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A Perfect Linear Cu–NNN–Cu Unit Inside the Cryptand Cavity and Perchlorate Entrapment within the Channel Formed by the Cascade Complex

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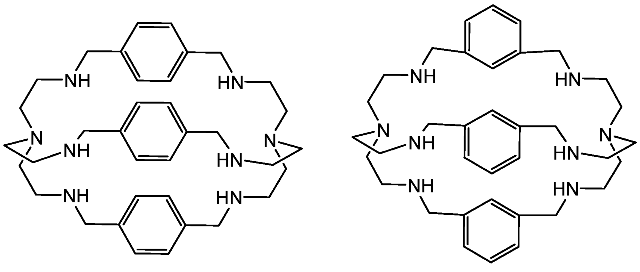
Dicopper complexes of bis-tren cryptand $\mathbf{L_1}$ having 1,4-xylyl spacers, becoming a potential receptor for perfect linear recognition of N$_3^-$, generate a Cu–NNN–Cu unit inside the cryptand cavity. Solid-state packing of this cascade complex shows the formation of a thorough channel which encapsulate perchlorate anion within the channel.

Homo dinuclear metal complexes of azacryptands such as $\mathbf{L_1}$ and $\mathbf{L_2}$ (Chart 1) are suitable receptors for different anionic species.[1−6] This is because of two reasons: Each metal center is coordinated in an N4 environment of a tren subunit in a trigonal bipyramidal geometry leaving an axial site vacant for anion guest coordination or the axial site is coordinated to water molecule which might be replaced by anionic guests. Moreover, these cascade receptors (dinuclear metal complexes) provide an electrostatic field, developing from the pair of positively charged cations for geometrically well-defined coordinate bonds to each donor site from the bridging anion (e.g., NCO$^-$, N$_3^-$). In 1992, Drew et al. prepared a dicopper(II) μ-azido complex of $\mathbf{L_1}$, and its unusual spectroscopic properties were attributed to enforced collinearity of the M−NNN−M assembly.[1] Full structural characterization of the μ-azido cryptate was elusive until 1996 when Harding et al. reported an X-ray structure derived from a poor-quality data set of dicopper(II) μ-azido complexes of $\mathbf{L_2}$ showing a 1,3-briding mode of azide, i.e., the Cu−NNN−Cu unit inside the cryptand cavity having a less-regular environment at the copper centers; the CuNN angles (N represents azide nitrogens) are 166.80° and 162.94°, the CuNCu angle (where N is the center nitrogen atom of azide) is 175.41°, and the NNN angle is 177.29°.[4a] Structural characterization of a dinickel(II) μ-azido complex of $\mathbf{L_2}$ reported also shows deviation from perfect linearity of the M−NNN−M unit.[4b] The dicopper(II) complex of $\mathbf{L_2}$ also encapsulates other anions such as NCO$^-$.[4a] The Br$^-$ encapsulation in a dicopper(II) cryptate containing 2,5-dimethylfuran spacers instead of *m*-xylyl spacers in $\mathbf{L_2}$ has also been determined by X-ray diffraction studies.[6] While most of the researchers' efforts in structural elucidation of cascade complexation have been dedicated to the bis-tren cryptand $\mathbf{L_2}$ which contains rigid 3,5-xylyl spacers,[3−6] much less has been done with $\mathbf{L_1}$, which contains rigid 1,4-xylyl spacers.[2]

Chart 1. Octaamino Cryptand Having 1,4-Xylyl Spacers ($\mathbf{L_1}$) and 3,5-Xylyl Spacers ($\mathbf{L_2}$)



$\mathbf{L_1}$ $\mathbf{L_2}$

Recently, the cyanide-bridged and H$_3$O$_2^-$ -bridged complexes of dinuclear copper(II) cryptate of $\mathbf{L_1}$ have been reported.[2a,7] Herein we report crystallographic evidence of a perfect linear recognition of azide inside the cavity of

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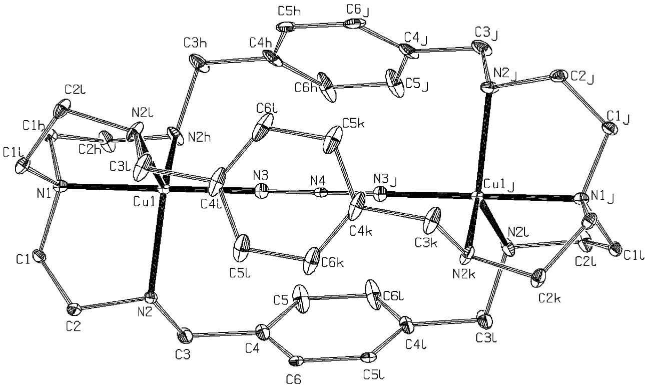

Figure 1. ORTEP diagram depicting the cationic part of the compound with atom-numbering scheme for compound **2**.

