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Cu₁₃{S₂CNⁿBu₂}₆(acetylide)₄⁺: A Two-Electron Superatom

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Dedicated to Professor Sunney Chan on the occasion of his 80th birthday

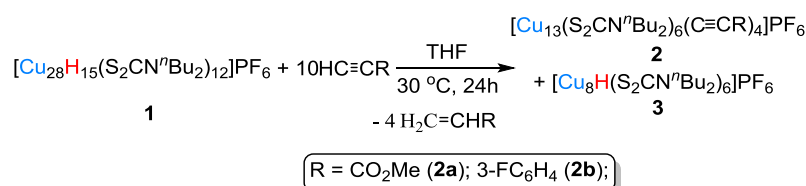
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Abstract: The first structurally characterized copper cluster having a Cu₁₃ centered cuboctahedral arrangement, a miniature of the bulk copper *fcc* structure, is revealed from the [Cu₁₃(S₂CNⁿBu₂)₆(C≡CR)₄](PF₆) (R = C(OMe), C₆H₄F) nanoclusters. Four among eight triangular faces of the cuboctahedron are capped by acetylide groups in a μ₃ fashion and each of the six square faces is bridged by a dithiolate ligand in a (μ₂, μ₂) fashion that subtends a truncated tetrahedron of 12 sulfur atoms. DFT calculations are fully consistent with a description of these Cu₁₃ clusters as 2-electron superatoms, *i.e.* a [Cu₁₃]¹¹⁺ core passivated by ten monoanionic ligands, with an *a₁* HOMO containing two 1S jellium electrons.

The chemistry of atomically precise, noble metal nanoclusters (NCs) has been booming during the last decade, due to their numerous properties with potential uses in nano-devices, imaging, medicine, and catalysis.^[1,2] Gold and (to a lesser extent) silver NCs of various sizes are well documented. In contrast, comparable copper NCs have remained ambiguous, in line with the fact that only a very small number of Cu(0) coordination complexes are known to date.^[3,4] In our search for silver and copper NCs, we have been able to synthesize several silver mixed-valent species,^[5] but so far could only isolate a series of air- and moisture-stable hydrido copper(I) cluster compounds, such as [Cu₇H(S₂CNⁿPr₂)₆], [Cu₈H(S₂CNⁿPr₂)₆]⁺, [Cu₂₈H₁₅(S₂CNⁿPr₂)₁₂]⁺, [Cu₂₀H₁₁{E₂P(OⁿPr)₂]₉] (E = S, Se) and [Cu₃₂H₂₀{S₂P(OⁿPr)₂]₁₂].^[6] As compared with gold and silver, the difficulty in the stabilization of copper oxidation states lower than +I is owed, at least in part, to the lower M(I)/M(0) half-cell potential of Cu (0.52 V) versus Ag (0.80 V) and Au (1.68 V).^[7] In fact, the only known copper NC with mixed-valent superatom type character, namely [Cu₂₅H₂₂(PPh₃)₁₂]⁺, which has a centered icosahedral [Cu₁₃]¹¹⁺ core, was very recently reported by Hayton and co-workers^[8a] by the reduction of Cu(I) salt in a ligand-deficient environment. A few mixed-metal nanoclusters are also known, namely the 8-electron [(CuCNⁿBu)₄(ZnCp⁺)₄],^[8b] and the 18-electron [Au_{12+n}Cu₃₂(SR)_{30+n}]⁴⁺ series.^[8c] In the following, we report the synthesis and characterization of a new copper NC which not only possesses a [Cu₁₃]¹¹⁺ unit but also exhibits a centered dodecahedral (or cuboctahedral) arrangement, *an unprecedented configuration in copper cluster chemistry*. Moreover and astonishingly, this is the only example with a centered-cuboctahedral structure for any discrete tridecanuclear cluster.^[9]



Scheme 1. Synthesis of Compounds **2a**, **2b** and **3**.

