

Squeezing the $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ Bridge by Cryptate EncapsulationAndrew D. Bond,[†] Sofia Derossi,[†] Frank Jensen,[†] Frank B. Larsen,[†] Christine J. McKenzie,[†] and Jane Nelson^{*‡}

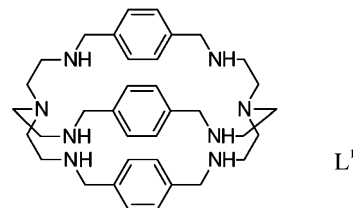
University of Southern Denmark, Department of Chemistry, Campusvej 55, 5230 Odense M, Denmark, and Biomedical Sciences, University of Ulster, Coleraine, BT52 1SA, Northern Ireland

Received April 5, 2005

Treatment of cryptand **L**¹ with Cu(II) generates a H_3O_2^- -bridged dicopper(II) cryptate, **2**, where the guest anion has responded to steric constraint by a significant shortening of the O–O distance to 2.325(9) Å; computational optimization at the B3LYP/6-31(d) level suggests that the bridging O–H \cdots O H-bond is bent ($\approx 157^\circ$) but that the barrier to interchange of the bridging H atom is low ($< 4 \text{ kJ mol}^{-1}$). This cryptate, rather than the $[\text{Cu}_2\text{L}^1\mu\text{CN}]^{3+}$ species recently claimed to derive from cleavage of the C–C bond of the solvent, is the product of acetonitrile recrystallization of the initially formed reaction product, **1**.

The secondary coordination of an anionic or other bridge between cations, themselves coordinated by a cryptand host, has some time ago been termed “cascade coordination”.¹ Implicit in this description is the expectation of isolating unusual chemical species and/or promoting unusual chemical reactivity deriving from coordination within the steric confines of the cryptand cavity. To date, however, such behavior has seldom been realized. In just a few favorable situations, cascade-type reactivity has been observed² within the azacryptand³ series of hosts. Our preliminary work in this area has concerned the activation of CO_2 toward reaction with OR^- ($\text{R} = \text{H}, \text{Me}$) under the influence of encrypted Lewis acidic cations from the first transition series ($\text{Co(II)}-\text{Zn(II)}$).² Despite the scarcity of authenticated examples of cascade reactivity, there are many examples of “cascade complexation”,^{4–8} which has come to describe simply the incorporation of anionic bridging ligands between the

coordinated cations of a cryptate. Often these ligands are held in unfamiliar geometries by the constraints of the cryptand skeleton, and this may be associated with unusual physical properties such as anomalous bridge-mediated magnetic interactions. Bridging ligands studied to date include N^{4-7} and $\text{O}^{2,8}$ donor ligands, both triatomic^{4–8} and monatomic.⁹ Reported here is a dicopper(II) cryptate encapsulating an exceptionally short $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ bridge.



When an acetonitrile solution of the tetraperchlorate salt of the *p*-xylyl-spaced dicopper(II) cryptate $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ (**1**) is allowed to evaporate slowly in air over several days, a green polycrystalline solid is obtained from the originally blue solution. Hexagonal plates of the product were obtained by ether diffusion into an acetonitrile solution of this solid, and single-crystal X-ray diffraction revealed these to be $[\text{Cu}_2\text{L}^1(\text{H}_2\text{O})(\text{OH})](\text{ClO}_4)_3$, **2** (Figure 1).¹⁰ The cryptate **2** contains a linear $[\text{Cu}-\text{O}\cdots\text{O}-\text{Cu}]$ unit that includes a remarkably short O \cdots O separation of 2.325(9) Å. That the bridging unit is H_3O_2^- is unambiguous on account of the requirement for charge balance in the structure. Experimental location of the H atoms within the $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$

* To whom correspondence should be addressed. E-mail: j.nelson@ulster.ac.uk.

[†] University of Southern Denmark.

[‡] Velux Visiting Professorship, University of Southern Denmark. Current address: Loughborough University, LE11 3TU, U.K.

