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Well-defined bridged dicopper(III) chloride, azide, and amino complexes

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The biologically relevant bis(μ-L)dicopper(III) core with modified bridging ligands (L = Cl, N_3, NMe_2), mimicking the enzyme oxidation bis(μ-oxo)copper(III) intermediates, was prepared from the heterocubane $[Cu(CF_3)_2(OH)]_4$ and fully characterized, including using X-ray crystallography. The electronic structure, effective oxidation state of copper, and natural charge distribution in these complexes were studied using DFT calculations. The oxidation state localized orbital (OSLO) method and XPS spectroscopy support a +3 oxidation state of copper in these complexes, albeit with highly covalent Cu–C bonding, which is the most profound in the *chlorido*-complex. The potential of these complexes in synthetic chemistry was demonstrated *via* azidotrifluoromethylation of an alkyne by the azido complex $[Cu(CF_3)_2(N_3)]_2$ furnishing a vinyl azide, and alcohol *O*-difluoromethylation by the copper chloride complex.

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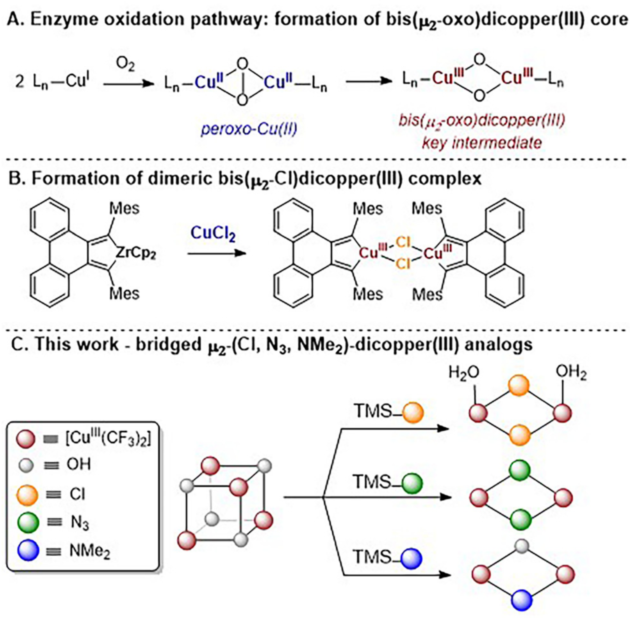
Introduction

Stabilization of copper in the high oxidation state (+3) is a fundamental challenge and is essential for advancing the understanding of aerobic oxidation and metalloenzyme systems,[1] as well as cross-coupling reactions.[2] In particular, bridged dicopper(III) species are key intermediates in biochemistry.[1,3] Here, dimeric bis(μ-oxo)copper(III) complexes are the key scaffolds in aerobic enzyme oxidation processes and oxygen activation, forming *via* rearrangement of the primary peroxo-copper(II) adducts (Scheme 1A).[3] Mimicking these intermediates by gaining insights into similar dimeric high-valent copper species is a timely and challenging task for inorganic and organometallic chemists, given the elusiveness of the high-valent copper. In particular, well-defined dimeric copper(III) hydroxide compounds L_n-Cu(III)-(μ_2-OH)-Cu(III)-L_n (where L_n = 2,6-pyridinedicarboxamide ligands) reported by Tolman are key models for putative intermediates in oxidation processes.[4] Recently, direct formation of the bridged oxo-dicopper(III) core in aerobic oxidation has been observed and studied using spectroscopic methods.[5] However, due to the low stability and propensity of amine- and azole-ligated bridged dicopper(III) complexes for reduction (including intramolecular charge transfer),[1,5] stabilization of well-defined dicopper(III) species is still difficult to realize.

