

Macrocyclic Copper(II) Complex with Unusual Involvement of btc^{4-} ($\text{btc} = 1,2,4,5\text{-Benzenetetra-carboxylate Ion}$) Ligand

Taeyeong Kim and Ju Chang Kim*

Department of Chemistry, Pukyong National University, Busan 48513, Korea. *E-mail: kimjc@pknu.ac.kr
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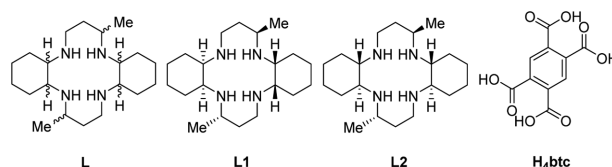
Aromatic polycarboxylate ligands in cooperation with transition metal complexes have been widely used as building blocks for the construction of coordination polymers and supramolecules.^{1–10} Among various aromatic polycarboxylates, 1,2,4,5-benzenetetra-carboxylate (btc) as bridging ligand is of special interest due to its following unique structural features.^{11,12} The COOH groups in H_4btc 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 polycarboxylate 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 $[\text{Cu}(\text{L1})](\text{ClO}_4)_2$ with H_4btc in basic condition to get insight into the copper(II) chemistry of **L1** with axial ligand btc , and obtained a copper(II) dimer $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2][\text{Cu}_2(\text{L1})_2(\mu\text{-btc}^{4-})] \cdot 2\text{ClO}_4 \cdot 1.454\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$ (**1**) in which the btc^{4-} 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 $[\text{Cu}(\text{L1})](\text{ClO}_4)_2$ and H_4btc in $\text{DMF}/\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{N}(\text{CH}_2\text{CH}_3)_3$. The complex **1** is composed of macrocyclic copper(II) cation $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2]^{2+}$, complex anion $[\text{Cu}_2(\text{L1})_2(\mu\text{-btc}^{4-})]^{2-}$, 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 $\text{Cu}-\text{O}$ distances ($\text{Cu}2-\text{O}1\text{W}$, 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 btc^{4-} ligand in **1**. The anionic part of **1** exhibits a macrocyclic copper(II) dimer bridged by btc^{4-} 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 $[\text{Cu}_2(\text{L1})_2(\mu\text{-btc}^{4-})]^{2-}$ of **1** shows a five-coordinate square pyramid with four $\text{Cu}-\text{N}$ and one $\text{Cu}-\text{O}$ bonds. The $\text{Cu}-\text{N}$ 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 H_4btc .

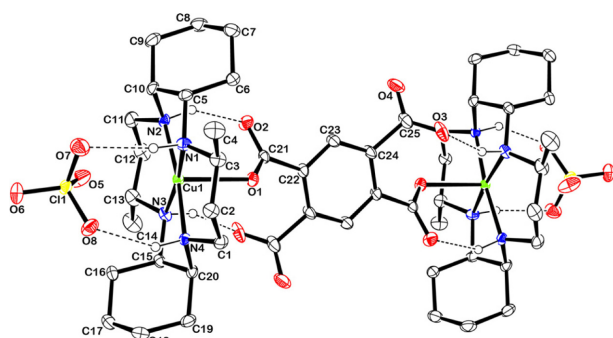


Figure 1. Structure of $[\text{Cu}_2(\text{L1})_2(\mu\text{-btc}^{4-})]^{2-}$ anion with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Cu1-N1, 2.0613(17); Cu1-N2, 2.0213(16); Cu1-N3, 2.0479(17); Cu1-N4, 2.0105(16); Cu1-O1, 2.3742(14); 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 $-x+1, -y+2, -z$.

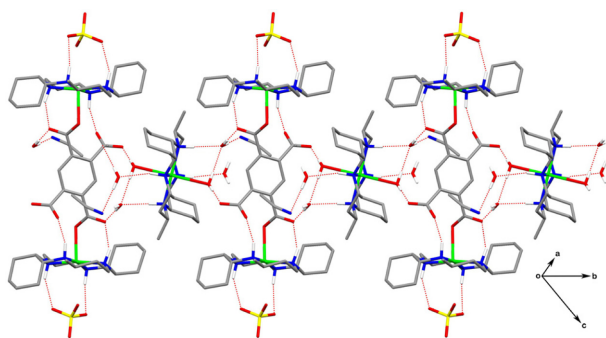


Figure 2. View of 1D supramolecule formed with hydrogen bonding interactions between $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2]^{2+}$ cation and $[\text{Cu}_2(\text{L1})_2(\mu\text{-btc}^{4-})]^{2-}$ anion.

