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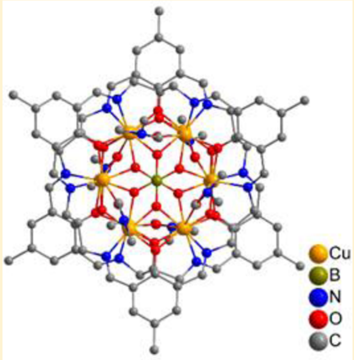
Antiferromagnetically Coupled Dimeric Dodecacopper Supramolecular Architectures of Macrocyclic Ligands with a Symmetrical μ_6-BO_3^{3-} Central Moiety

Santokh S. Tandon,*[†,‡] Scott D. Bunge,[‡] Sara A. Toth,[‡] Joaquin Sanchiz,[§] Laurence K. Thompson,[∥] and Jacob T. Shelley[‡]

[†]Department of Chemistry, Kent State University Salem, 2491 State Route 45 South, Salem, Ohio 44460, United States
[‡]Department of Chemistry, Kent State University, 1175 Risman Drive, Kent, Ohio 44242, United States
[§]Departamento de Química, Facultad de Ciencias, Universidad de La Laguna, 38206 Tenerife, Spain
[∥]Department of Chemistry, Memorial University, St. John's, Newfoundland A1B 3X7, Canada

Supporting Information



ABSTRACT: Reactions between 2,6-diformyl-4-alkyl(R)-phenol (R = CH_3 or $C(CH_3)_3$) and 1,3-diamino-2-hydroxypropane (1,3-DAP) in the presence of copper(II) salts ($Cu(BF_4)_2\cdot6H_2O$, $Cu(ClO_4)_2\cdot6H_2O/H_3BO_3/Ar$) and triethylamine (TEA) in a single pot result in self-assembly of dimeric dodecacopper supramolecular architectures of 30-membered hexatopic macrocyclic ligands (H_6L4 and H_6L5) with unique and fascinating structures having the BO_3^{3-} anion as the central species bonded to all six copper centers in a symmetrical fashion (μ_6-BO_3^{3-}). A number of closely related macrocyclic hexacopper complexes are reported: $\{[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)][BF_4]_2\cdot3C_3H_7NO\}_2$ (**1**) (DMF = C_3H_7NO), $\{[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}C_3H_7NO)_3][ClO_4]_3\cdot3C_3H_7NO\}_2$ (**2**), $\{[Cu_6(L5)(\mu_6\text{-}BO_3)(\mu\text{-}OH)(H_2O)_3(C_3H_7NO)][BF_4]_2\cdot6C_3H_7NO\cdot4C_2H_5OH\cdot2H_2O\}_2$ (**3**), $\{[Cu_6(L5)(\mu_6\text{-}BO_3)(\mu\text{-}CH_3OH)(CH_3OH)_2][ClO_4]_3\cdot10H_2O\}_2$ (**4**), and $\{[Cu_6(L5)(\mu_6\text{-}BO_3)(\mu\text{-}CH_3CO_2)(\mu\text{-}CH_3O)(CH_3OH)][BF_4]\cdot13CH_3OH\cdot8H_2O\}_2$ (**5**). A polymeric side product $\{[Cu_2(H_2L2)(CH_3OH)(BF_4)][BF_4]\}_n$ (**6**), involving a 2 + 2 macrocyclic ligand, was also isolated and structurally characterized. Complex **6** involves dinuclear copper(II) units linked through BF_4^- anions to form a novel 1D single-chain polymeric coordination compound. This appears to be the first report in which a central BO_3^{3-} species is linked to six copper(II) ions held together by a single macrocyclic ligand through three $\mu_{1,1}$-$O(BO_3^{3-})$ and three $\mu_{1,3}$-$O(BO_3^{3-})$ bridges. In complexes **1**–**5** the BO_3^{3-} is present in the center of the macrocyclic cavity and is bonded to all six metal centers arranged in a benzene-like hexagonal array. In the hexagonal array there are alternate double (μ-alkoxide and $\mu_{1,3}$-$O(BO_3^{3-})$) and (μ-phenoxide and $\mu_{1,1}$-$O(BO_3^{3-})$) bridges between the Cu(II) centers. The symmetrical hexa-bridging nature of μ_6-BO_3^{3-} is unprecedented in transition metal complex chemistry, and along with alkoxide and phenoxide bridges in the equatorial plane provides effective pathways for an overall antiferromagnetic exchange interaction between six copper(II) centers. In **1**, **3**, and **5** the BO_3^{3-} moiety is produced in one step (synthetic) by an unusual copper(II)-macrocycle complex catalyzed hydrolysis of BF_4^- ion in methanol. In **2** and **4** the central species (BO_3^{3-}) comes from boric acid (H_3BO_3) which is added to reaction mixture of $Cu(ClO_4)_2/H_6L4/H_6L5$ under inert conditions to confirm the identity of the central species.

INTRODUCTION

Metallo-supramolecular coordination clusters of transition metals have been studied intensely because of their widespread implications in homogeneous catalysis[1−3] and as enzyme models,[4−7] and also because of their potential applications in magnetic materials.[8−12] Multinucleating polytopic macrocyclic ligands provide an opportunity for the organization of groups of metal ions in a regular and controllable fashion, and many novel polymetallic systems have been produced from 2,6-diformyl-4-methylphenol (DFMP), first described by Pilkington and Robson.[13] This versatile building block has produced numerous polynucleating macrocyclic and noncyclic Schiff-base ligands, and a large number of multimetallic transition metal complexes of these multidentate polynucleating ligands have been reported.[13−28] Cyclodehydrative condensation reactions of 2,6-diformyl-4-alkyl(R)-phenol (R = CH_3, DFMP and R = $C(CH_3)_3$, DFTBP) with diamino alcohols are common, and result in mainly (2 + 2) macrocyclic rings (H_4L, H_4L1, H_4L2, and H_4L3, Figure 1) encompassing 1−4 metal centers in the macrocyclic cavity [Ba, Cu_2, Ni_2, Co_2, Zn_2, Mn_2, Pb_2, Ni_4, Zn_4, mixed valence $Co_2^{II}Co_2^{III}$, mixed valence $Mn_2^{II}Mn_2^{III}$, Cu_4, and dimeric $(Cu_4)_2$].[15−21] Robson et.al.[22] reported that, in one unusual case, the reaction of DFMP with 2,6-diaminomethyl-4-

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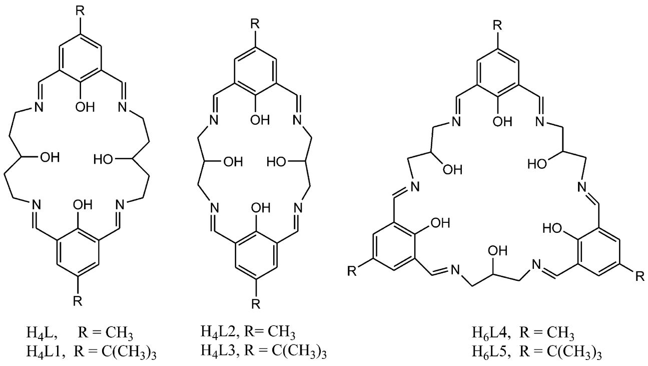


Figure 1. Structures of macrocyclic ligands.

methylphenol in the presence of copper(II) acetate results in the formation of a hexacopper cluster of an expanded (3 + 3) macrocycle with a distorted boat-shape conformation. In our lab a reaction of DFMP and 1,3-diamino-2-hydroxypropane in the presence of copper(II) nitrate and triethylamine led to the formation of a novel hexacopper complex of (3 + 3) macrocycle (H_6L4) in which six copper(II) ions are incorporated within the macrocyclic cavity in an unprecedented "benzene-like" array.[23,24] In this complex three hydroxide (μ-OH) groups are present within the macrocyclic cavity which along with alkoxide (μ-O) oxygens provide alternate μ-O (alkoxide) and μ-O/OH (phenoxide/hydroxide) bridging between three pairs of copper ions. In the overall structure two saucer-shaped Cu_6 rings are joined at the base by weak axial contacts between copper centers to form a dodecanuclear structure. In a recent preliminary communication[25] we described a modification of the earlier template synthesis, which has allowed the insertion of a seventh copper ion into the macrocyclic cavity effectively filling the hole at the center of the hexagonal arrangement of copper ions. In this complex two heptacopper(II) species are linked to form a dimeric structure with the two heptanuclear $(Cu(II)_7)$ halves joined by four μ-1,3-azide bridges. Coordination complexes in which 6 or 7 metal ions are held together within a single macrocyclic ring are very rare.[22−25] Recently, a few reports describe a 3 + 3 condensation of diformyldihroxybenzene with substituted phenylenediamines, and the incorporation of three Zn(II) ions in the macrocyclic ring, with extra-ring coordination of four additional Zn(II) ions in a heptazinc cluster.[29a−c] Hexazinc and dimeric dodecazinc complexes of this macrocyclic ligand have also been reported.[29d] Expanded cyclization to form a closely related 6:6 macrocyclic system indicates six potential ring coordination sites, but no complexes are reported.[30]

In this Article, we describe the synthesis, structural characterizations, and magneto-structural investigations of five dimeric dodecacopper supramolecular metalloclusters **1**−**5** of two 3 + 3 hexatopic macrocyclic (30-membered) ligands (H_6L4 and H_6L5) which have six tridentate (NO_2) preorganized pockets capable of encapsulating six metal centers within the macrocyclic ligand, but in this case a BO_3^{3-} species occupies the central ring cavity, bonded to all six copper centers through three $\mu_{1,1}$-O and three $\mu_{1,3}$-O bridges. This creates a very unusual μ_6-bridging mode of an isolated borate ion in transition metal clusters. The magnetic exchange interactions in **1** are dominated by strong overall antiferromagnetic coupling between the copper(II) centers. A 1D single-chain polymeric copper(II) complex $\{[Cu_2(H_2L2)(CH_3OH)(BF_4)](BF_4)\}_n$ (**6**) of 2 + 2 macrocyclic ligand (H_4L2) composed of dinuclear (Cu_2) units bridged through BF_4^- ions was obtained as a side product along with complex **1**. The overall magnetic exchange interactions within all the complexes (**1**−**6**) are dominated by the strong antiferromagnetic coupling between the copper(II) centers.