The trifluoromethyl group is known to stabilize high oxidation states due to stabilizing metal-to-ligand π-back donation and contraction of σ-orbitals on a high-valent metal.[2c,6] These factors preclude reductive elimination. We have envisioned the use of a tetrameric copper(III) trifluoromethyl hydroxide recently discovered by us[7] for accessing novel dimeric Cu(III) species bearing two trifluoromethyl groups. Very recently, we have used this starting material to prepare copper(III) carboxylates,[7a] 1,3-diketonates,[7a] bench-stable synthetically useful scorpionates,[8] and dimeric bridged


A. Enzyme oxidation pathway: formation of bis(μ_2-oxo)dicopper(III) core

B. Formation of dimeric bis(μ_2-Cl)dicopper(III) complex

C. This work - bridged μ_2-(Cl, N_3, NMe_2)-dicopper(III) analogs

Scheme 1 Key binuclear dicopper(III) core in enzyme oxidation, its chlorine-bridged analogue stabilized in a bulky environment, and this work.

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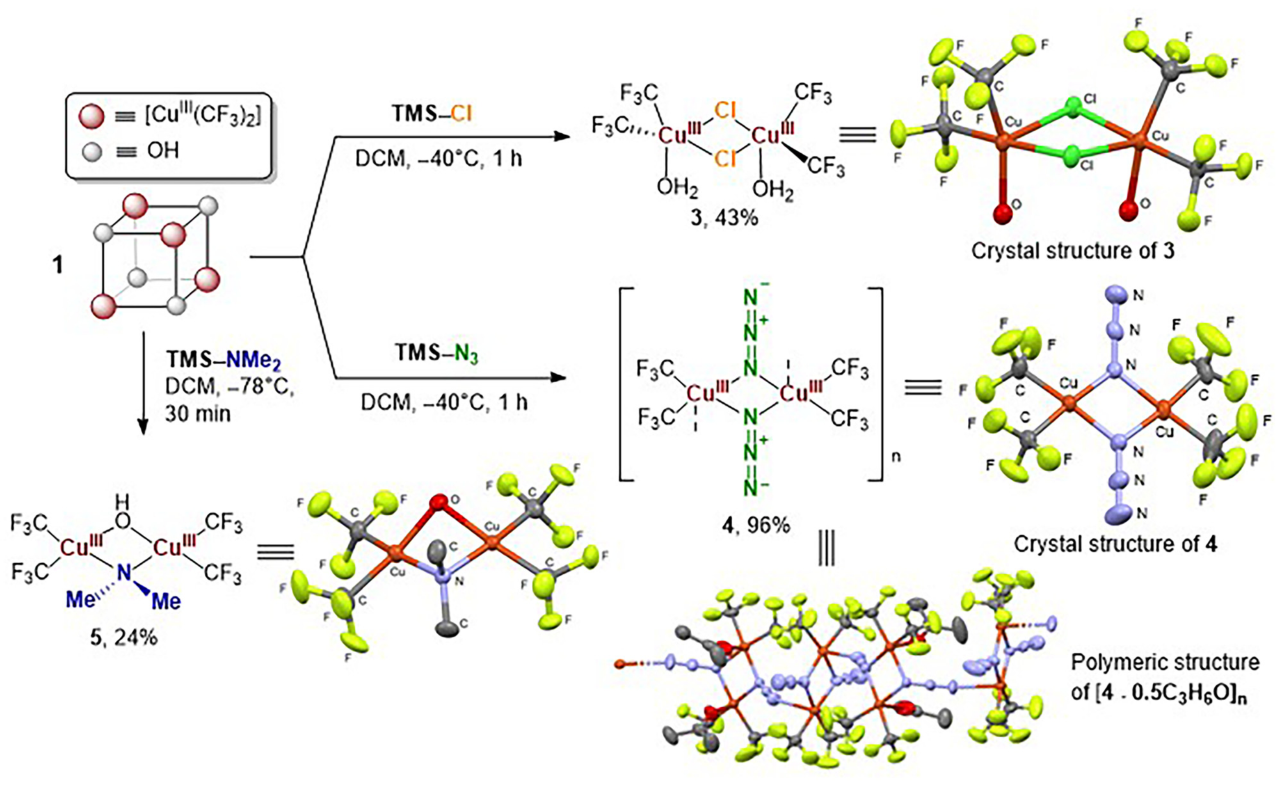
copper(III) hydroxides.[7b] To the best of our knowledge, dicopper(III) cores with other bridging ligands apart from oxo- and hydroxide groups are very rare. Only a single report of a well-defined bridged formally copper(III) chloride complex was made in 2022, where this unique core was stabilized in a metallacycle (Scheme 1B).[9] Nitrogen-bridged dicopper(III) complexes could be stabilized by a complex macrocyclic pyrazole–imidazolium NHC ligand,[10] whereas formation of an elusive phenoxide-bridged mixed Cu(II)–Cu(III) complex was observed spectroscopically from the well-defined Cu(II) dimer.[11] A common theme around all these species is the presence of bulky substituents (such as mesityl)[9] or a macrocyclic environment[10] to shield the high-valent copper centre. The use of trifluoromethyl groups for stabilization is a conceptually different alternative strategy. Herein we report the isolation of novel elusive μ_2-chlorido-, μ_2-azido- and μ_2-dimethylamino-dicopper(III) complexes prepared from an easily accessible tetrameric hydroxide $[Cu(CF_3)_2(OH)]_4$ (**1**) with their characterization studies including X-ray crystallography and oxidation state analysis (Scheme 1C).

