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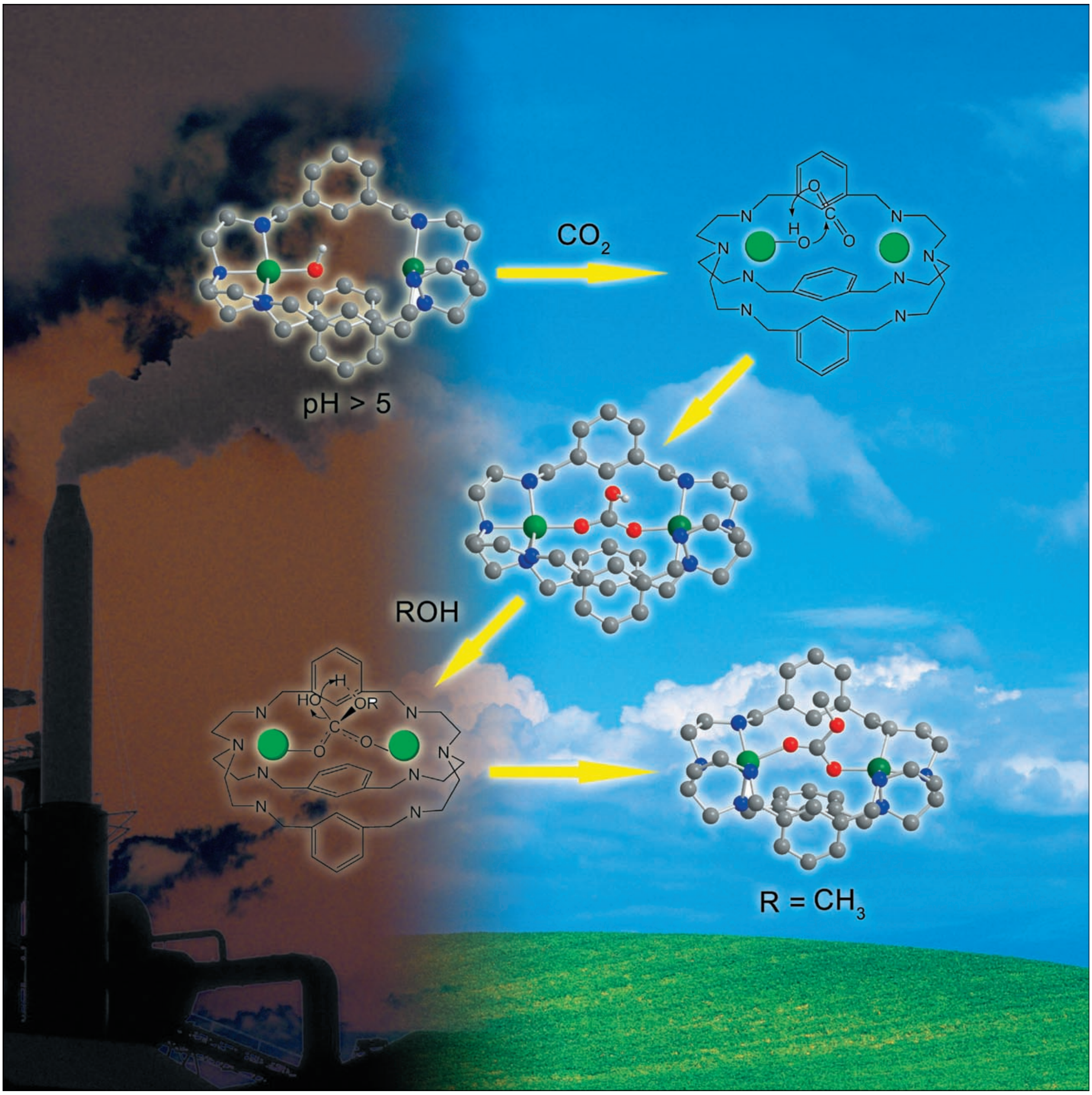
CO_2 Fixation and Transformation by a Dinuclear Copper Cryptate under Acidic Conditions

Jia-Mei Chen, Wei Wei, Xiao-Long Feng, and Tong-Bu Lu*[a]



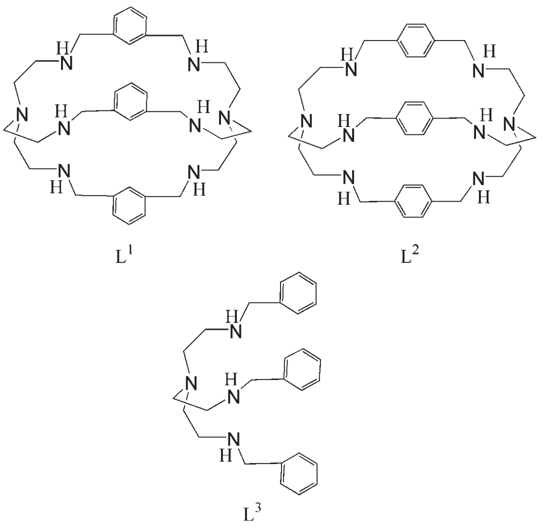
Abstract: CO_2 fixation and transformation by metal complexes continuously receive attention from the viewpoint of carbon resources and environmental concerns. We found that the dinuclear copper(II) cryptate $[Cu_2L^1](ClO_4)_4$ (**1**; $L^1 = N[(CH_2)_2NHCH_2(m\text{-}C_6H_4)CH_2\text{-}NH\text{-}(CH_2)_2]_3N$) can easily take up atmospheric CO_2 even under weakly acidic conditions at room temperature and convert it from bicarbonate into carbonate monoesters in alcohol solution. The compounds $[Cu_2L^1(\mu\text{-}O_2COH)](ClO_4)_3$ (**2**), $[Cu_2L^1(\mu\text{-}O_2COR)](ClO_4)_3$ (**3**: $R = CH_3$; **4**: $R = C_2H_5$; **5**: $R = C_3H_7$; **6**: $R = C_4H_9$; **7**: $R = C_5H_{11}$; **8**: $R = CH_2CH_2OH$), $[Cu_2L^1(\mu\text{-}O_2CCH_3)](ClO_4)_3$ (**9**), and $[Cu_2L^1(OH_2)(NO_3)](NO_3)_3$ (**10**) were characterized by IR spectroscopy and ESI-MS. The crystal structures of **2**–**6** and **10** were studied by single-crystal X-ray diffraction analysis. On the basis of the crystal structures, solution studies, and DFT calculations, a possible mechanism for CO_2 fixation and transformation is given.

Keywords: absorption · carbon dioxide fixation · copper · cryptands · density functional calculations

Introduction

The chemical fixation and transformation of atmospheric CO_2 have been of long-standing interest, as excess CO_2 is an atmospheric pollutant.[1] CO_2 can potentially be used as a substrate for storing solar energy[2] and as an attractive C1 feedstock for the preparation of useful carbon-containing compounds its reaction with metal complexes.[3] So far, a great deal of research has been done on the reactivity of CO_2, including its hydration products such as HCO_3^-[4] and CO_3^{2-},[5] as well as its derivatives such as alkyl carbonate[6–8] and carbamate.[9] Kato and Ito[7] found that a mononuclear metal–tetraazacycloalkane complex in alcohol can take up atmospheric CO_2 under alkaline conditions and fix it as the carbonate monoester at the metal center. Dinuclear macrocyclic complexes have also been reported for CO_2 fixation and transformation.[8] In general, CO_2 uptake takes place in basic or neutral reaction media;[5,7] few metal complexes can fix atmospheric CO_2 under acidic conditions.[8a]

We focused our attention on the polyaza cryptands L^1 and L^2 (Scheme 1), which incorporate tripodal skeleton groups and contain two binding subunits located at the two poles of the structures, as well as their dinuclear metal complexes, as they have unique recognition and catalytic properties with regard to various small molecules and ions.[10–14] We previously demonstrated that the C−C bond of acetonitrile can be cleaved by the dinuclear copper complex $[Cu_2L^2](ClO_4)_4$ at room temperature to generate the cyano-bridged complex $[Cu_2L^2(CN)](ClO_4)_3$ and methanol.[14] Based on this work, we presumed that the dinuclear copper complex $[Cu_2L^1](ClO_4)_4$ (**1**), which has a structure similar to $[Cu_2L^2](ClO_4)_4$, may also cleave the C−C bond of acetonitrile. However, no cyano-bridged dinuclear complex was formed under similar reaction conditions. Instead, **1** easily absorbed atmospheric CO_2 in weakly acidic reaction media at room temperature to form the bicarbonate-bridged complex $[Cu_2L^1(\mu\text{-}O_2COH)](ClO_4)_3$ (**2**), which further reacted with primary alcohols to generate carbonate monoesters of $[Cu_2L^1(\mu\text{-}O_2COR)](ClO_4)_3$ (**3**: $R = CH_3$; **4**: $R = C_2H_5$; **5**: $R = C_3H_7$; **6**:



Scheme 1. Structures of L^1, L^2, and L^3.