■ EXPERIMENTAL SECTION

Physical Measurements. Infrared spectra were recorded as Nujol mulls using a PerkinElmer FT-IR instrument, and UV−vis spectra of the powdered compounds were obtained as Nujol mulls or in DMF solution using a Cary 5E spectrometer. Microanalyses were carried out using a Leco CHNS-Analyzer. Magnetic measurements were performed on the X-ray samples by sealing the crystals immediately after taking them out of the mother liquor under argon to avoid loss of coordinated/lattice solvent molecules. Magnetic susceptibility measurements on polycrystalline samples of **1**−**6** were carried using a Quantum Design SQUID magnetometer. The dc measurements were performed in the temperature range 1.9−300 K at applied magnetic fields of up to 1 T. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants, and experimental susceptibilities were also corrected for the magnetization of the sample holder.

High-Resolution Mass Spectrometry (HRMS) Measurements. High-resolution mass spectra of the reaction products were obtained with an Orbitrap-based mass spectrometer (Exactive Plus, Thermo Scientific, Bremen, Germany) equipped with a heated electrospray ionization (ESI) source (HESI II probe, Thermo Scientific, Bremen, Germany). Crystallized reaction products were dissolved in LC−MS grade (Optima, Fisher Scientific, Pittsburgh, PA) methanol, water, and acetic acid (75:24:1). These solutions were directly infused into the ESI source at a flow rate of 5 μL/min with a syringe pump (Fusion 100T, Chemyx, Inc., Stafford, TX). The ESI source was operated at 4 kV with a sheath gas flow rate of 10 (manufacturers units); the heater on the source was turned off. Mass spectra were recorded in the positive ionization mode with a scan range m/z 150−1800, a mass resolving power setting of 140 000, and an automatic gain control (AGC) target value of 1×10^6 ions. To ensure very high mass accuracy, found to be better than 1 mmu, the instrument was mass calibrated daily and a lock mass of m/z 371.10124, due to polysiloxane, was used throughout. All mass spectral data were collected and processed with the Xcalibur software (ver. 3.0, Thermo Scientific, San Jose, CA).

Materials. 2,6-Diformyl-4-alkyl(R)phenol species were prepared by the reported method,[31] and 1,3-diamino-2-propanol was supplied by Aldrich. All other chemicals used (solvents and metal salts) were analytical or reagent grade and employed without further purification.

Synthesis of complexes. ***Caution!*** *Perchlorate complexes of metal ions involving organic ligands are potentially explosive. Only small quantities of the complexes should be prepared, and these should be handled with care.*

In some of the complexes, there are significant differences between the most reasonable formula based on the elemental analysis (analytical formula), and that obtained from X-ray crystallography (see the Synthesis of the Complexes section). This is due to the recrystallization of these complexes from a mixture of DMF:EtOH/MeOH:$(C_2H_5)_2O$ and ligation of the solvent molecules (DMF, MeOH, EtOH, or H_2O) with the metal ions or present in the crystal lattice. Some or all of the solvent molecules are lost when air-dried for analysis, as evidenced by crumbling of the crystals to form powder. The CHN analysis of these complexes was carried out before recrystallization, unless otherwise stated. The formulas used in the text are the ones obtained from the single crystal X-ray diffraction studies.

$\{[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)][BF_4]_2\cdot 3C_3H_7NO\}_2$ (**1**). 2,6-Diformyl-4-methylphenol (DFMP) (0.50 g, 3.0 mmol) dissolved in hot methanol (30 mL) was added to a methanolic solution (30 mL) of $Cu(BF_4)_2\cdot 6H_2O$ (2.1 g, 6.1 mmol) dropwise with constant stirring. The brownish green solution obtained was stirred under reflux for 10 min. A solution of 1,3-diamino-2-hydrohypropane (1,3-DAP) (0.27 g, 3.0 mmol) in 15 mL of methanol was added to the reaction mixture dropwise over a period of 5 min followed by a solution of

triethylamine (TEA, 0.61 g, 6.0 mmol) in 5 mL of methanol. A dark green reaction mixture formed and was stirred under reflux for ca. 40 h. After addition of 30 mL of ethanol, the reaction mixture was further stirred under reflux for 2 h. Some bluish green solid appeared in the dark green solution. The reaction mixture was concentrated to ca. 10 mL and was left at room temperature after adding 10 mL of ethanol. The bluish green solid that separated was filtered off, and washed with ethanol (3 × 5 mL). (Yield: 0.90 g, 62% based on DFMP.) Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of **1** in DMF:EtOH (1:1) mixture. IR spectrum: $\upsilon(H_2O/CH_3OH)$, 3355 cm^{-1}; $\upsilon C{=}N$, 1652 cm^{-1}; υBF_4, 1097, 1045, 1004, 979 cm^{-1}. UV–vis spectrum: 600 and 310 nm. Anal. (air-dried sample) Found (%): C, 30.25; H, 3.10, N, 5.75. Calcd (%) for $Cu_6(C_{36}H_{36}N_6O_6)(BO_3)(BF_4)_3(H_2O)_5$: C, 30.04; H, 3.22; N, 5.84.

$\{[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}C_3H_7NO)_3][ClO_4]_3\cdot 3C_3H_7NO\}_2$ **(2)**. This reaction was carried out in thoroughly degassed solvent and under argon atmosphere. DFMP (0.33 g, 2.0 mmol) dissolved in 30 mL of hot methanol was added to a solution of copper(II) perchlorate hexahydrate $[Cu(ClO_4)_2.6H_2O]$ (1.5 g, 4.0 mmol) in 20 mL of the same solvent dropwise with constant stirring. A light brownish green solution formed, which was stirred under reflux for 10 min, and a solution of boric acid (H_3BO_3) (0.12 g, 2.0 mmol) in 10 mL of methanol was added dropwise with stirring under reflux. The reaction mixture was refluxed further for 10 min, and a solution of 1,3-DAP (0.18 g, 2.0 mmol) dissolved in 15 mL of methanol was added dropwise in ca. 5 min followed by a solution of TEA (0.50 g, 5.0 mmol) in 5 mL of the same solvent. A dark green solution that formed was stirred under reflux for 36 h. The color of solution changed to bluish green, and the reaction mixture was left undisturbed at ambient temperature for 3 days. A bluish green solid that separated was filtered off and washed with methanol (3 × 3 mL). Crystals suitable for X-ray study were obtained by slow diffusion of diethyl ether into a solution of **2** in DMF:MeOH (1:1) mixture strictly under argon in a drybox. IR spectrum: $\upsilon(H_2O)$, 3540, 3339 cm^{-1}; $\upsilon C{=}N$, 1652 cm^{-1}; υClO_4, 1097, 1067, 1044 cm^{-1}. UV–vis spectrum: 595 and 308 nm. (Yield: 0.66 g, 61% based on DFMP.) Anal. (air-dried sample, before recrystallization) Found (%): C, 26.50; H, 3.39; N, 5.72. Calcd (%) for $Cu_6(C_{36}H_{36}N_6O_6)(BO_3)(ClO_4)_3(H_2O)_{12}$: C, 26.97; H, 3.77; N, 5.24.

Preparative details for complexes **3**–**5** are available as Supporting Information

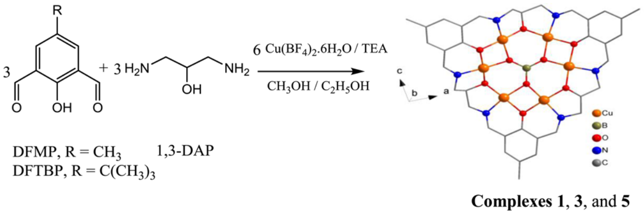
$\{[Cu_2(H_2L2)(CH_3OH)(BF_4)](BF_4)\}_n$ **(6)**. In order to explore the possibility of the formation of 4 + 4 or 2 + 2 macrocycle along with 3 + 3 macrocycle in the reactions reported in the present paper, we planned to investigate the filtrate after the separation of complex **1** in more detail. A solution of $Cu(BF_4)_2\cdot 6H_2O$ (0.10 g, 0.30 mmol) in 5 mL of methanol was added dropwise to the filtrate after the separation of complex **1**. The reaction mixture was stirred at ambient temperature for 10 min and filtered. The filtrate was left undisturbed at room temperature. After 1 week dark green crystals suitable for X-ray study formed, were filtered off, and were washed with ethanol (2 × 2 mL). IR spectrum: $\upsilon(CH_3OH)$, 3526 cm^{-1}; $\upsilon C{=}N$, 1636 cm^{-1}; υBF_4, 1096, 1046, 973 cm^{-1}. (Yield: 0.025 g, 3% based on DFMP.) Anal. (air-dried sample) Found (%): C, 38.42; H, 3.73; N, 7.13. Calcd (%) for $[Cu_2(C_{24}H_{26}N_4O_4)(CH_3OH)(BF_4)](BF_4)0.5H_2O$: C, 38.68; H, 4.03; N, 7.22.