- (1) Lehn, J.-M. *Pure Appl. Chem.* **1980**, 52, 2441. Lehn, J.-M. *Science* **1985**, 227, 549.
- (2) Dussart, Y.; Harding, C. J.; Dalgaard, P.; McKenzie, C. J.; Kadirvelraj, R.; McKee, V.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **2002**, 1704.
- (3) Nelson, J.; McKee, V.; Morgan, G. *Prog. Inorg. Chem.* **1998**, 47, 168.
- (4) Drew, M. G. B.; Hunter, J.; Marrs, D.; Nelson, J.; Harding, C. *J. Chem. Soc., Dalton Trans.* **1992**, 3235.
- (5) Harding, C. J.; Lu, Q.; Malone, J. F.; Marrs, D. J.; Martin, N.; McKee, V.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1995**, 1739.
- (6) Lu, Q.; Latour, J.-M.; Harding, C. J.; Martin, N.; Marrs, D. J.; McKee, V.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1994**, 1471.

- (7) Harding, C. J.; Mabbs, F. E.; MacInnes, E. J. L.; McKee, V.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1996**, 3227. Escuer, A.; Harding, C. J.; Dussart, Y.; Nelson, J.; McKee, V.; Vicente, R. *J. Chem. Soc., Dalton Trans.* **1999**, 223.
- (8) McKee, V.; Nelson, J.; Town, R. *Chem. Soc. Rev.* **2003**, 32, 309.
- (9) Lu, Q.; Harding, C. J.; McKee, V.; Nelson, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1798.
- (10) Details of the structure determination for **2**: $\text{C}_{36}\text{H}_{57}\text{Cl}_3\text{Cu}_2\text{N}_8\text{O}_{14}$, $f_w = 1059.33$, trigonal, $P31c$, $a = 9.8716(7)$, $c = 25.642(2)$ Å, $V = 2164.0(3)$ Å³, $Z = 2$, $T = 180(2)$ K, $d_{\text{calcd}} = 1.626 \text{ g cm}^{-3}$; $R1$ ($I > 2\sigma(I)$) = 0.045, $wR2$ (all data) = 0.140, $\text{GOF} = 1.06$, CCDC-250369 . The H atom position inferred from difference Fourier syntheses was included in the final model with 50% site occupancy (thereby summing to a total of 3 H atoms per cryptate), refined with a tightly restrained O–H distance and a constrained isotropic displacement parameter ($1.2 \times U_{\text{eq}}(\text{O})$).

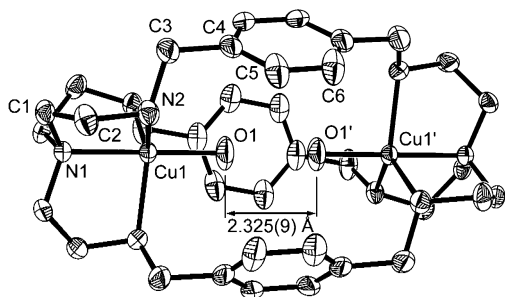


Figure 1. Structure of the cryptate cation in the crystal structure of **2** showing displacement ellipsoids at 30% probability (H atoms omitted).

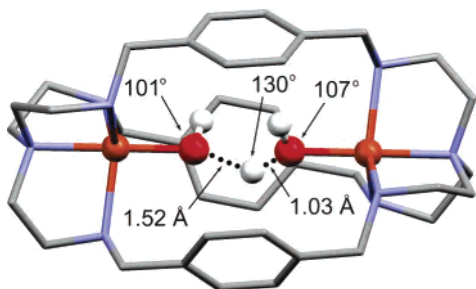


Figure 2. H atom positions in the $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ bridge derived from optimization at the B3LYP/6-31G(d) level within a constrained cryptate skeleton.

bridge is problematic, not only on account of their minimal X-ray scattering power, but also by the location of the cryptate on a site of 32 (D_{3h}) point symmetry within the crystal structure. This renders the two O atoms crystallographically equivalent, so that the H atoms of the $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ bridge must be described as disordered.¹¹ One possible H atom position could be inferred from a difference Fourier synthesis, providing six symmetry-generated positions lying on cones about the $\text{Cu}-\text{O}\cdots\text{O}-\text{Cu}$ axis with half-angle $\text{Cu}-\text{O}-\text{H} = 114(2)^\circ$.

