Supramolecular Assembly with Calix[6]arene and Copper Ions − Formation of a Novel Tetranuclear Core Exhibiting Unusual Redox Properties and Catecholase Activity

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The supramolecular biomimetic chemistry based on calix[6]arene N-ligands has been further explored. A tris(imidazole)Cu^I complex was treated with 1 mol-equiv. of cuprous ion under dioxygen to produce a tetranuclear cupric species. X-ray structural determination of this novel Cu_4 complex revealed that the self-inclusion of an imidazolyl coordinating arm into the hydrophobic calixarene cavity provides the base of coordination for a $\{ClImCu(OH)_2CuIm_2\}_2$ assembly. The Cu_4 core is maintained in solution and is stable even in a coordinating solvent such as acetonitrile. Magnetic susceptibility measurements evidenced a strong antiferromagnetic coupling in each $Cu(OH)_2Cu$ subunit with $J = -408\ cm^{-1}$. The complex displayed catecholase activity in the presence of 3,5-di-*tert*-butylcatechol behaving as a four-electron hole with, however, a sluggish $Cu^I_4 \rightarrow Cu^{II}_4$ regeneration through O_2 autooxidation. Finally, electrochemical studies revealed two oxidative reversible processes that successively gave rise to a $\{Cu^{II}Cu^{III}\}\{Cu^{II}_2\}$ and a $\{Cu^{II}Cu^{III}\}_2$ mixed-valence species that could be characterized by UV/Vis and EPR spectroscopy. The overall structure and behavior of this tetranuclear complex is reminiscent of multicopper enzymes.

Introduction

The synthesis of polynuclear complexes that can be studied in solution is an important topic in view of the potential role of such species in multi-metal-centered catalysis in both biological and industrial reactions. Multi-copper-containing oxygenases and oxidases have been intensively studied in recent years.[1−3] Indeed they have revealed a synergism between the copper sites on the activation of O_2. While dinuclear systems are now fairly well documented,[4] clusters of higher nuclearity appear more difficult to study. Several tetranuclear copper complexes have been described recently, displaying a wide diversity of structures of the metal cluster.[5−7] However, little information concerning their redox properties has been reported,[8] partly because of their lack of stability in solution.

In the recent past, we have been particularly interested in the synthesis, structural characterization and reactivity of copper complexes containing calix[6]arene-based N-ligands. We have shown that these supramolecular systems provide remarkable models for the type 2 active sites of copper enzymes in both Cu^I and Cu^{II} states.[9−11] In the process of studying the reactivity of the tris(imidazole)-based mononuclear cuprous complexes,[10] we have found that, in the presence of a second mol-equiv. of Cu^I, they can give rise to highly stable tetranuclear species. Here, we report the synthesis and structural characterization of a novel complex presenting a $[Cu_2(OH)_2]_2$ core with some very interesting redox properties.

Results

Synthesis and Characterization of $[Cu_4(X_6Me_3Imme_3)_2(OH)_4(Cl)_2](PF_6)_2$ (2)

Equimolar quantities of ligand $X_6Me_3Imme_3$ [12] and CuCl were first allowed to react in THF under argon to produce the cuprous complex $[Cu(X_6Me_3Imme_3)Cl]$ (**1**) that slowly precipitated out of the solution (Scheme 1). Upon

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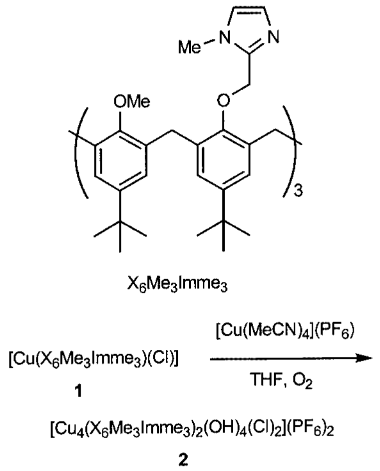
the addition of 1 mol-equiv. of $[Cu(MeCN)_4](PF_6)$ followed by dioxygen bubbling, a green solution was obtained and a blue precipitate slowly formed overnight. The isolated solid **2** was quite soluble in chlorinated solvents. Besides the absorptions characteristic of $X_6Me_3Imme_3$ and PF_6^-, the IR spectrum displayed a strong absorption at 3510 cm^{-1} that can be assigned to OH ligands. The UV/Vis spectrum in CH_2Cl_2 exhibited features at 359 and 633 nm attributed to LMCT (hydroxide or chloride to Cu^{II}) and d-d transitions, respectively. The EPR spectrum (100 K in CH_2Cl_2 or CH_2Cl_2/MeCN) showed only very weak signals at $g = 2$ and 4. The half field lines indicate the presence of exchange-coupled Cu^{II} ions,[13] whereas the signal at $g = 2$ may be attributed to traces of monomeric cupric impurities. The ^1H NMR spectrum presented both well-defined and broad peaks. However, most of the resonances were located in the diamagnetic region, suggesting an antiferromagnetic coupling between the copper ions. Elemental analysis of compound **2** was in good agreement with the formula $[Cu_4(X_6Me_3Imme_3)_2(OH)_4(Cl)_2](PF_6)_2$. Finally, the dicationic nature of complex **2** was confirmed by ES-MS analysis performed either in CH_2Cl_2 or MeCN solution. It is noteworthy that the ES-MS experiment showed that the tetranuclear entity was conserved in solution even in a dissociating and coordinating solvent such as MeCN.



