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Preparation and characterization of mono- and hetero-dinuclear complexes with a dicompartmental macrocyclic ligand containing hexa- and penta-coordination sites

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Abstract

A novel hetero-dinucleating macrocyclic Zn(II)–Ni(II) complex was prepared by a stepwise procedure. The prepared mono- and dinuclear macrocyclic complexes were characterized by elemental analysis, IR, NMR spectroscopies, and molar conductance measurements. Characterization results confirm the expected C_2 symmetry geometry for mononuclear macrocyclic zinc complex with *trans* disposed pyridyl ligands. In contrast, the X-ray crystal structure of the dinuclear macrocyclic Zn(II)–Ni(II) complex reveals a C_1 symmetry geometry so that, Zn(II) ion is located in six-coordination site with *cis* disposed pyridyl ligands and the penta-dantate compartment is occupied by Ni(II) ion in a square pyramidal geometry. The thermogravimetric analysis (DTA/TG) of binuclear complex is also investigated.

Keywords: Dicompartmental ligand; Hetero-dinuclear complex; Macrocyclic complex; Zn(II)–Ni(II) complex; Thermogravimetric analysis

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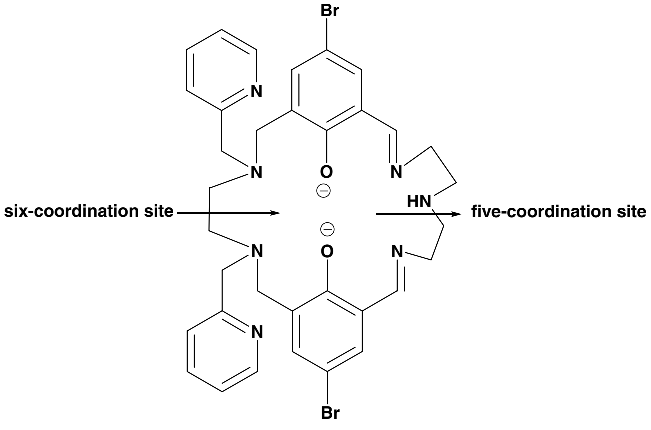
The design and synthesis of unsymmetrical dicompartmental ligands and their binuclear complexes have earned increasing interest over the past decade [1,2] due to their possibility to mimic the active sites of the metalloenzyme [3], their ability to stabilize unusual oxidation states and mixed-valence compounds [4], their interesting catalysis properties [5] and also their possibilities for the mutual influence of two metal centers on the electronic, magnetic and electrochemical properties of such system [6]. Recently, we prepared new mono-metallic complexes with phenol-based macrocyclic dicompartmental ligand shown in **A**. Such ligands contain two compartments: one includes six-coordination atoms (N_4O_2), and the other with a penta-dentate N_3O_2 donor set.



A

The idea behind this design was the expectation that the substrate would bind to the coordinatively unsaturated metal and be reduced by both metals. In order to fulfill this

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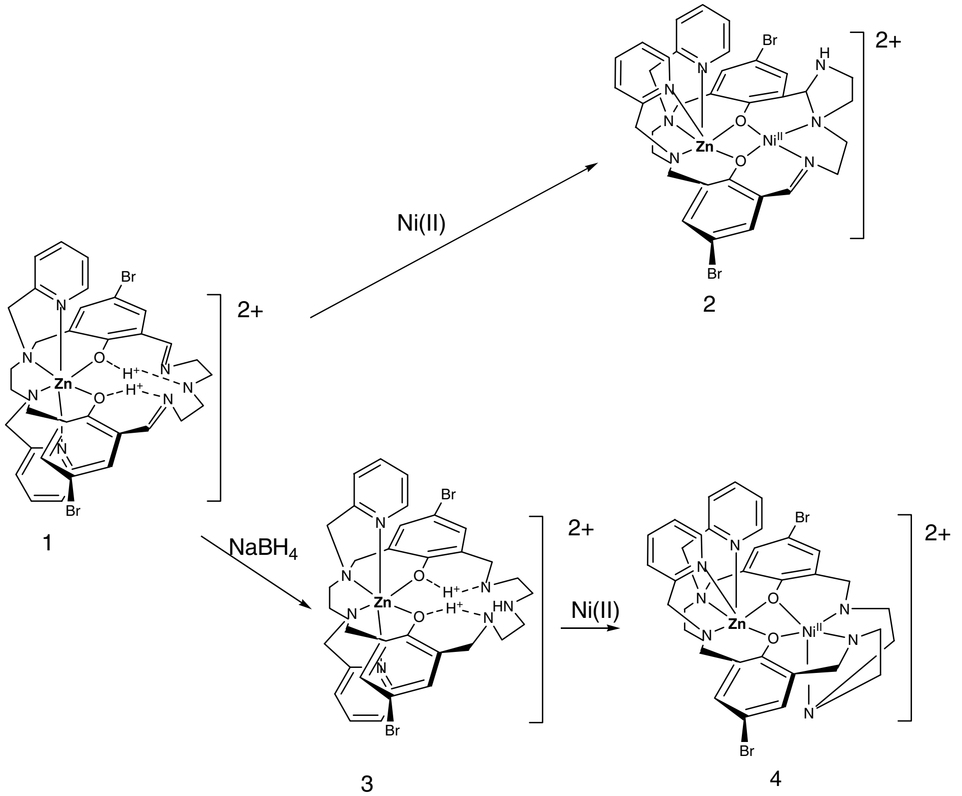

