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Controlled syntheses of heterodinuclear complexes of a dicompartmental macro-acyclic ligand with hexa and tetra coordination sites

Hamid Golchoubian [a,*], Hamid Reza Mardani [a], Giuseppe Bruno [b], Hadi Amiri Rudbari [b]

[a] Department of Chemistry, University of Mazandaran, Babolsar 47416-95447, Iran
[b] Dipartimento di Chimica Inorganica, Vill. S. Agata, Salita Sperone 31, Università di Messina, 98166 Messina, Italy

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ABSTRACT

Two phenol-based unsymmetrical dinucleating macro-acyclic ligands (LH_2), which can contiguously accommodate two metal ions, one in a hexa-coordinate (N_4O_2) site and the other in a tetra-coordinate (N_2O_2) site, and their heterodinuclear complexes $[ZnLM^{II}]^{2+}$, where M = Cu or Ni, were prepared using a stepwise method. One of the ligand systems (L^3H_2) comprises an ethylenediamine link in the N_4O_2 compartment, whereas the other (L^6H_2) includes an 1,3-diaminopropane link. Both ligands contain two methyl arms attached to the nitrogen atoms in the N_2O_2 coordination site. The mononuclear complex of the type $[ZnL^3(H^+)_2]^{2+}$ has a C_2-symmetrical structure. When a second metal is incorporated, however, the resultant heterodinuclear complexes $[ZnL^3M^{II}]^{2+}$ provide a non-symmetrical structure due to the occurrence of geometrical isomerization. In contrast, the mononuclear complex of the type $[ZnL^6(H^+)_2]^{2+}$ demonstrated a mixture of topological isomers and the structures of the resultant heterodinuclear complexes $[ZnL^6M^{II}]^{2+}$, remained constant without a change in the structures with respect to the mononuclear complex. The origins of the structural variations are discussed. The structures of the complexes were studied by NMR, IR, UV–Vis spectroscopies and X-ray crystallography.

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1. Introduction

We have been interested in the synthesis of dicompartmental ligands and their heterodinuclear complexes for many years. We recently prepared macro-acyclic complexes of type 1, shown in Scheme 1, which comprise two proximal compartments, one a six-coordinate, hexadentate (N_4O_2) site and the other a four-coordinate, tetradentate O_2N_2(imine) site [1]. The tetra coordination site also includes two alkyl groups attached to the azomethine moieties. It was found that during the preparation of a heterodinuclear complex from the corresponding mononuclear complex, one of the alkyl groups attached to the azomethine nitrogen atom was eliminated, along with a change in topology around the metal ion in the N_4O_2 compartment such that the pyridyl ligands disposed themselves from *trans* in the mononuclear complex to *cis* in the dinuclear complexes, as shown in Scheme 2. This unusual structural change and the alkyl elimination are believed to be interrelated and arise from a number of factors associated with the chelate ring size in the N_4O_2 compartment and steric hindrance and/or the lack of flexibility in the N_2O_2 compartment. Our previous study showed that the ethylenediamine chelate bite angle in the mononuclear complexes is about 80°. This constricted angle causes the opposite phenolate–O–Zn–O–phenolate angle to expand (104°) beyond a value which can accommodate a second neighboring metal ion tightly by the O_2N_2(imine) donor set. Thus, the dinuclear complexes are highly strained and the system relieves this strain by considerable topological rearrangement. Additionally, this rearrangement forces the alkyl groups attached to the azomethine moieties to become close to each other. Meanwhile, the imine groups restrict the flexibility of the alkyl azomethine. Thus, the transmitted steric strain causes the elimination of one of the alkyl groups attached to the imine nitrogen atom. If this analysis is correct we speculate that the corresponding amine ligand might impose a greater flexibility to the macro-acyclic ligand and would cause a change in the stereochemistry of the dinuclear complexes compared to those of the imine ligand. Additionally, it was expected that the expansion of the chelate bite angle in the N_4O_2-coordination site by replacing the ethylenediamine link with a 1,3-diaminopropane link would provide conformational flexibility to the ligand system. In fact, this flexibility would be transmitted to the whole conformational framework of the coordinated ligand so that the structural rearrangement and alkyl elimination would be excluded.

The objective of this paper, aside from an interest in investigating the factors which influence the topology and alkyl elimination in macro-acyclic dinuclear complexes, which is peculiar in the field of coordination chemistry, is that we require a C_2-symmetrical

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* Corresponding author. Tel./fax: +98 1125342350.
E-mail address: h.golchobian@umz.ac.ir (H. Golchoubian).