To probe the structural features of the central $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ bridge, calculations were performed at the B3LYP/6-31G(d) level using the GAMESS-US program.¹² Optimization of the three H atom positions with the remainder of the structure constrained to the observed X-ray geometry suggests that the $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ unit comprises two $\text{Cu}-\text{OH}$ groups connected by a bridging H atom (Figure 2). The $\text{Cu}-\text{O}-\text{H}$ angles of 107° and 101° for the nonbridging H atoms are consistent with the H atom positions suggested by the X-ray data. The geometry around the bridging H atom is asymmetric, with $\text{O}-\text{H}$ distances of 1.03 and 1.52 Å and an $\text{O}-\text{H}-\text{O}$ angle of 130° . Full

- (11) The H atom positions may be clarified further by neutron diffraction only if they display long-range translational order. Although the local relative arrangement of the three H atoms is likely to be comparable in each cryptand cavity, the relative position of these three atoms about the C_3 axis of the cryptand is likely to be variable. In that case, neutron diffraction would again provide only a disordered model in space group $P31c$. Similarly, a locally unconstrained refinement of the H atom positions (see for example: Thomas, J. *Solid State Ionics* **1995**, *77*, 275) is not feasible in the absence of long-range translational order.
- (12) (a) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347; <http://www.msg.ameslab.gov/GAMESS/>. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

optimization of the entire complex at the B3LYP/6-31G(d) level displaces the oxygen atoms slightly from the C_3 axis and causes the $\text{O}-\text{H}-\text{O}$ angle around the bridging H atom to expand to 157° . The optimized $\text{Cu}\cdots\text{Cu}$ distance is 6.20 Å, compared to the experimental value of 6.1213(12) Å. This agreement is representative for the employed level of theory.

The full system is too large to allow frequency calculations that would enable location of transition structures for interchanging H atoms in the $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ unit. Instead, we have estimated the energetic barriers by a series of constrained optimizations: the barrier for H atom transfer between the two $\text{Cu}-\text{OH}$ groups is estimated to be less than 4 kJ mol^{-1} , while the barrier for interchanging the bridging and terminal hydrogens is approximately 10 kJ mol^{-1} . These small values suggest clearly that the positions of the H atoms in the central $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ bridge are fluctuating rapidly, so that the concept of a unique molecular structure becomes blurred. If the H atoms were described in a quantum-mechanical sense, they would be delocalized over a significant volume of the internal cryptate space. Such delocalization would be consistent with the observed time- (and space-) averaged D_{3h} structure.

Formation of the short $\text{O}\cdots\text{O}$ distance in **2** may be attributed to the collinear $[\text{Cu}-\text{O}\cdots\text{O}-\text{Cu}]$ geometry that arises from the constraints of cryptand encapsulation. All other well-established $[\text{M}-\text{OH}\cdots\text{H}_2\text{O}-\text{M}]^{n+}$ complexes to date exhibit bent $[\text{M}-\text{O}\cdots\text{O}-\text{M}]$ geometries with significantly greater $\text{O}\cdots\text{O}$ distances.¹³ For example, an acyclic pyrazolate-hinged dinucleating ligand furnishes a copper(II) complex in which a $[\text{Cu}-\text{OH}\cdots\text{H}_2\text{O}-\text{Cu}]^{3+}$ unit is bent with an $\text{O}\cdots\text{O}$ distance of 2.442(7) Å,¹⁴ some 0.117 Å greater than in **2**. We have identified only one other $[\text{M}-\text{OH}_x\cdots\text{H}_y\text{O}-\text{M}]^{n+}$ system that displays a comparable $\text{O}\cdots\text{O}$ distance: the copper(II) coordination polymer, catena(μ -benzenehexacarboxylato)decaaquatricopper(II) dihydrate is proposed to contain an approximately collinear $[\text{Cu}-\text{OH}_2\cdots\text{H}_2\text{O}-\text{Cu}]^{4+}$ unit in which the $\text{O}\cdots\text{O}$ distance is 2.321 Å.¹⁵ Although assigned as $[\text{Cu}-\text{OH}_2\cdots\text{H}_2\text{O}-\text{Cu}]^{4+}$, the protonation state in that case is not as well defined as that in **2**.

