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Synthesis and structural characterization of inverse-coordination clusters from a two-electron superatomic copper nanocluster†

Kiran Kumarvarma Chakravarti,†a Rhone P. Brocha Silalai,†a Jian-Hong Liao,a Samia Kahal,b Yu-Chiao Liu,c Jyh-Fu Lee,d Ming-Hsi Chiang,c Jean-Yves Saillard b and C. W. Liu id

We have synthesized and structurally characterized a series of centred cuboctahedral copper clusters, namely [Cu12(S2CNR2)3(C≡CR)4](PF6), 1a–d (where a: R = 9Bu, R′ = CO2Me; b: R = 9Bu, R′ = CO2Et; c: R = 9Pr, R′ = CO2Et; d: R = 9Pr, R′ = 3,5-(CF3)2C6H3); [Cu12(μ12-Cl)(S2CNR2)3(C≡CR)4](PF6), 2a–c; [Cu12(μ12-Cl)(S2CNR2)3(C≡CR)4](PF6), 3a–e (where e: R = 9Bu, R′ = Ph); [Cu12(μ12-Br)(S2CNBu2)3(C≡CPh)4](PF6), 4e; and [Cu12(μ12-Cl)(μ12-Cl)(S2CNBu2)4(C≡CCO2Me)4]5a. Cluster 1a is the first structurally characterized copper cluster having a Cu12 centered cuboctahedral arrangement, a miniature of the bulk copper fcc structure. Furthermore, the partial Cu(0) character in the 2-electron superatoms 1 was confirmed by XANES. Inverse coordination clusters 2–5 are the first examples of copper clusters containing main group elements (Cl, Br, S) with a hyper-coordination number, twelve. A combined theoretical and experimental study was performed, which shows that the central copper (formally Cu1−) in nanoclusters 1 can be replaced by chalcogen/halogen atoms, resulting in the formation of clusters 2–5 which show enhanced luminescence properties and increase in the ionic component of the host–guest interaction as Br = Cl > S > Cu, which is consistent with the Cu–X Wiberg indices. The new compounds have been characterized by ESI-MS, 1H, 13C NMR, IR, UV-visible, emission spectroscopy, and the structures 2a–b, 3d–e, 4e and 5a were established by X-ray diffraction analysis.

Introduction

The concept of inverse coordination, as recently defined by Haiduc,2 applies to metal complexes in which the arrangement of acceptor and donor sites is opposite to that occurring in Werner-type coordination complexes. Inverse coordination complexes are formed around a non-metal species as the central atom (ion) surrounded by a number of metal atoms (ions) connected or not by internal bridging (intramolecular) linkers. Thus, discarding the nature of metal–metal interactions (if any), inverse coordination complexes can be simply viewed as transition-metal clusters (with or without metal–metal bonding) encapsulating a main-group anion.

In recent years, our group has developed the chemistry of anion-encapsulated CuI and AgI clusters bridged by dichalcogenolate ligands (dithiocarbamates and dichalcogenophosphates). Various high-coordination numbers have been observed and rationalized for anions located at the centre of such d10-metal clusters.3 For instance, cubic metal clusters containing an octa-coordinated encapsulated anion are known (Chart 1, left side).4 Nona-coordination of a halide or a chalcogenide, where the encapsulated anion lies at the center of an M11 pentacapped trigonal prism (Chart 1, middle), has also been shown to exist.4 Later, we reported the first example of a dodeca-coordinated iodide lying at the center of an Ag12

![Chart 1 Geometries of hyper-coordinated anions.](image-url)
cuboctahedron (Chart 1, right side).\(^4\) Lang and coworkers reported a cluster having a similar coordination environment for iodide in a cuboctahedral copper core.\(^4\) It is worth noting that in the examples illustrated in Chart 1, no formal covalent bonding exists between the \(d^{10}\) metal centers, but only some metalophilic interactions.\(^6\)

Understanding the mechanisms of nanocluster (NC) formation and reactivity is an important step toward the tailoring of new functional materials.\(^4\) A substitution reaction is a typical chemical reaction where an atom or a functional group of a molecule is replaced by another atom or functional group.\(^7\)

Compared to substitution reactions on a terminal ligand, substituting an inversely coordinated anion is much more difficult to perform due to the relatively high activation energy associated with this process.\(^8\) As far as we know, organometallic complexes with a main-group element in a very high coordination number have never been synthesized via the substitution reaction.