X-ray Crystal Structure Information. X-ray crystallography was performed by mounting a crystal onto a thin glass fiber from a pool of Fluorolube and immediately placing it under a liquid N_2 cooled stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out using APEX2 version 2013.2 software package[32,33] and XSHELL software.[34] The crystallographic data for **1**–**6** complexes are given in Supporting Information Table S1.

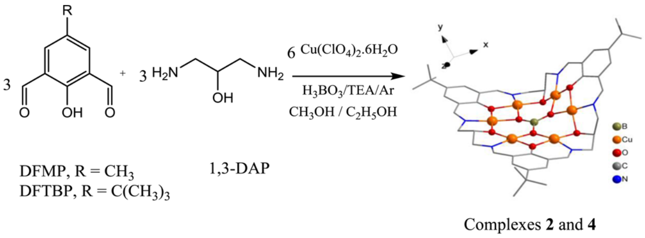
RESULTS AND DISCUSSION

Synthesis of the Complexes. All complexes reported in this Article are prepared in a single pot by reacting 2,6-diformyl-4-alkyl(R)phenol (R = CH_3, DFMP; R = $C(CH_3)_3$, DFTBP) with 1,3-diamino-2-hydroxy propane (1,3-DAP) in the presence of copper(II) salts ($Cu(BF_4)_2$ and $Cu(ClO_4)_2/H_3BO_3$/Ar) and triethylamine (TEA) under slightly varied conditions. In each case self-assembly results in the formation of dimeric dodecacopper supramolecular assemblies (**1**–**5**) of 3 + 3 macrocyclic ligands (H_6L4 and H_6L5) and 1D single-chain polymeric complex **6** as a side product in **1**. Cyclodehydrative condensation (3 + 3) between DFMP/DFTBP and 1,3-DAP in the presence of $Cu(BF_4)_2{\cdot}6H_2O$ and triethylamine (TEA) results in the formation of dimeric dodecacopper assemblies (**1**, **3**, and **5**) of hexatopic macrocyclic ligands (H_6L4 and H_6L5) which encapsulate 6 metal centers in the macrocyclic cavity (Scheme 1). In each hexacopper unit six copper(II) ions are arranged in a benzene-like hexagonal array within the macrocyclic ring, and the central hole in the macrocyclic cavity is filled by BO_3^{3-} which is linked to all six copper(II) centers. The BO_3^{3-} moiety present in the center of the macrocyclic cavity is presumably produced by the hexacopper(II) complex assisted hydrolysis of BF_4^- anion. In our opinion this is a very unique reaction and is the first example in which BF_4^- ion is hydrolyzed directly to BO_3^{3-} in a single synthetic step by a copper complex under very mild conditions. A recent report suggests the hydrolysis of BF_4^- to $[BO_2(OH)]^{2-}$ in a polynuclear cobalt cluster.[35] It is not easy to ascertain with certainty the identity of the central species. This could be the CO_3^{2-} ion probably formed from CO_2 present in the atmosphere as reported recently in lanthanide(III) clusters.[36−39] These two species (BO_3^{3-} and CO_3^{2-}) are very similar in dimensions but differ from each other only in their charge. It is extremely difficult to figure out with certainty a charge difference of one unit in huge coordination clusters involving six metal centers, a hexa-anionic macrocyclic ligand, and several other charged species like BF_4^-, CH_3O^-, $CH_3CO_2^-$, OH^-, etc. In order to identify the central species with certainty, we planned to carry out the above reactions in the presence of $Cu(ClO_4)_2{\cdot}6H_2O$ and boric acid (H_3BO_3) in place of $Cu(BF_4)_2{\cdot}6H_2O$ (Scheme 2) in degassed solvents under argon. We were very fortunate to get the desired compounds (**2** and **4**) from these reactions and to get crystals suitable for X-ray study. Complexes **2** and **4** have essentially the same structural cores in the basal plane as present in **1**, **3**, and **5** with BO_3^{3-} filling the central cavity, connected to all six copper(II) ions. These complexes (**2** and **4**) are similar to those produced using $Cu(BF_4)_2$, thus proving the point beyond any doubt that the central species is BO_3^{3-} not CO_3^{2-} and is formed from the

Scheme 1. Reactions between DFMP/DFTBP and 1,3-DAP in the Presence of $Cu(BF_4)_2{\cdot}6H_2O$ Form Hexacopper(II) Complexes 1, 3, and 5 of Macrocyclic Ligands H_6L4 and H_6L5



Scheme 2. Reactions between DFMP/DFTBP and 1,3-DAP in the presence of $Cu(ClO_4)_2{\cdot}6H_2O/H_3BO_3$ under Argon (Ar) Form Hexacopper(II) Complexes 2 ($R = CH_3$) and 4 ($R = C(CH_3)_3$) of Macrocyclic Ligands H_6L4 and H_6L5



copper complex assisted hydrolysis of BF_4^- ions in slightly basic medium.

We believe that under the stated reaction conditions tetrafluoroborate (BF_4^-) ion is activated by coordination to the Cu_6 complex to react with water to form tetrahydroxyborate ions ($B(OH)_4^-$) in a series of steps which exist in equilibrium with boric acid (H_3BO_3) according to the following reactions:

$$BF_4^- + 4H_2O \xrightarrow{[Cu_6L]^{6+}/TEA} B(OH)_4^- + 4HF$$

$$B(OH)_4^- + H^+ \rightleftharpoons H_3BO_3 + H_2O$$

It is well-documented in the literature that the formation of tetrahydroxyborate ion in aqueous solution is responsible for the acidity of boric acid.[40] The identity of the central species as BO_3^{3-} is further corroborated by the fact that when the same reactions were carried out in the absence of BF_4^- ion or H_3BO_3, that is, with $Cu(NO_3)_2$ or $Cu(ClO_4)_2$ under exactly the same reaction conditions, hexacopper(II) complexes $[Cu_6(L4)(\mu_2\text{-}OH)_3]X_3$ (X = NO_3 or ClO_4) with three bridging hydroxide ions (μ_2-OH^-) present within the macrocyclic cavity providing single-atom bridges between three pairs of copper ions with an empty space in the center of macrocyclic cavity (Figure 2) instead of BO_3^{3-} were formed.[22,23] The same reaction [$Cu(NO_3)_2$/DFMP/1,3-DAP/TEA/NaN_3] when carried out in the presence of sodium azide resulted in the formation of a heptacopper(II) complex with the seventh copper filling the central cavity (Figure 3) which dimerized to form tetradecanuclear copper(II) complex $[Cu_7(L4)(\mu_3\text{-}OCH_3)_3(\mu_3\text{-}OH)_2(CH_3OH)_2(NO_3)(H_2O)(N_3)_2]_2(NO_3)_4{\cdot}9H_2O$.[25]

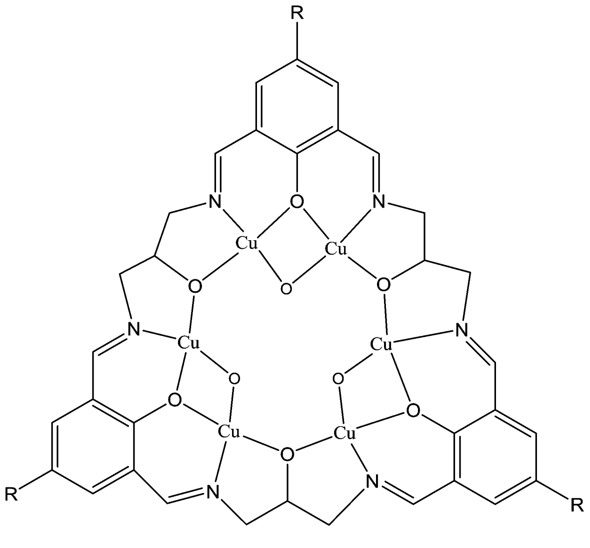


Figure 2. Structural representation of a cationic core $[Cu_6L4(\mu_2\text{-}OH)_3]_2^{6+}$ in hexacopper complexes.

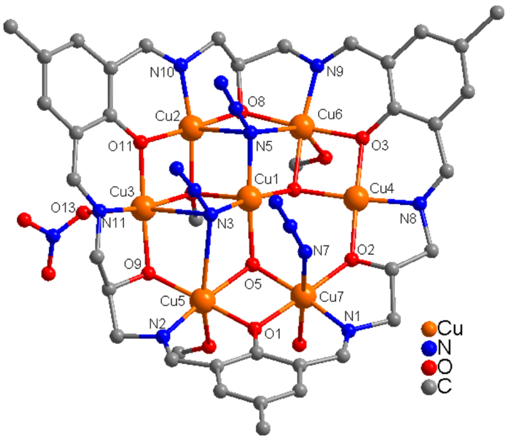


Figure 3. Structural representation of a heptacopper half.

High-resolution/high-accuracy mass spectrometry measurements were used to confirm the identity of the central BO_3^{3-} species in these complexes. The superb mass resolution and accuracy allow elemental composition to be determined with some *a priori* knowledge of elements likely to be found in the compound. The full mass spectrum of complex **2** is shown in Supporting Information Figure S1, and the isotopic pattern of the base peak from the mass spectrum of **2** is shown in Figure 4a. The most likely molecular formula for this species was found to be $[C_{38}H_{39}O_{11}N_6BCu_6]^{2+}$, which would correspond to acetate adducted onto the hexacopper(II) macrocyclic complex cation, $[Cu_6(C_{36}H_{36}N_6O_6)(BO_3)]^{3+}$, in **2**, where the acetate would come from the electrospray solvent conditions. This molecular formula was further confirmed by matching the distinct isotopic pattern of **2** (Figure 4a) with a simulated mass spectrum for the aforementioned ion (Figure 4b). The presence of boron in complex **2** is further confirmed by the presence of the low-mass isotopic peak at m/z 571.42887. This lower mass isotopic peak was observed for every detected species from the macrocyclic complex **2** which has only one boron atom in the central BO_3^{3-} species. Boron has a unique isotopic pattern, compared to other elements that could be in the reaction products, where the most abundant isotope (B-11) is higher in mass; boron-10 has a natural abundance of ~25% compared to that of boron-11. Thus, when boron is present in a molecule, there will be an isotopic feature lower in mass than the nominal mass of the compound, as was the case here. These facts clearly indicate that, in the present complexes (**1**−**5**), the central species is BO_3^{3-} and either is formed by the hydrolysis of BF_4^- (**1**, **3**, and **5**) or comes from the HBO_3 used in the reactions (**2** and **4**).

