Note

Macrocyclic Copper(II) Complex with Unusual Involvement of btc⁴⁻ (btc = 1,2,4,5-Benzenetetracarboxylate Ion) Ligand

Taeyeong Kim and Ju Chang Kim*

Department of Chemistry, Pukyong National University, Busan 48513, Korea. *E-mail: kimjc@pknu.ac.kr (Received February 15, 2019; Accepted February 21, 2019)

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Aromatic polycarboxylate ligands in cooperation with transition metal complexes have been widely used as building blocks for the construction of coordination polymers and supramolecules.¹⁻¹⁰ Among various aromatic polycarboxylates, 1,2,4,5-benzenetetracarboxylate (btc) as bridging ligand is of special interest due to its following unique structural features.^{11,12} The COOH groups in H₄btc could afford versatile coordination environment to metal ions depending on the degree of deprotonation. The COOH and deprotonated COO groups in the btc moieties can participate in hydrogen bonding interactions as hydrogen bond donors and/or acceptors. In addition, the COOH/COO groups can be tilted from the plane of the phenyl ring upon coordination. All these structural features of btc moieties are favorable to allow the rich coordination modes of COOH and/or COO groups to metal ions. Provided that the macrocyclic metal complexes get involved, the nature of macrocycles is another factor which influences the structural motifs of polycarboxylato macrocyclic metal complexes.

Numerous metal complexes of macrocycles L1 and L2, and their derivatives, have been reported since the pioneering work of Kang et al. on the nontemplate synthesis of macrocyclic ligands L and its isomers (Scheme 1).¹³⁻²¹ Although the macrocycles L1 and L2 to metal ions show similar coordination behaviors, the axial coordination of metal complexes of L1 and L2 is known to be affected by the stereochemistry of cyclohexane rings fused on the cyclam skeleton. Interestingly enough, structurally significant examples of axial interactions between macrocyclic metal complexes and axial ligands are frequently observed with macrocycle L1.^{16–21} Most of the earlier reports ascribed the reactivity differences of axial coordination of metal complexes with L1 and L2 to the structural characteristics of the macrocycles L1 and L2.16,17,20,21 However, more examples of metal complexes, especially with L1, are highly required to better understand the factors which influence the axial coordination of macrocyclic metal complexes. Therefore, we attempted the reaction of macrocyclic copper(II) complex $[Cu(L1)](ClO_4)_2$ with H₄btc in basic condition to get insight into the copper(II) chemistry of L1 with axial ligand btc, and obtained a copper(II) dimer $[Cu(L1)(H_2O)_2][Cu_2(L1)_2(\mu-btc^{4-})]\cdot 2ClO_4 \cdot 1.454CH_3CN$ $\cdot 6H_2O$ (1) in which the btc⁴⁻ ligand bridges two copper(II) macrocycles L1. Herein we describe the details of the synthesis and crystal structure of 1 in this report.

The complex 1 (violet plates) was crystallized from the 3:1 molar reaction of $[Cu(L1)](ClO_4)_2$ and H₄btc in DMF/ CH₃CN/H₂O/N(CH₂CH₃)₃. The complex 1 is composed of macrocyclic copper(II) cation $[Cu(L1)(H_2O)_2]^{2+}$, complex anion $[Cu_2(L1)_2(\mu-btc)]^{2-}$, and $2ClO_4^-$ counter anions. The structure of cationic part of 1 in which two aqua ligands axially coordinated to central copper(II) ion with long Cu-O distances (Cu2-O1W, 2.713 Å) due to Jahn-Teller effect is normal (*Fig.* S1, *Table* S1). The cationic part plays an important role in the formation of 1D supramolecule as well as the participation of btc⁴⁻ ligand in 1. The anionic part of 1 exhibits a macrocyclic copper(II) dimer bridged by btc⁴⁻ ligand (*Fig.* 1). Ultimately, along with cationic part, the whole structure of 1 extends by hydrogen bonding interactions to form a 1D supramolecule (*Fig.* 2).