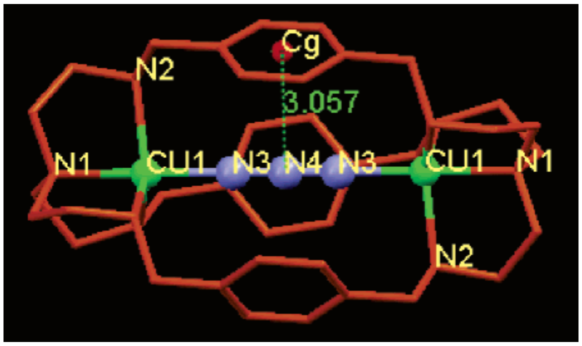

Figure 2. MERCURY diagram depicting the cationic part of the compound showing the Cg···N_4 interaction in compound **2**; Cg represents the centroid of the phenyl moiety.

dinuclear copper(II) cryptates of $\mathbf{L_1}$, and to the best of our knowledge, no structural characterization of a perfect linear M−NNN−M unit has been reported so far.[8] Moreover, this study shows perchlorate encapsulation inside the channel formed by the solid state aggregation of cascade complex.

The macrobicyclic cryptand $\mathbf{L_1}$ and tetraperchlorate salt of the *p*-xylyl-spaced dicopper(II) cryptate $[Cu_2L_1](ClO_4)_4\cdot4H_2O$ (**1**) were synthesized according to the literature procedure.[7,9] When an acetonitrile/water solution of the **1** in presence of sodium azide is allowed to evaporate slowly in air, a dark green crystal suitable for X-ray diffraction study is obtained from the solution.[10] Single-crystal X-ray diffraction revealed these to be $[Cu_2(N_3)\mathbf{L_1}]\cdot(ClO_4)_3$ (**2**) (Figure 1).[11] Compound **2** crystallizes in Trigonal space group $P\bar{3}_1c$ in the dimeric Cu(II) complex with the azide anion bridging co-linearly the copper centers inside the cryptand cavity. The molecule possesses a C_3 symmetry passing through the apical nitrogens N1, central metal ion Cu1, and the azido nitrogens N3 and N4 (Figure 2). In addition to this C_3 symmetry, a C_2 symmetry bisecting the C5−C6 bond of the phenyl ring and the azide nitrogen N4 is also present in the cation. The geometry around both the symmetry-related Cu(II) centers of the dimeric unit can be described as "trigonal bypyrmidal" with a perfect trigonal base provided by the coordination of the secondary amino Nitrogen N2 from symmetry-oriented cryptand arms with a distance Cu1···N = 2.125(4) Å. The angles of the symmetrically coordinated secondary amine from the amino cryptand arms forming the trigonal base is ∠N2−Cu1−N2 = 119.11(3)°. The axial coordination is provided by the apical bridgehead nitrogen N1 from the cryptand and the azido nitrogen N3 in a μ-1,3 bridging mode connecting the metal centers colinearly via the M−NNN−M assembly, creating a dinuclear copper azido cascade complex. The axial coordination distances of the nitrogen atoms N1 and N3 from the cryptand and azide moiety are Cu−N1 = 2.037(6) Å and Cu···N3 = 1.928(6) Å, respectively, indicating a stronger coordination through the azide anions. The trans angle ∠N(3)−Cu(1)−N(1) = 180.0° clearly signifys the perfect triogonal geometry around Cu(II). The 3-fold symmetry of the molecule, in fact favoring a $\pi-\pi$ stacking interaction between the azide and the symmetrically disposed phenyl rings with a distance N4···Cg = 3.057 Å where Cg is the centroid of the phenyl rings (Figure 2). The Cu···Cu separation distance in the azido bridged unit in complex **2** is 6.188 Å, which is slightly higher than dicopper(II) μ-azido complex of $\mathbf{L_2}$ (Cu···Cu = 6.057 Å). This fine-tuning in distance between metal centers in the case of **2** might be responsible for perfect linear recognition of azide bridging between two copper centers having ∠Cu−N−N, ∠Cu−N−Cu, and ∠N−N−N all are 180.0°.

The packing diagram of compound **2** viewed down *c* axis is depicted in Figure 3. Both the perchlorates located from the difference Fourier map have a C_3 symmetry with the Cl2 located at the origin. As discussed earlier, the azide anion being involved in cascade coordination to generate the dinuclear Cu(II) compound with the azacryptand host is noteworthy. However, the screw-related adjacent layers of the cryptand moiety orient themselves creating thorough hexagonal channels down the *c* axis, making themselves available for the encapsulation of the perchlorate counteranion residing at the origin.

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(8) A CSD search (CSD version 5.27, November 2005) was performed for $\mathbf{L_1}$ and $\mathbf{L_2}$. There were 12 hits for $\mathbf{L_1}$ and 36 hits for $\mathbf{L_2}$. There was no structural characterization of a perfect linear M−NNN−M unit reported inside the cryptand cavity.