Scheme 1. Synthesis of tetranuclear complex **2**

Crystal Structure of 2

The molecular structure of this tetranuclear complex is depicted in Figure 1 and selected interatomic distances and angles are listed in Table 1. It presents an inversion center in the middle of a "stepped-cubane" Cu_4O_4 core, located between two tris(imidazolyl)calix[6]arene-based ligands that are stacked head to head. The metallic core can be viewed as two Cu_2O_2 units linked together, in which the two copper ions have a different coordination sphere.

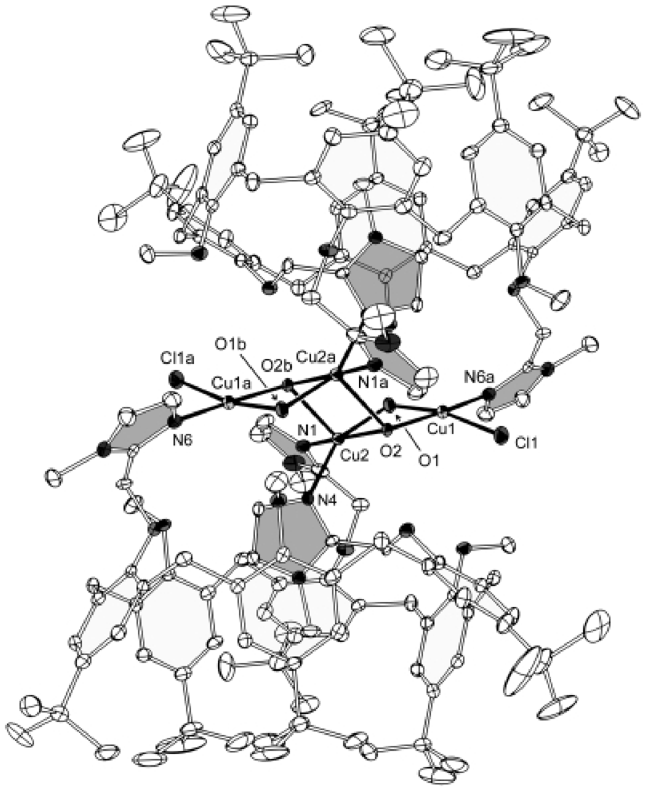


Figure 1. Crystal structure of $[Cu_4(X_6Me_3Imme_3)_2(OH)_4(Cl)_2](PF_6)_2$ (**2**) showing ellipsoids at 20% probability; hydrogen atoms, hexafluorophosphate counterions and solvent of crystallization have been omitted for clarity

Table 1. Selected interatomic distances [Å] and angles [°] for **2**

Interatomic distances[a]			
Cu1−Cl	2.230(5)	Cu2−N4	1.994(6)
Cu1−O1	1.910(6)	Cu2−O2a	2.272(7)
Cu1−O2	1.965(5)	Cu1···Cu2	2.983(1)
Cu1−N6a	1.986(7)	Cu1···Cu2a	3.770(1)
Cu2−O1	1.932(5)	Cu2···Cu2a	3.056(2)
Cu2−O2	1.988(7)	O1···O2	2.46(1)
Cu2−N1	1.97(1)	O2···O2a	2.98(2)
Angles			
Cu1−O1−Cu2	101.8(3)	Cl1−Cu1−O2	93.8(3)
Cu1−O2−Cu2	97.9(5)	N6a−Cu1−O2	170.8(3)
Cu1−O2−Cu2a	125.6(3)	N4−Cu2−O2	94.2(3)
Cu2−O2−Cu2a	91.5(3)	N4−Cu2−N1	93.5(4)
O1−Cu1−O2	78.7(3)	N1−Cu2−O2	168.1(3)
O1−Cu2−O2	77.6(3)	N1−Cu2−O1	91.4(3)
O1−Cu2−O2a	110.7(3)	N4−Cu2−O1	153.0(3)
O2−Cu2−O2a	88.5(3)	N1−Cu2−O2a	99.9(3)
Cl1−Cu1−N6a	95.1(3)	N4−Cu2−O2a	94.5(3)
Cl1−Cu1−O1	168.2(2)		

[a] Symmetry transformation for equivalent atoms: $1 - x$, $-y$, $1 - z$.