Polymeric 1D single-chain complex **6** is obtained as a side product by the addition of copper(II) tetrafluoroborate to the filtrate of complex **1**. In complex **6** a one-dimensional single-chain structure results from the bridging of the cationic dinuclear subunits of a 2 + 2 macrocyclic ligand (H_2L2) through BF_4^- anions. This indicates that in these reactions both 2 + 2 (H_4L2) tetratopic and 3 + 3 (H_6L4/H_6L5) hexatopic macrocyclic ligands can be formed and their copper(II) complexes separate out of the reaction mixture due to the difference in their solubilities. The hexacopper complexes have

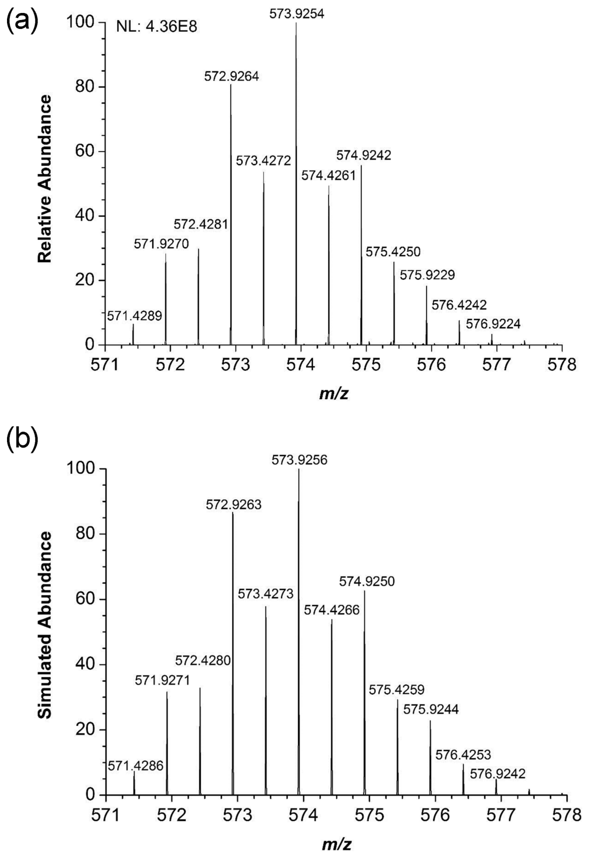


Figure 4. (a) High-resolution mass spectrum of complex **2**. (b) Simulated mass spectrum for $[C_{38}H_{39}O_{11}N_6BCu_6]^{2+}$ ion present in **2**.

less solubility than the dicopper complexes and come out of the reaction mixture first followed by the dicopper complexes. We have already seen that the reactions between DFMP/DFTBP and 1,3-DAP in the presence of metal salts (Cu(II), Co(II), Ni(II), Pb(II), and Zn(II) salts) in the absence of TEA always result in the formation of only dinuclear complexes of 2 + 2 macrocyclic ligands (H_4L2 and H_4L3),[17,18] whereas the reactions in the presence of TEA produce hexanuclear complexes[23,24] (Cu(II) and Ni(II)) and a heptanuclear complex[25] of 3 + 3 macrocyclic ligands depending upon the metal salts and the reaction conditions.

Description of Structures. In compounds **1**−**5** the basic structural core $[Cu_6(\mu_6\text{-}BO_3)L^{6-}]^{3-}$ (Figure 5) is the same, but the molecular formulas and the structures are significantly different due to the presence of different axial ligands [anionic species (CH_3O^-, $CH_3CO_2^-$, BF_4^-, ClO_4^-) and molecular species (H_2O, C_3H_7NO, CH_3OH)]. In these complexes, DMF solvent, due to its moderate coordination ability, seems to play an important role in crystal formation and gives crystals suitable for X-ray diffraction studies. The structural details of complexes **1** and **2** are discussed in detail, while the structures of complexes **3**−**5** are included in the Supporting Information.

*$\{[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)][BF_4]_2\cdot 3C_3H_7NO\}_2$ (**1**).* The basic structural core $[Cu_6(\mu_6\text{-}BO_3)L^{6-}]^{3-}$ (Figure 5) in **1**−**5**, which comprises six copper(II) ions, a 30-membered hexa-anionic hexatopic macrocyclic ligand [$L4^{6-}$ (**1** and **2**) or $L5^{6-}$ (**3**, **4**, and **5**)], and a central BO_3^{3-} ion, is present in all hexacopper complexes which dimerize to form dodecacopper assemblies (**1**−**5**). Compounds **1** and **3** crystallize in the monoclinic space group $C2/c$, and **2** crystallizes in the hexagonal space group $R\overline{3}$, whereas **4** and **5** crystallize in the monoclinic crystal systems and space group $P2_1/c$. The overall molecular structures of these complexes and the stereochemistries at the copper centers have significant differences due to different numbers and different modes of coordination of the anionic species (CH_3O^-, ClO_4^-, BF_4^-, $CH_3CO_2^-$) and the solvent (H_2O, C_3H_7NO, CH_3OH) molecules. The macrocyclic ring encapsulates six metal centers in its cavity which are arranged in a distorted hexagonal ring. The BO_3^{3-} species is present in the center of the macrocyclic cavity and is bonded to all six copper(II) centers through two sets of alternating bridges: three one-atom $\mu_{1,1}$-O(BO_3^{3-}) and three three-atom $\mu_{1,3}$-O(BO_3^{3-}) bridges. In all these complexes H_6L4 and H_6L5 act as hexanucleating, hexatopic [NO_2 pockets], hexa-anionic, dodecadentate ligands utilizing their full potential which is a rare feature in itself. The crystallographic details of **1**−**6** are listed in Table S1 in Supporting Information. Crystals suitable for X-ray studies were obtained either directly from the reaction mixture or by recrystallization from DMF:MeOH:EtOH(ether).

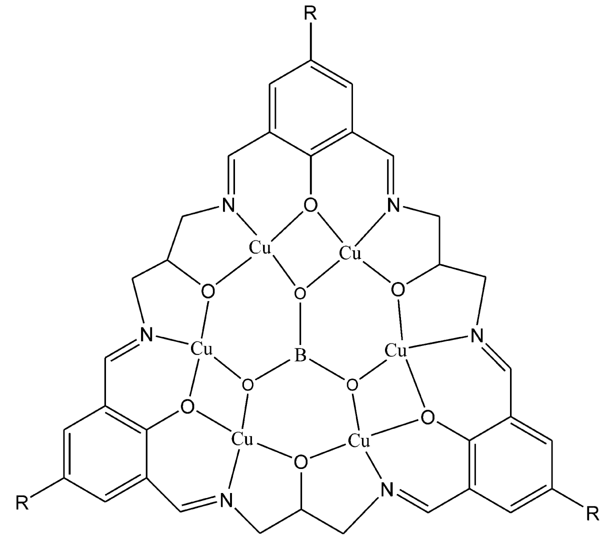


Figure 5. Basic hexacopper structural core present in **1**−**5** with central μ_6-BO_3^{3-} species bonded to all six copper centers.

The overall molecular structure of $\{[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)][BF_4]_2\cdot 3C_3H_7NO\}_2$ (**1**) consists of two hexanuclear halves joined by two axial μ_3-O(3)(μ_6-BO_3^{3-})−Cu(3) bridges. The structure of a hexanuclear half $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)]^{2+}$ is illustrated in Figure 6, and dimeric structure is shown in Figure 7a,b, respectively. The bond distances and angles relevant to the copper coordination spheres in **1** are given in Supporting Information Table S2. The structure of **1** consists of a Cu_6 unit with a distorted hexagonal arrangement of the six copper(II) centers, bridged alternately by (μ-phenoxide and $\mu_{1,1}$-O-(BO_3^{3-})) and (μ-O(alkoxide) and $\mu_{1,3}$-O(BO_3^{3-})) pairs, with the remarkable incorporation of a BO_3^{3-} ion at the center of the Cu_6 hexagon bonded to all six metal centers. Cu(1), Cu(2), Cu(4), and Cu(5) are square pyramidal, with long axial contacts (2.418−2.543 Å to DMF, BF_4^-, DMF, and μ-H_2O, respectively). Cu(3) and Cu(6) can also be described as square pyramidal with relatively longer axial (2.8542(47) and 2.634 Å)) contacts with O(3)(BO_3^{3-}) of neighboring hexacopper units and μ-H_2O, respectively. The Cu(1), Cu(6); Cu(2), Cu(3); and Cu(4), Cu(5) copper pairs, which are bridged by

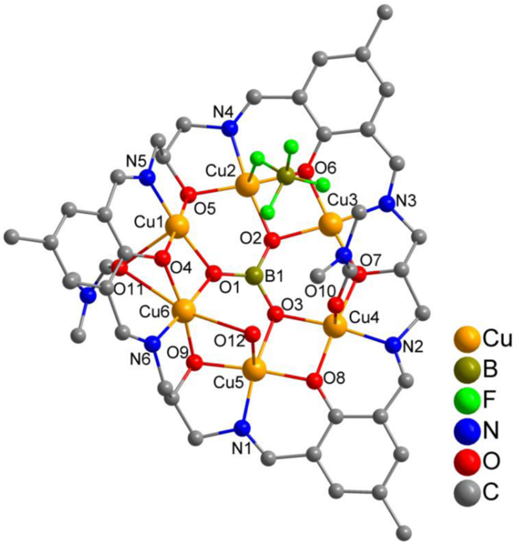


Figure 6. Structural view of $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)]^{2+}$ cation (**1**) (hydrogen atoms are omitted for clarity).