The centered icosahedron is the most compact arrangement for a 13-atom unit and it is very common in transition metal clusters. In the case of gold and silver, for instance, several examples of clusters containing icosahedral $\{M_{13}\}$ cores have been characterized through single crystal X-ray study and theoretical computations.^[5,10] On the other hand, recent efforts by Zeng *et al.* have led to the isolation of a couple of *fcc*-configured NCs, namely $Au_{28}(SPh-t-Bu)_{20}$ and $Au_{36}(SPh-t-Bu)_{24}$.^[11,12] This splits the previous idea that non-*fcc* configurations would be more stable than *fcc*-linked cuboctahedral configurations.^[13] Nevertheless discrete centered-dodecahedral $\{M_{13}\}$ cores within molecular clusters are scarce. Related notable crystal structures deposited in the Cambridge Structural Database (v 5.37) are as following: a Pt@Pt₁₂ cuboctahedron which is edge-bridged by two extra Pt atoms and stabilized by carbonyl and phosphine ligands,^[14] and an Ag@Ag₁₂ cuboctahedron with each triangular face capped by one iron tetracarbonyl unit.^[15]

Previously we have demonstrated that hydrides in copper clusters stabilized by dichalcogenolates are substantially hydridic in nature.^[6d] Thus terminal alkynes are sufficiently acidic to react with $[Cu_{28}H_{15}(dtc)_{12}]^+$ (*dtc* = di-butylthiocarbamate = $S_2CN^oBu_2$) to yield a brand new NC formulated as $[Cu_{13}(dtc)_6(acetylide)_4]^+$, (**2**, see Scheme 1) which has a centered cuboctahedral $[Cu_{13}]^{11+}$ core possessing two cluster electrons. A tenfold excess of methyl propiolate was added to a THF suspension of $[Cu_{28}H_{15}(S_2CN^oBu_2)_{12}]^+$, and the reaction mixture was stirred at 30 °C for 24 hours. The color of the suspension changed from orange to deep red, and a dark green solid deposited from the solution. Workup of this mixture leads to the isolation of $[Cu_{13}\{S_2CN^oBu_2\}_6\{C\equiv CC(O)OMe\}_4](PF_6)$ (**2a**) as a dark red solid in 73% yield. Presumably, the hydrogen generated in situ during the reaction was used to partially reduce the excess alkyne (4 of the 10 equiv of alkyne were reduced to the alkene; see the Supporting Information, Figure S1) as well as some Cu^I species to Cu⁰. $[Cu_{13}\{S_2CN^oBu_2\}_6\{3-FC_6H_4C\equiv C\}_4](PF_6)$ (**2b**, 49% yield) was formed under similar reaction conditions by replacing methyl propiolate with 3- $FC_6H_4C\equiv CH$. In both cases, **3** has been isolated as byproduct in 10-15% yield. **2a** and **2b** were fully characterized by single crystal X-ray diffraction and a broad set of standard chemical characterization methods including multinuclear NMR spectroscopy, ESI mass spectrometry, and X-ray photoelectron spectroscopy (XPS). The positive-ion ESI mass spectrum of **2a** and **2b** clearly displays a prominent band for the molecular ion $[2a]^+$ at *m/z* 2382.8 (calcd 2382.6), $[2b]^+$ at *m/z* 2526.7 (calcd 2526.7), and their simulated isotopic patterns match well with the experimental observations (Figures S2, S3). Most importantly, with one PF_6^- counterion, six *dtc* and four alkynyl anionic ligands, the formal global oxidation state of the 13-atom metal core should be +11. This makes compounds **2** mixed-valent complexes, undermore precisely 2-electron superatoms. Notably, only three 2-electron NCs are known: $[Cu_{25}H_{22}(PPh_3)_{12}]^+$,^[8] $[Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8]$,^[16] and $[Ag_{16}(SC_6H_3F_2)_{14}(dppe)_8]$ (*dppe* = 1,2-bis(diphenylphosphino)-ethane).^[17]