The dicopper(II) cryptate/solvent system described herein

- (13) (a) Ghiladi, M.; Gomez, J. T.; Hazell, A.; Kofod, P.; Lumtscher, J.; McKenzie, C. J. *J. Chem. Soc., Dalton Trans.* **2003**, 1320. (b) Hazell, A.; Jensen, K. B.; McKenzie, C. J.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 3127. (c) Ardon, M.; Bino, A.; Jackson, W. G. *Polyhedron* **1987**, *6*, 181. (d) Ruf, M.; Weis, K.; Vahrenkamp, H. *J. Am. Chem. Soc.* **1996**, *118*, 9288. (e) Meyer, F.; Rutsch, P. *Chem. Commun.* **1998**, 1037. (f) Jarjayes, O.; Du Moulinet D'Hardemare, A.; Durif, A.; Averbuch-Pouchot, M.-T. *Acta Crystallogr.* **1998**, *C54*, 931. (g) Poussereau, S.; Blondin, G.; Cesario, M.; Guilhem, J.; Chottard, G.; Gonnet, F.; Girerd, J.-J. *Inorg. Chem.* **1998**, *37*, 3127. (h) Buchler, S.; Meyer, F.; Kaifer, E.; Pritzkow, H. *Inorg. Chim. Acta* **2002**, *337*, 371. (i) Justel, T.; Bendix, J.; Metzler-Nolte, N.; Weyhermüller, T.; Nuber, B.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 35. (j) Kong, D.; Xie, Y. *Inorg. Chim. Acta* **2002**, *338*, 142.
- (14) Siegfried, L.; Kaden, T. A.; Meyer, F.; Kircher, P.; Pritzkow, H. *Dalton Trans.* **2001**, 2310.
- (15) Zhao, M.-G.; Liu, C.-O.; Shi, J.-M.; Xu, W. *Transition Met. Chem.* **2003**, *28*, 525. The standard uncertainty of the $\text{O}\cdots\text{O}$ distance is not quoted in this case, but it is unlikely to differ significantly from 2.325(9) Å observed in **2**. Although both O atoms are designated as water molecules by Zhao et al., the location of the H atoms in this unit is highly uncertain. There are many noncoordinated carboxylate groups in the local vicinity, and it is possible that one or even both O atoms of the $[\text{Cu}-\text{OH}_x\cdots\text{H}_y\text{O}-\text{Cu}]^{n+}$ bridge belong to hydroxide groups.

is identical to that previously reported to promote cleavage of the C–C bond of acetonitrile to yield the cyanide-bridged complex, $[\text{Cu}_2\text{L}^1(\text{CN})]^{3+}$ (**3**).¹⁶ During our work with this system, we have been unable to replicate this potentially very significant example of cascade reactivity. Although our routine procedure for purification of all cascade complexes is recrystallization from acetonitrile, we have never been aware of the formation of even a trace of cyano-bridged cryptate in the absence of added cyanide reagent (see Supporting Information). Formation of **3** is clearly recognizable by an obvious change of solution color to bright green, and **3** is readily distinguished from **2** by characteristic signatures in ESR, IR, and UV–vis spectroscopies.¹⁷ Powder X-ray diffraction analysis of our bulk material confirms it

(16) Lu, T.; Zhuang, X.; Li, Y.; Chen, S. *J. Am. Chem. Soc.* **2004**, 126, 4761.

(17) Bond, A. D.; Derossi, S.; Harding, C. J.; McInnes, E. J.; McKee, V.; McKenzie, C. J.; Nelson, J.; Wolowska, J. *J. Chem. Soc., Dalton Trans.* **2005**, 2403.

to be almost exclusively **2**; certainly there is no observable trace of **3**. Thus, at least in our hands, there is no evidence to support the claim¹⁶ of quantitative C–C bond cleavage by “cascade reaction” of acetonitrile with **1**.

Acknowledgment. J.N. thanks University of Southern Denmark for hospitality and the Velux Foundation for financial support during her stay in Odense. The Danish Natural Science Research Council (SNF) and Carlsbergfondet are also thanked for financial support (A.D.B., C.J.M.). J.N. also acknowledges the assistance of a Leverhulme Emeritus Fellowship during the preparation of this manuscript.

Supporting Information Available: Synthesis details, table of indexed PXRD peak positions, and refined lattice parameters for the bulk sample of **2** and comparison to simulated PXRD for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0505091