The coordination geometry about the copper(II) ion in the anionic part $[Cu_2(L1)_2(\mu-btc^{4-})]^{2-}$ of 1 shows a five-coordinate square pyramid with four Cu-N and one Cu-O bonds. The Cu-N distances of 2.0613(17) Å, 2.0213(16) Å, 2.0479(17) Å, 2.0105(16) Å are typical for those found in square pyra-



Scheme 1. Molecular structures of L, L1, L2, and H4btc.



Figure 1. Structure of $[Cu_2(L1)_2(\mu-btc^{4-})]^{2-}$ anion with atomlabeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Cu1-N1, 2.0613(17); Cu1-N2, 2.0213(16); Cu1-N3, 2.0479(17); Cu1-N4, 2.0105(16); Cu1-O1, 2.3742(14); C21-O1, 1.255(2); C21-O2, 1.262(3); C25-O3, 1.260(6); C25-O4, 1.247(6); N1-Cu1-N2, 84.26(7); N1-Cu1-N4, 93.06(6); N2-Cu1-N3, 96.59(7); N3-Cu1-N4, 85.15(7); N1-Cu1-O1, 100.03(6); N2-Cu1-O1, 95.39(6); N3-Cu1-O1, 87.25(6); N4-Cu1-O1, 92.11(6). Symmetry codes: #1 -x+1,-y+1,-z #2 -x+1,-y+2,-z.



Figure 2. View of 1D supramolecule formed with hydrogen bonding interactions between $[Cu(L1)(H_2O)_2]^{2+}$ cation and $[Cu_2(L1)_2(\mu-btc^{4-})]^{2-}$ anion.

midal copper(II) ions.^{22,23} The Cu-O distance of 2.3742(14) Å is longer than those observed in similar geometries of carboxylate/formato copper(II) macrocycles ([Cu(L2)(H₂btc²⁻)]; $Cu-O=2.2539(13) \text{ Å},^{22} [Cu(L2)(O_2CH)] \cdot H_2O; Cu-O=2.2343(15)$ Å).²³ The copper atom lies slightly above the four N atom mean plane of the macrocycle (0.132 Å). The macrocyclic ligand skeleton in 1 adopts the most stable trans III (R,R,S,S) conformation as usual.²⁴ Each pair of N-H groups is pre-organized with its role in profacial selection of perchlorate anion binding through hydrogen bonding interactions. One of the pertinent features observed in the structure 1 is the unusual involvement of btc4- bridging ligand. Although there have been many reports on the transition metal macrocyclic complexes with btc moieties, the btc⁴⁻ coordination to the macrocyclic copper(II) ions is rare and unusual (Scheme S1).12,22,25-27 To our best knowledge, this is the first example of the involvement of btc⁴⁻ ligand in the macrocyclic copper(II)