In each discrete subunit, the Cu−O bond lengths (1.91−1.99 Å) as well as the Cu···Cu and O···O distances [*d*(Cu1···Cu2) = 2.98 Å; *d*(O1···O2) = 2.46 Å] are similar to those reported for other bis(μ-hydroxo)dicopper(II) complexes.[14] A global charge of 2+, attested by the presence of two PF_6^- counter anions, indicates that the bridging oxygen atoms belong to hydroxo ligands (their hydrogen atoms could not be determined experimentally). The Cu_2O_2 subunit is asymmetric with bridging angles Cu1−O1−Cu2 and Cu1−O2−Cu2 angles equal to 101.8 and 97.9°, respectively. Cu1 lies in a square-planar geometry provided by one chloride ion, one calixarene-linked imidazole group and the two bridging hydroxide ions. Cu2 is coordinated in a distorted square-based pyramid ($\tau = 0.26$).[15] The base of the pyramid is constituted by the two bridging hydroxide ions and two imidazole moieties attached to the second calixarene ligand. The fifth ligand is a hydroxo group belonging to the other Cu_2O_2 core. The corresponding axial bond Cu2−O2a [2.272(7) Å] is indeed much longer than the equatorial bonds Cu2−O1 and Cu2−O2. The intersubunit distance between the two central copper ions of the tetranuclear core is only slightly longer than the Cu···Cu intrasubunit distance [*d*(Cu2···Cu2a) = 3.05 Å versus *d*(Cu1···Cu2) = 2.98 Å]. Interestingly, the calix[6]arene structures are in a cone conformation with one of the imidazole arms folded into the cavity. One C−N bond of the included imidazole ring faces an aromatic C−C bond of the host at a distance of 3.80 Å. The *N*-methyl group also stands at a relatively short distance from one of the calixarene aromatic rings (3.66 Å from the methyl group to the centroid of the aromatic ring). These observations are indicative of stabilizing π−π and CH−π host−guest interactions.[16]

Magnetism

The magnetic properties of the tetranuclear complex **2** are depicted in Figure 2. The $\chi_M T$ value at 300 K (0.66 $cm^3 \cdot K \cdot mol^{-1}$) is lower than expected for four noninteracting copper(II) ions (1.6 $cm^3 \cdot K \cdot mol^{-1}$) and decreases upon cooling. This behavior is characteristic of a strong antiferromagnetic interaction between the copper ions. The plateau of $\chi_M T$ below 70 K is due to uncoupled copper(II) impurities. As explained above, **2** can be described as two (μ-hydroxo)copper(II) binuclear subunits. As far as the magnetic properties are concerned, a weak interaction is expected between the two subunits. Let us briefly review some magneto-structural correlations concerning the bis(μ-hydroxo)-bridged copper(II) binuclear complexes. Hatfield et al. have shown that the singlet−triplet gap in such compounds varies in a regular way with the Cu−O−Cu bridging angle.[17] For bridging angles larger than 98° antiferromagnetic interactions are observed. With an average bridging angle Cu1−O−Cu2 of 99.8° in the $Cu1Cu2O_2$ subunit of **2**, a strong antiferromagnetic interaction between the copper(II) ions Cu1−Cu2 is expected. Therefore, on the first attempt, we tried to fit magnetic data using a modified Bleaney−Bowers equation taking into account the presence of two subunits. Paramagnetic impurities were accounted for by a Curie law. By least-squares fitting of the magnetic data, the following values were found: $g = 2.06$, $J = -408$ cm^{-1}, $C = 0.065$ $cm^3 \cdot K \cdot mol^{-1}$. The reliability factor $[R(\chi_M) = \Sigma(\chi_M^{obs} - \chi_M^{calc})^2/\Sigma(\chi_M^{obs})^2]$ is then $7 \cdot 10^{-5}$. On the second attempt we tried to fit the data with a tetranuclear model using complete diagonalization of the hamiltonian matrix. Interestingly, there is no improvement in the quality of the fit by using a tetranuclear model. Moreover, the *J* value for the dinuclear subunit does not change and good fits are obtained with positive and negative values for the interaction between the two central copper ions Cu2 and Cu2a. This is not unexpected; the antiferromagnetic interaction between the copper ions in the dinuclear subunits is so strong that it is not possible to measure the weakest interaction at low temperature because the dinuclear subunits are already diamagnetic at this temperature. The *J* value of −408 cm^{-1} found for the dinuclear subunit is in agreement with the theoretical calculation and the data published in the literature for an asymmetric unit.[18]