Results and discussion

Inspired by the reactivity of the easily available high-valent copper hydroxide $[Cu(CF_3)_2(OH)]_4$ (**1**) as a hydroxide base,[7] we attempted substitution of the hydroxyl group with a strong acid (HCl) or a secondary amine ($HNMe_2$), which could result in dehydration and formation of the corresponding formally copper(III) chloride "$Cu(CF_3)_2Cl$" or amino species. However, for reaction products formed in this direct method, decomposition occurred even below −40 °C. Moreover, the use of other common acidic chloro-dehydrative agents such as $SOCl_2$ and $POCl_3$ was also unsuccessful. Therefore, we envisioned the use of trimethylsilyl derivatives as functional group transfer reagents. To our delight, the reaction of heterocubane **1** with 2 equivalents of TMSCl (**2a**) at −40 °C afforded a new product, **3**, formed as yellow crystals, which after recrystallization could be identified as di-(μ_2-chlorido)-diaqua-tetrakis(trifluoromethyl) dicopper(III), a dimeric formally copper(III) complex with bridging μ_2-chlorido ligands and two water molecules coordinated in apical positions (Scheme 2). X-ray crystallography revealed that the geometry of the well-known binuclear bis(μ_2-oxo)-dicopper(III) core is significantly altered when two hydroxyl ligands are replaced with chlorine atoms as in compound **3**. Two copper centers with two chloride ligands form a rectangle with two nearly equal Cl–Cu–Cl (87.32(3)°) and two Cu–Cl–Cu (91.37(3)°) angles. There are two short Cu–Cl bonds (2.2181(8) Å) at the opposite sides of the Cu–Cl–Cu–Cl rectangle, and two significantly longer (2.7572(9) Å) contacts in the apical positions to the respective copper centers. This is remarkably different from the known dimeric square-shaped copper(III) chloride core, with nearly equal (2.318 and 2.327 Å) Cu–Cl distances.[9] Water molecules lie nearly in the same plane as two



Scheme 2 Synthesis of bridged Cu(III) dimers chlorido-Cu(III) **3**, azido-Cu(III) **4**, and μ_2-(dimethylamino)-μ_2-(hydroxy)-Cu(III) **5**. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

trifluoromethyl groups and one of the chloride ligands, in *cis*-configuration to each other. The Cu–O bond lengths are 1.946 (2) Å, which indicates stronger coordination in contrast to the previously reported copper(III) complex with water as a weakly coordinated ligand (Cu–O = 2.316(1) Å).[7]