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[a] J.-M. Chen, W. Wei, X.-L. Feng, Prof. Dr. T.-B. Lu
MOE Key Laboratory of Bioinorganic and Synthetic Chemistry
State Key Laboratory of Optoelectronic Materials and
School of Chemistry and Chemical Engineering
Sun Yat-Sen University
Guangzhou 510275 (China)
Fax: (+86) 20-84112921
E-mail: lutongbu@mail.suysu.edu

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Table 1. Crystallographic data for **2–6** and **10**.

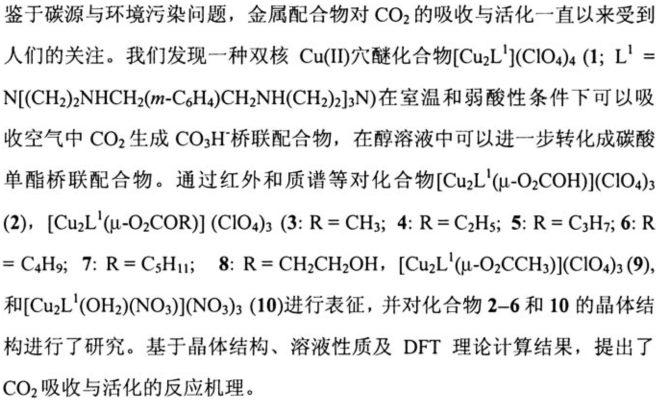
Compound	**2**·2CH$_3$CN	**3**·2CH$_3$CN	**3**·4.5CH$_3$CN·0.5H$_2$O	**4**·2CH$_3$CN	**5**·CH$_3$CN	**6**·CH$_3$CN	**10**·2H$_2$O
Formula	$C_{41}H_{61}Cl_3Cu_2N_{10}O_{15}$	$C_{42}H_{63}Cl_3Cu_2N_{10}O_{15}$	$C_{47}H_{71}Cl_3Cu_2N_{12.5}O_{15.5}$	$C_{43}H_{65}Cl_3Cu_2N_{10}O_{15}$	$C_{42}H_{64}Cl_3Cu_2N_9O_{15}$	$C_{43}H_{66}Cl_3Cu_2N_9O_{15}$	$C_{36}H_{60}Cu_2N_{12}O_{15}$
M_r	1167.43	1181.45	1290.58	1195.48	1168.45	1182.48	1028.04
Crystal size [mm^3]	0.36 × 0.23 × 0.22	0.42 × 0.35 × 0.27	0.42 × 0.34 × 0.34	0.62 × 0.51 × 0.49	0.58 × 0.46 × 0.40	0.55 × 0.50 × 0.42	0.29 × 0.28 × 0.22
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1$	$P2_1$	$P2_1/c$
a [Å]	16.975(7)	16.861(5)	14.338(4)	16.8448(15)	11.5642(2)	11.582(5)	14.367(2)
b [Å]	16.631(7)	17.197(6)	14.378(4)	17.5221(16)	14.199(3)	14.176(6)	14.154(2)
c [Å]	19.188(8)	19.640(6)	16.080(4)	19.6620(18)	15.587(3)	15.490(7)	23.347(3)
α [°]	90	90	79.734(5)	90	90	90	90
β [°]	109.444(9)	113.186(6)	67.938(4)	113.509(2)	91.303(5)	91.748(6)	111.690(7)
γ [°]	90	90	87.829(4)	90	90	90	90
V [Å^3]	5108(4)	5253(3)	3021.5(13)	5231.7(8)	2558.8(9)	2541.9(19)	4411.5(10)
Z	4	4	2	4	2	2	4
μ [mm^{-1}]	1.064	1.039	0.909	1.023	1.062	1.070	1.046
Reflections collected	22832	31309	26098	28237	12657	15791	24199
Unique reflections (R_{int})	7097 (0.0440)	11456(0.0359)	13081(0.0345)	10451(0.0236)	9255(0.0248)	9864(0.0340)	9676(0.0738)
GOF on F^2	1.089	1.015	1.069	1.032	1.016	1.013	0.995
$R1$,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0627, 0.1692	0.0639, 0.1649	0.0639, 0.1675	0.0587, 0.1622	0.0456, 0.1032	0.0423, 0.1050	0.0741, 0.1861
$R1$,[a] $wR2$[b] (all data)	0.1006, 0.1969	0.1145, 0.2032	0.1170, 0.1987	0.0821, 0.1871	0.0723, 0.1206	0.0595, 0.1160	0.1964, 0.2595

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2\}^{1/2}$, in which $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$ and $P = (F_0^2 + 2F_c^2)/3$.

R = C_4H_9; **7**: R = C_5H_{11}; **8**: R = CH_2CH_2OH). Although Martell and co-workers[11] and Nelson and co-workers[12] found that the reaction of Cu($C1O_4$)$_2$ with L^1 in water and CH_3OH/CH_3CN gave the products [Cu$_2$L^1(μ-CO$_3$)(H$_3$O)]Br$_3$ and [Cu$_2$L^1(μ-O$_2$COCH$_3$)](ClO$_4$)$_3$, respectively, the reaction mechanism has not been established.

To investigate the mechanism of CO$_2$ fixation and transformation by [Cu$_2$L^1]$^{4+}$, and to understand why [Cu$_2$L^1]$^{4+}$ prefers CO$_2$ fixation to C−C bond cleavage of acetonitrile, μ-O$_2$COH-bridged cryptate **2** and a series of μ-O$_2$COR$^-$-bridged dinuclear copper(II) cryptates **3–8** were synthesized. For comparison, dinuclear copper(II) cryptates [Cu$_2$L^1(μ-O$_2$CCH$_3$)](ClO$_4$)$_3$ (**9**) and [Cu$_2$L^1(OH$_2$)(NO$_3$)](NO$_3$)$_3$ (**10**), as well as the mononuclear compound [CuL^3(H$_2$O)](ClO$_4$)$_2$, were also prepared. A reasonable mechanism for CO$_2$ fixation and transformation is presented herein, based on crystal structures, solution studies, and DFT calculations. The difference in reactivity between [Cu$_2$L^1]$^{4+}$ and [Cu$_2$L^2]$^{4+}$ is also discussed in this paper.

Abstract in Chinese:



鉴于碳源与环境污染问题，金属配合物对 CO$_2$ 的吸收与活化一直以来受到人们的关注。我们发现一种双核 Cu(II)穴醚化合物[Cu$_2$L^1](ClO$_4$)$_4$ (**1**; L^1 = N[(CH$_2$)$_2$NHCH$_2$(*m*-C$_6$H$_4$)CH$_2$NH(CH$_2$)$_2$]$_3$N)在室温和弱酸性条件下可以吸收空气中 CO$_2$ 生成 CO$_3$H$^-$桥联配合物，在醇溶液中可以进一步转化成碳酸单酯桥联配合物。通过红外和质谱等对化合物[Cu$_2$L^1(μ-O$_2$COH)](ClO$_4$)$_3$ (**2**)，[Cu$_2$L^1(μ-O$_2$COR)] (ClO$_4$)$_3$ (**3**: R = CH$_3$; **4**: R = C$_2$H$_5$; **5**: R = C$_3$H$_7$; **6**: R = C$_4$H$_9$; **7**: R = C$_5$H$_{11}$; **8**: R = CH$_2$CH$_2$OH，[Cu$_2$L^1(μ-O$_2$CCH$_3$)](ClO$_4$)$_3$ (**9**), 和[Cu$_2$L^1(OH$_2$)(NO$_3$)](NO$_3$)$_3$ (**10**)进行表征，并对化合物 **2–6** 和 **10** 的晶体结构进行了研究。基于晶体结构、溶液性质及 DFT 理论计算结果，提出了 CO$_2$ 吸收与活化的反应机理。

Results and Discussion

The reaction of Cu(ClO$_4$)$_2$·6H$_2$O and L^1 in methanol at pH 5–6 gave a blue mixture of **2** and **3** within a few minutes, which was dissolved in acetonitrile and evaporated slowly at room temperature to give blue crystals of **2**·2CH$_3$CN and **3**·4.5CH$_3$CN·0.5H$_2$O. Slow evaporation of a solution of **1** in acetonitrile in an open vessel at room temperature afforded blue crystals of **2**·CH$_3$CN. Cryptate **2** reacted further with primary alcohols to form monoalkylcarbonate-bridged cryptates **3–8**.