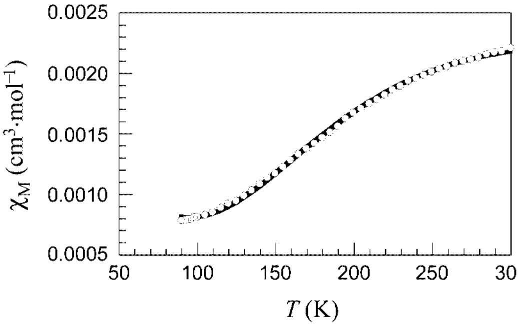


Figure 2. Plot of χ_M vs. *T* for **2**: (o) experimetal data, (−) best fit

Catecholase Activity

(μ-Hydroxo)dicopper(II) centers have been found in several active sites of enzymes.[1,2] Among the so-called type 3 copper proteins, catechol oxidase[3] catalyzes the two-electron oxidation of catechols to quinones. As complex **2** may be viewed as a dimeric form of a type 3 center, we thought of testing its activity in oxidation catalysis. Therefore, we studied the ability of compound **2** to dehydrogenate 3,5-di-*tert*-butylcatechol (dtbc) to 3,5-di-*tert*-butyl-*o*-quinone (dtbq). The reaction was conducted in a 0.088 mM dichloromethane solution of **2** with various concentrations of dtbc. Immediately after introduction of dtbc, we observed the bleaching of the initially blue solution, indicative of reduction of the four copper(II) centers to copper(I). The redox process was monitored by UV/Vis spectroscopy (see Figure 3). The absorption at 400 nm, characteristic of the *o*-quinone product ($\varepsilon = 1900$ $M^{-1} \cdot cm^{-1}$), revealed the formation of 2 equiv. of dtbq. After this first very fast process, the absorption at 400 nm only slowly increased at a rate (2.2 h^{-1}) that was independent of the dtbc concentration. This shows that the tetranuclear complex **2** is an excellent oxidant for dtbc. However, its subsequent regeneration through autooxidation of the cuprous species is slow, leading to sluggish catalytic activity.

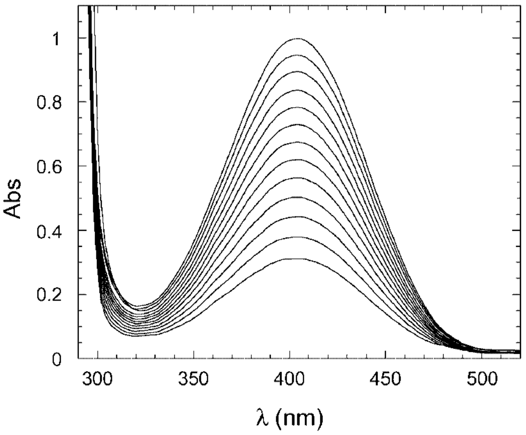


Figure 3. UV/Vis spectra of the formation of the *o*-quinone band recorded every 10 min (CH_2Cl_2 solution, [**2**] = 0.088 mM, $[dtbc]_0$ = 10.3 mM)

Electrochemistry

The electrochemical behavior of this complex has been examined in different solvents. The most interesting results were obtained in MeCN, although compound **2** is only sparingly soluble in this solvent. In pure PhCN or CH_2Cl_2 (in which **2** is highly soluble), the voltammograms displayed an elusive behavior with oxidation peaks of very low intensity. However, addition of MeCN as a co-solvent allowed the recovery of the interesting redox properties that are described as follows. On the one hand, cyclic voltammetry (CV) in the cathodic range only showed a broad peak corresponding to the reduction of some of the copper centers down to Cu^0. This is indeed indicated by the presence of an anodic redissolution peak on the reverse scan (Figure 4). In the anodic range on the other hand, two nearly reversible one-electron processes were observed at $E'°(1) = 0.11$ V [$\Delta E_p(1) = 320$ mV] and $E'°(2) = 0.66$ V [$\Delta E_p(2) = 100$ mV] with $i_{pa}/i_{pc} \approx 1$. The corresponding waves were better defined when scanning from the more anodic potential, i.e. when the totally oxidized form was generated at the surface of the electrode prior to scanning. It is noteworthy that the intensity of the peaks was much lower than those observed for the monomeric calix[6]arene-based N_3Cu family,[9,19] indicating slower diffusion processes. Rotating disk voltammetry (RDV) displayed two successive oxidation waves with a different height. The first well-defined oxidation wave was followed by a second one that was broader and 1.5 to 2 times less intense. Bulk electrolyses and coulometries gave a number of exchange electrons close to one for each oxidation step.[20] They also result in total dissolution of **2** in MeCN. After the exhaustive electrolysis of the solution (2 electrons), the RDV showed a broad composite reduction wave at a half-wave potential between the two initial oxidation waves. Evolution of the EPR spectrum was monitored after each step of the electrolysis. After a one-electron oxidation, a well-defined EPR spectrum was observed (150 K, frozen MeCN solution). The corresponding parameters ($g_{\perp} = 2.07$, $g_{//} = 2.30$, $A_{//} = 140$ G) are typical of a magnetically isolated Cu^{II} ion sitting in a distorted square-based pyramidal environment. Interestingly, after the second one-electron exchange, an identical spectrum was recorded with double intensity, however. By UV/Vis spectrophotometry (Figure 5), the two successive oxidations resulted in the disappearance of the LMCT band and a shift of the d−d transition from 633 to 720 nm. Both oxidation steps are chemically reversible, as indicated by the restoration of the initial voltammetric and spectroscopic characteristics of the solution after counter-electrolyses.