Recently, we reported the synthesis and characterization of a series of group 11 cuboctahedral metal NCs of the general formula \([\text{Cu}_{12}^\text{I}_{12}^\text{III}(\text{S}_2\text{CNR}_2)_3](\text{C}_n\text{CR}_2)_3]^+(M = \text{Cu}, \text{Ag}, \text{Au}).\(^9\) In a first approximation, the bonding within these 2-electron superatoms can be described as resulting from the interaction of an encapsulated and formally \(M^\text{−}\) anion with a cuboctahedral cage composed of twelve \(\text{Cu}^\text{I}\) ions. One fascinating query is whether it should be possible to substitute the encapsulated closed-shell \(M^\text{−}\) anion by a closed-shell main-group anion, and further on, to replace this encapsulated main-group element by another one, the corresponding substitution reactions occurring without cluster disintegration.

Herein, we report the detailed synthesis and characterization of chalcogen- and halogen-centred copper cuboctahedra. The compounds exhibit three distinct features: (1) the \(\text{Cu}_{12}^\text{I}_{12}^\text{III}\) framework stabilized by both dithiocarbamate (dtc) and acetylide ligands is unprecedented; (2) the reported \(\mu_{12}^\text{II}\) S species are the very first compounds exhibiting a twelve-coordinated chalcogen encapsulated in a copper cluster; (3) the reported \(\mu_{12}^\text{II} \text{Cl}\) species constitute the only third example of a twelve-coordinated halogen in coordination chemistry.

**Results and discussion**

**Synthesis and characterization**

Previously we have demonstrated that the hydrides present in the copper(i) cluster \([\text{Cu}_{25}^\text{II}^\text{III}(\text{dtc})_{12}]^+(\text{dtc} = \text{di-butylidithiocarbamate} = \text{S}_2\text{CN}^\text{−}\text{Bu}_2)\) react with the acidic protons of terminal alkynes to liberate molecular hydrogen, which subsequently reduces the excess of alkynes to alkenes, as well as parts of \(\text{Cu}^\text{I}\) to \(\text{Cu}^\text{II}.\(^8\) The generation of alkynyl ligands in the reaction medium leads eventually to the formation of a brand-new NC formulated as \([\text{Cu}_{13}^\text{II}(\text{dtc})_6(\text{alkynyl})_4]^+\) (1), which has a centered cuboctahedral \([\text{Cu}_{13}^\text{III}]\) core possessing two 4s cluster electrons (1S\(^2\) closed-shell configuration within the spherical jellium or superatom paradigm).\(^8\) In a typical experiment, to a THF suspension of \([\text{Cu}_{28}^\text{II}^\text{III}(\text{S}_2\text{CNR}_2)_{12}]^+\), a ten-fold excess of terminal alkylene was added and the reaction mixture was stirred at 30 °C for 24 hours. The solution undergoes a color change from orange to deep red, resulting in the deposition of a dark green solid.

Workup of this mixture leads to the isolation of \([\text{Cu}_{13}^\text{II}^\text{III}(\text{S}_2\text{CNR}_2)_{12}](\text{C}_n\text{CR}_2)_3]^+(\text{PF}_6)^−\) (1) as a dark red solid in 40–70% yield (1a (70%): \(\text{R} = \text{Bu}\), \(\text{R}^\prime = \text{CO}_2\text{Me}\); 1b (42%): \(\text{R} = \text{Bu}, \text{R}^\prime = \text{CO}_2\text{Et}\); 1c (65%): \(\text{R} = \text{iPr}, \text{R}^\prime = \text{CO}_2\text{Et}\); 1d (55%): \(\text{R} = \text{Pr}, \text{R}^\prime = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\)). In all the cases \([\text{Cu}_{13}^\text{II}^\text{III}(\text{S}_2\text{CNR}_2)_{12}]^+\) and the corresponding alkane (methyl acrylate for \(\text{a}\), ethyl acrylate for \(\text{b}\), \(\text{c}\), and 1,3-bis(trifluoromethyl)-5-vinylbenzene for \(\text{d}\)) have been isolated as byproducts. The hydrogen gas released from the reaction of the terminal alkylene’s acidic hydrogen with the hydrides of \([\text{Cu}_{28}^\text{II}^\text{III}(\text{S}_2\text{CN}^\text{−}\text{R}_2)_{12}]^+\) is assumed to be the reductant for the partial conversion of the alkylene to an alkane.

