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Preparation of heterodinuclear complexes with phenol-based compartmental ligands containing hexa- and tetradentate coordination sites

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ABSTRACT

A series of mono- and heterodinuclear complexes of type ML^nH_2 and ML^nM' where M = Co^{III}, Cr^{III}, Zn^{II} and M′ = Cu^{II}, Zn^{II} have been synthesized and characterized. The non-macrocyclic ligands L^nH_4 contain two geometrically distinct compartments, hexa- (N_4O_2) and tetradentate (O_4) compartments which are bridged by phenolic oxygen atoms. The dinuclear complexes were prepared in stepwise reactions. The non-macrocyclic ligand showed a site specificity of metal ions upon the synthetic procedure. The results obtained reveals that in case of using ligand L^2H_4 only an isomer (*trans*-pyridines and *cis*-phenolates) among three possible geometrical isomers is formed. The metal site scrambling in the prepared complexes were not also observed in the reaction conditions used. The crystal structure of $[Cr^{III}L^2H_2]ClO_4$ was determined and discussed.

1. Introduction

The study of heterodinuclear metal complexes is of current interest in unique physicochemical properties and functions associated with metal–metal interaction [1] or cooperative effect of a pair of dissimilar metal ions [2–6]. So far, many efforts have been developed to the design of compartmental ligands possessing two dissimilar metal bonding sites with respect to the nature of donor atoms, the cavity size and the steric requirement for coordination of metal ions [7–13]. The term "compartmental" was introduced to indicate a ligand containing two adjacent dissimilar coordination sites [14]. Among many different types of dinucleating ligands, the phenol-based compartmental ligand attracted particularly wide attention of scientists [9–13,15,16]. Until now various type of dicompartmental ligands including the end-off, the side-off and the macrocyclic and non-macrocyclic types have been developed [1,5,8,17–19]. Among these, the special attention has been focused on the pendent arm unsymmetrical compartmental ligands as shown in Fig. 1 and their metal complexes [20-23]. The heterodinuclear complexes of these ligands were prepared by a stepwise reactions. The pendent arms in these dicompartmental ligands could have additional potential ligating groups or having lack of coordinating ability. An elegant development of unsymmetrical dicompartmental ligand was introduced by Bosnich and co-workers [12] as shown by 2 in Fig. 1. This type of ligand is interesting in several aspects such as the hexadentate coordination site (N_4O_2) and the tetradentate coordination site (N_2O_2) can accommodate different metal ions with different coordination numbers and geometrical environments [15,23–25]. Mono- and dinuclear complexes of macrocyclic ligands of type **2** have been prepared, and their structures and reactivities were investigated by Bosnich [9–12,23,26–28], Busch [7], and us [6,15,16,29]. These studies demonstrated that although the macrocyclic ligand **2** is suitable for preparation of homodinuclear complexes it is not useful for synthesis of heterodinuclear complexes because the both coordination sites could be occupied by introduction of metal ion into this macrocyclic ligand. As a result, the preparation of heterodinuclear complexes requires a sequential steps in which involves in the formation of the mononuclear complexes first, the formation of the second compartment and finally the introduction of the second metal ion into it. Acyclic compartmental ligands type **3** in Fig. 1 containing one N_4O_2- and O_4-coordination sites were also prepared by Bosnich and co-workers [10]. This dicompartmental ligand forms mononuclear complexes where the metal ion is probably in the N_4O_2 site. The insolubility of these complexes precluded attempts to synthesis dinuclear complexes. Another issue regarding with pendent arms dicompartmental ligands is the topology of the pendent arms groups around the metal ions in the mono- and dinuclear complexes. The results show that when ethylenediamine link is present in the N_4O_2 site mononuclear complexes with a C_2-symmetric structure with *trans*-pyridines and *cis*-phenolates isomer is produced, but with a trimethylenediamine link the acyclic mononuclear complex

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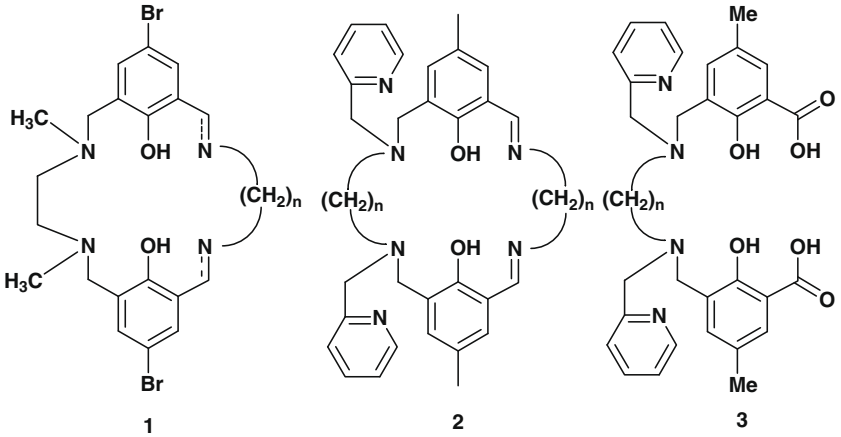
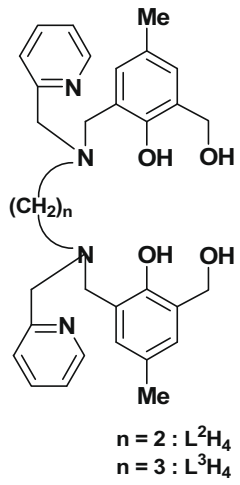


Fig. 1. Phenol-based macrocyclic and non-macrocyclic dicompartmental ligands with pendent arms.