The single crystal X-ray structures of **2a** (Figure 1) and **2b** (Figure S4) show clearly the Cu@Cu₁₂ cuboctahedral architecture of the cations.^[18] To the best of our knowledge, this core unit is the first example of a copper-centered Cu₁₃ cuboctahedron, identical to that observed in the *fcc* structure of bulk copper. This configuration represents a marked contrast with the centered icosahedral geometry observed in the core unit of $[Ag_{20}\{S_2P(O^oPr)_2\}_{12}]$, $[Ag_{21}\{S_2P(O^oPr)_2\}_{12}]^+$, and $[Au_{13}(PPhMe_2)_{10}Cl_2]^{3+}$.^[5,19] The central copper (Cu1) plays a template role in the formation of this large cluster, and strongly binds to the twelve other Cu atoms. Whereas a couple of examples of Au₁₂ and Ag₁₂ dodecahedra encapsulating a sodium or silver atom, respectively, are known,^[14, 20] **2** is the first example of a copper cuboctahedron encapsulating another atom. It is worthwhile to mention that no guest element exists in the dodecahedral structures of $[Cu_{12}S_8]^{4-}$,^[21a] $[Cu_{12}(NPh)_8]^{4-}$,^[21b] $[(^tBu_3SiP)_6Cu_{12}]$,^[21c] and $[Cu_{12}E_6(PR_3)_8]$ (E = S, Se, Te).^[21d] The six square faces of the cuboctahedron in **2** are all capped by six *dtc* ligands that bridge four metal centers in a (μ_2, μ_2) binding mode. The twelve sulfur atoms thus form a truncated tetrahedral cage. Only half of the eight triangular faces of the cuboctahedron are capped by alkynyl groups in a $\mu_3-\eta^1$ fashion. Each of the twelve outer Cu atoms is tri-coordinated to two S and one C atoms in a somewhat pyramidalized trigonal fashion (**2a**: $\angle S(1)-Cu(2)-C(55)$ 117.7(5) $\angle S(1)-Cu(2)-S(3)$ 105.8(2)). As a result, **2** has an idealized *T_d* symmetry.

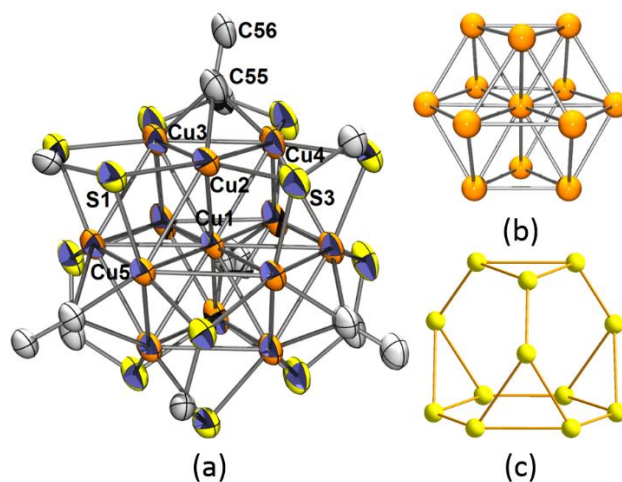


Figure 1. (a) View of the structure of the cluster cation of **2a** with 30% thermal probability ellipsoids. All N^tBu_2 and $C(O)OCH_3$ moieties are omitted for clarity; (b) the centred cuboctahedron framework of 13 copper atoms; (c) the 12 sulfur atoms in a truncated tetrahedral geometry which surround the copper core.

Table 1. Selected bond lengths (Å) and bond angles (°) for **2a**, **2b** and **2'**.

	2a	2b	2' (T_d)
$Cu_{cent}-Cu_{cubo}$	2.605(3) – 2.669(3) avg. 2.636(3)	2.601(2)-2.666(2) avg. 2.645(2)	2.660
$Cu_{cubo}-Cu_{cubo}$	2.522(4) – 2.786(3) avg. 2.636(3)	2.484(1)-2.792(2) avg. 2.645(2)	2.595-2.725 avg. 2.660
$Cu_{cubo}-S$	2.257(6) - 2.320(6) avg 2.289(6)	2.338(2)-2.268(3) avg. 2.299(3)	2.344
$Cu_{cubo}-C$	2.001(2)-2.076(2) avg 2.035(2)	1.977(1)-2.092(1) avg. 2.039(1)	2.053
$C\equiv C$	1.187(19)-1.213(7) avg 1.202(12)	1.201(2)-1.231(1) avg. 1.216(15)	1.221
$Cu(3)-Cu(2)-Cu(4)$	61.13(9)°	59.67(6)°	60°
$Cu(3)-Cu(2)-Cu(5)$	88.63(9)°	87.07(5)°	90°
$C(55)\equiv C(56)-C(57)$	177(2)°	175(2)°	180°

