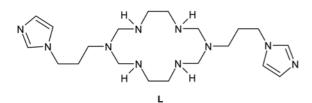# Synthesis, Crystal Structures and Properties of Macrocyclic Copper(II) Complexes Containing Imidazole Pendants

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Coordination polymers have been received considerable interest due to their interesting structural aspects as well as potential applications.[1-6] Especially, the transition metal complexes containing hexaazamacrocycles with pendant arms have been synthesized and characterized in order to inspect how the pendants affect the whole molecular structure.[7-13] Various pendants have been employed by the change of padlock primary amines to investigate the coordination chemistry in hexaazamacrocyclic metal complexes. Typical examples of primary amines used include methylamine/ ethylamine,[7] ethanolamine,[8,9] β-aminopropionitrile,[10] (*R/S*)-α-methylbenzylamine,[11] 2-thiophenemethylamine,[12] 4-(aminomethyl)pyridine,[13] and 1-(3-aminopropyl)imidazole.[9] In particular, the functional pendants which can act as hydrogen bond donors and/or acceptors, C-H⋯π interactions, and π-π interactions in addition to metal-ligand coordination bonds have been widely investigated due to the advantage in the self-assembly of coordination polymers and/or metallo-supramolecular polymers.[2,8,9,12-15] In the previous work, on the effects of macrocyclic pendants hydroxyethyl[9] and propylimidazole groups[15] with axial aromatic carboxylate ligands, we reported 1D hexaazamacrocyclic nickel(II) coordination polymers which further extend their structures through intermolecular hydrogen bonds and π-π interactions to form multidimensional supramolecular polymers. Herein, we synthesized and structurally characterized new hexaazamacrocyclic copper(II) complexes in which the macrocycle contains propylimidazole pendants in order to get further insight into the role of pendants to the coordination polymers. The details of the structures and properties of [Cu₃(**L**)₂(bpdc)(H₂O)₄] (bpdc)₂·18H₂O (**1**) and [Cu(**L**)(H₂O)₂](ndc)·8H₂O (**2**) (**L** = 3,10-bis{3-(1-imidazolyl)propyl}-1,3,5,8,10,12-hexaazacyclotetradecane, bpdc = 4,4'-biphenyldicarboxylate, ndc = 2,6-naphthalenedicarboxylate) are discussed in this report.

The complex **1** was prepared by the reaction between equimolar amounts of [Cu(**L**)](ClO₄)₂ and bpdc. As illustrated in Figure 1, the structure of **1** consists of three independent copper(II) ions. The first copper(II) ion (Cu1) is coordinated by the macrocycle and a bridging bpdc ligand to form a 1D coordination polymer, extending to an axial direction. The second copper(II) ion (Cu2) is also coordinated by the macrocycle, but the axial positions of the second copper(II) ion are occupied by aqua ligands. The coordination geometry around the third copper(II) ion (Cu3) is fulfilled with four imidazole pendants from the macrocycles and two aqua ligands, and shows a tetragonally distorted octahedron. The whole structure for **1** is charge balanced with copper(II) macrocycles, one coordinated bpdc lagand and two uncoordinated bpdc ions. The molecular structure of **1** contains three different series of 1D coordination polymeric chains (Figure 2). The first chain is composed of copper(II) (Cu1) macrocycles and bpdc ligands (-Cu1-bpdc-Cu1-bpdc-) which extends to an axial direction. The second polymeric chain is composed of another copper (II) (Cu2) macrocycles and the third copper(II) ions (Cu3) (-Cu2-imidazole pendant-Cu3-imidazole pendant-Cu2-). The last polymeric chain consists of copper(II)
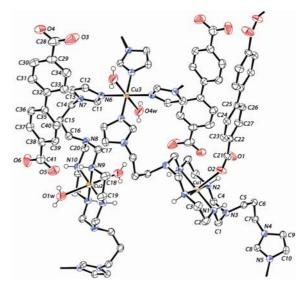

Figure 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms other than those of aqua ligands and on the secondary nitrogen atoms of the macrocycles are omitted for clarity. Selected interatomic distances (Å): Cu1-O2, 2.511(2); Cu2-O1W, 2.551(3); Cu3-O4W, 2.573(3).
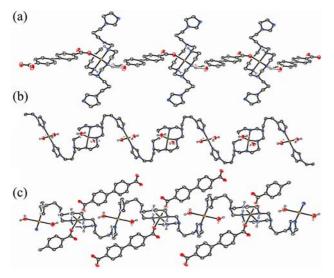
Figure 2. View of three different series of 1D coordination polymers in **1** (a) The first chain is composed of Cu1 macrocycles and bpdc ligands (-Cu1-bpdc-Cu1-bpdc-) (b) The second chain is composed of Cu2 macrocycles and Cu3 ions (-Cu2-imidazole pendant-Cu3-imidazole pendant-Cu2-) (c) The third chain is composed of Cu1 macrocycles and Cu3 ions (-Cu1-imidazole pendant-Cu3-imidazole pendant-Cu1-).
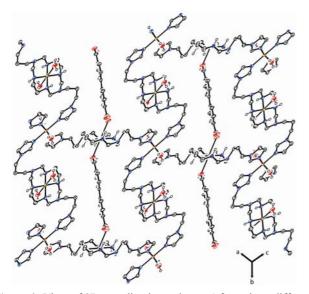