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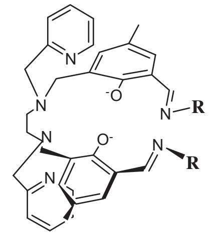

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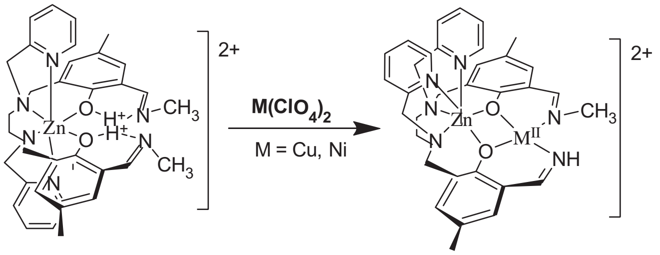
Scheme 1. The macro-acyclic dicompartmental ligand.



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Scheme 2. Synthetic scheme for previously prepared heterodinuclear complexes.

structure to bring two contiguous metal ions to interact through the oxygen atoms of bridging phenolate groups, which is a necessary prelude to our ultimate goal of studying cooperative chemical reactivity.

2. Experimental

2.1. Materials and methods

All of the chemicals and solvents were purchased from Aldrich and Merck. The dialdehyde complexes [Zn(II)L^1] (**3**), [Zn(II)L^5] (**7**) [2] and [ZnL^2(H$^+$)$_2$](ClO$_4$)$_2$ (**4**) [1] were synthesized as previously described. All the samples were dried to constant weight under a high vacuum prior to analysis. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker 400 MHz DRX spectrometer. IR spectra were recorded as pressed KBr discs using a Bruker FT-IR instrument. Electronic spectral measurements were carried out using a Baric2100 model UV–Vis spectrophotometer in the range 200–900 nm. C, H and N elemental analyses were performed on a LECO 600 CHN elemental analyzer. Absolute metal percentages were determined by a Varian-spectra A-30/40 atomic absorption-flame spectrometer. Conductivity measurements were carried out at 25 °C with a Jenway 400 conductance meter using 10^{-3} M solutions of the complexes in CH$_3$CN.

Caution: Perchlorate salts are potentially explosive and should be handled with appropriate care.

2.2. Preparation of the complexes

2.2.1. [Zn^{II}L^3(H$^+$)$_2$](ClO$_4$)$_2$·C$_2$H$_5$OH (**5**)

To a stirred solution of [ZnL^2(H$^+$)$_2$](ClO$_4$)$_2$, (300 mg, 0.370 mmol) in CH$_3$CN (7 mL) at 0 °C was added dropwise over 15 min a solution of NaBH$_4$ (284 mg, 0.74 mmol) in ethanol (7 mL). The intense yellow color of the imine disappeared rather abruptly near the end of the addition. The resultant colorless solution was warmed to 25 °C over 30 min. Acetic acid (168 μL, 3.26 mmol) was added to the reaction mixture and a small amount of gas evolution was observed. The solution was heated to 90 °C and the solvents were slowly distilled off over 1 h until a colorless solid precipitated. The suspension was cooled to 25 °C over 30 min. The solid was collected, washed with EtOH (1 × 3 mL), Et$_2$O (2 × 5 mL) and *n*-hexane (2 × 5 mL), and dried under vacuum. The crude solid was recrystallized from CH$_3$CN/EtOH as follow: the crude compound was dissolved in CH$_3$CN (ca. 4 mL) at room temperature and the solution was filtered. To the CH$_3$CN solution was added absolute ethanol (ca. 4 mL) and the resulting solution was placed in a small flask, which was then put in a jar containing ethanol (ca. 25 mL). This jar was capped to allow for slow diffusion of ethanol into the solution. After several days the crystalline complex was collected and dried under vacuum. Yielded 207 mg, 67%. The crystals were suitable for X-ray crystallography. Λ_m: 270.46 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for C$_{34}$H$_{44}$N$_6$O$_{10}$Cl$_2$Zn·C$_2$H$_5$OH (M_w = 879.13 g mol^{-1}): C, 49.18; H, 5.73; N, 9.56; Zn, 7.44. Found: C, 49.44; H, 5.35; N, 9.18; Zn, 7.50%. FT-IR (KBr, cm^{-1}): 3430 (b), 3068 (s), 2921 (s), 1603 (s), 1473 (s), 1272 (s), 1098 (s), 624 (m). ^{1}H NMR (400 MHz, CD$_3$CN), δ (ppm): 1.14 (t, *J* = 6.8, 3H, –C*H*$_3$, ethanol); 2.18 (s, 6H, Ar–C*H*$_3$); 2.22 (s, 6H, –N–C*H*$_3$); 2.71, 2.84 (syst AB, J_{AB} = 9.5 Hz, 4H, –N–C*H*$_2$–C*H*$_2$–N–); 3.50, 4.15 (syst AB, J_{AB} = 13.0 Hz, 4H, –N–C*H*$_2$–Ar); 3.55 (m, *J* = 6.0 Hz, 2H, C*H*$_2$, ethanol); 3.77, 4.23 (syst AB, J_{AB} = 13.0 Hz, 4H, –N–C*H*$_2$–Py); 3.89 (d, *J* = 8 Hz, 4H, –NH–C*H*$_2$–Ar); 3.92 (s, H, *OH* ethanol); 6.66 (s, 2H, Ar–*H*); 6.83 (s, 2H, Ar–*H*); 7.11 (d, *J* = 9.0 Hz, 2H, Py–*H*); 7.32 (t, *J* = 6.0 Hz, 2H, Py–*H*); 7.77 (t, d, *J* = 7.5, 1.3 Hz, 2H, Py–*H*); 8.76 (d, *J* = 6.0 Hz, 2H, Py–*H*). ^{13}C NMR (CD$_3$CN), δ (ppm): 17.77 (*C*H$_3$, ethanol); 19.17 (*C*H$_3$–Ar); 30.83 (–HN–*C*H$_3$); 52.39 (–*C*H$_2$–N–); 58.57 (–N–*C*H$_2$–Ar); 58.85 (–N–*C*H$_2$–Py); 56.98 (*C*H$_2$, ethanol); 61.27 (–HN–*C*H$_2$–Ar); 117.89 (quaternary Ar); 121.80 (Py); 122.56 (quaternary Ar); 122.87 (Py); 123.51 (quaternary Ar); 130.60 (Ar); 133.32 (Ar); 139.16 (Py); 148.62 (Py); 156.54 (quaternary Ar); 162.68 (quaternary Py).

