZnX_2 and $[ZnX_2.L]$ (where X= Cl or NO_3; L = L^1 or L^2 or L^3 or L^4 or L^5) are listed in Table 1. It may be seen that $Zn3p_{1/2}$ photoelectron peaks binding energy values

Table 1. $Zn3p_{1/2}$, $S2p$, $Cl2p$ and $N1s$ binding energies (eV) in ZnX_2 and $[ZnLX_2]$ complexes

Sl. no.	Ligand, salt and complexes	$Zn3p_{1/2}$	$S2p$	$Cl2p$	$N1s$
1.	Ligand L^1	-	166.2	-	-
2.	Ligand L^2	-	166.2	-	-
3.	Ligand L^3	-	166.2	-	-
4.	Ligand L^4	-	166.2	-	-
5.	Ligand L^5	-	166.2	-	-
6.	$ZnCl_2$	88.4	-	202.4	-
7.	$[ZnL^1Cl_2]$	87.2	168.4	203.8	-
8.	$[ZnL^2Cl_2]$	87.2	168.4	203.8	-
9.	$[ZnL^3Cl_2]$	87.2	168.4	203.8	-
10.	$[ZnL^4Cl_2]$	87.2	168.4	203.8	-
11.	$[ZnL^5Cl_2]$	87.2	168.4	203.8	-
12.	$Zn(NO_3)_2$	88.6	-	-	404.6
13.	$[ZnL^1(NO_3)_2]$	87.4	168.6	-	405.8

Table-1 (contd.)

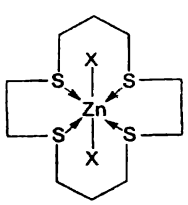
14.	$[ZnL^2(NO_3)_2]$	87.4	168.6	-	405.8
15.	$[ZnL^3(NO_3)_2]$	87.4	168.6	-	405.8
16.	$[ZnL^4(NO_3)_2]$	87.4	168.6	-	405.8
17.	$[ZnL^5(NO_3)_2]$	87.4	168.6	-	405.8

were observed more in metals than in metal complexes. It suggested that Zn ion have more electron density in complexes than metal salts due to involvement of metal ion in coordination[11]. Further, S2*p* photoelectron peak shows a single symmetrical peak with higher binding energies in $[ZnCl_2.L]$ complexes than free ligand S2*p* photoelectron peak, which concluded that sulfur atom of ligand is coordinated to metal ion[11]. While in $[Zn(NO_3)_2.L]$ complexes N1*s* photoelectron peak was also observed, which have shown higher binding energy value than $Zn(NO_3)_2$, suggesting coordination of nitrogen atom in $[Zn(NO_3)_2.L]$ complexes[11].

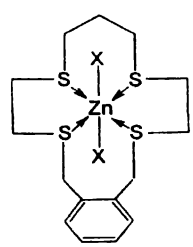
Experimental

All solvents were reagent grade and purified before use. Macrocyclic ligands L^1 = 1,4,8,11-tetrathiacyclotetradecane; L^2 = 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane; L^3 = 3,6,10,13-tetrathiacyclotetradecane-1-ol; L^4 = 4,5-benzo-3,6,10,13-tetrathiacyclotetradecane-1,8-diol; L^5 = 4,5,11,12-dibenzo-3,6,10,13-tetrathiacylotetradecane-1,8-diol; were prepared as given in literature[9,10].

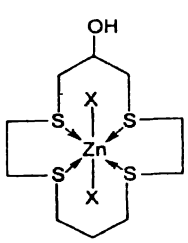
Preparation of $[ZnX_2.L]$ complexes (where X = Cl or NO_3) : To a solution of ZnX_2 (X= Cl or NO_3) (0.1 mmol) in dry C_2H_5OH is mixed (0.1 mmol) prepared ligand L^1 or L^2 or L^3 or L^4 or L^5 in dry C_2H_5OH solution. The mixture was refluxed for 3–4 h, the solid product was obtained, filtered, washed with dry C_2H_5OH and dried over P_4O_{10}. On the basis of these physico-chemical studies of these complexes it can be concluded a tentative structure is as shown in Figs. 1 and 2.



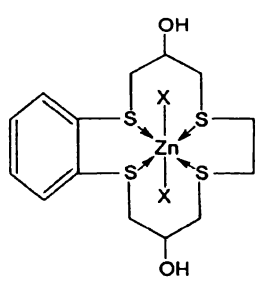
L^1 = 1,4,8,11-Tetrathiacyclotetradecane



L^2 = 13,14-Benzo-1,4,8,11-tetrathiacyclopentadecane

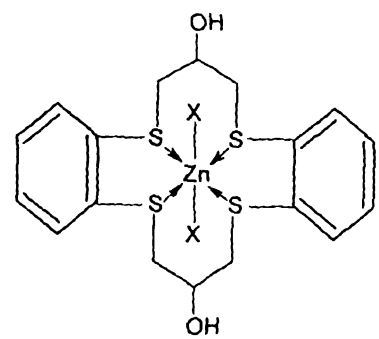


L^3 = [14]aneS$_4$-ol



L^4 = 4,5-Benzo-3,6,10,13-tetrathiacyclotetradecane-1,8-diol

Fig. 1. Structure of $[ZnX_2.L]$ (where X = Cl or NO_3; L = L^1 or L^2 or L^3 or L^4).



L^5 = 4,5,11,12-Dibenzo-3,6,10,13-tetrathiacyclotetradecane-1,8-diol

Fig. 2. Structure of $[ZnX_2.L]$ (where X = Cl or NO_3; L = L^5).

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