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NEW DINUCLEAR ZINC(II) OCTAAZA MACROCYCLIC COMPLEX: CONDUCTOMETRIC STUDY, SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

The new complex $[\text{Zn}_2(\text{tpmc})\text{NO}_3](\text{NO}_3)_3 \cdot \text{CH}_3\text{OH}$, where *tpmc* is *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, have been synthesized and characterized. The conductometric technique played a guiding role in planning experiment with this large macrocyclic ligand. In IR spectrum sharps are shown coordinated and ionic nitrate ions which are in agreement to proposed formula by elemental analysis. Molar electrical conductivities indicated assumption that the complex is about a 1:3 electrolyte type. The optimized complex structure is obtained by molecular modeling and DFT calculations.

INTRODUCTION

In recent years, macrocyclic polyamine ligands and their complexes have been attractive due to specific structures and properties, as well as possibility of their application [1]. *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (*tpmc*) is one of the *cyclam* derivatives with eight nitrogen atoms as possible coordinate places. Until today, *tpmc* complexes with only few metals (mostly with Cu (II) ions) are synthesized, and they have shown different electrochemical properties [2], as well as, antibacterial and cytotoxic activity [3].

The goal of the present investigation is to study the stoichiometry of the complexation of *tpmc* with Zn(II) ions and to find the most convenient solvent for synthesis, by using the conductometric titration. Base on this results, here we report the synthesis, characterization and proposed structure of the first binuclear zinc complex with *tpmc* containing nitrate ligand as a bridging ligand.

EXPERIMENTAL

Measurements: Elemental analysis (C, H, N) was carried out by standard micro methods at the Center of Instrumental Analysis, University of Belgrade. IR spectra (KBr disc technique) were recorded on a Perkin-Elmer FTIR 31725 X spectrophotometer. Molar electrical conductivities of the complex ($c = 1 \times 10^{-3} \text{ mol/dm}^3$) solution in acetonitrile was measured at room temperature using a Jenway 4010 conductometer.

Conductometric procedure: The experimental procedure for conductometric titrations was reported in our previous work [2]. The conductance measurements were performed on a digital conductometer WTW model 330i (Germany).

Preparation of compounds: N,N',N'',N''' -tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (*tpmc*) was prepared using previously described method [4]. *Synthesis of $[Zn_2(tpmc)NO_3](NO_3)_3 \cdot CH_3OH$:* The ligand (*tpmc*) was suspended in to a mixture methanol:water at 50 °C. To this solution was added a methanol solution of zinc(II)-nitrate hexahydrate and mixture was stirred more than hour at 65 °C and then cooled to room temperature. The white crystals which formed were filtered off and washed with ethanol (yield 129 mg, 53%). The crystals were recrystallized from a mixture of water and ethanol (1:1 v/v). Anal. Calc. for $C_{35}H_{48}N_{12}O_{13}Zn_2$: C 43.09, H 4.96, N 17.23. Found: C 42.81, H 4.83, N 17.08%. IR (KBr, cm^{-1}): 2868.9 $\nu(\text{CH}_2)$, 1610 $\nu(\text{Py})$, 1477.9 $\nu(\text{CH}_2)$, 1361.4 $\nu(\text{NO}_3)$ and 1021.3 cm^{-1} $\nu(\text{NO}_3)$.

Computational details: Optimization of the complex was done with DFT method, more specifically B3LYP functional and 6-31G(d,p) basis set. For the zinc atoms lanl2dz basis set was used with effective core potential (ECP) for inner electrons.

RESULTS AND DISCUSSION

Complexation of *tpmc* with Zn^{2+} ions was examined by conductometric titration method in ethanol and methanol solution. Based on previously reported conductometric results [2] in acetonitrile and aqueous solution and obtained results for titration in ethanol and methanol solution (Figure 1), for synthesis was chosen methanol due to distinct breaking point which indicate a formation of a relatively stable 2:1 ($Zn:tpmc$) complex.