Scheme 1. Synthetic scheme for the mono- and dinuclear macrocyclic complexes.

objective it requires the relatively close juxtaposition of two metal centers and the metal-bridging ligand–metal lie roughly in the same plane. This unsymmetrical dicompartmental ligands provide discrete hetero-dinuclear core complexes and we will investigate which particular ligand features ensure that this be so. Our previous work demonstrated that introduction of a second metal into N_3O_2 cavity of the mono-metallic Zn complex in which two of the three nitrogen atoms are in imines forms resulted in hetero-bimetallic Zn(II)–M(II) complexes with unusual structure as shown in Scheme 1 compound **2**. First, the molecules essentially possess an unsymmetrical structure so that, the pyridyl ligands were not *trans* but were located on the same side of the mean macrocyclic plane. Second, the existence of a five-membered hetero-cycle ring attached to the diethylenetriamine link as a result of an intramolecular rearrangement. Third, the Ni(II) ion occupies a square planar geometry and bind to an aminic and an iminic nitrogen atom of the diethylenetriamine link as well as bind to the two phenolic oxygen atoms. However, our previous works with the analogous ligand system and with a 1,3-trimethylendiamine in place of diethylenetriamine link showed that the Ni ion held a five-coordination environment with a solvent molecule as a fifth ligand [7]. Since we are interested in studying the influence of ligand modification on the geometry of the metals in both coordination sites of macrocyclic ligand here, we wish to report the synthesis and crystal structure of hetero-dinuclear macrocyclic complex of Zn(II)–Ni(II) derived from reduction of diimine moieties of penta-coordination site based on consecutive reactions depicted in Scheme 1.

Compound **1** with diimine moieties in the five-coordination site was prepared according to our previous report [8] and used as starting material to prepare mono-metallic and hetero-dinuclear complexes. The corresponding amine complex **3** was prepared by BH_4^- reduction of compound **1** as pale yellow solid almost a quantitative yield [9]. Subsequently, the nickel ion was introduced in the acetonitrile solution of compound **3**. Under these reaction conditions, hetero-dinuclear Zn(II)–Ni(II) complex **4** was obtained with moderate yield [10].

Molar conductance of the mono- and dinuclear complexes measured in acetonitrile solution is consistent with 2:1 electrolytes. The electronic absorption spectra of the mono- and dinuclear complexes were recorded in room-temperature acetonitrile solution over the range 300–800 nm. The hetero-dinuclear Zn(II)–Ni(II) complex displayed two weak bands at 585 nm ($32.1\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$) and 672 nm ($8.1\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$) attributed to the d–d transitions of Ni(II). These are characteristic of a five-coordinated spin-free Ni(II) structure in the acetonitrile solvent although it is difficult to distinguish clearly between trigonal bipyramidal and square pyramidal structure for Ni(II) [11,12]. In addition, compound **4** as well as compound **3** demonstrated two intense bands at around 350 nm and 415 nm which are assigned as metal to phenolate charge transfer transitions [13,14]. The infrared spectra of the binuclear complexes of diimine compound **2** and its amine counterpart **4** are generally similar but at the same time complicated. Significant differences in the spectra between the imines and amines are the emergence of another sharp, but weak band at 3326 cm^{-1} which is attributed to the N–H stretch of the quaternized amine of the –NH moiety of diethylenetriamine link (–NH–CH$_2$Ph) [11], and the disappearances of the strong band at 1643 cm^{-1}, corresponding to the C=N stretch of the imine groups [15]. Appearance of a band near 1550 cm^{-1} for all of the complexes is assigned to the skeletal vibration of the aromatic rings [16]. The presence of a sharp band at 2316 cm^{-1} for **4** is due to the presence of lattice CH$_3$CN. The appearance of strong bands at about 1022 cm^{-1} and 917 cm^{-1}, which are common in both compounds correspond to the anti-symmetric stretching and anti-symmetric bending vibration modes of perchlorate ions, respectively [17].