single-atom [μ-O(phenol) and $\mu_{1,1}$-O(borate)] bridges, involve much shorter Cu···Cu distances (2.801−2.946 Å) than those bridged by a single [μ-O(alkoxide)] and a triatomic [$\mu_{1,3}$-O(borate)] bridges (Cu···Cu = 3.155−3.399 Å). The Cu(1)···Cu(2) and Cu(5)···Cu(6) distances (3.155 and 3.028 Å) are relatively much shorter than the Cu(3)···Cu(4) distance (3.399 Å as a result of the bend in the macrocyclic ring falling roughly on the O(5)−O(1)−O(9) axis). O(12) of the water molecule (μ-H_2O) provides an asymmetric axial bridge between Cu(5), Cu(6) pair. These bridging patterns between copper centers differ markedly from those already reported in hexacopper complexes[23,24] or a heptacopper complex[25] with these macrocyclic ligands. The phenolic and alkoxide bridges generate six- and five-membered chelate rings, respectively, whereas the borate bridges [$\mu_{1,1}$-O(BO_3^{3-}) and $\mu_{1,3}$-O(BO_3^{3-})] generate alternating four- and six-membered chelate rings, respectively. This gives rise to a unique bridging pattern in which the BO_3^{3-} ion provides three single-atom bridges ($\mu_{1,1}$-O) between three pairs of copper(II) ions and three three-atom ($\mu_{1,3}$-O_2) bridges between three other pairs of metal centers, thus acting as hexatopic species (μ_6-BO_3^{3-}). To the best of our knowledge this feature has never been reported previously in transition metal complexes.

The alternating 6,6,5,5 chelate ring arrangement in the outer part of the macrocycle would be expected to create a fairly flat hexagonal ring of copper centers as observed previously in hexacopper complexes.[23,24] However, in **1**, two-thirds of the macrocyclic ring, holding four copper centers, is flat with a slight deviation (0.0446 Å) from the mean plane, whereas one-third of the ring, holding two copper centers, is bent upward, thus causing significant distortion of the macrocyclic ring. This appears to be the result of the incorporation of the borate ion, and suggests that the μ_6-BO_3^{3-} ion is slightly smaller than the macrocyclic cavity. The bending may also be attributed partly to the bridging water molecule (μ-O(12)). Furthermore, this O(12) is hydrogen bonded to O(10) with a distance of 2.80 Å, typical for hydrogen bonding. This hydrogen bonding may further stabilize the bending of the molecule.

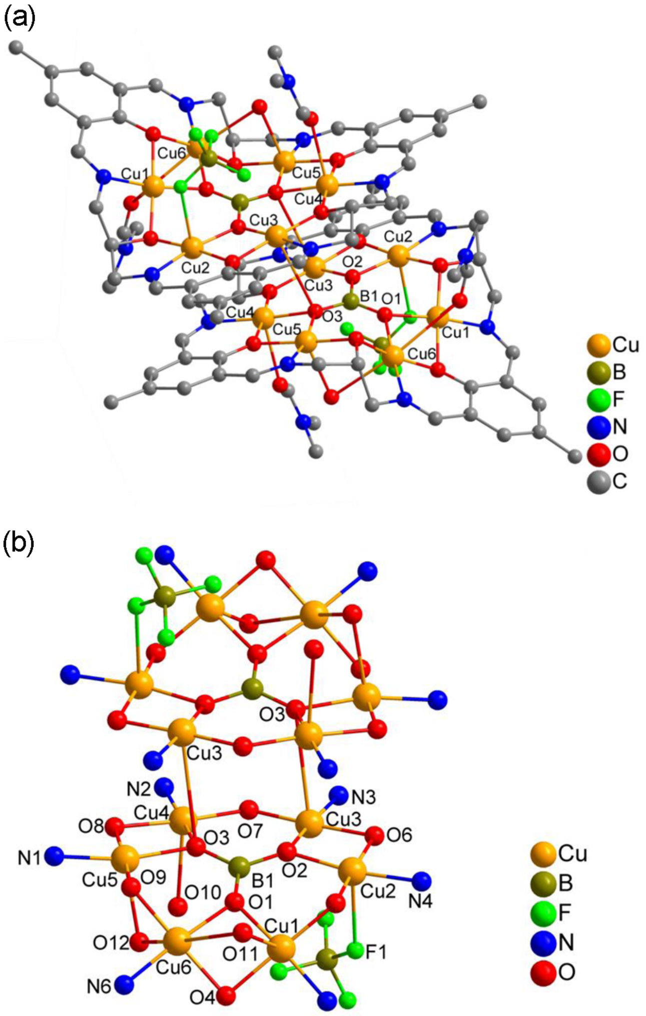


Figure 7. (a) Structural view of dimeric dodecacopper cation $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)]_2^{4+}$ (**1**) (hydrogen atoms are omitted). (b) Structural view of dimeric dodecacopper cation $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)]_2^{4+}$ (**1**) showing only coordinating atoms.

The bond angle sum at copper centers Cu(1) to Cu(6) lies in the range 359.4(3)−360.3(3)°, which is close to the ideal value of 360°, thus indicating a planar arrangement of NO_3 donor set at each metal center. Copper−oxygen (1.878(5)−1.990(5) Å) and copper−nitrogen (1.909(7)−1.957(6) Å) bond distances are quite short, as expected for polymetallic complexes of macrocyclic ligands of this type.[23−25] The sums of the bond angles around the phenoxide bridges (O(4) 339.2(4)°, O(6) 355.6(4)°, O(8) 360.0(4)°) and the alkoxide bridges (O(5) 334.3(4)°, O(7) 358.8(4)°, O(9) 326.8(4)°) indicate that for O(4), O(5), and O(9) there is considerable pyramidal distortion, while the others are close to planar. This is consistent with macrocyclic planarity in two-thirds of the ring and a bend involving the remaining third. The sum of angles at the boron (B(1)) atom (359.9(7)°) of the central species (BO_3^{3-}) is indicative of a planar arrangement around B. The sum of the angles at the borate oxygen atoms [O(1) 355.2(4)°, O(2) 356.2(4)°, and O(3) 357.0(4)°] reveals a slight deviation from planarity at the oxygen atoms. The Cu−O(a1koxide)−Cu bridge angles fall in the range 104.0(3)−129.3(3)°, while Cu−O(phenoxide)−Cu and Cu−O(borate)−Cu bridge angles fall in the ranges 91.3(2)−99.0(2)° and 93.7(2)−97.2(2)°, respectively, suggesting the possibility of fairly strong antiferromagnetic and also ferromagnetic spin-exchange interactions between the copper centers in the hexanuclear unit (*vide infra*).

A view of the dimeric cation $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}H_2O)(C_3H_7NO)_2(BF_4)]_2^{4+}$ (**1**) is illustrated in Figure 7a,b in which two hexacopper macrocyclic rings are coupled together by an axial bridging interaction in which μ_3-O(3) of $\mu_6\text{-}BO_3^{3-}$ not only bridges copper pair Cu(4), Cu(5) within the same ring, but also provides a bridge to copper atom, Cu(3), on the other macrocyclic ring generating a dimeric dodecacopper supramolecular architecture. The molecular symmetry dictates that this interhexacopper bridging also involves the symmetry related atoms, and so the two metallocycle rings are held together by two long axial [O(3)−Cu(3), (2.8542(49) Å] bridges leading to a chair-like conformation for each macrocyclic ring and an overall double inverted chair conformation in which two halves are bridged via the convex surfaces.

$\{[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}C_3H_7NO)_3][ClO_4]_3\cdot 3C_3H_7NO\}_2$ (2). Complex **2** is prepared by reacting DFMP with 1,3-DAP in the presence of $Cu(ClO_4)_2/H_3BO_3$/TEA in degassed solvents under argon atmosphere to confirm the indentity of the central species as $\mu_6\text{-}BO_3^{3-}$. Bluish green crystals of **2** for X-ray structural analysis were obtained by layering a solution of **2** in a mixture of DMF:EtOH (1:1) with diethyl ether in degassed solvents in a drybox under argon. The overall molecular structure of **2** is composed of two hexacopper halves linked together by six (μ_3-O)−Cu intermacrocycle bridges. The structure of the hexacopper monomeric cationic unit is shown in Figure 8, and that of the dimeric dodecacopper metallocluster is depicted in Figure 9a,b. The bond distances and angles relevant to the copper coordination spheres are given in Supporting Information Table S3. Compound **2** crystallizes in the hexagonal space group $R\bar{3}$ and contains a hexanuclear $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}C_3H_7NO)_3]^{3+}$ cationic core with trifold symmetry, a feature that is entirely different from those of all other complexes produced from these macrocyclic ligands. In **2**, three identical symmetry related dicopper units are present in the form of a distorted hexagonal ring inside the macrocyclic cavity which has a boat-like conformation (Figure 8). The coordination pattern of the macrocyclic ligand [hexanucleating, hexa-anionic, dodecadentate (N_6O_6)] and the presence of $\mu_6\text{-}BO_3^{3-}$ as central species in **2** is exactly the same as seen in **1** and other hexanuclear copper(II) complexes (**3**−**5**) of these ligands, clearly indicating that the central species is BO_3^{3-} and that it comes from H_3BO_3. In **2**, the basic structural core (Figure 8) in the equatorial plane is identical to that of **1**. In the axial plane, the three bridging bidentate DMF ($\mu\text{-}C_3H_7NO$) molecules cause trifold bending of the macrocyclic ring. In **2** the macrocyclic cavity is occupied by a symmetrical BO_3^{3-} moiety [O(4)−B(1)−O(4) = 120.01° and B(1)−O(4) = 1.379 Å] which is bonded to all six copper centers through two types of bridges: (1) three one-atom ($\mu_{1,1}$-O(BO_3^{3-})) intradinuclear bridges linking copper(II) ions within three identical dinuclear units and (2) three three-atom ($\mu_{1,3}$-O(BO_3^{3-})) interdinuclear bridges linking copper centers between dinuclear units. In each dinuclear unit the two copper ions are bridged through μ-O (phenoxide) and $\mu_{1,1}$-O(BO_3^{3-}) bridges. The dinuclear units are bridged through three interdimer bridges: an μ-O(alkoxide), a $\mu_{1,3}$-O(BO_3^{3-}), and a $\mu_{1,1}$-O(DMF). The intradimer and interdimer copper−copper distances are 2.920 and 3.060 Å, respectively, which are quite short and comparable to similar distances observed in doubly or triply bridged copper centers in other hexacopper complexes with these ligands.[23−25] The bridging ($\mu_6\text{-}BO_3^{3-}$) pattern of the central species is exactly identical to one observed for **1**. The macrocyclic ring in **2** has a symmetrical boat/shallow bowl-shape conformation which is entirely different from that observed in **1**, **3**, **4**, and **5**.