X-ray Structures

Attempts to solve the structures of **7**, **8**, and **9** were unsuccessful owing to the poor quality of the crystals; the crystal structures of the other complexes **2–6** and **10** were determined by X-ray crystallography (Table 1). During the period of this research, the structure of **2**·CH$_3$CN was reported.[8b] The structure of **2**·2CH$_3$CN is similar to that of **2**·CH$_3$CN. In **2**·2CH$_3$CN, each Cu^{II} ion is five-coordinated with four nitrogen atoms of L^1 and one oxygen atom of μ-O$_2$COH$^-$, and

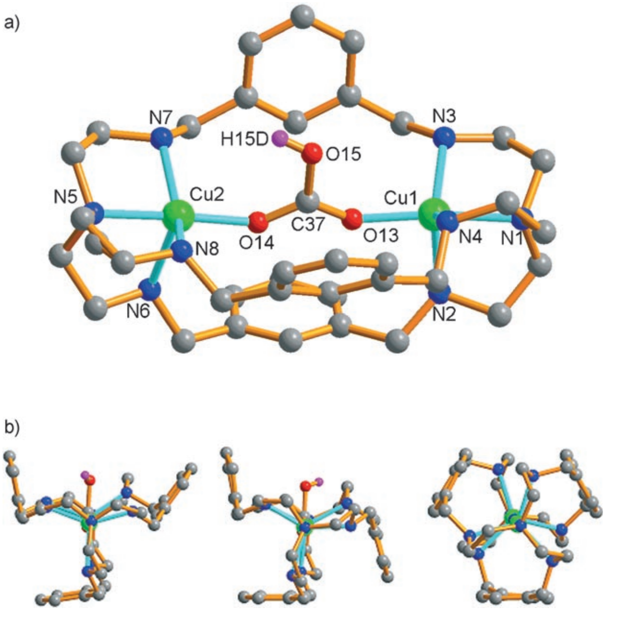


Figure 1. a) Structure of $[Cu_2L^1(\mu\text{-}O_2COH)]^{3+}$ in **2**·2CH_3CN. b) View of the cryptate cations along the Cu_2 axis, showing the different conformations of the ligands: form A (left) in **2**·2CH_3CN, form B (middle) in **2**·CH_3CN, and rigid tripodal skeleton (right) in $[Cu_2L^2(CN)]^{3+}$.

the $\mu\text{-}O_2COH^-$ ligand shows a symmetrical bridging mode (Figure 1 a) with a Cu···Cu separation of 6.01 Å. For each Cu center, one Cu−N bond (Cu1−N2 and Cu2−N6) is longer than the other four Cu−N/O bonds (Table 2). The parameters (τ) for the geometry of the five-coordinated Cu^{II} ions[15] are 0.81 for Cu1 and 0.60 for Cu2 ($\tau = 1.00$ for TBP (trigonal bipyramidal) and 0.00 for SP (square pyramidal)), thus indicating that distorted TBP geometry are adopted at both Cu1 and Cu2, with Cu2 showing more deviation from TBP geometry. In $[Cu_2L^2(CN)](ClO_4)_3$,[14] the τ value for each Cu^{II} ion is 1.00, which indicates that the geometry at each Cu^{II} ion is ideal TBP. The different geometries at the Cu^{II} ions in **2**·2CH_3CN and $[Cu_2L^2(CN)](ClO_4)_3$ are caused by the different conformations of the cryptands (Figure 1 b). In **2**·2CH_3CN, L^1 adopts the conformation form A, in which the two phenyl rings are oriented in the same direction, leading to distorted TBP geometry at Cu^{II}. In $[Cu_2L^2(CN)](ClO_4)_3$, however, the rigid tripodal skeleton of L^2 makes the Cu^{II} ions prefer TBP to SP geometry. In **2**·CH_3CN, L^1 adopts the conformation form B (Figure 1 b), in which the two phenyl rings are oriented in opposite directions. This indicates that the conversion of form A into form B does not involve a high energy barrier.

The cryptates **3**–**6** show similar structures (Figure 2), in which each Cu^{II} ion is also five-coordinated with four nitrogen atoms of L^1 and one oxygen atom of the corresponding bridging carbonate monoester. The τ values for Cu^{II} ions in **3**–**6** range from 0.80 to 0.32, which indicates that distorted TBP or SP geometry is adopted at the Cu^{II} ions. In **3**–**6**, all the $\mu\text{-}O_2COR^-$ ligands show an unsymmetrical bridging mode, and this leads to significant contraction of Cu···Cu separations (5.64–5.78 Å) relative to that in **2** (Table 2). The Cu−O bonds in the symmetrical mode are close to those in the unsymmetrical mode (Table 2), thus indicating that the unsymmetrical nature of the bonding is mainly due to the different C−O−Cu angles. In addition, all the L^1 cryptands in **3**–**6** adopt the conformation form B.

In **10**, both Cu^{II} ions are five-coordinated (Figure 3): Cu1 is bound to four nitrogen atoms of L^1 and one oxygen atom of NO_3^-, and Cu2 is coordinated to four nitrogen atoms of L^1 and one water molecule. The τ values are 0.42 and 0.75 for Cu1 and Cu2, respectively, which indicates that the geometry at Cu1 is distorted SP, whereas the geometry at Cu2 is closer to TBP. In **10**, the Cu···Cu separation of 6.521 Å is much longer than those in **2**–**6**. There is an intramolecular hydrogen bond between the coordinated water molecule (H14A) and a noncoordinated oxygen atom (O11) of NO_3^-; the O14···O11 distance is 2.726 Å, and the O14−H14A···O11 angle is 170.4°.

Table 2. Selected bond lengths [Å] and angles [°] for **2**–**6** and **10**.

	2·2CH_3CN	**3**·2CH_3CN	**3**·4.5CH_3CN·0.5H_2O	**4**·2CH_3CN	**5**·CH_3CN	**6**·CH_3CN	**10**·2H_2O
Cu1−O13	1.911(5)	1.940(5)	1.936(3)	1.941(4)	1.938(3)	1.934(3)	1.969(5)
Cu2−O14	1.922(6)	1.995(5)	1.941(4)	1.953(3)	1.946(4)	1.938(4)	1.933(5)
Cu1−N1	2.040(5)	2.043(4)	2.041(4)	2.043(3)	2.049(4)	2.045(4)	2.042(5)
Cu2−N5	2.040(6)	2.039(4)	2.030(4)	2.042(3)	2.041(4)	2.027(4)	2.009(5)
Cu1−N2	2.218(6)	2.145(5)	2.144(4)	2.117(4)	2.097(4)	2.150(3)	2.262(6)
Cu1−N4	2.103(5)	2.088(4)	2.081(4)	2.089(3)	2.161(4)	2.096(4)	2.073(5)
Cu1−N3	2.110(5)	2.139(5)	2.168(4)	2.197(4)	2.162(4)	2.156(4)	2.061(5)
Cu2−N8	2.08(2)	2.085(4)	2.083(4)	2.101(3)	2.072(4)	2.070(4)	2.061(7)
Cu2−N7	2.092(5)	2.090(4)	2.104(4)	2.085(4)	2.088(4)	2.068(4)	2.087(5)
Cu2−N6	2.271(6)	2.187(5)	2.207(4)	2.224(4)	2.258(4)	2.237(4)	2.147(6)
C37−O13−Cu1	145.0(5)	121.5(5)	124.3(3)	122.7(3)	124.2(3)	123.3(3)	
C37−O14−Cu2	141.2(7)	150.2(5)	159.1(4)	160.6(4)	159.8(4)	158.3(4)	
Cu1···Cu2	6.008	5.641	5.739	5.776	5.746	5.724	6.521
τ(Cu1/Cu2)	0.81/0.60	0.66/0.32	0.80/0.50	0.73/0.50	0.79/0.42	0.78/0.41	0.42/0.75