The ^{1}H NMR spectrum of mononuclear complex **3** obtained in acetonitrile-d$_3$ solution suggested a structure of C_2 symmetry topology in which the pyridine moieties are disposed *trans* (see **3** in Scheme 1). The ^{1}H NMR spectrum of **3** revealed a broad signal constituting two protons at 9.64 ppm. This signal is assigned to the presence of two protons in the O$_2$N$_3$ compartment as was observed for its analogous macrocyclic complexes [18]. It suggests that there is bonded hydrogen between the phenoxide and amine ligands [17]. Addition of D$_2$O to the NMR sample causes rapid proton–deuterium exchange as evidenced by the disappearance of proton signals which exist in the O$_2$N$_3$ cavity and N–H amines of the diethylenetriamine link.

The X-ray analysis of compound **4** was determined [19]. An ORTEP view of this compound is shown in Fig. 1 together with the numbering scheme.

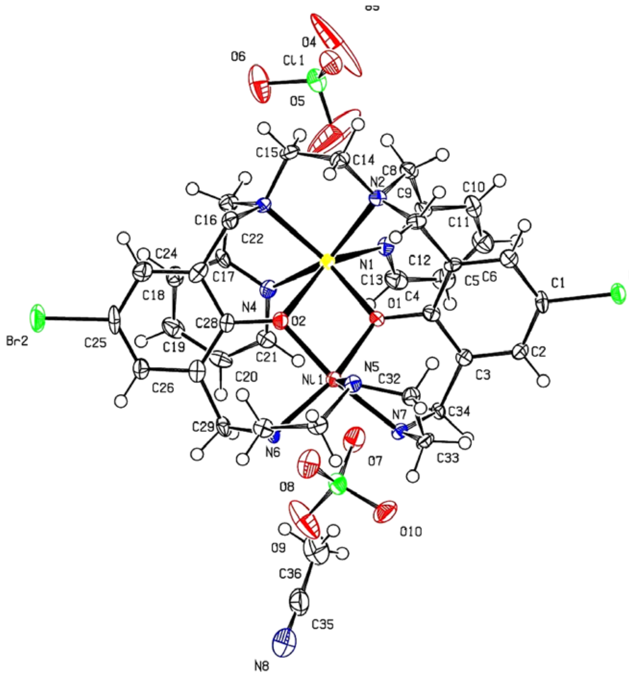

Fig. 1. ORTEP diagram of hetero-dinuclear macrocyclic complex [Zn–Ni]ClO$_4$ with atom labels and numbering scheme. Selected bond lengths (Å) and angles (°): Zn–O(1) 2.006(4), Zn–O(2) 2.287(4), Zn–N(1) 2.208(5), Zn–N(2) 2.199(5), Zn–N(3) 2.164(5), Zn–N(4) 2.128(5), Ni–O(1) 1.995(4), Ni–O(2) 1.967(4), Ni–N(5) 2.033(5), Ni–N(6) 2.065(5), Ni–N(7) 2.091(5), and N(1)–Zn–N(2) 78.51(19), N(3)–Zn–N(4) 80.42(19), O(1)–Zn–O(2) 69.71(15), O(1)–Zn–N(4) 115.64(19), O(1)–Zn–N(3) 146.64(18), O(1)–Zn–N(2) 90.68(18), O(1)–Zn–N(1) 89.07(18), N(2)–Zn–N(3) 82.50(19), N(1)–Zn–N(4) 91.32(19), N(2)–Zn–N(4) 151.8(20), N(3)–Zn–N(1) 112.01(19), N(4)–Zn–O(2) 80.28(18), O(2)–Zn–N(3) 85.82(16), O(2)–Zn–N(2) 120.67(17), O(2)–Zn–N(1) 150.35(17), N(5)–Ni–N(6) 85.60(19), O(1)–Ni–N(5) 106.74(19), O(2)–Ni–N(6) 90.83(18), O(2)–Ni–O(1) 76.91(17), O(2)–Ni–N(6) 90.83(18), O(1)–Ni–N(6) 164.45(18), N(5)–Ni–N(7) 85.44(19), N(6)–Ni–N(7) 101.14(19), O(1)–Ni–N(7) 89.47(18), O(2)–Ni–N(7) 164.30(18).