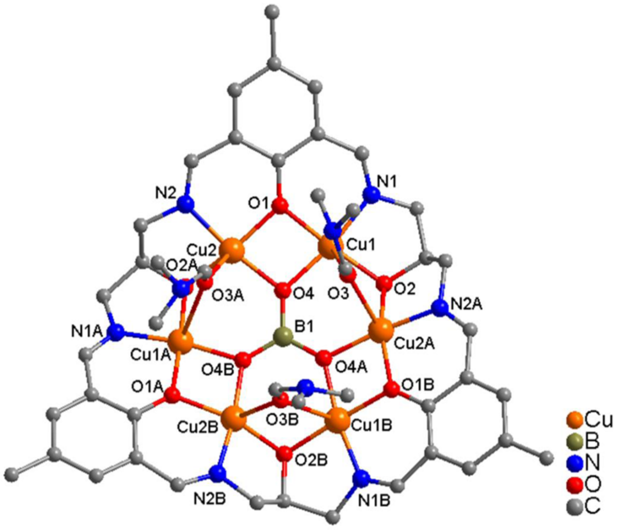


Figure 8. Structural view of hexacopper cation $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}C_3H_7NO)_3]^{3+}$ in **2**.

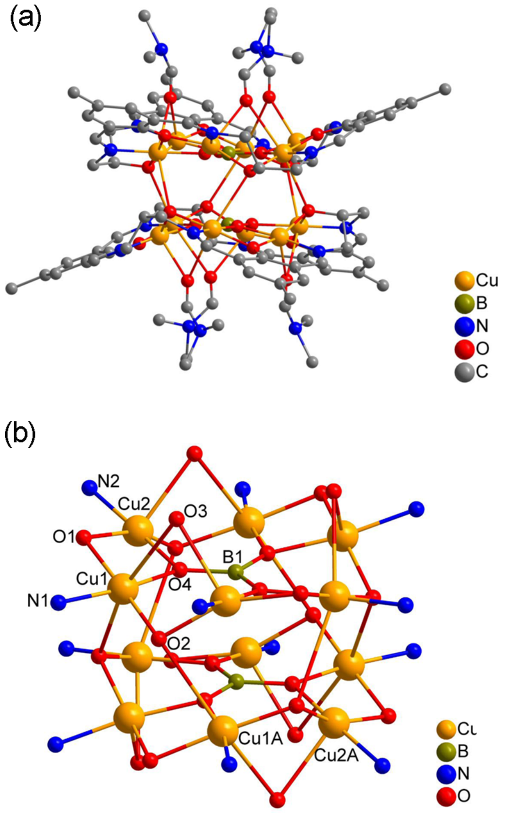


Figure 9. (a) Structural view of dimeric cation $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}C_3H_7NO)_3]_2^{6+}$ in **2** (hydrogen atoms are omitted for clarity). (b) Structural view of dimeric cation $[Cu_6(L4)(\mu_6\text{-}BO_3)(\mu\text{-}C_3H_7NO)_3]_2^{6+}$ in **2** showing only coordinating atoms.

The sums of the angles at copper centers in each dinuclear unit [Cu(1) 360.07° and Cu(2) 360.70°] are very close to the

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idealized value of 360°, indicating a planar arrangement at each copper(II) center in the equatorial plane (NO_3 donor set) with quite short copper−oxygen (1.902(4)−1.948(5) Å) and copper−nitrogen (1.925(6)−1.928(5)Å) distances which are comparable to those reported for other hexacopper complexes in this Article. The sums of the bond angles around the phenoxide bridge (O(1) 358.6(4)°) show a fairly planar arrangement around this bridge for effective magnetic interactions. The sum of the angles around the alkoxide bridge (O(2) 327.7(3)°) shows a pyramidal distortion and indicates much deviation from planarity. The sums of the angles around the oxygen bridge from DMF molecule (O(3) 359.56(4)°) reveal a fairly planar arrangement around this bridge. The sum of angles at the boron (B) atom [359.91(4)°] and at the oxygen atoms [O(4) 358.7(8)°] of the central species (BO_3^{3-}) are indicative of a planar arrangement at the B atom and a fairly planar arrangement at the oxygen atoms. The bridge angles at Cu−O(2)(alkoxide)−Cu [104.0(2)°], Cu−O(1)-(phenoxide)−Cu [97.7(2)°], and Cu−O(4)(borate)−Cu [99.62(19)°] bridges in the equatorial plane suggest anti-ferromagnetic and ferromagnetic spin-exchange interactions between the Cu(II) centers in the hexanuclear unit. The overall geometry at each copper center within the hexacopper unit is slightly distorted square pyramidal with relatively longer axial interactions with the oxygen atom of unsymmetrical bridging DMF molecules (Cu(1)−O(3) = 2.358 Å and Cu(2)−O(3) = 2.651 Å). Three symmetry related alkoxy oxygen atoms (μ_3-O_2) not only bridge three copper pairs [Cu(1), Cu(2)] within the same ring, but also provide longer interhexacopper axial bridges [Cu(1)−O(2)] to copper atoms on the other macrocyclic ring. The molecular symmetry dictates that this intermacrocycle bridging also involves the symmetry related atoms, and so the two metallocycle rings are held together by six long copper−oxygen (3.8542(47) Å) interhexacopper bridges to produce dimeric dodecacopper assembly (Figure 9a,b) in which each copper acquires distorted octahedral geometry. Each hexacopper, macrocycle half is dished slightly in the center, with the appearance of a shallow bowl or boat, and the two halves are bridged via the convex surfaces.

$\{[Cu_6(L5)(\mu_6\text{-}BO_3)(\mu\text{-}OH)(H_2O)_3(C_3H_7NO)][BF_4]_2\cdot 6C_3H_7NO\cdot 4C_2H_5OH\cdot 2H_2O\}_2$ (**3**). The structures of monomeric hexacopper and dimeric dodecacopper complex **3** are similar to that of **1** and are depicted in Supporting Information Figures S2−S4, respectively. The detailed structural discussion is included as Supporting Information. In **3**, two of the three oxygen atoms [μ_3-O(1) and μ_3-O(2)] of the central (μ_6-BO_3^{3-}) species, in addition to providing bridges between copper pair Cu(1), Cu(2) and Cu(3), Cu(4) within the same macrocyclic ring, also provide bridges to Cu(3) and Cu(2) on the other macrocyclic ring, respectively, generating a dimeric complex (Supporting Information Figures S3 and S4) in which two macrocycle rings are held together through convex surfaces as in **1**. The interhexacopper bridging also involves the symmetry related atoms so that the two macrocycle rings are held together by four long axial oxygen−copper interhexacopper [O(1)−Cu(3), 2.8359(3) Å and O(2)−Cu(2), 2.9865(13) Å] bridges leading to distorted octahedral geometry for Cu(2) and Cu(3) in a dimeric complex. This mode of interhexacopper bridging is different from that observed in **1** and **2** where two rings are held together by 2 and 6 axial bridges, respectively. The bond distances and angles for **3** are given in Supporting Information Table S4.

$\{[Cu_6(L5)(\mu_6\text{-}BO_3)(\mu\text{-}CH_3OH)(CH_3OH)_2][ClO_4]_3\cdot 10H_2O\}_2$ (**4**). Complex **4** was prepared using $Cu(ClO_4)_2$/L5/H_3BO_3/Ar like complex **2**. The crystal structure of **4** could not be refined well, but all atoms have been located. The structural detail is included in Supporting Information. This structure is similar to other hexacopper complexes reported in this investigation with BO_3^{3-} in the central cavity (Supporting Information Figure S5) dimerizing to dodecanuclear complex (Supporting Information Figure S6). The formation of **4** further confirms the identity of the central species as BO_3^{3-}. Crystallographic information (Supporting Information Table S1) and bond distances and angles for **4** are given in Supporting Information Table S5.