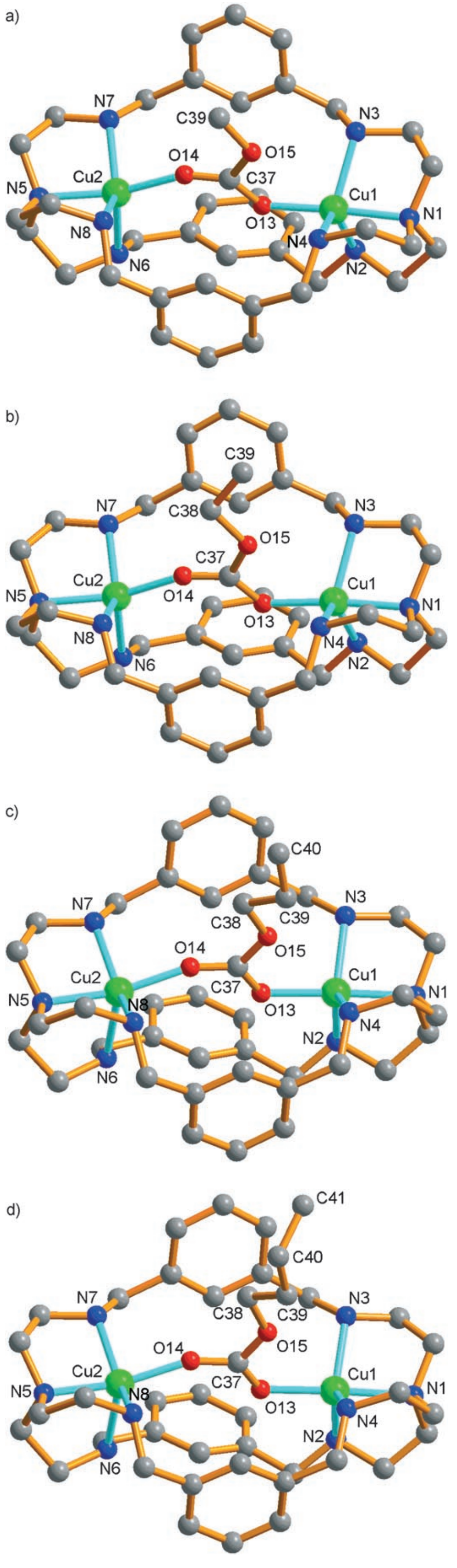


Figure 2. Structures of the cryptate cations in a) **3**, b) **4**, c) **5**, and d) **6**.

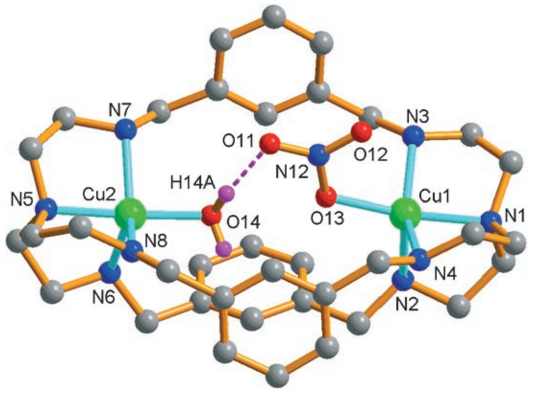


Figure 3. Structure of $[Cu_2L^1(NO_3)(H_2O)]^{3+}$ in **10**.

CO_2 Fixation and Transformation: IR and ESI Mass Spectra

The existence of the bicarbonate bridging ligand in **2**, and the μ-O_2COR^- bridging ligands in **3–8**, are further proved by their IR and electrospray ionization (ESI) mass spectra. The IR spectrum of **2** shows bicarbonate-related vibrations at 1553 and 1331 cm^{-1} for **2**·CH_3CN, and at 1551 and 1405 cm^{-1} for **2**·$2CH_3CN$.[16] All the μ-O_2COR^--bridged complexes of **3–8** showed two stretching vibration bands of the OCO_2 groups at around 1630 and 1330 cm^{-1}.[7,8,12]

The fixation of atmospheric CO_2 by **1** was confirmed by ESI-MS (see Supporting Information, Figure S1). Initially, **1** in acetonitrile showed four species: $[Cu_2L^1-H]^{3+}$, $[Cu_2L^1-2H]^{2+}$, $[Cu_2L^1-3H]^{+}$, and $[Cu_2L^1(ClO_4)-2H]^{+}$. After the solution was kept at room temperature in an open vessel for a few hours, these four peaks almost disappeared, and three new species corresponding to $[Cu_2L^1(HCO_3)]^{3+}$, $[Cu_2L^1(HCO_3)(ClO_4)]^{2+}$, and $[Cu_2L^1(CO_3)]^{2+}$ were observed. However, when the solution was left under nitrogen atmosphere for 7 days, only the new species $[Cu_2L^1(OH)-H]^{2+}$ was observed, and no species corresponding to HCO_3^-- or CO_3^{2-}-bridged dicopper cryptates were present. This clearly indicates that the bicarbonate anion in **2** comes from the hydration of atmospheric CO_2. Furthermore, in the presence of more strongly coordinating anions such as acetate and NO_3^-, Cu^{II} reacted with L^1 in air to give the acetate-bridged dicopper complex **9** and the NO_3^--coordinated dicopper complex **10**, respectively, instead of the bicarbonate-bridged complex. This indicates that CO_2 fixation is prohibited when the axial positions of Cu^{II} are occupied by strongly coordinating anions.

For **2**·CH_3CN and **2**·$2CH_3CN$, the ESI mass spectra show the existence of both carbonate and bicarbonate species with substantial intensity. The appearance of carbonate is probably due to the removal of protons during the ionization process. All monoalkylcarbonato species gave rise to distinct peaks corresponding to $[Cu_2L^1(\mu\text{-}O_2COR)(ClO_4)_2]^{+}$, $[Cu_2L^1(\mu\text{-}O_2COR)ClO_4]^{2+}$, and $[Cu_2L^1(\mu\text{-}O_2COR)]^{3+}$, respectively, which supports the monoalkylcarbonato-bridged dicopper structures. Furthermore, when **2** reacted with CD_3OH instead of CH_3OH, the peaks corresponding to $[Cu_2L^1(\mu\text{-}O_2COR)(ClO_4)_2]^{+}$ and $[Cu_2L^1(\mu\text{-}O_2COR)ClO_4]^{2+}$

shifted from $m/z = 999$ and 450, respectively, in methanol to $m/z = 1004$ and 452 in [D$_4$]methanol. (For **3** and **3a** ($[Cu_2L^1(\mu\text{-}O_2COCD_3)](ClO_4)_3$), the trivalent species were not observed.) This clearly indicates that transformation from HCO_3^- to $ROCO_2^-$ takes place in primary alcohols. However, no transforming reaction occurred in the secondary alcohol *i*PrOH (see Supporting Information, Figure S2). This could be attributed to the limited space in the cryptate,[8a] which allows the formation of monoalkylcarbonates of primary alcohols, but not higher alcohols, between two copper atoms.

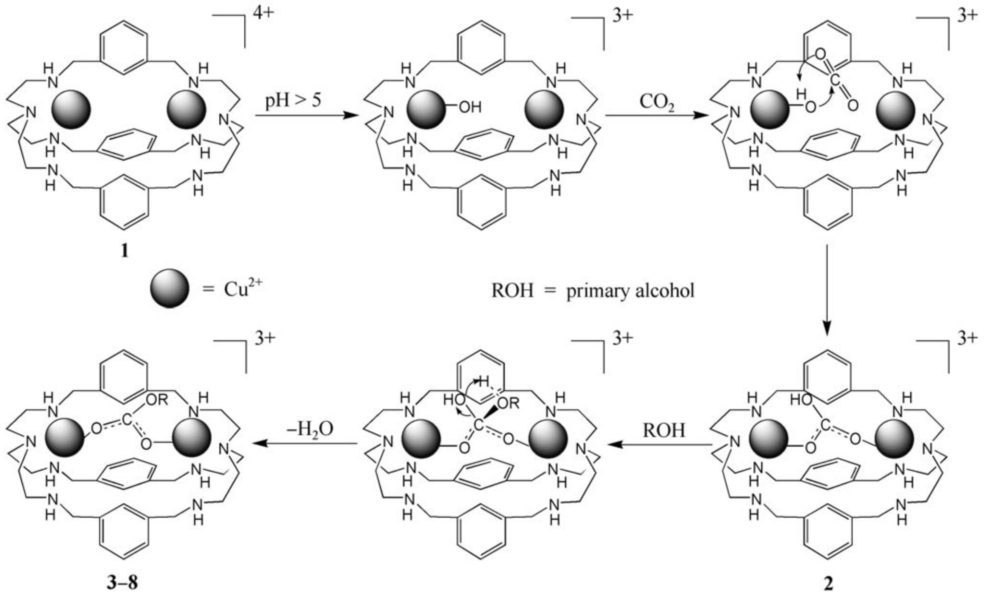
DFT Calculations

The geometry-optimized structural parameters are in reasonable agreement with the structures determined by X-ray crystallography (see Supporting Information, Table S2). The slight discrepancies are probably the consequence of crystal-packing forces and the presence of counteranions and solvent molecules in the solid-state structures. All the cations of **2–6** showed similar frontier molecular orbitals, in which the HOMOs and LUMOs are mainly from L^1 and from both $L^1$and copper, respectively (see Supporting Information, Figure S4 and Table S3); the $\mu\text{-}O_2COH^-$ and $\mu\text{-}O_2COR^-$ bridges showed little contribution to the frontier molecular orbitals. This implies that the esterification of $\mu\text{-}O_2COH^-$ does not significantly modify the stability of **2–6**. On the basis of the calculated frontier-molecular-orbital energies (see Supporting Information, Tables S3 and S4), all the cations of **2–6** showed similar HOMO and LUMO orbital energies, which also indicates that these cations have similar stability. During the optimization, the coordination mode of $\mu\text{-}O_2COH^-$ in **2** changed from symmetrical to asymmetrical, whereas the $\mu\text{-}O_2COR^-$ anions in **3–6** retained the asymmetrical mode. This suggests that the asymmetrical mode is more stable than the symmetrical.