The success of substitution of a hydroxyl group with chloride prompted us to explore substitution of a hydroxyl with a chemically similar pseudohalide. Importantly, coordination of azido groups to transition metals can take place *via* either one or both terminal nitrogen atoms, and thus formation of different isomers could be envisioned. To our delight, the reaction of $TMSN_3$ (**2b**) with heterocubane **1** at −40 °C afforded a bridged neutral copper(III) azide $[Cu(CF_3)_2(\mu\text{-}N_3)_2Cu(CF_3)_2]$ compound **4** with μ_2-κ_1-coordination of azide groups. It can be crystallized from a DCM/pentane mixture and can exist both in dimeric and polymeric forms. If the crystallization occurs in the presence of acetone, units of **4** with and without solvent form a coordination polymer of the composition $[Cu(CF_3)_2(\mu\text{-}N_3)_2Cu(CF_3)_2\cdot 0.5C_3H_6O]_n$. The monomer unit of **4** is rhombus-shaped with four nearly equal Cu–N distances of 1.950–1.956 Å, which are slightly elongated in the solvated unit in the presence of coordinated acetone molecules. Surprisingly, compound **4** was found to be more stable than the respective chloride complex **3** and thus can be safely handled even under ambient conditions.

With these neutral halide and pseudohalide complexes in hand, we attempted to substitute one of the hydroxyl ligands with an amino group, which can be more challenging due to a stronger Si–N bond and instability of the formally copper(III) amino species. Application of (*N*,*N*-dimethylamino)trimethylsilane as a reaction partner at −78 °C afforded a very unstable binuclear complex **5** with bridging dimethylamino- and hydroxyl groups (Scheme 2). Attempts to substitute both hydroxyl groups in an excess of silane led to decomposition, which can be attributed to very low stability of the bis(amino) dicopper(III) complex.

The crystal structure of **5** with the μ_2-(dimethylamino)-μ_2-(hydroxy)dicopper(III) core with square-planar copper centers revealed that both dimethylamino and hydroxyl groups are strongly coordinated, as shown by copper–oxygen distances of 1.850(4) and 1.878(4) Å, whereas the Cu–N bonds lengths are 1.949(5) and 1.960(5) Å. The two N–Cu–O angles are 80.2(2)° and 79.3(2)° respectively.

With the structure of the complexes established, we investigated the bonding situation in these compounds using DFT calculations, as well as their structure in solution by optimization of geometry taken from the XRD at the B3LYP-D3(BJ)/ZORA-def2-TZVP level with a CPCM(DCM) solvation model. The geometry of **3** in DCM solution features more symmetrical tetragonal units with Cu–Cl distances of 2.330 and 2.353 Å compared to more significant differences in the crystal structure, and elongated Cu–O bonds for coordinated water molecules (Fig. 1). Both calculated frontier orbitals for all three complexes are mixed with predominantly ligand-centered character. The HOMO of the complex **5** has the most significant contribution of the NMe_2 ligand, which could be the most reactive part of the molecule. LUMOs of the both complexes are centered along the Cu–C bonds, thus with a strong σ* ($Cu–CF_3$) character, which resembles known copper trifluoromethyl complexes.[6–8] The natural bonding orbital (NBO) analysis at the ωB97X-D3(BJ)/def2-QZVPPD//B3LYP-D3(BJ)/ZORA-def2-TZVP level of theory revealed the positive NPA charge of +0.99 on copper for complex **3** and +1.06 and +1.10 for complexes **4** and **5**, respectively, slightly higher than for copper(III) species with three trifluoromethyl groups[6b,c] and slightly lower than in the initial hydroxide **1**.[7] A similar result (NPA +1.026) was observed recently for a nitrogen-coordinated Cu(III)-pseudopeptide complex.[12] In contrast to two $Cu–CF_3$ bonds with a high degree of covalency (WBI = 0.50 in all three complexes), the Cu–Cl bonds in **3** display a relatively low degree of covalency (WBI = 0.19–0.22 for all contacts) comparable to both Cu–N (WBI = 0.23) and Cu–O (WBI = 0.18) coordination in the case of **5**.