Scheme 1. Phenol-based dialcoholic non-macrocyclic dicompartmental ligands.

contains all three possible topological isomers of *cis*-pyridines and *cis*-phenolates, *cis*-pyridines and *trans*-phenolates, and *trans*-pyridines and *cis*-phenolates [10]. However, the dinuclear macrocyclic complexes containing ethylenediamine link in the N_4O_2-coordination site forming C_1 structure with *cis*-pyridine ligands irrespective of the span of the N_2O_2 link [28].

Phenol-based compartmental ligands L^nH_4, in Scheme 1, having two dissimilar compartments N_4O_2 and O_4 metal-binding sites sharing the phenolic oxygen atoms, have been introduced by us through a four-step preparation procedure with a total yield of 38% [29]. These ligands, L^nH_4 (n = 2 and 3), were used for preparation of heterodinuclear complexes. The propose of this study was to investigate (i) the site specificity of the metal ion upon the synthetic procedure, (ii) the stereochemistry of the metal in the hexacoordination site, and (iii) the potential occurrence of the scrambling of the metal ions between two different coordination sites during the synthesis of heterodinuclear complexes.

2. Experimental

2.1. Materials and measurements

All reagents were commercial materials and were used as received. The dialdehyde ligand $[Co^{III}L^4](ClO_4)$ was prepared by the published method [12]. All the samples were dried to constant weight under a high vacuum prior to analysis. *Caution:* perchlorate salts are potentially explosive and should be handled with appropriate care.

Conductance measurements were made at 25 °C with a Jenway 400 conductance meter on 1.00×10^{-3} M samples in acetonitrile or DMSO. Infrared spectra (potassium bromide disk) were recorded using a Bruker FT-IR instrument. The electronic absorption spectra were measured using a Braic2100 model UV–Vis spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 and 400 DRX Spectrometer. 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. Electrospray mass studies were conducted on a VG Quattro II (Fision) triple-quadruple electrospray mass spectrometer with methanol and acetonitrile as the mobile phases.

2.2. Syntheses

2.2.1. Ligand L^nH_4

1,6-Bis(2-pyridyl)-2,5-bis(2-hydroxy-3-hydroxymethyl-5-methylbenzyl)-2,5-diazahexane (L^2H_4) and 1,7-bis(2-pyridyl)-2,6-bis-(2-hydroxy-3-hydroxymethyl-5-methylbenzyl)-2,6-diazaheptane (L^3H_4) were prepared according to published procedure except that *p*-cresol was used instead of 4-chlorophenol [29] with total yields of 37% and 42%, respectively, based on starting material of *p*-cresol.

Characterization data for L^2H_4: selected IR data (cm^{-1}): 3139 (O–H), 1601 (aromatic C=N), 1593 (aromatic C=C), 1467 (Ph-O). ^{1}H NMR (300.13 MHz in $CDCl_3$) δ: 1.63 (t, J = 7.0 Hz, 2H, ArCH$_2$-O*H*), 2.25 (s, 6H, *CH*$_3$-Ph), 2.76 (s, 4H, N–C*H*$_2$–C*H*$_2$–N), 3.65 (s, 4H, ArC*H*$_2$–N(amine)), 3.74 (s, 4H, Py-C*H*$_2$–N(amine)), 4.63 (d, J = 7.0 Hz, 4H, ArC*H*$_2$-OH), 6.65 (s, 2H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 7.16 (d, J = 4.0 Hz, 2H, Py-*H*), 7.19 (d, d, J = 5.2, 4.0 Hz, 2H, Py-*H*), 7.61 (d, d J = 5.2, 1.4 Hz, 2H, Py-*H*), 8.52 (d, J = 1.4 Hz, 2H, Py-*H*), 11.00 (br s, 2H, Ar-O*H*). ^{13}C NMR (75.03 MHz in $CDCl_3$) 20.7 (*C*H$_3$-Ph), 51.2 (Ph-*C*H$_2$–N(amine)), 51.9 (Py-*C*H$_2$–N(amine)), 54.9 (N–*C*H$_2$–*C*H$_2$–N), 61.5 (Ph-*C*H$_2$OH), 122.0 (*C*-aromatic), 122.5 (*C*-aromatic), 123.5 (*C*-aromatic), 125.7 (*C*-aromatic), 129.1 (*C*-aromatic), 129.5 (*C*-aromatic), 129.4 (*C*-aromatic), 137.0 (*C*-aromatic), 148.2 (*C*-aromatic), 150.1 (*C*-aromatic), and 160.5 (*C*-aromatic). When one drop of D_2O was added to the ^{1}H NMR sample, the broad signals at 11.00 and 1.63 ppm disappeared and the doublet at 4.63 ppm sharpened into a singlet at 4.53 ppm. The high-resolution mass spectrum showed the dominant peaks at m/z = 543.2971 (calculated value = 543.29) to be due to the monoposi-