2.2.2. [Zn^{II}L^{4}Cu^{II}](ClO$_4$)$_2$·0.5H$_2$O (**6**)

To a solution of [Zn^{II}L^3(H$^+$)$_2$](ClO$_4$)$_2$ (110 mg, 0.132 mmol) in CH$_3$CN (4 mL) was added dropwise a solution of Cu(ClO$_4$)$_2$·6H$_2$O (52 mg, 0.14 mmol) in ethanol (5 mL) and LiOH·H$_2$O (20 mg, 0.3 mmol) in methanol (3 mL). The green mixture that formed was stirred for 10 min and NH$_4$ClO$_4$ (300 mg, 2.5 mmol) in ethanol (5 mL) was then added to the resulting solution. The solution was partially concentrated at room temperature to reduce the CH$_3$CN content; diethyl ether was then added in portions (2 × 5 mL) and the solution was allowed to stand overnight. The resultant brown solid was collected and washed with water (2 × 2 mL), ethanol (2 × 3 mL), ether (3 × 3 mL) and *n*-hexane (3 × 3 mL). The crude compound was recrystallized with the same procedure as described above, yielding brown needles (103 mg, 75%). *Anal.* Calc. for C$_{34}$H$_{43}$Cl$_2$CuN$_6$O$_{10.50}$Zn (M_w = 903.60 g mol^{-1}): C, 45.19; H, 4.80; N, 9.30; Cu, 7.03; Zn, 4.24. Found: C, 45.94; H, 4.93; N, 9.88; Cu, 7.13; Zn, 4.41%. Λ_m: 223 Ω^{-1} mol^{-1} cm^2. FT-IR (KBr, cm^{-1}): 3436 (b), 3276 (s), 2919 (s), 1606 (s), 1477 (s), 1265 (s), 1100 (s), 623 (m).

2.2.3. [Zn^{II}L^6(H$^+$)$_2$](ClO$_4$)$_2$·H$_2$O (**8**)

To a stirred suspension of compound **7**, [Zn^{II}L^5], (0.9 g, 1.5 mmol) in ethanol (25 mL) was added dropwise over 10 min a solution of methylamine hydrochloride salt (0.3 g, 3.6 mmol) in ethanol (15 mL). After the addition was completed, all the starting materials were dissolved. The resulting yellow solution was then stirred for 12 h at room temperature. A yellow-orange solid precipitated almost immediately after the addition of a filtered solution of NH$_4$ClO$_4$ (1.2 g, 9.9 mmol) in ethanol (15 mL). The solid was collected and washed successively with EtOH (2 × 10 mL), Et$_2$O (2 × 5 mL) and hexane (2 × 5 mL), and then dried under vacuum. The solid consisted of a mixture of isomers (as discussed in the text) in a 51:43:6 ratio (as determined by ratio of C=N–CH$_3$ signals at 3.33, 3.30 and 3.25, 3.26 ppm, respectively). The crude compound was recrystallized by diffusion of diethylether into a CH$_3$CN

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