complex. Versatile modes of btc moieties such as H4btc, H3btc⁻, H₂btc²⁻, Hbtc³⁻, and btc⁴⁻ could be theoretically possible depending on the degree of deprotonation. However, the dianion H₂btc²⁻ is the most commonly observed in the macrocyclic btc complexes.^{15,22,26,27} The participation of H₃btc⁻ and H₄btc has also been reported.^{12,26} But we have never had the chance to meet the Hbtc³⁻ and btc⁴⁻ moieties in the macrocyclic btc complexes. The difficulty of obtaining the highly deprotonated Hbtc³⁻ and btc⁴⁻ ligands in the macrocyclic metal complexes is originated from the reprotonation of deprotonated btc species during the crystallization process even under the excess use of triethylamine. Thus, the COO and adjacent COOH groups on the 1,2- and 4,5- positions of phenyl ring form intramolecular hydrogen bonds, leading a coplanar H₂btc²⁻ anion, respectively.⁴ In the complex anion $[Cu_2(L1)_2(\mu-btc^{4-})]^{2-1}$ in 1, all four COO groups are tilted from the plane of the phenyl ring for their favorable hydrogen bonding interactions as hydrogen bond acceptors toward nearby hydrogen bond donors. The dihedral angles between the carboxylate and the phenyl ring in btc⁴⁻ is 45.13° (O1C21C22C24), 46.35° (O2C21C22C23), 41.61° (O3C25C24C22), and 53.79° (O4C25C24C23), respectively. The macrocycle L1 consisting of two cis-fused cyclohexane rings on the cyclam skeleton which is more steric demand also contributes to the nonplanarity of COO groups. Apart from the Cu-O bonds in 1, two kinds of hydrogen bonds between copper(II) macrocycles and btc⁴⁻ play a part in the formation of copper(II) dimer as well as the involvement of btc^{4-} ligand in 1 {D-H...A = N2-H2N...O2: d(H...A) = 1.94, d(D...A) = 2.848(2), \angle (DHA) = 148.9°; D-H...A = N3-H3N...O3#1; d(H...A) $= 1.95, d(D...A) = 2.909(3), \angle (DHA) = 159.5^{\circ};$ symmetry code: $\#1=x+1,-y+1,-z\}$ (Fig. 1, Table S1). The sixth vacant site about the copper(II) ion is blocked by a perchlorate ion, which interacts with the preorganized N-H groups of the macrocycle by way of N-H...O hydrogen bonds {D-H...A =N1-H1N...O7: d(H...A) = 2.15, d(D...A) = 3.129(3), \angle (DHA) $= 164.6^{\circ}$; D-H...A = N4-H4N...O8; d(H...A) = 2.23, d(D...A) $= 3.147(2), \angle$ (DHA) $= 151.8^{\circ}$ } (*Fig.* 1, *Table* S1). Perchlorate ions are crucial for the presence of btc4- ligands, where they play a role in balancing the charge of the whole molecule 1. The $[Cu(L1)(H_2O)_2]^{2+}$ cation also assists the engagement of btc⁴⁻ in 1 through intermolecular hydrogen bonding interactions between the COO group of btc⁴⁻ and the agua ligand of $[Cu(L1)(H_2O)_2]^{2+}$ {D-H...A = O1W-H1WA...O4: d(H...A) $= 2.07, d(D...A) = 2.908(6), \angle (DHA) = 179.2^{\circ}, Fig. 1, Fig. 3,$ Table S1}.

Consequently, the aforementioned versatile hydrogen bonding interactions arising from the N-H groups of the macrocycle, $[Cu(L1)(H_2O)_2]^{2+}$ cation, btc^{4-} ligand, and



Figure 3. View of hydrogen bonding interactions between $[Cu(L1) (H_2O)_2]^{2+}$ cation and $[Cu_2(L1)_2(\mu-btc)]^{2-}$ anion.

perchlorate ions in the crystalline state along with the use of sterically demand macrocyclic ligand L1 are believed in assisting the rare involvement of btc^{4–} ligand in 1.

Microanalytical analysis agrees with the structure determined by X-ray diffraction methods. Two weak bands at 3245 and 3156 cm⁻¹ in the IR spectrum can be assigned to N-H stretching of the macrocycle. The broad band at 3460 cm⁻¹ is originated from the O-H stretching of lattice water molecules. The strong absorptions at 1561 cm⁻¹ (v_{as}COO), 1411 cm⁻¹ (v_sCOO) are observable due to btc^{4–} ligand. The strong bands at 1076 cm⁻¹ (v_{as}Cl-O) and 625 cm⁻¹ (δ O-Cl-O) suggest the presence of uncoordinated perchlorate ions in 1.^{23,28} Electronic spectrum of **1** in DMF shows a band maximum at 555 nm which is typical for copper(II) complexes.

In summary, we successfully prepared and structurally characterized the complex 1 in which the btc^{4–} ligand bridges the copper(II) macrocycles L1, resulting in the formation of macrocyclic copper(II) dimer. The unusual involvement of btc^{4–} in 1 is ascribed to the presence of multiple types of hydrogen bonds between the btc^{4–} ligand and the copper(II) macrocycles. The btc^{4–} in 1 works as a ligand to coordinate to copper(II) ions as well as hydrogen bonds between the copper(II) macrocycles and perchlorate ions also contribute to the involvement of btc^{4–} in 1. The steric demand copper(II) macrocycle L1 causes the COO groups of btc^{4–} to tilt from the phenyl ring, allowing the favorable environments of COO groups to act as hydrogen bond acceptors.