A cuboctahedral configuration of twelve metal atoms around the central $\mu_{12}-Cu$ in **2** generates a geometric entity derived from the *fcc* packing of elemental copper. The Cu-Cu distances in **2a** and **2b** range 2.522(4)-2.786(3) and 2.484(1)-2.792(2) Å respectively, and are shorter than the average Cu-Cu distances (2.845 Å) observed in the cuboctahedral $[Cu_{12}S_8]^{4-}$.^[21a] The average $Cu_{cent}-Cu_{cubo}$ bond length {2.636(3) Å (**2a**), 2.645(2) Å (**2b**)}, is comparable to that of $Cu_{cent}-Cu_{icos}$ (2.635 Å) in $[Cu_{25}H_{22}(PPh_3)_{12}]Cl$ and ca. 0.1 Å larger than that in metallic copper.^[22] Though $[Cu_{20}H_{11}\{Se_2P(O^iPr)_2\}_9]$ also consists of a distorted cuboctahedral Cu_{13} core of which the central copper atom is further linked to a hydride, the Cu-Cu distances are in the range 2.5051(4)-3.0911(6) Å.^[6] The Cu-S bond lengths, averaging 2.289(6) Å in **2a** and 2.299(3) Å in **2b**, are comparable to the average Cu-S distances in $[Cu_8(H)(S_2CN^iPr)_6]^+$ (2.314(2)

Å) with a similar ligand S...S bite distance of 3.044 Å.^[6a] The average Cu-C bond distance 2.035(2) Å (**2a**), 2.039(1) Å (**2b**) is less than the sum of covalent radii for σ bonding alkynes.^[23] The values of the four C \equiv C–C angles of the four acetylide ligands in **2a** deviate from linearity by 3°, 9°, 10° and 16°, respectively; whereas in the case of **2b** the deviations are only 4°, 5°, 8° and 8°. Similar bonding modes of acetylide ligands have also been observed in other trinuclear copper(I) acetylide complexes.^[23] The cluster shows significant distortions away from the idealized T_d symmetry, which could arise from the different electronic and steric requirements of the alkynyl and dtc ligands.

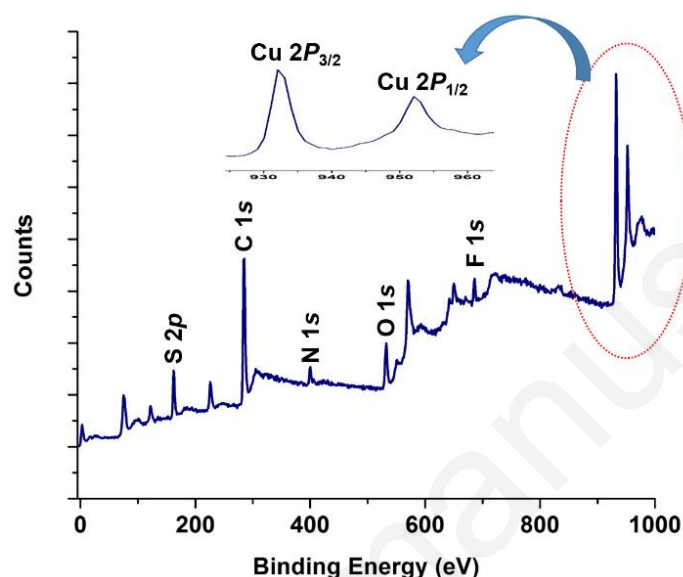


Figure 2. XPS survey spectrum of cluster **2a**. It identifies the presence of Cu, S, C, N, F and O. The inset shows the expanded XPS spectrum in the Cu 2p region of cluster **2a**. Sharp peaks with narrow width are observed.

X-ray photoelectron spectroscopy (XPS) has been used to evaluate the chemical states of the metal cores in nano-material studies. The spectrum in the Cu 2p region shows two peaks identical for **2a**, **2b** at 932.0 and 952.0 eV (Figure 2, S5), which have been assigned to $2p_{3/2}$ and $2p_{1/2}$ features of Cu(0). Binding energy (BE) of Cu(I) $2p_{3/2}$ in Cu_2O is 932.1 eV.^[24] Thus, the BE values are within the range of Cu(0) and Cu(I). XPS features of all other expected elements fitted exactly with that of the expected elements. The results strongly confirmed the existence of N and O, which were demonstrated by the peak of N 1s at 400.0 eV and O 1s at 532.0 eV. The S 2p region shows a $2p_{3/2}$ feature at 162.0 eV, characteristic of thiolate and the C1s binding energy seen is at 285.0 eV, characteristic of the ligand chain.