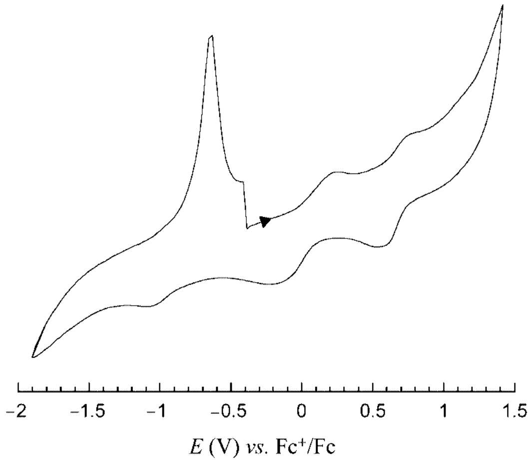


Figure 4. Cyclic voltammetry of complex **2** (1.5 mM in CH_3CN) + Bu_4NPF_6 (0.1 M) at a Pt electrode

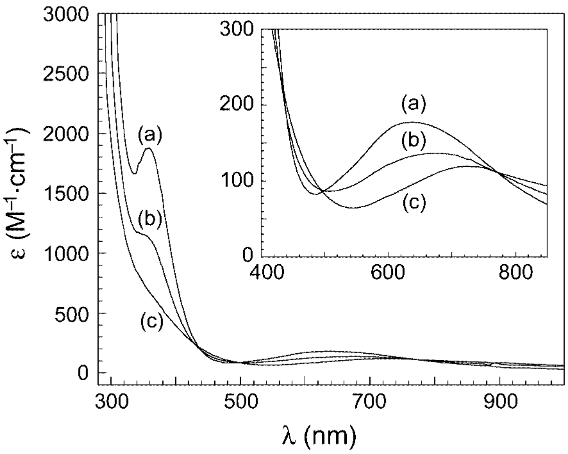
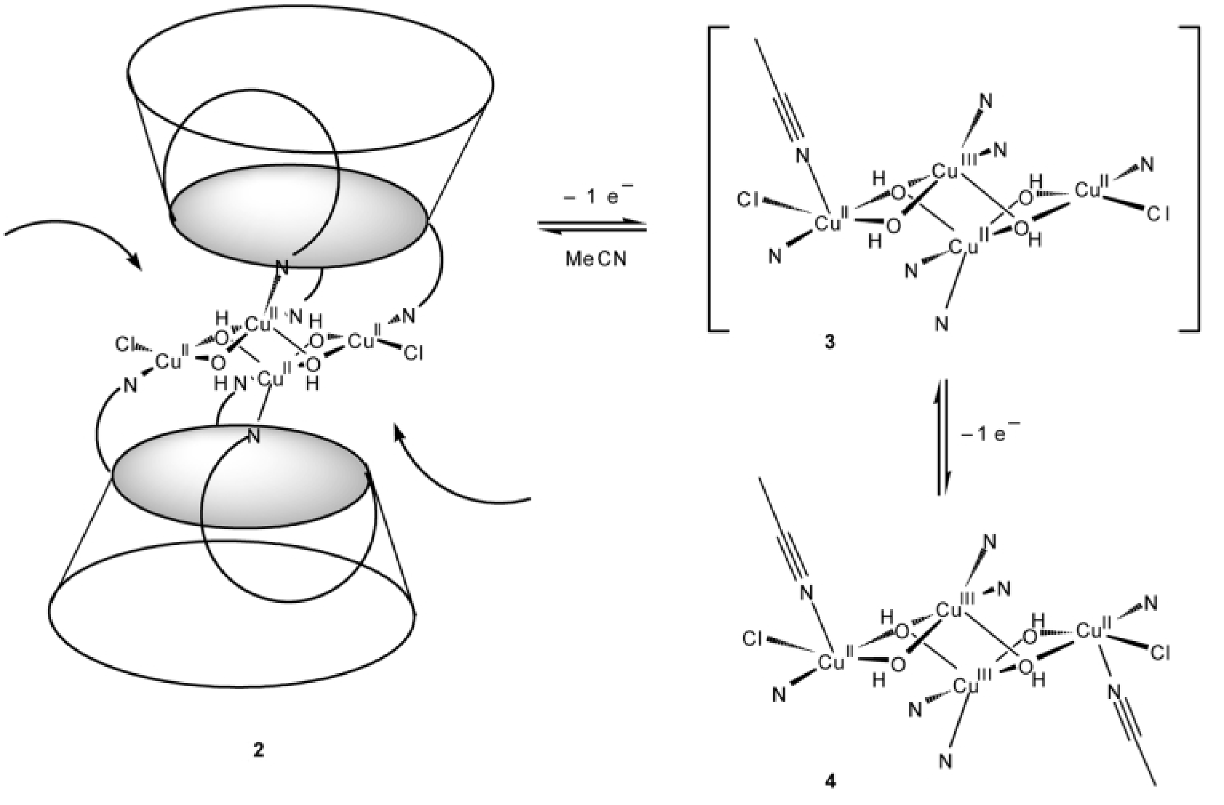