With insights into the structure and natural charge distribution in these dimeric formally copper(III) cores, we analysed the oxidation state in these complexes. The oxidation state assignment in formally copper(III) complexes has been a subject of long debates, since the occurrence of an inverted ligand field, predominantly ligand-centered LUMOs, and increased d-shell population point to the assignment of high-valent copper in these complexes as copper(I).[13] However, the concept of oxidation states is formal by IUPAC definition.[14] Furthermore, re-assessment of this assignment using XAS,[15] XPS[2d,8,12,16] and the recently developed OSLO (Oxidation State Localized Orbitals)[17] method provides more evidence for the existence of Cu(III),[6b,8] despite the fact that the d^8-configuration is almost never the case in these compounds according to DFT calculations of the orbital population.[8,12,13] X-ray photoelectron spectroscopy results for the chloride **3** and azide **4** complexes support the +3 oxidation state (see the SI for details). The binding energy of $Cu2p_{3/2}$ was found to be 936.2 eV for the chloride (**3**) and 935.8 eV for the azide (**4**), which excellently matches the literature reports, where the binding energies of 936 ± 1 eV indicate the copper(III) oxidation state, *ca.* 2 eV higher than that of the respective Cu(II) species.[2d,8,12,16] The binding energies of $Cu2p_{1/2}$ were found to be *ca.* 956 eV (956.2 eV for **3** and 955.4 eV for **4**). These XPS results also corroborate the characteristics of the inorganic cuprate(III) species.[18] Due to the instability of the complex **3** under XPS irradiation, the Cu(I) decomposition product with a binding energy of 932 eV was detected under inert conditions.

According to the OSLO calculations (Table 1), the Cu(III) oxidation state is also supported for all three complexes. However, for the chloride **3**, the assignment is the least clear, which is reflected by high FOLI value close to the most ambiguous case (FOLI = 2), as well as low Δ-FOLI values below the confidence value of 0.5 indicating clear OSLO assignment.[17] This discrepancy can be explained by strong π-donor properties and polarizability of chloride, where π-donation significantly increases the electron density on the copper atom, which additionally results in a lower NPA charge in the chloride complex (see above). Amino- and azido-complexes **4** and **5** are less electron-rich and are more clearly described as Cu(III) com-