^1H and ^{13}C NMR spectra show one set of signals illustrating that the molecule is symmetric in solution (Figure S6-S9). FT-IR spectra of **2a**, **2b** (Figure S10, S11) show that the $\nu(\text{C}\equiv\text{C})$ stretching frequencies of the coordinated $\text{RC}\equiv\text{C}^-$ ligands are lower than the values found for the free ligands ($\nu(\text{HC}\equiv\text{CC}(\text{O})\text{OMe}) = 2129$, $\nu(\text{HC}\equiv\text{CC}_6\text{H}_4\text{F}) = 2107 \text{ cm}^{-1}$). **2a** and **2b** show a band at 2017.5 and 2009.1 cm^{-1} respectively. These values are slightly higher than that for $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CCOO})(\mu_3\text{-OCH}_3)]$ (1976 cm^{-1}).^[25] The UV-vis spectrum of **2a** shows broad multiband optical absorption bands (at 345, 506, 526, 556 nm) and an intense absorption band at 287 nm (Figure S12), whereas the same number of absorption band with shifted positions (at 304, 335, 510, 539, and 568 nm) were also observed in **2b** (Figure S13). The low-energy bands could be assigned by TDDFT calculations to a HOMO-LUMO transition, *i.e.*, a metal to metal to ligand charge transfer (MMLCT, see below and Figure S14). Compounds **2a**, **2b** are not emissive in both the solid state and solution under UV-irradiation even at 77K. Electrochemical properties of **2a** and **2b** were investigated in CH_2Cl_2 solution at various temperatures. Cyclic voltammograms (CVs) of **2a** at 273 K displayed an irreversible reduction process at $E_{\text{pc}} = -1.94 \text{ V}$ (vs. Fc^+/Fc) and two quasi-reversible oxidation events at $E_{1/2} = -0.05$ and $+0.34 \text{ V}$ (Figure 3). At 237 K, reversibility of all

redox waves was slightly improved (Figure S15). Every redox reduction was a one-electron event according to differential pulse voltammetric measurements. The two oxidation peaks, which correspond to the $[\text{Cu}_{13}]^{12+}$ and $[\text{Cu}_{13}]^{13+}$ species, respectively (vide infra), are separated by ~ 400 mV and structural modification might occur upon oxidation owing to quasi-reversibility of the waves at low temperatures. A similar behaviour was observed for the **2b** analogue (Figure S16). Enhanced current amplitude for the return cathodic wave of the first oxidation event was revealed at 243 K at a scan rate of 1.6 V/s. It is suggested that **2a** is more stable than **2b** towards oxidation because the HOMO of **2a** (see below) is stabilized by the stronger electron-withdrawing group on the acetylide.

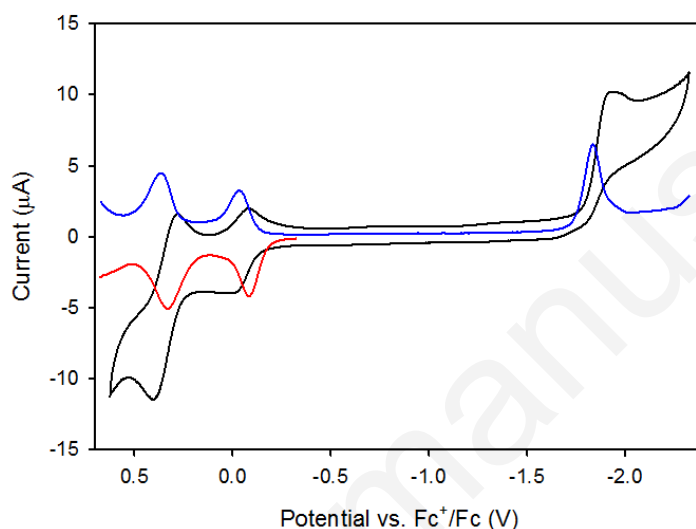


Figure 3. Cyclic voltammogram (black line) and differential pulse voltammograms (anodic scan in blue and cathodic scan in red, amplitude 50 mV, pulse period 0.5 s, pulse width 50 ms) of **2a** (0.75 mM) at 273 K in CH_2Cl_2 under N_2 atmosphere (3 mm vitreous carbon electrode, 0.1 M $[n\text{-Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$).