EXPERIMENTAL

Materials and Measurements

All chemicals were commercially available from Aldrich and were used without further purification. Water was distilled before use for all procedures. IR spectra were recorded on a JASCO FT-IR-4000 spectrophotometer with Nujol mull (KBr discs) in the 4000-400 cm⁻¹. Electronic spectrum using sample diluted with DMF was recorded with a Shimadzu UV-2600 recording spectrophotometer. Elemental analyses were performed on a VarioMICRO analyzer. The free ligand L1 and precursor complex [Cu(L1)](ClO₄)₂ were prepared according to the literature methods.¹³ Caution! The perchlorate salts are potentially explosive and should be handled in small quantities.

Synthesis of $[Cu(L1)(H_2O)_2][Cu_2(L1)_2(\mu-btc)]$ (1)

The complex $[Cu(L1)(H_2O)_2][Cu_2(L1)_2(\mu-btc)]$ (1) was prepared by adding an aqueous solution of 1,2,4,5-btc (102 mg, 0.4 mmol) and 1 mL of triethylamine to a mixture of DMF and acetonitrile (30 mL, 1:1 v/v) solution of $[Cu(L1)](ClO_4)_2$ (240 mg, 0.4 mmol). The mixture was left at ambient conditions in an open beaker. Violet crystals of 1 were obtained in a week. Suitable crystals for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under a microscope. Anal. Calc.

Table 1. Crystal data and structure refinement for 1

	1
Empirical formula	$C_{72.91}H_{142.36}Cl_2Cu_3N_{13.45}O_{24}$
Formula weight	1853.09
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	9.3618 (8)
<i>b</i> (Å)	13.8049 (11)
<i>c</i> (Å)	17.9693 (15)
α (°)	68.000 (2)
β(°)	78.583 (2)
γ (°)	86.534 (2)
V (Å ³)	2110.4 (3)
Z	1
D _{calcd} (Mg/m ³)	1.458
Absorption coefficient (mm ⁻¹)	0.894
Independent reflections	9762 [R(int) = 0.0336]
Goodness-of-fit on F ²	1.049
Final R indices $[I \ge 2\sigma(I)]$	R ₁ =0.0355, <i>w</i> R ₂ =0.0846
R indices (all data)	R_1 =0.0476, wR_2 =0.0933

for C_{72.91}H_{142.36}Cl₂Cu₃N_{13.45}O₂₄: C, 47.25; H, 7.69; N, 10.17. Found C, 47.11; H, 7.66; N, 9.95%. IR [Nujol, cm⁻¹]: 3460 (vOH), 3245, 3156 (vNH), 1561 (v_{as}COO), 1411 (v_sCOO), 1076 (v_{as}Cl-O), 625 (δ O-Cl-O). UV/Vis [DMF; λ_{max} /nm (ϵ , M⁻¹ cm⁻¹)]: 555 (140).

X-ray Crystallography

Crystallographic data for 1 are summarized in *Table* 1. Bruker APEX2 X-ray diffractometer with Mo-K_{α} radiation ($\lambda = 0.71073$ Å) was used for data collection. To collect sufficient data, a combination of ϕ and ω scans with κ offsets were used. The data frames were integrated and scaled using the Denzo-SMN package.²⁹ The structure was solved and refined, using the SHELXTL\PC V6.1 package.³⁰ Refinement was performed by full-matrix least squares on F^2 , using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

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Supplementary Materials. CCDC No. 1895324 (1) contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/data_request/cif. Versatile modes of btc, Structure of complex cation $[Cu(L1)(H_2O)_2]^{2+}$, IR and Visible spectra, CIF file for 1 (*Scheme* S1, *Figs.* S1-S3, *Table* S1).

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