A number of features of this structure are worth noting. The pyridyl groups are *cis*-disposed whereas the monometallic complex **3** possess symmetric structure with *trans* disposed pyridyl ligands. An explanation for this occurrence has been offered previously [8]. However, the zinc ion is coordinated in a distorted octahedral structure. The Ni(II) ion is penta-coordinated with (N$_3$O$_2$) coordination sphere and its geometry is very close to a perfect square pyramidal with the O(1), O(2), N(6), N(7) forming the basal plane and N(5) occupying the axial position. According to Addison and Rao [20], the distortion of the square pyramidal geometry towards trigonal bipyramidal can be described by geometrical parameter $\tau = |\beta - \alpha|/60$, where β and α are the bond angles involving the *trans* donor atoms in the basal plane. The τ values are 0 and 60 for perfect square pyramidal and trigonal bipyramidal geometries, respectively. The τ value for the coordination around the nickel atom is 0.003, confirming the square pyramidal geometry. The deviation of the nickel is 0.172 Å from the basal plane. Third, the apical Ni–N(5) moiety of the diethylenetriamine link is directed on the opposite side of the mean macrocyclic plane to the two *cis* pyridyl ligands. This arrangement reduces the steric repulsion between pyridyl groups and the apical moiety of the diethylenetriamine link. Also two five-membered rings formed as a result of the coordination of diethylenetriamine to the nickel ion and have envelope configurations. The angle N(6)–Ni–N(7) is unusually large (101.14°) and deviate considerably from the ideal value of 90°. The Ni–N and Ni–O bond distances range from 1.995 to 2.091 Å. The Zn$\cdots$Ni intermetallic separation bridged by the two phenolic oxygen atoms is 3.272 Å.

The absolute configuration of the molecule was determined by X-ray diffraction and the topological chirality about the Zn(II) is Λ, Δ, Λ. In addition, both amine groups N(3) and N(4) are in the *meso* (R,S) configuration which is required for *cis*-pyridine topology [21]. The nitrogen atoms in the N$_3$O$_2$ site, N(6) and N(7) are in the *meso* (R,S) configuration as well.

The thermal analysis of the compound **4** was evaluated by thermogravimetric analysis (TG and DTA) between ambient temperature and 700 °C in argon (10 °C min^{-1}) (Fig. 2). According to structure data, there is a lattice ace-

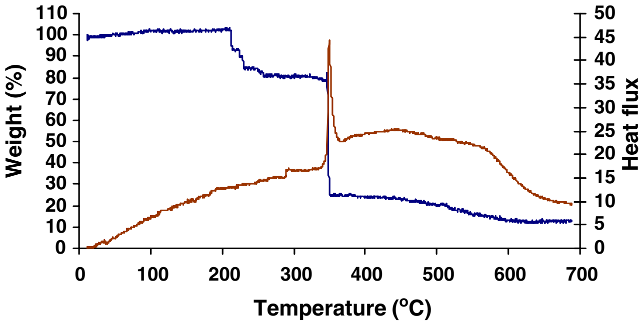

Fig. 2. TG and DTA curves for compounds **4**.

tonitrile molecule in compound **4**. Thus, during heating, it was lost with an endothermic associated process below 45 °C. The next weight loss is apparent between 210 and 260 °C and can be attributed to the loss of two pyridyl moieties (–CH$_2$–Py) corresponding to 17% of the weight loss (calculated 17%). The complex further started decomposition at 350 °C and completed at ca. 600 °C to yield residue corresponding to ZnO/NiO (found/calc. 13/14%). It is worth noting that the compound exhibited a very exothermic decomposition, leading to an overflow of the temperature regulation.

Acknowledgement

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Appendix A. Supplementary material

CCDC 644065 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.05.017.