The Mulliken and natural electron charges on copper, L^1, $\mu\text{-}O_2COH^-/\mu\text{-}O_2COR^-$ bridges, the carbon atoms in the bridges of the cations of **2–6**, and the uncoordinated O_2COH^-/O_2COR^- ions are listed in the Supporting Information (Table S5). The Mulliken and net natural electron charges of the $\mu\text{-}O_2COH^-$ bridge in $[Cu_2L^1(\mu\text{-}O_2COH)]^{3+}$ are -0.47 (Mulliken population analysis; MPA) and -0.85 (natural population analysis; NPA), which indicates very significant electron donation from the $\mu\text{-}O_2COH^-$ group to the d orbitals of Cu^{II} after formation of $\mu\text{-}O_2COH^-$-bridged **2**. The electronic charge of the carbon atom in the $\mu\text{-}O_2COH^-$ bridge thus becomes much more positive (MPA = 0.86, NPA = 1.09) compared with that in the uncoordinated O_2COH^- group (MPA = 0.62, NPA = 0.98). This indicates that the O_2COH^- anion is activated after coordination to Cu^{II}, that is, the electrophilic reactivity of the carbon atom in the $\mu\text{-}O_2COH^-$ bridge is increased through ligand coordination with Cu^{II}, so it is more susceptible to nucleophilic attack by the solvent.

Mechanism of CO_2 Fixation and Esterification

Although it is well-known that the fixation of CO_2 by metal complexes in basic solution occurs via hydroxo species to afford metal carbonate derivatives,[5,7,17] the fixation of CO_2 in acidic media is rather unusual, and only a few such examples have been reported so far.[8a] We have now found that $[Cu_2L^1](ClO_4)_4$ can easily fix atmospheric CO_2 in the form of the bicarbonate in neutral or even weakly acidic media. CO_2 fixation by $[Cu_2L^1]^{4+}$ may follow a mechanism analogous to that for bicarbonate formation. As shown in Scheme 2, the initially coordinated water molecule loses a proton to give the species $[Cu_2(OH)L^1]^{3+}$. OH^- then attacks the carbon atom in CO_2 to form the $\mu\text{-}O_2COH^-$-bridged cryptate $[Cu_2L^1(\mu\text{-}O_2COH)]^{3+}$ (**2**). Interestingly, the corresponding mononuclear complex $[Cu(tren)(H_2O)](ClO_4)_2$



Scheme 2. Proposed mechanism for CO_2 fixation and esterification by $[Cu_2L^1]^{4+}$.

(tren = tris(2-aminoethyl)amine) does not take up atmospheric CO_2, and $[\{Cu(tren)\}_2(\mu\text{-}O_2COH)](ClO_4)_3$ could only be obtained by adding HCO_3^- in acidic medium.[18] The ability of $[Cu_2L^1]^{4+}$ to fix atmospheric CO_2 in weakly acidic medium may be due to the extremely low pK_a value of the $[Cu_2L^1(OH)]^{3+}$ species (4.58[11]), which enables it to take up CO_2 at $pH > 5$.

Nelson and co-workers[12] presumed that the generation of $O_2COCH_3^-$ by $[Cu_2L^1]^{4+}$ in methanol may occur through CO_2 insertion into the M−OCH_3 bond. If alkylcarbonate formation depended on this event, the mononuclear complex $[CuL^3]^{2+}$ in methanol should easily generate the complex $[CuL^3(O_2COCH_3)]^+$. However, ESI-MS revealed that the corresponding mononuclear complexes $[Cu(tren)(H_2O)](ClO_4)_2$ and $[CuL^3(H_2O)](ClO_4)_2$ in CH_3OH/CH_3CN (1:1) did not generate the methylcarbonate species, even when $NaOCH_3$ was added and the solution left in the open for 3 days (see Supporting Information, Figure S3). This suggests that alkylcarbonate formation does not result from CO_2 insertion into the M−OCH_3 bond. In fact, alkylcarbonate formation may involve two steps: the formation of the intermediate $[Cu_2L^1(\mu\text{-}O_2COH)]^{3+}$, and its esterification with primary alcohols. Furthermore, $\mu\text{-}O_2COH^-$ formation is necessary for esterification, as only synchronous activation by two Cu^{II} atoms on $\mu\text{-}O_2COH^-$ will lead to increased positive charge on the carbon atom in the $\mu\text{-}O_2COH^-$ bridge, so that electrophilic attack by the primary alcohol can take place. On the basis of our ESI-MS results and DFT calculations, there is no doubt that the esterification of **2** proceeds via tetrahedral intermediates as shown in Scheme 2. In the process of esterification, the electrophilic carbon atom of $\mu\text{-}O_2COH^-$ in **2** is attacked by the primary alcohol to form a tetrahedral intermediate, which is then converted into the $\mu\text{-}O_2COR^-$-bridged cryptates $[Cu_2L^1(\mu\text{-}O_2COR)]^{3+}$ by elimination of water.

Reactivity Controlled by Ligand Conformation

Although L^1 and L^2 have similar structures, they show different reactivity. The dinuclear complex $[Cu_2L^1]^{4+}$ dissolved in acetonitrile easily absorbed atmospheric CO_2 in an open vessel to form the $\mu\text{-}O_2COH^-$-bridged cryptate $[Cu_2L^1(\mu\text{-}O_2COH)]^{3+}$ within a few minutes, as monitored by UV/Vis spectroscopy (see Supporting Information, Figure S5). $[Cu_2L^1(\mu\text{-}O_2COH)]^{3+}$ does not cleave the C−C bond of acetonitrile as the axial positions of both Cu^{II} ions are occupied by the $\mu\text{-}O_2COH^-$ bridge. On the contrary, $[Cu_2L^2]^{4+}$ in acetonitrile does not take up atmospheric CO_2, so the axial sites can be occupied by acetonitrile; thus, $[Cu_2L^2]^{4+}$ can cleave the C−C bond of acetonitrile to form the cyano-bridged complex $[Cu_2L^2(CN)]^{3+}$ and methanol.

As shown in Figure 1b, the three phenyl rings of L^2 adopt a rigid triangular conformation, and the conformational conversion from stable triangle to form A or B goes through a large energy barrier. As a consequence, it is difficult for large molecules or anions to enter the binding cavity of $[Cu_2L^2]^{4+}$, hence it does not fix atmospheric CO_2. The only exception is $[Cu_2L^2(im)](ClO_4)_3$ (im = imidazolate),[19] in which L^2 adopts the conformation form A. In this complex, the imidazolate ligand is located between two parallel phenyl rings to form a sandwichlike structure with strong $\pi\cdots\pi$ interactions between the imidazolate and the two phenyl rings. The strong $\pi\cdots\pi$ interaction means that L^2 can overcome the energy barrier of conversion from triangle to form A to form the stable complex $[Cu_2L^2(im)](ClO_4)_3$. The conformation of L^1 is more flexible than that of L^2; two of three phenyl rings in L^1 can rotate to some degree to generate a larger window in the binding cavity (Figure 1b), which can accommodate planar O_2COH^- and O_2COR^- groups. Therefore, $[Cu_2L^1]^{4+}$ can take up atmospheric CO_2 to form **2** and transform it into **3**–**8** in the presence of primary alcohols. For secondary alcohols such as *i*PrOH, no esterification occurs due to the limited cavity space. This sterically induced selective esterification may be potentially useful for the synthesis of symmetric or unsymmetric carbonate esters.

Conclusions

In summary, a bicarbonate-bridged and a series of monoalkylcarbonate-bridged cryptates have been synthesized. $[Cu_2L^1](ClO_4)_4$ (**1**) absorbs atmospheric CO_2 easily to form the $\mu\text{-}O_2COH^-$-bridged complex **2** even under acidic conditions because of the extremely low pK_a value of the intermediate $[Cu_2L^1(OH)]^{3+}$; this process follows the mechanism of bicarbonate formation. The coordination of O_2COH^- to two Cu^{II} ions activates its carboxy carbon atom so that it is more easily attacked by primary alcohols to generate monoalkylcarbonate-bridged complexes **3**–**8** via tetrahedral intermediates. Notably, different metal ions may also play a crucial role in CO_2 fixation and transformation. Atmospheric CO_2 fixation and transformation by $[Cu_2L^1]^{4+}$ may potentially be used for the preparation of valuable carbon-containing compounds such as symmetrical and unsymmetric carbonate esters. Optimization efforts directed along these lines are currently ongoing in our group.