Figure 3. View of 2D coordination polymer **1** from three different series of 1D coordination polymers.

(Cu1) macrocycles and the third copper(II) ions (Cu3) (-Cu1-imidazole pendant-Cu3-imidazole pendant-Cu1-). The above three 1D coordination polymeric chains are intersected at the third copper(II) ions (Cu3), forming a 2D grid coordination polymer (Figure 3). The coordination environment around the first copper(II) ion (Cu1) shows a distorted octahedron in the chain direction with four Cu1-N bonds and two Cu1-O contacts. The four Cu1-N distances are in the range 2.005(3)-2.009(3) Å and shorter than the Cu1-O distance (2.511(2) Å). The second copper(II) ion is coordinated by four secondary nitrogen atoms of the macrocycle and two oxygen atoms of aqua ligands. The four Cu2-N distances are
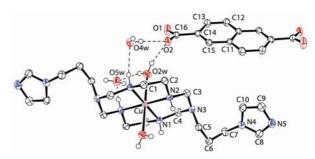

Figure 4. Molecular structure of **2** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Selected interatomic distance (Å): Cu1-O2W, 2.522(2).

in the range 2.011(3)-2.025(3) Å and shorter than the Cu2-O distance of 2.551(3) Å. Thus, the coordination environment of the second copper(II) is similar to that of the first copper(II) ion (Cu1). Interestingly, the third copper(II) ion (Cu3) which is coordinated by four imidazole pendants and two aqua ligands exists without macrocycles in the structure **1**. Since the equimolar amounts of reactants [Cu(**L**)](ClO$_4$)$_2$ and H$_2$bpdc with slight excess of NaOH were used during the synthesis, we believe that the third copper(II) ion (Cu3) was involved in the structure from the partial decomposition of [Cu(**L**)](ClO$_4$)$_2$. The coordination geometry around the third copper(II) ion (Cu3) exhibits again an axially elongated octahedron with four Cu3-N bonds and two Cu3-O contacts. The four Cu3-N distances are in the range 2.007(3)-2.023 Å and shorter than the Cu3-O distance of 2.573(3) Å. Overall, all three copper(II) ion geometries show Jahn-Teller distorted octahedrons, and the distances of Cu-N and Cu-O are comparable to those reported earlier in related systems.[16-19] The possible dianionic bpdc ligands in this molecule serve two functions. One is as a coordinated axial ligand (Cu1-O2), while the other is a counteranion to maintain the molecule as a charge-balanced species. It is well understood that the self-assembly of metal ion building blocks and dicarboxylate ligands yield 1D coordination polymers or monomers.[8,9,20,21] Thus, in order to achieve the construction of 2D coordination polymers, metal ion building blocks with polycarboxylate ligands having more than two carboxylate groups are expected to be involved.[22,23] However, we successfully constructed the 2D coordination polymer **1** by the reaction between metal ion building blocks and dicarboxylate ligands, where three independent 1D coordination polymers participate in the formation of a 2D coordination polymer.

By the reaction of copper(II) complex [Cu(**L**)](ClO$_4$)$_2$ with ndc, the complex **2** was isolated. In **2**, the copper ion is six-coordinate with bonds to the secondary amines of the macrocycle and axial aqua ligands. The ring closing tertiary amines as well as the pendant propylimidazoles are uninvolved in the copper(II) coordination sphere. Figure 4 shows the structure of **2** as determined by single crystal X-ray diffraction methods. The macrocyclic ligand skeleton of the complex adopts the classical *trans III* (*R,R,S,S*) conformation.[24] The Cu-N interatomic distances vary from

2.006(2) Å to 2.017(2) Å with an average distance of ~ 2.0155 Å, which is normal for such geometry. The axial Cu-O distances of 2.522(2) Å are long, as is expected for a d^9 copper(II) ion, which is orbitally degenerate and susceptible to distortion.[25] Nevertheless, it falls in the shorter area compared to related systems.[18,19] In **2**, axial aqua ligands are involved in forming two kinds of hydrogen bonded rings and are expected to be stabilized (Table S2). The reasons for the shorter Cu-O distances in **2** compared to the other closely related diaqua complexes are suggested by the combined effects of reduced steric hindrances of the macrocyclic ligand and of the presence of additional hydrogen bonds as mentioned above. The counter anion ndc as well as pendant imidazole groups of the macrocycle do not involve in secondary interactions such as π-π stacking.