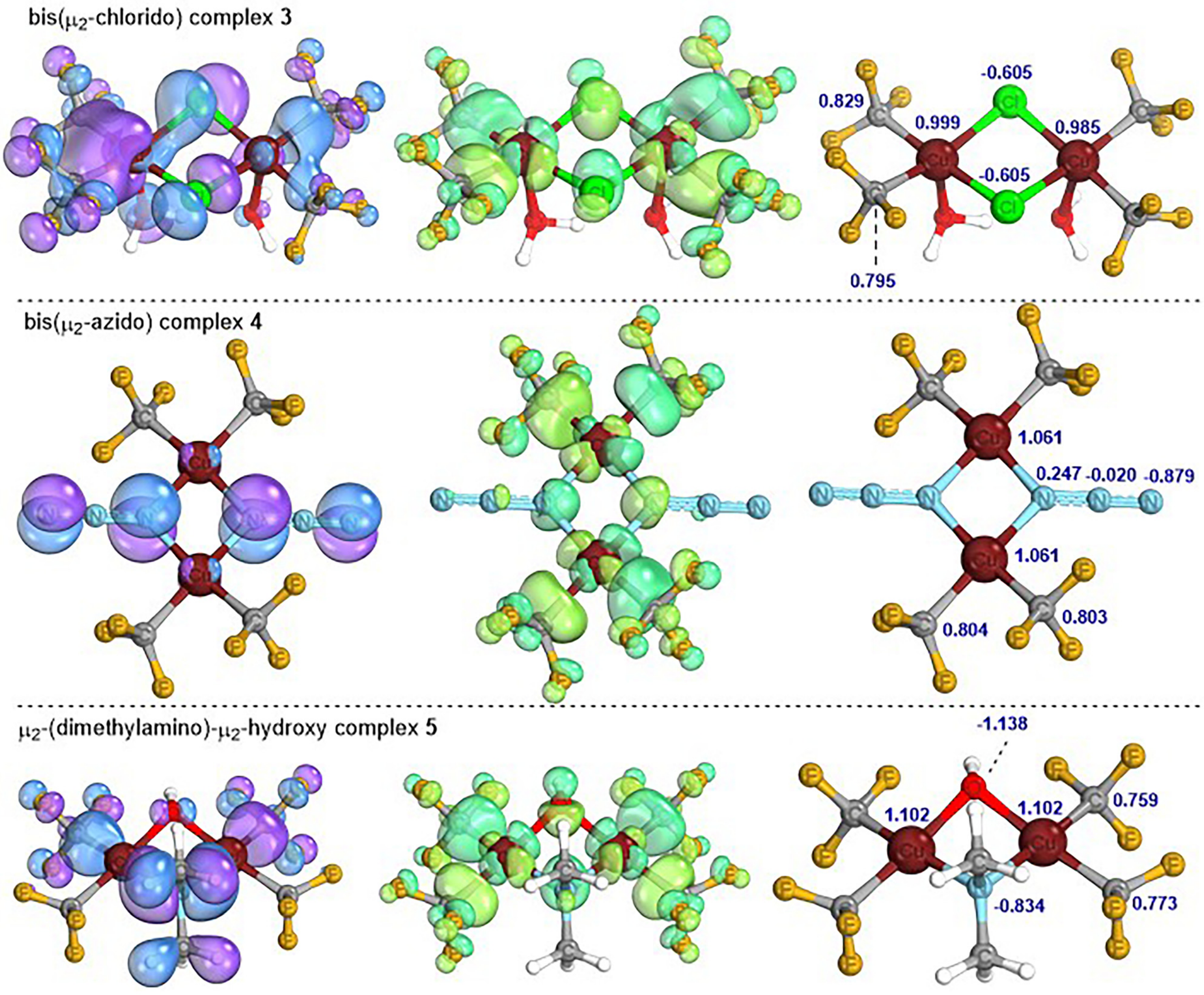


Fig. 1 Frontier orbitals of complexes **3**, **4** and **5** (left) and their natural charge distribution (right). Minimum structures (ωB97X-D3(BJ)/def2-QZVPPD//B3LYP-D3(BJ)/ZORA-def2-TZVP, CPCM(DCM)) with blue numbers corresponding to the NPA charges.

Table 1 Determination of the effective oxidation state in dimers **3–5** using the OSLO method. Single point energies were calculated at ωB97X-D3(BJ)/def2-TZVPPD//B3LYP-D3(BJ)/ZORA-def2-TZVP (level 1) or DLPNO-CCSD(T)/ZORA-def2-TZVP//B3LYP-D3(BJ)/ZORA-def2-TZVP (level 2) levels of theory

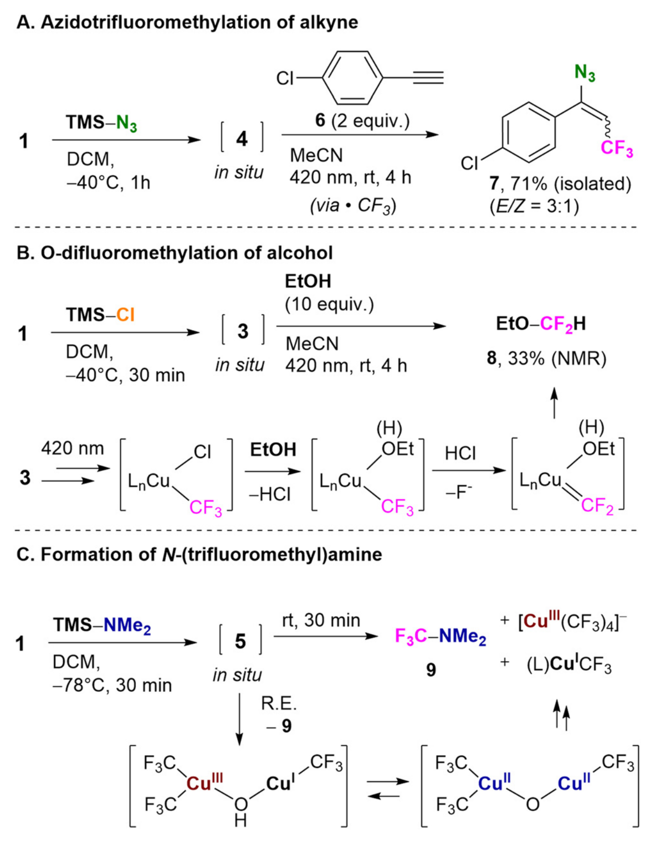
Compound	%Cu(3d) in the LUMO[a]	OS(Cu)[b] OSLO	FOLI (level 1)	Δ-FOLI (level 1)	FOLI (level 2)	Δ-FOLI (level 2)
3	32.8	+3	1.95	0.30	1.86	0.46
4	38.0	+3	1.92	0.41	1.69	0.74
5	39.5	+3	1.82	0.54	1.54	1.07
$[Cu(CF_3)_4]^-$	36.2	+3	1.56	1.11	1.26	2.50