Experimental Section

General

Ligand L^3 and its mononuclear complex $[CuL^3(H_2O)](ClO_4)_2$ were prepared by literature methods.[20] All other solvents and chemicals were commercially available and used without further purification. Elemental analysis was performed with an Elementar Vario EL elemental analyzer. IR spectra were recorded in the 4000–400-cm^{-1} region at room temperature by using KBr pellets and a Bruker EQUINOX 55 spectrometer. ESI mass spectra were recorded on a Thermo Finnigan LCQ DECA XP ion-trap mass spectrometer. pH values were measured with an HANNA pH213 meter with an HI1330 electrode. UV/Vis spectra were recorded on a Shimadzu UV-3150 spectrophotometer.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care.

Syntheses

L^1: Prepared by a modified literature method.[11] A solution of tris(2-aminoethyl)amine (1.51 g, 0.0103 mol) in CH_3OH (150 mL) was added dropwise to a stirred solution of benzene-1,3-dicarboxaldehyde (2.08 g, 0.0155 mol) in CH_3OH (300 mL) over 1 h. After the mixture was stirred at room temperature for 24 h, the resulting yellowish solution was reduced to 100 mL under reduced pressure. The solution was cooled to 0 °C on an ice bath, and $NaBH_4$ (4.30 g, 0.114 mol) was then added. The suspension was stirred at room temperature for 2 h, then heated to 50 °C and stirred at this temperature for an additional 20 h to ensure that the reduction was complete. The solvent was removed under reduced pressure, and water (50 mL) was added. The product was extracted with toluene. The organic phase was dried over $MgSO_4$ and filtered. Evaporation of the filtrate under reduced pressure yielded a yellowish oil. It was recrystallized from toluene to give a white solid (2.16 g, 70 %). MS (ESI): *m/z* calcd for $C_{36}H_{54}N_8$: 599.9 $[HL^1]^+$, 300.4 $[H_2L^1]^{2+}$; found: 600.2, 300.5; elemental analysis: calcd (%) for $C_{36}H_{54}N_8{\cdot}0.5H_2O$ ($L^1{\cdot}0.5H_2O$): C 71.13, H 9.12, N 18.43; found: C 70.74, H 9.32, N 18.02. L^1 easily absorbs atmospheric CO_2 to form $[H_2L^1]CO_3$. To obtain the CO_2-free ligand, the dry product L^1 was dissolved in a small amount of acetone, the solution was kept on an ice-bath, and excess $HClO_4$ was added dropwise to give a white precipitate. After the mixture was stirred for 15 min, the precipitate was filtered, washed with a small amount of acetone and diethyl ether, and then dried under vacuum to give the white solid $L^1{\cdot}8HClO_4$ (4.34 g, 86 %). MS (ESI): *m/z* calcd for $C_{36}H_{54}N_8HClO_4$: 350.7 $[H_3L^1ClO_4]^{2+}$, 300.4 $[H_2L^1]^{2+}$; found: 349.4, 300.5; elemental analysis: calcd (%) for $C_{36}H_{78}N_8Cl_8O_{40}$ ($L^1{\cdot}8HClO_4{\cdot}8H_2O$): C 27.96, H 5.08, N 7.24; found: C 28.32, H 4.82, N 7.31.

1: This reaction was carried out under nitrogen atmosphere. A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (2.10 g, 5.67 mmol) in anhydrous ethanol (12 mL) was added to a solution of $L^1{\cdot}8HClO_4$ (3.00 g, 2.14 mmol) and NaOH (0.67 g, 16.80 mmol) in anhydrous ethanol (250 mL). The mixture was stirred at room temperature for 15 min, and the blue precipitate formed was filtered, washed with ethanol and diethyl ether, and dried under vacuum to give **1** as a blue powder (1.74 g, 75 %). IR (KBr): $\tilde{\nu}$ = 1629, 1450 cm^{-1} (Ar); MS (FAB): *m/z* calcd for $[Cu_2L^1](ClO_4)_4$: 823.4 $[Cu_2L^1(ClO_4){-}2H]^+$; found: 823.0; elemental analysis: calcd (%) for $C_{36}H_{70}N_8Cu_2Cl_4O_{24}$(**1**$\cdot 8H_2O$): C 34.10, H 5.56, N 8.84; found: C 34.46, H 5.22, N 9.03.

2: The blue powder of **1** (1.00 g, 0.89 mmol) was dissolved in acetonitrile (20 mL) to give an acidic solution (an accurate pH value could not be obtained due to fluctuations). The solution was evaporated slowly in an open vessel at room temperature. After about 6 days, blue crystals of **2**$\cdot CH_3CN$ were obtained (0.69 g, 69 %); the remaining solution was still acidic. IR (KBr): $\tilde{\nu}$ = 1553, 1331 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_3H)L^1](ClO_4)_3$: 885.4 $[Cu_2(CO_3H)L^1(ClO_4)_2]^+$, 443.2 $[Cu_2(CO_3H)L^1(ClO_4)]^{2+}$, 393.0 $[Cu_2(CO_3)L^1]^{2+}$; found: 885.0, 441.6, 392.1; elemental analysis: calcd (%) for $C_{37}H_{61}N_8Cu_2Cl_3O_{18}$ (**2**$\cdot 3H_2O$): C 39.00, H 5.40, N 9.83; found:C 38.96, H 5.56, N 9.83 (in all cases, the crystals were dried under vacuum before elemental analysis).

The final pH values after crystallization of all the other cryptates **3**–**8** from acetonitrile were also in the acidic range. As the measurement of pH in acetonitrile might not be accurate, a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ and L^1 (2:1) in water was exposed to the atmosphere; the pH of this solution was 5.3. ESI-MS indicates that **2** was also formed in this solution, with a final pH value of 5.1. Thus, there is no doubt that fixing of atmospheric CO_2 can take place under acidic conditions.

3: The blue powder of **2** (0.50 g, 0.46 mmol) was dissolved in acetonitrile (10 mL) and methanol (8 mL). The solution was evaporated slowly at room temperature. After about one week, blue crystals of **3**$\cdot 2CH_3CN$ were obtained (0.41 g, 75 %). IR (KBr): $\tilde{\nu}$ = 1633, 1348 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_3CH_3)L^1](ClO_4)_3$: 999.9 $[Cu_2(CO_3CH_3)L^1(ClO_4)_2]^+$, 450.3 $[Cu_2(CO_3CH_3)L^1(ClO_4)]^{2+}$; found: 998.9, 450.1; elemental analysis: calcd (%) for $C_{38}H_{63}N_8Cu_2Cl_3O_{18}$ (**3**$\cdot 3H_2O$): C 39.57, H 5.51, N 9.72; found: C 39.32, H 5.33, N 9.91.

Alternative method for **2** and **3**: A solution of $L^1{\cdot}8HClO_4$ (0.50 g, 0.36 mmol) and NaOH (0.11 g, 2.8 mmol) in methanol (35 mL) was added dropwise to a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.35 g, 0.94 mmol) in methanol (2 mL) to obtain a pH value of 5–6. After the mixture was stirred at room temperature for 15 min, the blue precipitate formed was filtered and washed with methanol. The precipitate contained a mixture of **2** and **3** (as indicated by ESI-MS). The precipitate was then dissolved in acetonitrile (5 mL), and the solution was filtered. The filtrate was evaporated slowly at room temperature. After about 5 days, blue crystals of **2**$\cdot 2CH_3CN$ (0.09 g, ≈22 %) and **3**$\cdot 4.5CH_3CN{\cdot}0.5H_2O$ (0.06 g, 13 %) were obtained from the solution (yields based on the isolated crystals; there was still a large amount of product in solution). **2**: IR (KBr): $\tilde{\nu}$ = 1551, 1405 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_3H)L^1](ClO_4)_3$: 885.4 $[Cu_2(CO_3H)L^1(ClO_4)_2]^+$, 443.2 $[Cu_2(CO_3H)L^1(ClO_4)]^{2+}$, 393.0 $[Cu_2(CO_3)L^1]^{2+}$; found: 885.1, 442.9, 392.2; elemental analysis: calcd (%) for $C_{37}H_{61}N_8Cu_2Cl_3O_{18}$ (**2**$\cdot 3H_2O$): C 39.00, H 5.40, N 9.83; found: C 39.32, H 5.68, N 10.07. **3**: elemental analysis: calcd (%) for $C_{38}H_{62}N_8Cu_2Cl_3O_{17.5}$ (**3**$\cdot 2.5H_2O$): C 39.90, H 5.42, N 9.79; found: C 39.99, H 5.72, N 9.73.