The positive-ion ESI mass spectrum of 1b-d clearly displays a prominent band for the molecular ion \([\text{1b}^\text{−}\text{PF}_6]^\text{+}\) at \(m/z\) 2438.6 (calcd 2438.7), \([\text{1c}^\text{−}\text{PF}_6]^\text{+}\) at \(m/z\) 2270.3 (calcd 2270.5), \([\text{1d}^\text{−}\text{PF}_6]^\text{+}\) at \(m/z\) 2830.3 (calcd 2830.4) and their simulated isotopic patterns match well with the experimental observations (Fig. 1a, S1 and S2†). As said above, with two 4s(Cu) electrons delocalized on its 13-atom metal core, the cluster cation 1 is a mixed-valent species, more precisely 2-electron superatoms.\(^10\) Notably, only a few 2-electron copper NCs are known: \([\text{Cu}_{25}^\text{II}^\text{III}(\text{PhPh})_{12}]^+\), \([\text{Cu}_{25}^\text{II}^\text{III}(\text{PhPh})(\text{OAc})_{12}]^+\), and \([\text{Cu}_{20}^\text{II}^\text{III}(\text{CCPh})_{12}(\text{OAc})_{12}]^+\),\(^11\) and none of them has a cuboctahedral metal core.

![Fig. 1 Positive mode ESI-MS of 1b (a) and 2b (b). Insets: experimental and simulated mass spectra.](Image)


H and 13C NMR spectra of 1a-d show one set of signals, consistently with T₃ symmetry in solution (see below). Their FT-IR spectra show that the alkyne ν(C≡C) stretching frequencies are lower than in the corresponding alkyne (ν(HC≡CR) = 2129 cm⁻¹). 1a shows a band at 1721.5 cm⁻¹. This value is slightly higher than in [Cu₂(μ-dppm)₂(μ-η¹⁻¹-C≡CCOO)][μ-OCH₃] (1976 cm⁻¹). The effect of Cu oxidation state(s) and cluster nuclearity is evident in the Cu K-edge X-ray absorption near-edge spectra (XANES) of 1a-d (Fig. 2). At ~8979.8 eV, the edge position of 1a-d is very similar to that of copper NCs, [Cu₂Cl₂H₂(PPh₂Phen)₁₂]Cl and [Cu₂H₂(PPh₃)₁₂]Cl reported by Hayton and resides between values measured for Cu⁰ in the bulk foil (8979.0 eV) and Cu¹ in clusters such as [Cu₉(H)₁₃(S₂CNBu₂)₁₂]PF₆ (8980.1 eV) and [Cu₉(H)₃(S₂CNBu₂)₆]PF₆ (8980.3 eV). This is consistent with an average Cu oxidation state between 0 and +1 for 1a-d (Table 1).

Compound 2a has been synthesized by reacting 1a with a two-fold excess of K[S₂CNBu₂] and the reaction mixture was stirred for 24 hours at 0 °C (Scheme 1). The solution undergoes a color change from deep red to orange. Immediate workup of the mixture leads to the isolation of [S₂CNBu₂(C₂O)₆]PF₆ (8980.1 eV) and [Cu₈(H)₁₃(S₂CNBu₂)₆]PF₆ (8980.3 eV). This is consistent with an average Cu oxidation state between 0 and +1 for 1a-d (Table 1).

![Fig. 2 Comparison of Cu K-edge XANES profiles for Cu foil, CuCl, copper(0) hydrides and NCs 1a–d.](image)

| Material | Edge (eV) |
|----------|-----------|
| Cu foil  | 8979.0    |
| [Cu₁ الثن(PPh₃)₁₂]Cl | 8979.6    |
| [Cu₂Cl₂H₂(PPh₂Phen)₁₂]Cl | 8979.5    |
| [Cu₃(S₂CNBu₂)₆(C₂O)₆]PF₆ | 8979.8    |
| [Cu₃(S₂CNBu₂)₆(C₂OEt)₆]PF₆ | 8979.8    |
| [Cu₃(S₂CNPr₂)₆(C₂OEt)₆]PF₆ | 8979.8    |
| [Cu₃(S₂CNPr₂)₆(CF₃)₃CuH₁₃]PF₆ | 8979.7    |
| Cu₂O     | 8980.0    |
| [Cu₉(H)₁₃(S₂CNBu₂)₁₂]PF₆ | 8980.1    |
| [Cu₉(H)₃(S₂CNBu₂)₆]PF₆ | 8980.3    |
| [Cu(CH₃CN)₄]PF₆ | 8980.3    |
| CuCl     | 8981.6    |

a prominent band for the molecular ion [2a]⁺ at m/z 2351.6 (calcd 2351.7), [2b]⁺ at m/z 2407.5 (calcd 2407.7), [2c]⁺ at m/z 2239.0 (calcd 2237.5), and their simulated isotopic patterns match well with the experimental observation (Fig. 1b, 3s and 3t). The presence of a sulfide atom in 2a-c clearly originates from the dtc ligand. Indeed, the formation of S^2⁻ from the sulfur–carbon bond cleavage in dtc ligands has been well documented.