[a] Determined using Löwdin population analysis at the ωB97X-D3(BJ)/def2-TZVPPD//B3LYP-D3(BJ)/ZORA-def2-TZVP level of theory. [b] The determined oxidation state is the same for both levels used.

pounds by the OSLO method, in contrast to the predominantly ligand-centered LUMO suggesting ligand field inversion for all complexes.[13a]

Finally, we compared the correlation of the OSLO oxidation state assignments with the Cu(3d) contribution from the Löwdin population analysis in the LUMO orbital,[13a] which are very similar (32.8–39.5%) for all species considered here. However, a slightly diminished Cu(3d) character was indeed observed for the chloride **3** with the most ambiguous situation (Δ-FOLI < 0.5), which is reflected by a fragment population of the last OSLO of 43% on copper and 57% on the CF_3 group (see the SI for full details). No strong correlation was observed between %Cu(3d) and FOLI values in the OSLO system. Consistently higher FOLI and lower Δ-FOLI for neutral complexes than for anionic species[6c] such as the $[Cu(CF_3)_4]^-$ complex suggests higher bond covalency, whereas comparing Cu(3d) contributions directly does not reflect this tendency.

With these insights, reactivity and potential of complexes **3–5** in synthetic organic and organometallic chemistry were established (Scheme 3). The azide complex **4**, most stable of all three, was capable of trifluoromethylazidation of alkyne **6** under photochemical conditions (Scheme 3A) to furnish the vinyl azide **7** in 71% yield. Control experiments with TEMPO and detection of the TEMPO-CF_3 adduct supported the radical mechanism of this transformation (see the SI for full details), which is also reflected in the $\sigma^*(Cu–CF_3)$ character of the LUMO for complex **4** (Fig. 1 above). Moreover, a different mode of reactivity based on very recently reported difluorocarbene transfer from Cu–CF_3 complexes[19] was realized for the chloride complex **3**, to afford the alcohol difluoromethylation product **8** (Scheme 3B). While a direct difluorocarbene transfer is feasible in the presence of HCl,[19] electrophilicity of copper(III) or copper(II) chloride intermediates can enable both HCl generation due to fast ligand exchange and formation of the difluorocarbene intermediate.[20] Finally, formation of *N*-trifluoromethyl amine **9** was observed during decomposition of the pre-formed amino-complex **5** at room temperature. Formation of binuclear $Cu^{III}–Cu^{I}$ and $Cu^{II}–Cu^{II}$ complexes upon reductive elimination can be envisioned, which undergo quick degradation to form a mixture of $[Cu^{III}(CF_3)_4]^-$ and $Cu^{I}(CF_3)$ by-products, detected using ^{19}F NMR (Scheme 3C).



Scheme 3 Transformations and synthetic potential of dimeric formally copper(III) complexes **3–5** in alkyne difunctionalization (A), alcohol difluoromethylation (B), and amine *N*-trifluoromethylation (C).