3a: The blue powder of **2** (0.100 g, 0.092 mmol) was dissolved in acetonitrile (2 mL) and [D$_4$]methanol (1.5 mL). The solution was allowed to evaporate slowly in air at room temperature. After about 3 days, blue crystals of **3a** were obtained (0.076 g, 75 %). IR (KBr): $\tilde{\nu}$ = 1635, 1377 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_3CD_3)L^1](ClO_4)_3$: 1002.9 $[Cu_2(CO_3CD_3)L^1(ClO_4)_2]^+$, 451.7 $[Cu_2(CO_3CD_3)L^1(ClO_4)]^{2+}$; found: 1004.0, 452.0; elemental analysis: calcd (%) for $C_{38}H_{64}D_3N_8Cu_2Cl_3O_{20}$ (**3a**$\cdot 5H_2O$): C 38.28, H 5.91, N 9.40; found: C 38.01, H 5.58, N 9.34.

4–**8**: The blue powder of **2** was dissolved in acetonitrile and the corresponding alcohol. The solution was allowed to evaporate slowly in air at room temperature to give blue crystals. Yields: **4**: 0.05 g, 47 %; **5**: 0.04 g, 40 %; **6**: 0.07 g, 70 %; **7**: 0.06 g, 55 %; **8**: 0.07 g, 72 %.

4: IR (KBr): $\tilde{\nu}$ = 1630, 1325 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_2C_2H_5)L^1](ClO_4)_3$: 1013.9 $[Cu_2(CO_3C_2H_5)L^1(ClO_4)_2]^+$, 457.2 $[Cu_2(CO_3C_2H_5)L^1(ClO_4)]^{2+}$, 271.7 $[Cu_2(CO_3C_2H_5)L^1]^{3+}$; found: 1013.0, 457.1, 271.1; elemental analysis: calcd (%) for $C_{39}H_{65}N_8Cu_2Cl_3O_{18}$ (**4**$\cdot 3H_2O$): C 40.12, H 5.61, N 9.60; found: C 39.80, H 5.61, N 9.80.

5: IR (KBr): $\tilde{\nu}$ = 1638, 1326 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_2C_3H_7)L^1](ClO_4)_3$: 1028.0 $[Cu_2(CO_3C_3H_7)L^1(ClO_4)_2]^+$, 464.3 $[Cu_2(CO_3C_3H_7)L^1(ClO_4)]^{2+}$, 276.4 $[Cu_2(CO_3C_3H_7)L^1]^{3+}$; found: 1027.0, 464.1, 275.9; elemental analysis: calcd (%) for $C_{40}H_{71}N_8Cu_2Cl_3O_{20}$ (**5**$\cdot 5H_2O$): C 41.94, H 5.54, N 9.84; found: C 41.92, H 5.47, N 9.78.

6: IR (KBr): $\tilde{\nu}$ = 1634, 1329 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_2C_4H_9)L^1](ClO_4)_3$: 1042.0 $[Cu_2(CO_3C_4H_9)L^1(ClO_4)_2]^+$, 471.3 $[Cu_2(CO_3C_4H_9)L^1(ClO_4)]^{2+}$, 281.0 $[Cu_2(CO_3C_4H_9)L^1]^{3+}$; found: 1040.9, 471.1, 280.4; elemental analysis: calcd (%) for $C_{43}H_{66}N_9Cu_2Cl_3O_{15}$ (**6**$\cdot CH_3CN$): C 43.68, H 5.63, N 10.66; found: C 43.12, H 5.59, N 10.72.

7: IR (KBr): $\tilde{\nu}$ = 1638, 1403, 1323 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_2C_5H_{11})L^1](ClO_4)_3$: 1056.0 $[Cu_2(CO_3C_5H_{11})L^1(ClO_4)_2]^+$, 478.3 $[Cu_2(CO_3C_5H_{11})L^1(ClO_4)]^{2+}$, 285.7 $[Cu_2(CO_3C_5H_{11})L^1]^{3+}$; found: 1055.1, 478.1, 285.9; elemental analysis: calcd (%) for $C_{42}H_{75}N_8Cu_2Cl_3O_{20}$ (**7**$\cdot 5H_2O$): C 40.50, H 6.07, N 9.00; found: C 40.03, H 6.07, N 9.53.

8: IR (KBr): $\tilde{\nu}$ = 1642, 1403, 1323 cm^{-1} (OCO_2); MS (ESI): *m/z* calcd for $[Cu_2(CO_3CH_2CH_2OH)L^1](ClO_4)_3$: 1029.9 $[Cu_2(CO_3C_2H_4OH)L^1(ClO_4)_2]^+$, 465.2 $[Cu_2(CO_3C_2H_4OH)L^1(ClO_4)]^{2+}$, 277.0 $[Cu_2(CO_3C_2H_4OH)L^1]^{3+}$; found: 1029.0, 465.1, 276.5; elemental analysis: calcd (%) for $C_{39}H_{61}N_8Cu_2Cl_3O_{17}$ (**8**$\cdot H_2O$): C 40.82, H 5.36, N 9.77; found: C 40.45, H 5.42, N 9.99.

9: A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.105 g, 0.30 mmol) in methanol (5 mL) and acetonitrile (5 mL) was added to a solution of L^1 (0.087 g, 0.15 mmol) in methanol (5 mL) . The solution was stirred for 5 min, then a solution of sodium acetate (0.018 g, 0.22 mmol) in methanol (5 mL) was added. The resulting solution was evaporated slowly at room temperature. After about 2 days, blue crystals of **9** were obtained (0.084 g, 52 %). IR (KBr): $\tilde{\nu}$ = 1611, 1578, 1281 cm^{-1} (OCO); MS (ESI): *m/z* calcd for $[Cu_2(CO_2CH_3)L^1](ClO_4)_3$: 983.9 $[Cu_2(CO_2CH_3)L^1(ClO_4)_2]^+$, 442.2 $[Cu_2(CO_2CH_3)L^1(ClO_4)]^{2+}$, 261.7 $[Cu_2(CO_2CH_3)L^1]^{3+}$; found: 982.8, 441.9, 261.8; elemental analysis: calcd (%) for $C_{38}H_{55}N_8Cu_2Cl_3O_{15}$ (**9**$\cdot H_2O$): C 41.44, H 5.40, N 10.17; found: C 41.32, H 5.65, N 10.13.

10: A solution of L^1 (0.15 g, 0.25 mmol) in methanol (3 mL) and a solution of Na_2SO_4 (0.035 g, 0.25 mmol) in water (0.5 mL) was added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.12 g, 0.50 mmol) in methanol (3 mL). After the mixture was stirred at room temperature for 18 h, the blue precipitate formed was filtered out, and the filtrate was evaporated in air for 8 days to give blue crystals of **10**$\cdot 2H_2O$ (0.05 g, 18 %). IR (KBr): $\tilde{\nu}=1384$, 1017 cm^{-1} (NO_3^-); elemental analysis: calcd (%) for $C_{37}H_{63}N_{12}Cu_2O_{15.5}$ (**10**$\cdot 2.5H_2O\cdot CH_3OH$): C 42.28, H 6.04, N 15.99; found: C 42.04, H 6.16, N 16.12.

Crystal-Structure Determination

Single-crystal data for **2**$\cdot 2CH_3CN$, **3**$\cdot 2CH_3CN$, **3**$\cdot 4.5CH_3CN\cdot 0.5H_2O$, **4**$\cdot 2CH_3CN$, **5**$\cdot CH_3CN$, **6**$\cdot CH_3CN$, and **10**$\cdot 2H_2O$ were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with $Mo_{K\alpha}$ radiation (λ= 0.71073 Å). All empirical absorption corrections were applied by using the SADABS program.[21] The structures were solved with direct methods, which yielded the positions of all non-hydrogen atoms. These were first refined isotropically and then anisotropically. All hydrogen atoms (except those bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure-factor calculations in the final stage of full-matrix least-squares refinement. The carbonate monoester groups in **3**$\cdot 2CH_3CN$, **4**$\cdot 2CH_3CN$, and **6**$\cdot CH_3CN$, as well as the ClO_4^- anions in **5**$\cdot CH_3CN$ and **6**$\cdot CH_3CN$ were found to be disordered. All calculations were performed with the SHELXTL-97 system of computer programs.[22] The crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. CCDC-635603–635609 (**2**$\cdot 2CH_3CN$, **3**$\cdot 2CH_3CN$, **3**$\cdot 4.5CH_3CN\cdot 0.5H_2O$, **4**$\cdot 2CH_3CN$, **5**$\cdot CH_3CN$, **6**$\cdot CH_3CN$, and **10**$\cdot 2H_2O$, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/data_request/cif.