Figure 5. UV/Vis spectra of complex **2** in MeCN/CH_2Cl_2 (1:1) + Bu_4NPF_6 (0.1 M), before electrolysis (a), after one (b) and two (c) electron oxidation electrolysis; inset: enlarged 400−850 nm region

Discussion

The "stepped-cubane" structure of compound **2** is fairly uncommon for tetranuclear copper(II) complexes.[21] To the best of our knowledge, only one complex with similar Cu_4O_4 array has been previously reported.[22] Even more surprising is the exceptional stability of the tetranuclear core towards coordinating solvent or redox processes. The complex results from the spontaneous assembly of two calixarene-based tridentate N-ligands, four copper atoms, one dioxygen molecule and two chloride ions. The calixarene structures seem to be frozen in a cone conformation due to the self-inclusion of one of their imidazole arms. As a result, the supramolecular assembly[23] displays interesting features: it forms a sandwich that holds and protects the $\mathrm{Cu_4}$ metal core but simultaneously maintains a pathway for an external molecule to interact with it. As shown by the spontaneous dehydrogenation of 2 equiv. of dtbc into dtbq when complex **2** is introduced, the system can behave as a four-electron hole. On the other hand, the electrochemical studies showed that, in the cathodic range, complex **2** tends to decomposition after electrochemical reduction to $\mathrm{Cu^{I}}$; this is due to the poor ability of $\mathrm{OH^-}$ bridges to coordinate $\mathrm{Cu^{I}}$ centers.[24] In the anodic range complex **2** can undergo two sequential one-electron oxidation processes, giving finally rise to a bis(mixed-valence) tetranuclear $[(\mathrm{Cu^{II}Cu^{III}})]_2$ compound (**4**) (Scheme 2). Indeed, the central core of **2** is rich in anionic ligands with the two chloride and the bridging hydroxide ions. Together with the tetragonal environment of the copper ions, these features favor the stabilization of the copper(III) state. Formation of $\mathrm{Cu^{III}}$ derivatives, with a mixed-valence behavior, has been described in rare examples of $\mathrm{Cu_3}$ and $\mathrm{Cu_4}$ complexes of oxime derivatives.[25−27] The stabilization of $\mathrm{Cu^{III}}$ has been shown to be related to the electron-donating ability of the ligand in monomers[28] as well as in dimers.[29] In the present case, the reversibility, both electrochemical and chemical, of the redox process militates the integrity of the tetranuclearity of the system. The EPR study showed that the oxidation process gives rise to gradual apparition of magnetically isolated $\mathrm{Cu^{II}}$ ions. Hence, knowing that (i) the presence of MeCN is necessary for the observation of the redox systems, (ii) the spectroscopic data (NMR and UV/Vis) of **2** remained unchanged upon addition of MeCN to a $\mathrm{CH_2Cl_2}$ (or $\mathrm{CHCl_3}$) solution, and (iii) the EPR spectrum of the oxidized complex is typical of $\mathrm{Cu^{II}}$ sitting in a square-based pyramidal environment, we propose the sequence of reactions depicted in Scheme 2. The central copper atoms are successively oxidized to the diamagnetic $\mathrm{Cu^{III}}$ state leading to the formation of intermediate **3** and the final product **4**. At each step of the oxidation process, a peripheral $\mathrm{Cu^{II}}$ ion (Cu1) neighboring a central $\mathrm{Cu^{III}}$ (Cu2) becomes magnetically isolated and possibly five-coordinate due to the binding of acetonitrile in the axial position.[30] It is noteworthy that, conversely, oxidation of the peripheral Cu1 copper ions would have led to a weakly coupled dinuclear copper(II) central unit for the deoxidized species with a characteristic triplet EPR spectrum, not observed. The splitting into two one-electron redox systems, instead of a two-electron oxidation process, could result from an original cooperative/interactive phenomenon between the two dimeric units of the $\mathrm{Cu_4}$ core, which should thus be considered as a pair of interacting dimers, as has been proposed in other cases.[25] This is in accordance with the dependence on the scan direction for CV and change from a two-to-one RDV wave



Scheme 2. Proposed electrochemical oxidation pathway for **2** in the presence of MeCN; the arrows emphasize the most accessible sites of the $\mathrm{Cu_4O_4}$ core for an external molecule

after electrolysis, which is indicative of a structural rearrangement of the $[(Cu_2)_2]$ core upon oxidation.