Conclusions

In conclusion, novel well-defined dimeric formally Cu(III) complexes with bridging chloro, azido- and amino-ligands were prepared and fully characterized. The molecular structures in the solid state, the natural charge distribution, and the effective oxidation state of these complexes were studied using DFT calculations, including the OSLO method, which support an assignment of a +3 oxidation state to copper in these complexes. We believe that the structure of these complexes will open new avenues in the use of high-valent copper dimers in organic synthesis and biochemistry and encourage further studies of this unique family of copper(III) complexes derived from the parent cubane base $[Cu(CF_3)_2(OH)]_4$.

Experimental

Preparation of the bis(μ_2-chlorido)dicopper(III) complex 3

In a 10 ml round-bottom Schlenk flask under an argon atmosphere, to the solid heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol of monomer]), dry dichloromethane (1 ml) was added, and the mixture was cooled to −40 °C. Trimethylsilyl chloride (25 µl, 0.2 mmol, 2 equiv.) was added with vigorous stirring. The mixture was stirred at −40 °C for 1 hour; during this time the solution turned an intense yellow. It was concentrated to *ca.* 0.2 ml volume under vacuum, then layered with pentane (*ca.* 2 ml) containing 0.5% acetone. Crystallization at −40 °C for 2 days afforded yellow crystals of bis(μ_2-chlorido)-diaqua-tetrakis(trifluoromethyl)dicopper(III) **3** with the composition $[Cu(CF_3)_2Cl·H_2O]_2$ (11 mg, 43%), which were dried under a stream of argon at −40 °C to −20 °C and collected.

Preparation of the bis(μ_2-azido)dicopper(III) complex 4

In a 10 ml round-bottom Schlenk flask under an argon atmosphere, to a solution of heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol of monomer]), dry dichloromethane (0.5 ml) was added and the mixture was cooled to −40 °C. $TMSN_3$ (26.3 µl, 0.2 mmol, 2 equiv.) was added with vigorous stirring. The mixture was additionally stirred for 1 hour at −40 °C, then connected to high vacuum and evaporated to dryness while warming up to room temperature to completely remove silanol by-products and afford complex **4** $[Cu(CF_3)_2(\mu_2-N_3)]_2$ as a bright yellow solid (23.5 mg, 96%). Single crystals for X-ray crystallography were grown from 1 : 1 pentane/DCM with or without addition of 0.5% acetone at −20 °C.

Preparation of the μ_2-(dimethylamino)-μ_2-hydroxy-dicopper(III) complex 5

In a 10 ml Schlenk tube under an argon atmosphere, to solid heterocubane **1** (21.8 mg, 0.025 mmol [0.1 mmol monomer]), dry dichloromethane (1 ml) was added and the mixture was cooled to −78 °C (acetone/dry ice). (*N*,*N*-Dimethylamino)trimethylsilane (8 µl, 0.05 mmol, 0.5 equiv.) was added with vigorous stirring *via* a syringe. The resulting orange mixture was stirred at −78 °C for 30 minutes, then layered with pentane (*ca.* 3 ml). Crystallization in the freezer at −80 °C for 2 days afforded orange crystals of dimeric μ_2-(dimethylamino)-μ_2-hydroxy-tetrakis(trifluoromethyl)dicopper(III) **5** (5.6 mg, 24%), which were immediately collected for X-ray crystallography and other measurements. The compound undergoes slow decomposition even at −78 °C, and decomposes within minutes under ambient conditions to form a dark green residue.

Author contributions

V. Motornov conceived the idea, led the project, acquired the funding, conducted the experiments and most calculations, and wrote the manuscript. N. Limberg performed X-ray crystal structure measurements and partially conducted the calculations. Both authors contributed to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data are available in the supplementary information (SI) of this article. Supplementary information: experimental procedures, computational and crystallographic details, and analytical data. See DOI: **https://doi.org/10.1039/d6qi00530f**.

CCDC 2533527 (**3**), 2533528 (**5**), 2539161 (the acetone solvate of **4**) and 2551392 (**4**) contain the supplementary crystallographic data for this paper.[21a–d]

Acknowledgements

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