

Zn^{II} complexes of cyclic tetradentate thioethers

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Abstract : A new series of 14- and 15-membered tetrathia macrocyclic complexes, [MLX₂] [M = Zn^{II}; X = Cl or NO₃; L = L¹ = 1,4,8,11-tetrathia cyclotetradecane; L² = 13,14-benzo-1,4,8,11-tetrathia cyclotetradecane-1-ol; L³ = 3,6,10,13-tetrathia cyclotetradecane-1-ol; L⁴ = 4,5-benzo-3,6,10,13-tetrathia cyclotetradecane-1,8-diol; L⁵ = 4,5,11,12-dibenzo-3,6,10,13-tetrathia cyclotetradecane-1,8-diol] have been prepared. The complexes have been characterized on the basis of elemental analysis, 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 known¹. It acts as a very good ligating atom when in the form of the sulfide ion (S²⁻) 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 Me₃[16]aneS₄, [16]aneS₄, [14]aneS₄ and [12]aneS₄ 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. L¹ = 1,4,8,11-tetrathia cyclotetradecane; L² = 13,14-benzo-1,4,8,11-tetrathia cyclotetradecane-1-ol; L³ = 3,6,10,13-tetrathia cyclotetradecane-1-ol; L⁴ = 4,5-benzo-3,6,10,13-tetrathia cyclotetradecane-1,8-diol; L⁵ = 4,5,11,12-dibenzo-3,6,10,13-tetrathia cyclotetradecane-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 $\pm 0.5\%$ from C, H, N, Zn and Cl. The low molar conductance data in DMF (20-30 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of these complexes indicates that

all these are non-electrolytes⁸. All the prepared ligands show $\nu_{\text{C-S}}$ 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 $\nu_{\text{Zn-S}}$ vibration^{9,10}.

The Zn2p_{1/2,3/2} and S2p binding energies (eV) data of ZnX₂ and [ZnX₂.L] (where X = Cl or NO₃; L = L¹ or L² or L³ or L⁴ or L⁵) are listed in Table 1. It may be that Zn2p_{1/2} photoelectron peaks binding energy

Table 1. Zn2p_{1/2}, S2p, Cl2p and N1s binding energies (eV) in ZnX₂ and [ZnX₂.L] complexes

Sl. no.	Ligand, salt and complexes	Zn2p _{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 ¹ Cl ₂]	87.2	163.4	203.8	-
8.	[ZnL ² Cl ₂]	87.2	163.4	203.8	-
9.	[ZnL ³ Cl ₂]	87.2	163.4	203.8	-
10.	[ZnL ⁴ Cl ₂]	87.2	163.4	203.8	-
11.	[ZnL ⁵ Cl ₂]	87.2	163.4	203.8	-
12.	Zn(NO ₃) ₂	88.6	-	-	404.6
13.	[ZnL ¹ (NO ₃) ₂]	87.4	163.6	-	405.8