$\{[Cu_6(L5)(\mu_6\text{-}BO_3)(\mu\text{-}CH_3CO_2)(\mu\text{-}CH_3O)(CH_3OH)]BF_4\cdot 13CH_3OH\cdot 8H_2O\}_2$ (**5**). The molecular structures of hexacopper monomer and dimeric dodecacopper complex **5** are shown in Supporting Information Figures S7−S9, respectively. The bond distances and angles relevant to the copper coordination spheres are given in Supporting Information Table S6. In **5**, the coordination mode, the bridging pattern of the macrocyclic ligand in the basal plane, and the presence of a central μ_6-BO_3^{3-} species bonded to all six copper centers providing three alternating one-atom ($\mu_{1,1}$-O(BO_3^{3-})) and three three-atom ($\mu_{1,3}$-O(BO_3^{3-})) bridges is the same (Supporting Information Figure S7) as those present in other similar complexes (**1**−**4**) reported in this Article. The detailed structural discussion of **5** is included as Supporting Information. In **5**, one of the three oxygen atoms (μ_3-O(12)) of the central μ_6-BO_3^{3-} ion, in addition to bridging a copper pair (Cu(3), Cu(4)) within the same hexacopper monomer, provides a longer axial intermacrocycle bridge to Cu(2) on the other macrocyclic ring generating a dimeric cluster (Supporting Information Figures S8 and S9) in which two hexacopper rings are coupled from convex surfaces. As in **1**, the molecular symmetry dictates that this interhexacopper bridging also involves the symmetry related atoms, and so the two rings are linked together by two axial [O(12)−Cu(2) (2.8107(47) Å] bridges, thus leading to a chair-like conformation for each macrocyclic ring and a double inverted chair-like conformation for the dimeric cluster.

In hexacopper complexes (**1**−**5**) the interatomic B−O distances (1.36−1.39 Å) are significantly longer than C−O distances (1.24−1.34 Å) reported by Kruger et al.[41] in dinuclear and hexanuclear copper(II) complexes involving bridging carbonate groups (μ-CO_3^{2-}), which further supports the assignment of the central species as BO_3^{3-}. Also, the process of structural refinement replacing BO_3^{3-} with CO_3^{2-} resulted in a poor data set with higher *R* values suggesting that the Cu_6-complex with BO_3^{3-} is more stable and the central species is BO_3^{3-}.

$\{[Cu_2(H_2L2)(CH_3OH)(BF_4)](BF_4)\}_n$ (**6**). The single crystal X-ray diffraction study shows that the structure of **6** consists of a 1D single chain resulting from the bridging of the dinuclear cationic units $[Cu_2(H_2M2)(CH_3OH)(BF_4)]^+$ through BF_4^- anions. The molecular structure of slightly asymmetric complex **6** is shown in Figure 10, and the relevant bond distances and angles are listed in Supporting Information Table S7. In complex **6**, H_4L2, potentially an octadentate (N_4O_4) tetra-anionic tetranucleating macrocycle, acts as hexadentate (N_4O_2) dianionic, dinucleating ligand (H_2L2^{2-}) binding through four imine nitrogen atoms and two deprotonated phenoxide oxygen atoms, thereby bridging two copper(II) ions in close proximity into a dinuclear unit. The secondary alcohol groups remain protonated and are not coordinated within the macrocyclic complex itself and adopt *exo*-ring conformations with the

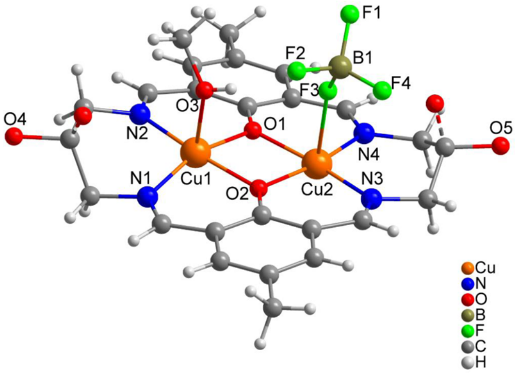

Figure 10. Structural representation of a dinuclear cationic unit $[Cu_2(H_2L2)(CH_3OH)(BF_4)]^+$ (**6**). Dashed line (---) indicates that O(5) is distorted over two positions and treated as half occupancy. (Hydrogen atoms are omitted for clarity.)

oxygen atom disordered over two positions, a feature which has been observed before in comparable complexes.[18] This is probably due to the smaller size (20-membered) of the macrocyclic ring which appears to be too small to accommodate four metal centers contrary to a 24-membered macrocyclic ring which invariably accommodates 4 metal centers within the macrocyclic cavity.[15,16,19,21] In each dinuclear unit two copper(II) ions are bridged through two phenoxide oxygen (μ-O) bridges providing effective pathways for very strong antiferromagnetic magnetic exchange interactions between copper(II) ions.

The stereochemistry at Cu(1) can best be described as slightly distorted square pyramidal with two phenoxide O atoms and two imine N atoms in the equatorial plane and a methanolic O atom in the axial plane. The stereochemistry at Cu(2) is slightly distorted octahedral with two phenoxide O and two imine N atoms in the equatorial plane and two F atoms from terminal and bridging BF_4^- anions in the axial plane. The sum of the angles in the basal plane of Cu(1) and Cu(2) are 359.11(14)° and 360.04(14)°, respectively, indicating planar arrangements around these metal centers. The Cu−N and Cu−O bond distances in the basal plane lie in the ranges 1.939(4)−1.972(4) and 1.958(3)−1.972(3) Å, respectively, typical for similar dinuclear units of macrocyclic ligands.[18,20] The axial Cu(1)−O(3) (methanol) and Cu(2)−F(1) (terminal BF_4^-) distances of 2.291(3) and 2.394(3) Å, respectively, are relatively much longer than equatorial distances. The cationic dinuclear units $[Cu_2(H_2L2)(CH_3OH)(BF_4)]^+$ are linked through a relatively longer Cu(2)−F(3) (bridging BF_4^-) bond, 2.518 Å, to form one-dimensional single chains (Figure 11). In a dinuclear unit the bridge angles at phenoxide oxygen atoms O(1) and O(2) are 103.53(14)° and 103.61(14)°, respectively. The sums of the angles around the phenoxide bridging O atoms, O(1) and O(2), are 358.9(7)° and 359.1(7)°, respectively, and indicate almost planar arrangements at these atoms. The Cu(1)−Cu(2) distance of 3.088 Å in a dinuclear unit is similar to the distance found in other dinuclear and tetranuclear copper, cobalt, nickel, manganese, and zinc complexes with the same and similar ligands.[15−20] The copper atoms (Cu(1) and Cu(2)) have a 0.107 Å mean displacement from the plane of the equatorial N_2O_2 donor set. There is H-bonding interaction between hydrogen atom of protonated uncoordinated alkoxy group on the macrocyclic ligand and the F(3) atom of the bridging tetrafluoroborate (μ-BF_4^-) ion. There are no close connections between the single chains to form 2D or 3D structures. A small portion of a 1D single chain along the *c*-axis is shown in Figure S10 in the Supporting Information.

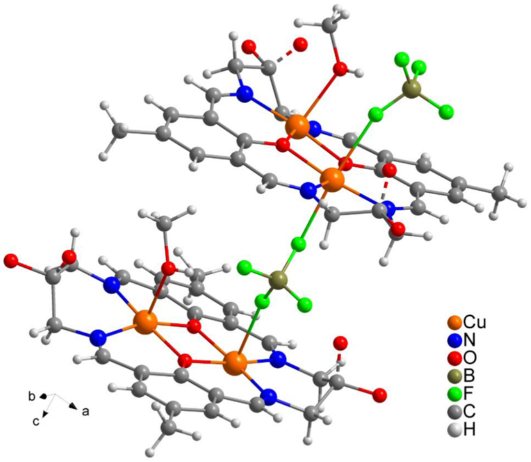

Figure 11. Perspective view of a portion of 1D single-chain of $\{[Cu_2(H_2L2)(CH_3OH)(BF_4)](BF_4)\}_n$ (**6**). (Hydrogen atoms are omitted for clarity.)

Magnetic Properties. The variable temperature magnetic data of complex **1** (2−300 K) (Figure 12) show a profile of molar susceptibility with a shallow maximum at ∼140 K, and a sharp rise at low temperatures. This signals dominant net intramolecular antiferromagnetic exchange. The χT value at 300 K (1.8 $cm^3\ mol^{-1}$ K) is somewhat lower than expected for six noninteracting spin doublets (expected $\chi T = 6(N\beta^2g^2/3k)S(S+1) \approx 2.4\ cm^3\ mol^{-1}\ K$ with $g = 2.1$ and $S = {}^1/_2$) and, on lowering temperature, continuously decreases aproaching to zero at 2 K. All Cu(II) ions can be considered in the framework of six $d_{x^2-y^2}$ spin centers connected by all oxygen bridges, with relatively short Cu−O contacts. However, the borate bridge itself would probably provide too long a pathway for any significant internal exchange via the B atom, and so can effectively be ignored, at least compared with the μ-O(phenol) and $\mu_{1,1}$-O(borate) bridges. Therefore, a realistic approach would include just the direct oxygen bridges.

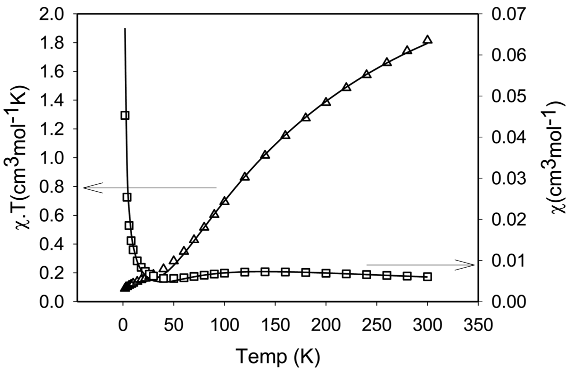

Figure 12. Variable temperature magnetic data for **1**.