Computational Details

DFT calculations and geometry optimizations were performed with the Gaussian 03 package[23] by using the B3LYP functional,[24] the 6-31G(d) basis set, and default settings for the convergence criteria. On the basis of the corresponding crystal structures, the structure of the cations of **2**$\cdot CH_3CN$, **3**$\cdot 2CH_3CN$, **4**$\cdot 2CH_3CN$, **5**$\cdot CH_3CN$, and **6**$\cdot CH_3CN$ were fully optimized on isolated entities in vacuum without any symmetry constraints. Wavefunction stability calculations were performed to confirm that the calculated wavefunctions corresponded to those of the ground state. Atomic charges were calculated by using MPA[25] and NPA[26] as implemented in Gaussian 03. GaussSum[27] was used to calculate the contributions from groups of atoms to each molecular orbital. Graphical representations of the orbitals were produced by the gOpenMol[28] graphics program. For reasons of computational expense due to the large size of our systems, frequency calculations were not carried out on the minima. The optimized Cartesian coordinates are given in Table S1 of the Supporting Information. Selected bond lengths and angles for the optimized geometries of the cations of **2**–**6** are summarized in Table S2. The orbital energies (ε) and composition (in terms of Cu, L^1, and the bridges) of the frontier molecular orbitals are listed in Table S3.

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[1] a) K. Caldeira, A. K. Jain, M. I. Hoffert, *Science* **2003**, *299*, 2052–2054; b) D. S. Jenkinson, D. E. Adams, A. Wild, *Nature* **1991**, *351*, 304–306.

[2] a) J. R. Bolton, *Science* **1978**, *202*, 705–711; b) R. Eisenberg, D. G. Nocera, *Inorg. Chem.* **2005**, *44*, 6799–6801.

[3] a) D. A. Palmer, R. van Eldik, *Chem. Rev.* **1983**, *83*, 651–731; b) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063–2095; c) W. Leitner, *Coord. Chem. Rev.* **1996**, *153*, 257–284; d) X. L. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27–59.

[4] a) Z. W. Mao, G. Liehr, R. van Eldik, *J. Am. Chem. Soc.* **2000**, *122*, 4839–4840; b) J. C. Kim, J. H. Cho, H. Kim, A. J. Lough, *Chem. Commun.* **2004**, 1796–1797.

[5] a) L. Y. Kong, Z. H. Zhang, H. F. Zhu, H. Kawaguchi, T. Okamura, M. Doi, Q. Chu, W. Y. Sun, N. Ueyama, *Angew. Chem.* **2005**, *117*, 4426–4429; *Angew. Chem. Int. Ed.* **2005**, *44*, 4352–4355; b) L. Y. Kong, H. F. Zhu, Y. Q. Huang, H. Kawaguchi, X. H. Lu, Y. Song, G. X. Liu, W. Y. Sun, N. Ueyama, *Inorg. Chem.* **2006**, *45*, 8098–8107; c) B. Verdejo, J. Aguilar, E. G. Espana, P. Gavina, J. Latorre, C. Soriano, J. M. Llinares, A. Domenech, *Inorg. Chem.* **2006**, *45*, 3803–3815; d) C. Bazzicalupi, A. Bencini, A. Bencini, A. Bianchi, F. Corana, V. Fusi, C. Giorgi, P. Paoli, P. Paoletti, B. Valtancoli, C. Zanchini, *Inorg. Chem.* **1996**, *35*, 5540–5548; e) A. Escuer, F. A. Mautner, E. Penalba, R. Vicente, *Inorg. Chem.* **1998**, *37*, 4190–4196; f) N. Kitajima, S. Hikichi, M. Tanaka, Y. Moro-oka, *J. Am. Chem. Soc.* **1993**, *115*, 5496–5508.

[6] a) M. H. Chisholm, F. A. Cotton, M. W. Extine, W. W. Reichert, *J. Am. Chem. Soc.* **1978**, *100*, 1727–1734; b) T. Tsuda, S. Sanada, K. Ueda, T. Saegusa, *Inorg. Chem.* **1976**, *15*, 2329–2332.

[7] a) M. Kato, T. Ito, *Inorg. Chem.* **1985**, *24*, 504–508; b) M. Kato, T. Ito, *Inorg. Chem.* **1985**, *24*, 509–514; c) M. Kato, T. Ito, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 285–294.

[8] a) B. Kersting, *Angew. Chem.* **2001**, *113*, 4109–4112; *Angew. Chem. Int. Ed.* **2001**, *40*, 3987–3990; b) S. Derossi, A. D. Bond, C. J. McKenzie, J. Nelson, *Acta Crystallogr. Sect. E* **2005**, *61*, m1379–m1382.

[9] a) W. E. Buhro, M. H. Chisholm, J. D. Martin, J. C. Huffmann, K. Folting, W. E. Streib, *J. Am. Chem. Soc.* **1989**, *111*, 8149–8156; b) E. García-España, P. Gaviña, J. Latorre, C. Soriano, B. Verdejo, *J. Am. Chem. Soc.* **2004**, *126*, 5082–5083; c) D. Dell'Amico Belli, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* **2003**, *103*, 3857–3897.

[10] a) V. McKee, J. Nelson, R. M. Town, *Chem. Soc. Rev.* **2003**, *32*, 309–325; b) M. A. Hossain, P. Morehouse, D. Powell, K. Bowman-James, *Inorg. Chem.* **2005**, *44*, 2143–2149.

[11] R. Menif, J. Reibenspies, A. E. Martell, *Inorg. Chem.* **1991**, *30*, 3446–3454.

[12] Y. Dussart, C. Harding, P. Dalgaard, C. McKenzie, R. Kadirvelraj, V. McKee, J. Nelson, *J. Chem. Soc. Dalton Trans.* **2002**, 1704–1713.

[13] a) J. L. Pierre, P. Chautemps, S. Refaif, C. Beguin, A. E. Marzouki, G. Serratrice, E. Saint-Aman, P. Rey, *J. Am. Chem. Soc.* **1995**, *117*, 1965–1973; b) C. J. Harding, V. McKee, J. Nelson, Q. Lu, *J. Chem. Soc. Chem. Commun.* **1993**, 1768–1770; c) C. J. Harding, F. E. Mabbs, E. J. L. MacInnes, V. McKee, J. Nelson, *J. Chem. Soc. Dalton Trans.* **1996**, 3227–3230; d) A. Escuer, C. J. Harding, Y. Dussart, J. Nelson, V. McKee, R. Vicente, *J. Chem. Soc. Dalton Trans.* **1999**, 223–228; e) A. D. Bond, S. Derossi, C. J. Harding, E. J. L. McInnes, V. McKee, C. J. McKenzie, J. Nelson, *Dalton Trans.* **2005**, 2403–2409.

[14] T. Lu, X. Zhuang, Y. Li, S. Chen, *J. Am. Chem. Soc.* **2004**, *126*, 4760–4761.

[15] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349–1356.

[16] M. Aresta, D. Ballivet-Tkatchenko, D. B. Dell'Amico, M. C. Bonnet, D. Boschi, F. Calderrazzo, F. Faure, L. Labella, F. Marchetti, *Chem. Commun.* **2000**, 1099–1100.

[17] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry, 6th ed.*, Wiley, New York, **1999**, p. 1225.

[18] Z. W. Mao, G. Liehr, R. van Eldik, *J. Chem. Soc. Dalton Trans.* **2001**, 1593–1600.

[19] X.-M. Zhuang, T.-B. Lu, S. Chen, *Inorg. Chim. Acta* **2005**, *358*, 2129–2134.

[20] a) M. A. Hossain, J. A. Liljegren, D. Powell, K. Bowman-James, *Inorg. Chem.* **2004**, *43*, 3751–3755; b) M. Schatz, M. Becker, O. Walter, G. Liehr, S. Schindler, *Inorg. Chim. Acta* **2001**, *324*, 173–179.

[21] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany), **1996**.
[22] G. M. Sheldrick, SHELXTL-97, Program for Crystal Structure Solution and Refinement, University of Göttingen, Göttingen (Germany), **1997**.
[23] Gaussian 03 (Revision B.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross,C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham,C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA (USA), **2003**.
[24] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[25] R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833–1840.
[26] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.
[27] M. N. O'Boyle, G. J. Vos, GaussSum 1.0, to be found under http://gausssum.sourceforge.net, Dublin City University, Dublin (Ireland), **2005**.
[28] a) L. Laaksonen, *J. Mol. Graphics* **1992**, *10*, 33–34; b) D. L. Bergman, L. Laaksonen, A. Laaksonen, *J. Mol. Graphics Modell.* **1997**, *15*, 301–306.

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