Conclusion

Under specific conditions, reaction of the tridentate calix[6]arene-based ligand $X_6Me_3Imme_3$ with 2 mol-equiv. of copper gives rise to a tetranuclear copper(II) complex that is very stable in solution. The molecular structure of this novel compound displays a rare "stepped-cubane" Cu_4O_4 core. It also points out the self-inclusion of one imidazole arm of the calixarene ligand into its cavity. Such a self-inclusion phenomenon should be controllable by the steric hindrance of the coordinating arm. This very interesting supramolecular feature suggests that novel geometries for the coordinated metal center are actually accessible within the calix[6]arene-based tripodal systems. We are currently exploring this structural aspect. The tetranuclear complex also presents remarkable stability and redox properties that are related to its supramolecular architecture. Indeed, it can either behave as a four-electron hole, displaying catecholase activity, or itself be reversibly oxidized into mixed-valence species $Cu_3^{II}Cu^{III}$ and $Cu_2^{II}Cu_2^{III}$. In the field of biomimetic modeling, its behavior evidences an interesting similarity with multicopper enzymes in which some copper centers are specifically devoted to electron transfer and others to interaction with the substrate.[27,31] We are now actively studying the potential electrocatalytic properties of this novel Cu_4 system with promising preliminary experiments.

Experimental Section

Materials and Methods: All solvents and reagents were obtained commercially. THF was distilled from sodium/benzophenone under argon. ^1H NMR spectra were recorded either with a Bruker ARX 250 or a Bruker AC200 spectrometer. IR spectra were recorded with a Perkin−Elmer 783 spectrometer. Elemental analyses were performed at the Institut de Chimie des Substances Naturelles, Gif sur Yvette, France. Electrochemical experiments were carried out under dry, dioxygen-free N_2 in a dry-box manufactured by Jacomex. The electrochemical cell was specifically designed to fit the rotating disk electrode (EDI Tacussel) for a minimum volume of solution in the main compartment. The auxiliary and reference (ferrocenium/ferrocene = Fc^+/Fc) electrodes were in separate compartments connected to the main compartment through ground joints terminated by frits (Vycor tips from PAR). For voltammetric measurements, a platinum disk (diameter 2 mm) was employed, and the electrolyses were performed with the same electrode, but rotated, equipped with a disk (diameter 4 mm). A model PAR 173 potentiostat equipped with a PAR 179 digital coulometric unit, was monitored by a PAR 175 programmer. The chart recorder was a T-2Y SEFRAM ENERTEC. EPR spectra were recorded using a Bruker Elexys spectrometer (X-band). The UV/Vis spectra were recorded with a Cary 50 spectrophotometer or a Hitachi U-2010 spectrophotometer. Magnetic measurements were performed with a Quantum Design SQUID MPMS5 magnetometer. The data were collected in the range 1.8−300 K for a powdered microcrystalline sample of **2** at 0.5 T. Diamagnetic corrections were applied based on Pascal's constant.

$[Cu(X_6Me_3Imme_3)(Cl)]$ (1): Under argon, dry THF (2 mL) was added to a mixture of CuCl (7.0 mg, 0.067 mmol) and $X_6Me_3Imme_3$ [12] (87.0 mg, 0.067 mmol). The mixture was stirred at 40 °C for 1 h. The colorless supernatant was separated from the slightly blue precipitate by centrifugation and concentrated under vacuum. Heptane (5 mL) was added and a white precipitate formed, which was isolated by centrifugation, washed with heptane (2 mL) and dried under vacuum at 30 °C for 12 h to yield a white powder (62.8 mg, 67%). Sometimes, precipitation occurred a few minutes after addition of THF to the starting materials. In this case, the mixture was stirred at room temperature for 2 h and the precipitate was collected by centrifugation and washed with heptane. ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 0.80 (s, 27 H, *t*Bu), 1.34 (s, 27 H, *t*Bu), 2.20 (s, 9 H, OCH_3), 3.22 (d, J = 14.2 Hz, 6 H, Ar-αCH_{eq}), 3.81 (s, 9 H, NCH_3), 4.43 (d, J = 14.7 Hz, 6 H, Ar-αCH_{ax}), 4.99 (s, 6 H, Im-αCH_2), 6.65 (s, 6 H, ArH), 6.94 (br. s, 6 H, ImH), 7.19 (s, 6 H, ArH) ppm. IR (KBr): $\tilde{\nu}$ = 1500, 1482, 1465, 1418, 1396, 1365 cm^{-1}. $C_{84}H_{108}ClCuN_6O_6$ (1396.79): calcd. C 72.23, H 7.79, N 6.02; found C 72.22, H 7.88, N 6.15.