The microanalyses for **1** and **2** were consistent with the composition determined by X-ray diffraction methods. The solid state electronic spectra of **1** and **2** show approximate absorption maxima at 530 nm (**1**) and 526 (**2**) nm, respectively, corresponding to a composite of three possible transitions d_{xy}, d_{xz}, $d_{yz} \rightarrow d_{x2-y2}$.[26] The assignment of three band maxima which is expected in **1** due to the presence of three different copper(II) ions was hampered with the broadness of the spectrum. The presence of water molecules was suggested by the broad absorptions at 3373 (**1**) and 3393 (**2**) (νOH) cm^{-1} in the IR spectra. In addition, weak bands at 3170 (**1**) and 3183 (**2**) (νNH) cm^{-1} indicate that the macrocyclic ligands are present in the complexes, respectively. The bands at 1590 (**1**) and 1629, 1564 (**2**) cm^{-1} were observable due to ν_{as}COO stretchings, respectively. The TGA curve for **1** showed a first weight loss of 15.2% (Calc. 15.1%) between 40 °C and 105 °C, corresponding to the loss of eighteen lattice water molecules. The loss of aqua ligands was observed over 105-184 °C range. On further heating, gradual weight loss was observed in the range 200-540 °C with the loss of bpdc and macrocycle ligands. The final residue (Obs. 8.5%), presumably the mixture of $Cu_2O + 0.5$ CuO (Calc. 8.5%) was remained above 540 °C. The TGA curve for **2** showed a first weight loss of 16.5% (Calc. 16.4%) over the range 40-82 °C, corresponding to the loss of eight lattice water molecules. The loss of aqua ligands was observed in the range 82-105 °C. On further heating, gradual weight loss was observed in 190-480 °C with the loss of ndc and macrocyclic ligands. Finally, the CuO residue (Obs. 8.7%, Calc. 9.0%) remained above 480 °C. The higher temperature range for the loss of aqua ligands in **1** compared to that in **2** is believed to be the presence of hydrogen bonds having more favorable hydrogen bond angles and distances (Tables S1 and S2).

In summary, we prepared and fully characterized two new hexaazamacrocyclic copper(II) complexes **1** and **2**. The structure of **1** consists of three independent copper(II) ions with each copper(II) ion having a different coordination environment. Three different 1D coordination polymers together with copper(II) ions and bpdc ligands are observed in **1**, which are interconnected at the Cu3 ion to form a 2D coordination polymer. In the structure **2**, the coordination

geometry about the copper(II) atom is a tetragonally distorted octahedron with four equatorial nitrogen atoms from the macrocycle and two axial oxygen atoms from aqua ligands. The pendant imidazole groups of the macrocycles and ndc do not involve in the copper(II) coordination sphere or show secondary interactions such as π-π stacking.

Experimental Section

Physical Measurements. All chemicals utilized in this investigation were obtained from commercial sources, were reagent grade, and were used without further purification. Distilled water was used for all procedures. Infrared spectra of solid samples were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer between 4000 cm^{-1} and 400 cm^{-1} as Nujol mulls on KBr discs. Solid state electronic spectra were measured by the diffuse reflectance method using samples diluted with BaSO$_4$ with a Shimadzu 2401 PC UV/vis recording spectrophotometer. The thermal and elemental analyses were performed at the analytical laboratory of Korea Research Institute of Chemical Technology, Daejeon, Korea.

Caution! The perchlorate salts are potentially explosive and should be handled in small quantities.