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/formate copper(II) macrocycles ($[\text{Cu}(\text{L2})(\text{H}_2\text{btc}^{2-})]$; Cu-O = 2.2539(13) Å,²² $[\text{Cu}(\text{L2})(\text{O}_2\text{CH})\cdot\text{H}_2\text{O}]$; 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 btc^{4-} bridging ligand. Although there have been many reports on the transition metal macrocyclic complexes with btc moieties, the btc^{4-} 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 btc^{4-} ligand in the macrocyclic copper(II)

complex. Versatile modes of btc moieties such as H_4btc , H_3btc^- , $\text{H}_2\text{btc}^{2-}$, Hbtc^{3-} , and btc^{4-} could be theoretically possible depending on the degree of deprotonation. However, the dianion $\text{H}_2\text{btc}^{2-}$ is the most commonly observed in the macrocyclic btc complexes.^{15,22,26,27} The participation of H_3btc^- and H_4btc has also been reported.^{12,26} But we have never had the chance to meet the Hbtc^{3-} and btc^{4-} moieties in the macrocyclic btc complexes. The difficulty of obtaining the highly deprotonated Hbtc^{3-} and btc^{4-} 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 $\text{H}_2\text{btc}^{2-}$ anion, respectively.⁴ In the complex anion $[\text{Cu}_2(\text{L1})_2(\mu\text{-btc}^{4-})]^{2-}$ 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 btc^{4-} 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 btc^{4-} 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), ∠(DHA) = 148.9°; D-H...A = N3-H3N...O3#1: d(H...A) = 1.95, d(D...A) = 2.909(3), ∠(DHA) = 159.5°; 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), ∠(DHA) = 164.6°; D-H...A = N4-H4N...O8: d(H...A) = 2.23, d(D...A) = 3.147(2), ∠(DHA) = 151.8°} (Fig. 1, Table S1). Perchlorate ions are crucial for the presence of btc^{4-} ligands, where they play a role in balancing the charge of the whole molecule **1**. The $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2]^{2+}$ cation also assists the engagement of btc^{4-} in **1** through intermolecular hydrogen bonding interactions between the COO group of btc^{4-} and the aqua ligand of $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2]^{2+}$ {D-H...A = O1W-H1WA...O4: d(H...A) = 2.07, d(D...A) = 2.908(6), ∠(DHA) = 179.2°, Fig. 1, Fig. 3, Table S1}.

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

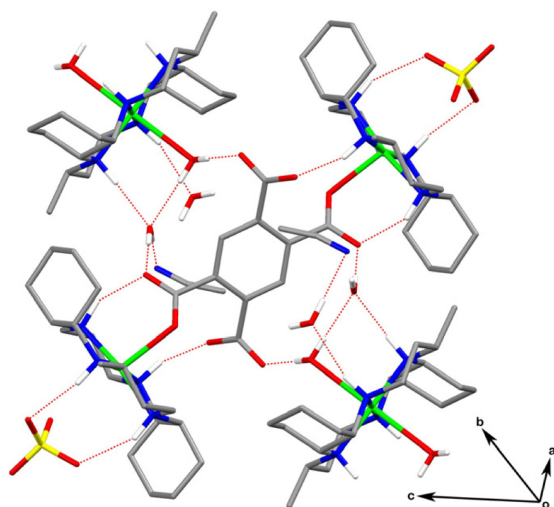


Figure 3. View of hydrogen bonding interactions between $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2]^{2+}$ cation and $[\text{Cu}_2(\text{L1})_2(\mu\text{-btc})]^{2-}$ anion.

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} (ν_{asCOO}), 1411 cm^{-1} (ν_{sCOO}) are observable due to btc^{4-} ligand. The strong bands at 1076 cm^{-1} ($\nu_{\text{asCl-O}}$) and 625 cm^{-1} ($\delta_{\text{O-Cl-O}}$) 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 bond acceptors. In terms of balancing the charge of **1**, 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 $[\text{Cu}(\text{L1})](\text{ClO}_4)_2$ were prepared according to the literature methods.¹³ Caution! The perchlorate salts are potentially explosive and should be handled in small quantities.

Synthesis of $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2][\text{Cu}_2(\text{L1})_2(\mu\text{-btc})]$ (**1**)

The complex $[\text{Cu}(\text{L1})(\text{H}_2\text{O})_2][\text{Cu}_2(\text{L1})_2(\mu\text{-btc})]$ (**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 $[\text{Cu}(\text{L1})](\text{ClO}_4)_2$ (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	$\text{C}_{72.91}\text{H}_{142.36}\text{Cl}_2\text{Cu}_3\text{N}_{13.45}\text{O}_{24}$
Formula weight	1853.09
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
<i>a</i> (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)
<i>V</i> (Å ³)	2110.4 (3)
<i>Z</i>	1
<i>D</i> _{calc} (Mg/m ³)	1.458
Absorption coefficient (mm ⁻¹)	0.894
Independent reflections	9762 [<i>R</i> (int) = 0.0336]
Goodness-of-fit on <i>F</i> ²	1.049
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0355, <i>wR</i> ₂ = 0.0846
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0476, <i>wR</i> ₂ = 0.0933

for $C_{72.91}H_{142.36}Cl_2Cu_3N_{13.45}O_{24}$: 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 ($\nu_{as}COO$), 1411 (ν_sCOO), 1076 ($\nu_{as}Cl-O$), 625 ($\delta O-Cl-O$). 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 ($\lambda = 0.71073 \text{ \AA}$) 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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