DFT calculations have been carried out at the PBE0/Def2-TZVP level on the simplified model $[\text{Cu}_{13}(\text{S}_2\text{CNH}_2)_6(\text{C}\equiv\text{CH})_4]^+$, (**2'**). Its optimized structure, characterized as an energy minimum (no imaginary frequency) was found to be of T_d symmetry. Its metrics match quite well with the X-ray data of **2a** and **2b** (see Table 1). The shortest Cu-Cu separations correspond to the edges of the triangular faces capped by the alkynyl ligands (2.595 Å) and the largest ones to those of the uncapped triangular faces (2.725 Å). In average, the dodecahedral edges are equal to the $\text{Cu}_{\text{cent}}-\text{Cu}_{\text{cubo}}$ distances (2.660 Å). The electronic structure of **2'** is fully consistent with that of a 2-electron superatom. Its Kohn-Sham MO diagram (Figure 4) exhibits a substantial energy gap of 3.08 eV separating the a_1 HOMO, which can be identified as the 1S jellium orbital, from the t_2 lowest unoccupied level, which can be viewed as the 1P jellium shell, mixed with ligand $d_{\text{TC}} \pi^*$ orbitals. The metal natural atomic orbital (NAO) charges are -0.54 and +0.69 for Cu_{cent} and Cu_{cubo} , respectively. This corresponds to the NAO configurations of $4s^{1.52}3d^{9.93}4p^{0.08}5s^{0.01}$ (Cu_{cent}) and $4s^{0.41}3d^{9.85}4p^{0.04}5s^{0.01}$ (Cu_{cubo}). This is consistent with the view of a formally central Cu^+ atom interacting with a $[\text{Cu}_{12}(\text{S}_2\text{CNH}_2)_6(\text{C}\equiv\text{CH})_4]^{2+}$ cage. The twelve pyramidalized Cu(I) centers of this cage are highly unsaturated, in such a way each of them bears a vacant sp-type orbital pointing towards the center of the cage. Due to significant overlap, the twelve sp-type combinations split in energy. The lowest one is a fully in-phase a_1 combination. This accepting orbital is well suited for interacting strongly with the 4s occupied orbital of the encapsulated Cu^+ atom, giving rise to the bonding a_1 HOMO of **2'** (Figure 4). This HOMO contains the two electrons associated with the jellium $1S^2$ configuration. On the other hand, the next bonding sp-type vacant combination of the twelve Cu(I) centers is of t_2 symmetry and matches with the vacant high-lying 4p orbitals of the encapsulated Cu^+ center, the resulting bonding combination being the t_2 LUMOs of **2'** which can be viewed as the

unoccupied jellium 1P level (with substantial ligand admixture). The computed Cu-Cu Wiberg indices are consistent with the existence of two bonding jellium electrons: +0.060 ($\text{Cu}_{\text{cent}}\text{-Cu}_{\text{cubo}}$) and +0.048 (avg. $\text{Cu}_{\text{cubo}}\text{-Cu}_{\text{cubo}}$). Based on the above analysis, one can anticipate that the $[\text{Cu}_{12}(\text{dtc})_6(\text{C}\equiv\text{CR})_4]^{2+}$ cage might be able to host various types of anions, not only 2-electron anions isolobal to Cu^{1+} , but also 8-electron anions such as halides or chalcogenides which have occupied valence orbitals perfectly suited for matching the a_1 and t_2 accepting orbitals of the cage. The oxidized forms of $\mathbf{2}'$, namely $[\text{Cu}_{13}(\text{S}_2\text{CNH}_2)_6(\text{C}\equiv\text{CH})_4]^{n+}$ ($n = 2, 3$) have also been calculated at the same level of theory. They correspond to the progressive depopulation of the Cu_{13} -centered $1a_1$ HOMO of $\mathbf{2}'$. Consistently, their optimized structures (characterized as true energy minima) retain the T_d symmetry, with a metal core expansion increasing with n ($\text{Cu}_{\text{cent}}\text{-Cu}_{\text{cubo}} = 2.734$ and 2.818 Å for $n = 2$ and 3 , respectively). These results are fully consistent with the CV experiments. The computed first and second ionization energies of $\mathbf{2}'$ are 8.06 and 10.84 eV respectively.