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(10) The complex of dicopper(II) cryptate of $\mathbf{L_1}$, **1** (0.5 mmol) was dissolved in 25 mL of acetonitrile/water (9:1) binary solvents. In this green solution, 35 mg (~0.5 mmol) of NaN_3 was added, and the solution was stirred at room temperature (RT) for 5 min. The dark green solution was filtered and allowed to sit at RT. After 3−4 days, green crystals suitable for single-crystal X-ray analysis were obtained which were collected by filtration. Yield of the first crop is 35%. Anal. Calcd for $C_{36}H_{54}N_{11}Cu_2Cl_3O_{12}$: C, 40.59; H, 5.11; N, 14.46%. Found: C, 40.42; H, 5.16; N, 14.40%.

(11) X-ray data for **2** is collected using Mo Kα (λ = 0.71073 Å) radiation on a SMART APEX diffractometer equipped with CCD area detector at 100 K. Crystals are selected from the mother liquor and immersed in Partone oil and then mounted. Data collection, data reduction, structure solution/refinement are carried out using the software package of SMART APEX. Graphics are generated using PLATON[11a] and MERCURY 1.3[11b]. All the structures are solved by direct methods and refined in a routine manner. Except the seconodary amine hydrogen all the other hydrogen atoms of the ligand moiety are stereochemically fixed. Crystal data for **2**: $C_{12}H_{16}ClCu_{0.67}N_{3.67}O_4$, FW = 353.43, hexagonal, $P\bar{3}_1c$, a = 9.7683(4) Å, b = 9.7683(4) Å, c = 25.864(2) Å, β = 120.0, V = 2137.3(2) Å^3, Z = 6, D_{calcd} = 1.648 g cm^{-3}, $F(000)$ = 1092, T = 100 K, R1 = 0.0670, and wR2 = 0.1538 for 1741 independent reflns with $I > 2\sigma(I)$, and R1 = 0.0713, wR2 = 0.1559, for all 12 132 reflns, GOF = 1.156 . (a) Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997. (b) *MERCURY 1.3 Supplied with Cabridge Structural Database*; CCDC: Cabridge, U.K., 2003−2004.

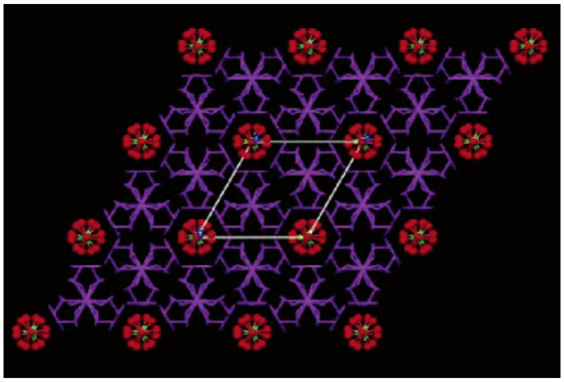

Figure 3. Packing diagram of complex **1** viewed down the *c* axis showing the close packing of the cryptand moiety creating a through hexagonal channel down the *c* axis encapsulating the perchlorate anion inside the cavity (hydrogen atoms attached to the cryptand and the second perchlorate anion are omitted for clarity).

The second perchlorate anion, having C_3 symmetry, is involved in one strong and two weak C−H⋯O interactions with the cryptand moiety. Thus, O2 and O3 are involved in C−H⋯O interactions with methylene hydrogens H1B and H2A. whereas O4 is making strong contact with phenyl hydrogen H5. Pertinent hydrogen-bonding interaction with symmetry code are C(1)−H(1B)⋯O(3): H(1B)⋯O(3) = 2.44 Å, C(1)⋯O(3) = 3.19(2) Å and ∠C(1)−H(1B)⋯O(3) = 134°; C(2)−H(2A)⋯O(2): H(2A)⋯O(2) = 2.52 Å, C(2)⋯O(2) = 3.21(1) Å ∠C(2)−H(2A)⋯O(2) = 128°; C(5)−H(5)⋯O(4): H(5)⋯O(4) = 2.18 Å, C(5)⋯O(4) = 3.12(2) Å, ∠C(5)−H(5)⋯O(4) = 178°. Salient features of the present investigation are the cascade coordination of the azide anion inside the cryptand cavity and the encapsulation of the perchlorate anion by the virtue of C_3 symmetry possessed by the cryptand cation to orient and self-assemble for making the thorough hexagonal channels. Even though the perchlorate anion inside the hexagonal channels is not involved in any classic H-bonding interaction with the cryptand moiety, the encapsulation of perchlorate anion can be attributed to the tubular electrostatic force down the *c* axis spawned by the surrounding azide cryptand with the perchlorate anions. The cascade complex of dicopper(II) cryptate of $\mathbf{L_1}$ described herein is an example of perfect linear orientation of M−NNN−M unit inside the cage, whereas those previously reported were either bent or near-linear. Sensing studies with this cascade complex are in progress.

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Supporting Information Available: CIF file of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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