In an initial attempt to understand the exchange picture, a hexacopper model with one averaged J value was examined (eq 1, $J_1 - J_6 = J$). A satisfactory fit could not be obtained. This is perhaps not surprising due to the wide variation in Cu−O−Cu angles. Refining the model to include six different J values, one for each adjacent copper pair (eq 1), was attempted.

$$\mathbf{H}_{ex} = -J_1(S_1\cdot S_2) - J_2(S_2\cdot S_3) - J_3(S_3\cdot S_4) - J_4(S_4\cdot S_5) - J_5(S_5\cdot S_6) - J_6(S_1\cdot S_6) \quad (1)$$

However, this did not provide a satisfactory solution either, despite revealing a mixture of antiferromagnetic and ferromagnetic connections, expected on the basis of the widely varying Cu−O−Cu bridge angles. Also, it would not provide a statistically meaningful solution because of the large number of variable parameters involved. Given the established correlations for J versus Cu−O−Cu bridge angle for dicopper complexes with Cu $d_{x^2-y^2}$ ground states,[42,43] estimates of J based on averaged Cu−O−Cu angles for single and double bridges were considered as a starting point. This was deemed reasonable on the basis that the major factor controlling exchange would be the Cu−O−Cu angle. The theoretically predicted J_1−J_6 values were thus included in the input file used in the MAGMUN4.1 fitting routine.[44] The variable temperature magnetic data were treated in the normal way, including g, and other variables (*vide infra*) using normal nonlinear regression procedures. A good "pseudofit" was obtained from 2 to 300 K (solid line Figure 12) for $J_1 = -207$ cm^{-1}, $J_2 = -9.5$ cm^{-1}, $J_3 = -424$ cm^{-1}, $J_4 = -19.0$ cm^{-1}, $J_5 = -130$ cm^{-1}, $J_6 = +187$ cm^{-1} ($g = 2.11(1)$, TIP = 310 × 10^{-6} cm^3 mol^{-1}, $\rho = 0.053$, $\theta = -0.8$ K, $10^2R = 2.08$; TIP = temperature independent paramagnetism, ρ = fraction paramagnetic impurity, θ = Weiss parameter); $R = [\sum(\chi_{obs} - \chi_{calc})^2/\sum\chi_{obs}^2]^{1/2}$). The input J values became adjusted slightly as a result of the fit, but ended up being very close to these original estimated input values. The revised J values are in line with the averaged Cu−O−Cu angles (111.4°, 98.2°, 129.3°, 99.0°, 104.0°, 91.3°, respectively), thus providing a reasonable appraisal of the exchange picture. It is notable that $J_6 = +187$ cm^{-1}, consistent with the very small angle, falls well below the point of "accidental orthogonality" for Cu−O−Cu (97.5°).[42,45]

The variable temperature magnetic data for compounds **2**−**5** are very similar, with χT in the range 2.1−2.2 cm^3 mol^{-1} K at 300 K, and dropping steadily to low values approaching zero at 2 K (0.1−0.5 cm^3 mol^{-1} K). The overall profiles are again consistent with the Cu_6 ring arrangements of Cu(II) ions, dominated by antiferromagnetic couplings. Given the serious limitations of dealing with such a complex spin-exchange model (*vide supra*), no further analysis of these data sets was attempted.

IR Spectroscopy. In the IR spectra of hexacopper complexes (**1**−**5**) a very strong sharp band at 1652−1653 cm^{-1} is typical for an imine stretch (υC=N) in 3 + 3 macrocyclic system (30-membered ring) coordinated to metal center.[23−25] This IR stretch can easily be used to differentiate a 3 + 3 macrocyclic ring from a 2 + 2 macrocyclic ring which shows this band at 1628−1640 cm^{-1}.[17,18,20] In the IR spectra of **1**−**5**, one or two broad bands in the region 3350−3596 cm^{-1} are due to υOH stretches of coordinated or uncoordinated H_2O, CH_3OH, or C_2H_5OH molecules. In the IR spectrum of **1** significant splitting of the band due to $\upsilon(BF_4^-)$ (1097, 1045, 1004, 979 cm^{-1}) suggests the presence of low symmetry coordinated along with an uncoordinated BF_4^- ion consistent with the X-ray structure. In the IR spectrum of **2**, the splitting of the band due to $\upsilon(ClO_4^-)$ (1045, 1067, 1082, 1097 cm^{-1}) suggests the presence of low symmetry perchlorate, indicating the presence of coordinated ClO_4^- and uncoordinated ClO_4^- which is not consistent with the X-ray structure which shows only uncoordinated ClO_4^- ions. The splitting can be attributed to H-bonding interaction involving ClO_4^-. In the IR spectra of **3** and **5** an unsplit strong band at 1051 cm^{-1} (**3**) and 1042 cm^{-1} (**5**), respectively, is due to uncoordinated $\upsilon(BF_4^-)$ ions consistent with X-ray structures. In **4** an unsplit strong band at 1098 cm^{-1} due to $\upsilon(ClO_4^-)$ shows the presence of uncoordinated ClO_4^- ions consistent with the X-ray structure. The IR spectrum of **6** shows a very strong sharp band at 1632 cm^{-1} due to coordinated υ(C=N) which is typical for dinuclear complexes of 2 + 2 macrocyclic ligands.[17,18,20] The splitting of the $\upsilon(BF_4)$ band (951, 999, 1060, and 1133 cm^{-1}) is indicative of low symmetry due to an interaction of tetrafluoroborate with Cu(2) at one of the axial position linking dinuclear units forming 1D single chain structure.

UV−Vis Spectroscopy. Electronic spectra of DMF solutions of complexes **1**−**5** exhibit two main bands at 595−600 and 305−310 nm (Figure 13). The broad band at 595−600 nm has been assigned to a d−d transition in copper(II) complexes with square planar or square pyramidal geometries.[20,46−48] The intense band at 305−310 nm is associated with ligand to metal charge transition.

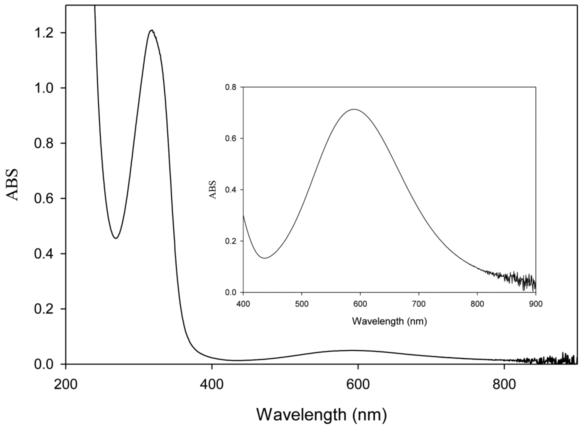

Figure 13. Electronic spectra of complex **1**.

CONCLUSIONS

A single pot self-assembly of dimeric dodecacopper supramolecular architectures of hexatopic, hexa-anionic, dodecadentate macrocyclic ligands (H_6L4 and H_6L5) with a symmetrical central species (μ_6-BO_3^{3-}) bonded to all six copper centers has been reported. A cationic core $[Cu_6(L4/L5)(\mu_6\text{-}BO_3)]^{n+}$ is present in the equatorial plane of these complexes, which differ in their molecular structures due to axial coordination with anionic/molecular species. In these complexes a central species (μ_6-BO_3^{3-}) provides three $\mu_{1,1}$-O and three $\mu_{1,3}$-O bridges to six copper(II) ions which are held together by a single macrocyclic ligand in a unique fashion not previously reported in transition metal complexes. The central species (μ_6-BO_3^{3-}) is produced in a single step by copper−macrocycle complex catalyzed hydrolysis of tetrafluoroborate ion (BF_4^-), which in our opinion constitutes first report. The identity of central species as BO_3^{3-} is established beyond any doubt from high-resolution/high-accuracy mass spectrometry measurements and by isolating complexes **2** and **4** by reacting $Cu(ClO_4)_2$/H_6L4 and H_6L5/HBO_3/TEA/Ar, which have molecular structures similar to **1**, **3**, and **5** obtained using $Cu(BF_4)_2$. In the dimeric assemblies, hexacopper monomeric units are held together by relatively longer two (**1** and **5**), four (**3** and **4**), or six (**2**) axial intermetallocycle (μ_3-Cu−O) bridges from convex surfaces generating dodecacopper complexes. These complexes exhibit overall antiferromagnetic spin-exchange interactions between copper(II) centers within the macrocyclic cavity. A polymeric side product of 2 + 2 macrocyclic ligand (H_4L2) with 1D single-chain structure (**6**) has been isolated and structurally characterized. We are in the process of carrying out similar reactions in the presence of other 3d transition metal ions and lanthanide (4f) metal ions.[49]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray acquisition and analysis, crystallographic details, selected bond distances and angles, details of structures of compounds **3**−**5**, χT vs T plots of compounds **2**−**5**, and synthetic details. X-ray crystallographic files in CIF format for the structures of **1**−**3**, **5**, and **6**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00771. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 892039 (**1**), 904707 (**2**), 956415 (**3**), 956414 (**5**), and 956295 (**6**). Copies of the data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/data_request/cif

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: standon@kent.edu. Fax: 1-330-332-9256. Phone: 1-330-337-4235.

Notes

The authors declare no competing financial interest.

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(44) *MAGMUN4.1*. MAGMUN4.1/OW01.exe is available as a combined package free of charge from the authors (http://www.ucs.mun.ca/~lthomp/magmun). MAGMUN has been developed by Dr. Zhiqiang Xu and OW01.exe by Dr. O. Waldmann. We do not distribute the source codes. The programs may be used only for

scientific purposes, and economic utilization is not allowed. If either routine is used to obtain scientific results, which are published, the origin of the programs should be quoted.

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