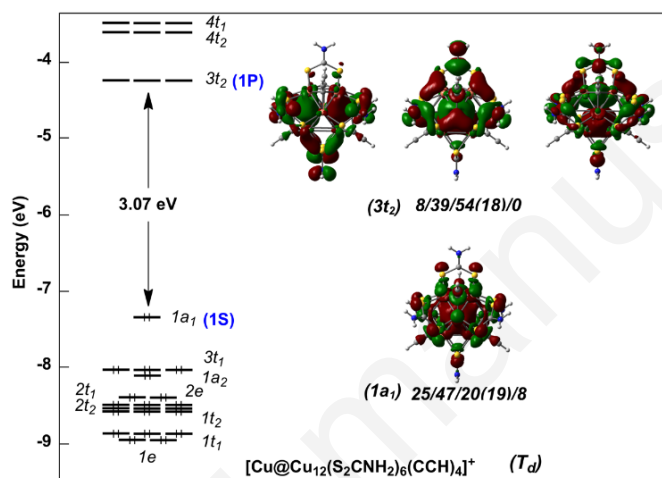


Figure 4. MO diagram of the $\mathbf{2}'$ model. The MO localization (in %) is given as follows: ($\mu_{12}\text{-Cu}$)/ $\text{Cu}_{12}/(\text{S}_2\text{CNH}_2)$ (of which S)/ $\text{C}\equiv\text{CH}$.

In summary, we have isolated and fully characterized $[\text{Cu}_{13}(\text{alkynyl})_4(\text{dtc})_6](\text{PF}_6)$ ($\mathbf{2}$), the first centred cuboctahedral copper NCs, a miniature of the bulk copper *fcc* structure, with partial $\text{Cu}(0)$ character. The Cu_{13} skeleton is capped on four among the eight triangular faces by acetylide groups, each of the six square faces of the cuboctahedron is bridged by a dithiocarbamate ligand. As a result, compound $\mathbf{2}$ has an idealized T_d symmetry. DFT calculations are fully consistent with a description of these species as 2-electron superatoms. Cyclic voltammetry experiments and DFT calculations suggest that the isolation of both $[\text{Cu}_{13}]^{12+}$ and $[\text{Cu}_{13}]^{13+}$ species is achievable. It is now clear that $\mathbf{1}$ could be a good source for larger Cu NCs with partial $\text{Cu}(0)$ character. Additionally, the unique reactivity of $\mathbf{1}$ opens the possibility for the development of reduction reactions of alkynes, and various carbonyl derivatives, including unsaturated ketones, esters and aldehydes. Such work is in progress.

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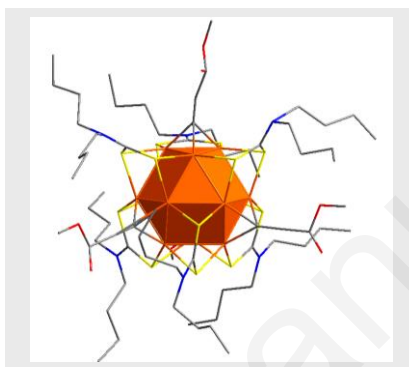
Keywords: centred cuboctahedron • nanoclusters • superatoms • copper • X-ray diffraction

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Entry for the Table of Contents

COMMUNICATION

The first structurally characterized Cu_{13} clusters having a centred-cuboctahedral unit, a miniature of the bulk Cu metal *fcc* structure, have been synthesized. The $[\text{Cu}_{13}]^{11+}$ core certified as a two-electron superatom is capped on four among the eight triangular faces by acetylide groups and each of the six square faces is bridged by a dithiolate ligand to yield T_d ideal symmetry.



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Page No. – Page No.

$[\text{Cu}_{13}\{\text{S}_2\text{CN}^t\text{Bu}_2\}_6(\text{acetylide})_4]^+$: A Two-Electron Superatom