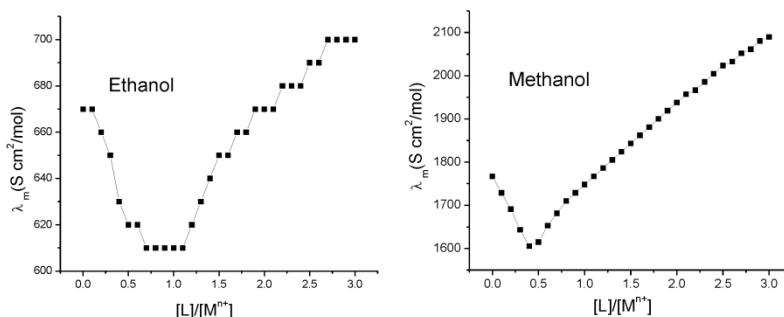


Figure 1. Plot of molar conductance, Λ , vs. V (cm³ of added ligand) for the binding of Zn^{2+} by *tpmc* in ethanol and methanol at 20 °C.

The complex was synthesized by the reaction of zinc(II)-nitrate hexahydrate and *tpmc* in 2:1 mole ratio. The results of elemental analysis are consistent with a binuclear structure of the obtained complex with the proposed formula $[Zn_2(tpmc)NO_3](NO_3)_3 \cdot CH_3OH$. In the IR spectrum of complex (Fig. 2b), a weak broad band at 2868.9 cm⁻¹ originates from the stretching vibrations of CH, and two medium bands at 1477.9 and 1445.1 cm⁻¹ from CH₂ bending vibrations. Sharp band at 1589.4 cm⁻¹ ascribed to skeletal vibration of the pyridine ring in the spectrum of free *tpmc* (Fig. 2a) is dislocated to 1610.1 cm⁻¹ upon coordination [3]. Strong a broad bands at 1361.4-1295.3 cm⁻¹ are assigned to coordinated nitrate, while a very strong band at 1021.3 cm⁻¹ is assigned to ionic nitrate [5].

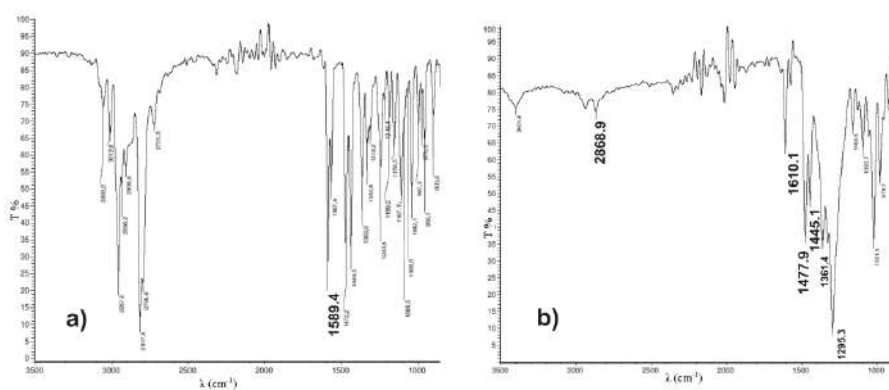


Figure 2. IR spectra of a) *tpmc* b) $[Zn_2(tpmc)NO_3](NO_3)_3 \cdot CH_3OH$.

DFT calculations and molecular modeling were employed for the optimization of the complex structure (Figure 3).

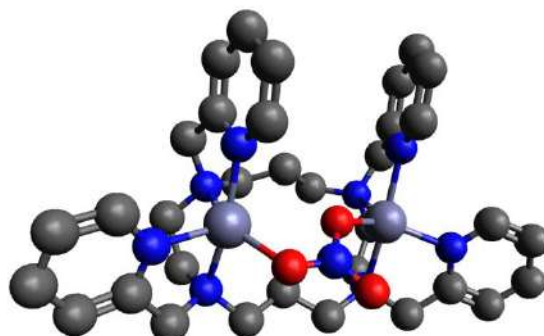


Figure 3. Optimized structure of $[\text{Zn}_2(\text{tpmc})\text{NO}_3]^{3+}$ complex ion. Colors: violet-zinc; red-oxygen; blue-nitrogen; grey-carbon

CONCLUSION

New binuclear Zn (II) complex with octaazamacrocyclic ligand, *tpmc*, was synthesized, characterized and theoretically optimized structure was proposed. The conductometric technique is convenient for investigation the complex formation between macrocyclic ligands and metallic ions because it provides voluble information for determining the most convenient solvent for synthesis and metal/ligand mole ratio.

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