Syntheses of Precursor Complexes [Cu(L+2H)](ClO$_4$)$_4$ and [Cu(L)](ClO$_4$)$_2$. The precursor complex [Cu(L+2H)](ClO$_4$)$_4$ was prepared according to the literature procedures with slight modifications by using Cu(OAc)$_2$·H$_2$O instead of Ni(OAc)$_2$·4H$_2$O.[13,15] Typical procedures are as follows. To a stirred methanol (40 mL) solution of Cu(OAc)$_2$·H$_2$O (2.5 g, 12.5 mmole) were slowly added ethylenediamine (1.7 mL, 25.0 mmole), paraformaldehyde (1.5 g, 50.0 mmole) and 1-(3-aminopropyl)imidazole (2.98 mL, 25.0 mmole). The mixture was refluxed for 1 day. The hot solution was filtered, and HClO$_4$ (60%, 10 mL) was added slowly to the filtrate. The solution was stored overnight in the refrigerator until purple needles [Cu(L+2H)](ClO$_4$)$_4$ formed. The crystals were filtered, washed with methanol and dried in air. Yield: ~20%. To a suspension of [Cu(L+2H)](ClO$_4$)$_4$ (1 g, 1.13 mmole) in water was added an excess amount of triethylamine (2 mL). The mixture was stored overnight in the refrigerator until purple blocks of [Cu(L)](ClO$_4$)$_2$ formed. The crystals were filtered, washed with water and dried in air. Yield: ~50%. Anal. Calc. for C$_{20}$H$_{38}$N$_{10}$O$_8$Cl$_2$Cu: C, 35.27; H, 5.62; N, 20.57. Found C, 35.33; H, 5.79; N, 19.48%. IR (Nujol, cm^{-1}): 3250, 3113 (νNH), 1612 (νC=N), 1073, 1042 (νCl-O), 623 (νCl-O).

Synthesis of [Cu$_3$(L)$_2$(bpdc)(H$_2$O)$_4$](bpdc)$_2$·18H$_2$O (1). Complex **1** was prepared by adding an aqueous solution of H$_2$bpdc (250 mg, 1.0 mmole) and a slight excess of NaOH to a DMF solution of [Cu(L)](ClO$_4$)$_2$ (680 mg, 1.0 mmole). Slow evaporation of the solution afforded purple needles of **1**. Suitable crystals for X-ray diffraction studies and other measurements were manually collected under a microscope. The yield was not determined. Anal. Calc. for C$_{82}$H$_{144}$N$_{20}$O$_{34}$Cu$_3$ (**1**): C, 45.92; H, 6.71; N, 13.05. Found: C, 46.64; H, 6.37; N, 13.10%. IR (Nujol, cm^{-1}): 3377 (νOH), 3170 (νNH),

Table 1. Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{82}H_{144}Cu_3N_{20}O_{34}$	$C_{32}H_{64}CuN_{10}O_{14}$
Formula weight	2144.79	876.47
Temperature (K)	150(1)	150(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.3041(3)	9.5995(2)
b (Å)	13.4866(3)	9.8569(3)
c (Å)	16.1856(4)	11.8941(5)
α (°)	69.9230(14)	89.8340(16)
β (°)	70.140(1)	87.379(2)
γ (°)	72.6340(13)	66.3820(17)
V (Å³)	2510.48(10)	1029.94(6)
Z	1	1
D_{calcd} (Mg/m³)	1.419	1.413
Absorption coefficient (mm⁻¹)	0.720	0.606
Independent reflections	11335 [R(int) = 0.0565]	4638 [R(int) = 0.0491]
Goodness-of-fit on F²	1.035	1.038
Final R indices [I > 2σ(I)]	$R_1 = 0.0615$, $wR_2 = 0.1565$	$R_1 = 0.0560$, $wR_2 = 0.1376$
R indices (all data)	$R_1 = 0.0986$, $wR_2 = 0.1813$	$R_1 = 0.0824$, $wR_2 = 0.1570$

1590 ($\nu_{as}COO$).

Synthesis of [Cu(L)(H₂O)₂](ndc)·8H₂O (2). To a DMF solution (10 mL) of [Cu(**L**)](ClO₄)₂ (680 mg, 1.0 mmol) was added an aqueous solution (20 mL) of K₂ndc (269 mg, 1.0 mmol), the mixture was allowed to stand in an open beaker at ambient temperature. After several days, purple blocks of **2** were obtained. Suitable crystals of **2** were picked up under a microscope for X-ray diffraction studies and subsequent measurements. The yield was not determined. Anal. Calc. for $C_{32}H_{64}CuN_{10}O_{14}$ (**2**): C, 43.85; H, 7.30; N, 15.97. Found C, 44.47; H, 6.72; N, 16.35%. IR (Nujol, cm⁻¹): 3393 (νOH), 3183 (νNH), 1629, 1564 ($\nu_{as}COO$).

X-ray Crystallography. A summary of selected crystallographic data for **1** and **2** is given in Table 1. X-ray data were collected on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). A combination of 1° ϕ and ω (with k offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[27] The structures were solved and refined, using the SHELXTL\PC V6.1 package.[28] Refinement was performed by full-matrix least squares on F^2, using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

Supplementary Material. CCDC 818103 and 818104 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif. Figures S1-S3 contain the IR spectra, vis spectra and TGA curves for **1** and **2**, respectively. Tables S1 and S2 contain the hydrogen bond data for **1** and **2**, respectively.

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