$[Cu_4(X_6Me_3Imme_3)_2(OH)_4(Cl)_2](PF_6)_2$ (2): Under argon, dry THF (4 mL) was added to a mixture of CuCl (12.5 mg, 0.126 mmol) and $X_6Me_3Imme_3$ (164 mg, 0.126 mmol). The mixture was stirred at room temperature for 30 min during which a white precipitate of $[Cu(X_6Me_3Imme_3)(Cl)]$ slowly appeared. $[Cu(CH_3CN)_4](PF_6)$ (47 mg, 0.126 mmol) was added to the reaction mixture. Dry oxygen was then bubbled into the solution, which turned green. A blue precipitate slowly appeared. After 2 h, the oxygen bubbling was stopped and the mixture was stirred overnight. The green supernatant was removed and the blue precipitate was washed with THF (5 × 2 mL), dissolved in CH_2Cl_2, filtered through Celite, precipitated with pentane and dried under vacuum to yield a blue powder (131 mg, 63%). M.p. >260 °C (dec.). ^1H NMR ($CDCl_3$, 250 MHz, 300 K): δ = 0.5, 0.77 (s, 18 H, *t*Bu), 0.91 (s, 18 H, *t*Bu), 1.28 (s, 18 H, *t*Bu), 1.38 (s, 18 H, *t*Bu), 1.43 (s, 18 H, *t*Bu), 1.51 (s, 18 H, *t*Bu), 1.89, 2.83, 2.90, 3.75, 4.30, 4.75, 5.98, 6.12 (s, 4 H, ArH), 6.52 (s, 2 H, ArH), 6.72 (s, 2 H, ArH), 6.82 (s, 2 H, ArH), 6.85 (s, 2 H,

Table 2. Crystallographic data for **2**

Empirical formula	$C_{88}H_{120}ClCu_2F_6N_7PO_{10}$
Formula mass	1743.47
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	15.663(1)
b [Å]	15.915(1)
c [Å]	22.803(1)
α [°]	73.72(1)
β [°]	72.36(1)
γ [°]	61.73(1)
V [Å^3]	4706.85(4)
Z	2
D_c [g cm^{-3}]	1.23
Crystal colour	blue
Crystal size [mm]	0.6 × 0.5 × 0.3
μ(Mo-K_α) [cm^{-1}]	5.65
Number of unique data	9955
Number of parameters refined	1044
Number of reflections used in refinement	9955
R [$F^2 > 4\sigma(F^2)$][34]	0.092
wR[a]	0.177
Goodness of fit	2.015
Residual Fourier [e Å^{-3}]	−0.69; 0.80

[a] $w = 1/[\sigma^2(F_o) + 0.03(F_o)^2]$.

ArH), 6.96 (s, 2 H, ArH), 7.2, 7.32 (s, 2 H, ArH), 7.70 (s, 2 H, ArH), 7.93 (s, 2 H, ArH), 8.04 (s, 2 H, ArH), 8.10 (s, 2 H, ArH), 9.85, 15.3 (br), 17, 18.1 (br), 21.9, 26.3, 30 (br), 31 (br), 32.5 (br) ppm. IR (KBr): $\tilde{\nu}$ = 3520 (OH), 1505, 1482, 1418, 1395, 1362, 1295, 1200, 842 (PF_6) cm^{-1}. UV/Vis (CH_2Cl_2, 25 °C): λ (ε) = 359 (1882), 633 (175 $M^{-1}\cdot cm^{-1}/Cu_4$) nm. ES-MS (CH_2Cl_2 or MeCN): m/z = 1494 [**2** − $2PF_6^-$]. $C_{168}H_{220}Cl_2Cu_4F_{12}N_{12}O_{16}P_2$ (3278.63): calcd. C 61.54, H 6.76, Cl 2.16, N 5.13; found C 61.23, H 6.61, Cl 2.56, N 4.97.

Crystal Structure Determination:[32] X-ray quality crystals of $[Cu_4(X_6Me_3Imme_3)_2(OH)_4(Cl)_2](PF_6)_2$ were obtained by slow diffusion of Et_2O into a CH_2Cl_2/MeCN or $CHCl_3$/MeCN solution of complex **2**. Data were collected at 223 K using a Nonius Kappa CCD diffractometer.[33] After a last series of Fourier analysis, two fragments remained partially resolved and were attributed to a disordered MeCN molecule and an incomplete ether solvent molecule. Crystallographic data are listed in Table 2.

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