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[9] *Synthesis of compound 3*: Caution: Perchlorate salts are potentially explosive and should be handled with appropriate care. To the stirred solution of compound **1** (500 mg, 2.7 mmol) in acetonitrile (5 mL) at 0 °C was added dropwise over 1 h, a solution of NaBH$_4$ (25 mg, 0.657 mmol) in acetonitrile (3 mL) and stirred for an additional 1 h at 0 °C. The resultant pale yellow mixture was allowed to stand for 2 h at room temperature. To the resultant pale yellow solution, acetic acid (0.23 mL, 3.89 mmol) was added and a small amount of gas evolution was observed. To the resulting solution, water (3 mL) was added. After addition of water, a fluffy pale yellow precipitate formed. Extra water (2 mL) was added and the solvents were distilled from the reaction mixture over 1 h until the total volume was less than 5 mL. The suspension was cooled to ambient temperature over 30 min and the pale yellow solid was collected, washed with water (2 × 10 mL), Et$_2$O (2 × 10 mL), hexane (2 × 10 mL) and dried under vacuum. The crude compound was recrystallized from acetonitrile–diethyl ether, which, yielded pale yellow needles (0.480 g, 96%). $\Lambda_m = 270\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for $C_{34}H_{41}N_7O_{10}Br_2Cl_2Zn$ (%): C, 40.68; H, 4.12; N, 9.77; Zn, 6.51. Found: C, 40.39; H, 4.01: N 9.74; Zn 6.69. FT-IR (KBr, cm^{-1}): 3326(m), 3342(b), 2927(b), 1650(s), 1600(m), 1540(s), 1452(s), 1276(m), 1106(s), 1022(s), 761(m), 619(m). ^{1}H NMR (500.13 MHz, CD$_3$CN): $\delta = 1.60$–1.90 (m, 3H), 2.86–2.90 (m, 12H), 3.40–4.20 (m, 12H), 6.98 (d, $J = 2.7$ Hz, 2H), 7.09 (d, $J = 2.7$ Hz, 2H), 7.17 (d, $J = 2.7$ Hz, 2H), 7.33 (t, $J = 5.9$ Hz, 2H), 7.80 (t, d, $J = 8.6$, 2.1 Hz, 2H), 8.77 (d, $J = 5.8$ Hz, 2H), 9.64 (br s, 2H). When one drop of D$_2$O was added to the ^{1}H NMR sample, the broad signal at 9.64 ppm and the multiplet signal at 1.60–1.90 ppm disappeared.

[10] *Synthesis of compound 4*: Complex **3** (201 mg, 0.20 mmol) was dissolved in CH$_3$CN (5 mL) followed by addition of Ni(ClO$_4$)$_2$ c-dot 6 H$_2$O (24.3 mg, 0.10 mmol) in acetonitrile (5 mL). To the resultant pale yellow solution was added Et$_3$N (56 μL, 0.40 mmol) in acetonitrile (1.5 mL) dropwise over 5 min. The resulting blue-green solution was stirred for 30 min and then was taken to dryness under reduced pressure. The resultant bluish green residue was washed with EtOH (2 × 2 mL), Et$_2$O (2 × 2 mL), and pentane (2 × 2 mL) and was recrystallized in acetonitrile–diethyl ether. Compound **4** was obtained as bright blue crystals (136 mg, 62%). A crystal suitable for X-ray crystal structure determination was grown by vapor diffusion of ethanol into a CH$_3$CN: ethanol solution of the complex. $\Lambda_m = 212\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for $C_{34}H_{39}N_7O_{10}Br_2Cl_2Zn$-$NiCH_3$ CN (%): C, 39.25; H, 3.84; N, 10.17; Zn, 5.94; Ni, 5.33. Found: C, 39.01; H, 4.16; N, 9.95; Zn, 6.03; Ni, 5.27. FT-IR (KBr, cm^{-1}): 3301(m), 3255(m), 2927(b), 1600(m), 1459(s), 1304(m), 1240(m), 1078(s), 754(m), 614(m).

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[19] Crystallographic analysis of **4**: Single crystal was mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα $\lambda = 0.71073$ Å). The complete conditions of data collection (Denzo software) [22]. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined on F^2 using the SHELXL97 software [23]. The absorption corrections were not applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97. Crystal data: $C_{36}H_{42}Br_2Cl_2N_8NiO_{10}Zn$, $M_r = 1101.56$, Crystal system: tetragonal; symmetry space group I-4; measurement temperature = 173(2) K, $a = 23.1986(5)$, $b = 23.1986(5)$, $c =$

15.5713(3), $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 90.00°$, $V = 8380.1(3)$ Å^3, $Z = 8$, $\mu = 3.112$, $D_c = 1.756$ g cm^{-3}, $F(000) = 4408.0$, cell measurement reflections used 21,430, $\theta_{\min}$–$\theta_{\max} = 0.998$–30.034, independent reflections = 34,409 ($R_{\text{int}} = 0.0878$), of which 9097 ($I > 2\sigma(I)$) were used for structure solution. The final $R_1 = 0.0587$, wR_2 (reflections) = 0.1315 (12,255), no. of parameters = 514, the goodness-of-fit on $F^2 = 1.140$.

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