Compounds 3a–d were isolated as yellow solids in 11–30% yield from the reaction of 1a-d with dichloromethane for three days under ambient conditions. This reaction also produced [Cu₁₁Cl₄(S₂CNBu₂)₆]⁺ and a series of chloride-centred Cu₁₂ cuboctahedral clusters with a different number of acetylide ligands [Cu₁₂(μ₁₂-Cl)ₖ[S₂CNBu₂]ₖ[C≡COO]ₖ]⁺ (k = 1–3), whose compositions were confirmed by ESI mass spectrometry (Fig. S6 and S7†). This result suggests that three among the four acetylide of compound 1a-d can be replaced by halides. The geometric structure of [Cu₁₁Cl₄(S₂CNBu₂)₆]⁺ is presumably similar to that of our previously reported [Cu₁₁(μ₁₀-Br)₅[μ₁₀-Br]₈(S₂P(OEt)₂)₆]⁺. Separation of these compounds by column chromatography was difficult. However, we were lucky to grow single crystals of 5a [Cu₁₂(μ₁₂-Cl)ₖ[S₂CNBu₂]ₖ[C≡COO]ₖ]⁺, which was characterized by X-ray crystallography (vide infra).

We have increased the yields in the production of compounds 3 by designing an alternative synthetic procedure. The direct synthesis involved the reaction of a terminal alkyne with a THF suspension of CuI salts and dtc ligands followed by the addition of few drops of triethylamine (Scheme 2). The reaction mixture was stirred at room temperature for ten minutes followed by the addition of tetrabutylammonium halide. The resulting solution was stirred for 12 hours, leading to the isolation of compounds 3e and 4e with 45% and 52% yields, respectively. The spectroscopic data of 3e and 4e are fully consistent with their X-ray structures described below (Fig. 3). The positive-ion ESI mass spectra clearly display a prominent band for the molecular ion [3a-PF₆]⁺ at m/z 2354.8 (calcd
2354.7), [3b-PF₆]⁺ at m/z 2410.7 (calcd 2410.7), [3c-PF₆]⁺ at m/z 2242.5 (calcd 2240.5), [3d-PF₆]⁺ at m/z 2802.3 (calcd 2802.5), [3e-PF₆]⁺ at m/z 2426.4 (calcd 2420.5), and their simulated isotopic patterns match well with the experimental observation (Fig. 4 and S6–S9†).

FT-IR spectra of 3e and 4e show that the ν(C≡C) stretching frequencies (2014, and 2015 cm⁻¹ respectively) are lower than the values found for the corresponding alkyne (ν(HC≡CPh) = 2110 cm⁻¹).

In solution, ¹H NMR spectra for compounds 2a, 3e and 4e were recorded at variable temperatures (183, 193, 243 and 273 K), which show only one set of ligands (in line with T₃ symmetry, Fig. S10†). ¹H and ¹³C NMR spectroscopic analyses of 5 show one set of ligands illustrating that the molecule is highly symmetric in solution. This is consistent with the ligand distribution pattern in 1, implying their similarity in structure. Indeed, the ¹H chemical shifts of 1a and 5a are similar but their integration ratios are different. Clusters 1–4 contain six dtc ligands and four alkyln groups, whereas the ¹H NMR spectrum of 5a shows the integration value of three alkyln groups for six n-butyl dtc ligands. The replacement of one of the alkyln groups with chloride is further confirmed by the ESI mass spectrum, where 5a shows the molecular ion [5a]⁺ peak at m/z 2308.4 (calcd 2306.6) (Fig. S11†).

**Structural analysis**

The single-crystal X-ray structures of 1a, 2a, 2b, 3d, 3e and 4e are given in Fig. 3a, b, S5, S13,† 3c and d respectively. Corresponding relevant metrical data are given in Table 2. They all clearly show an X-centered Cu₁₂ cuboctahedron (X = Cu (1), S (2), Cl (3d, 3e), Br (4e)). The six square faces of the Cu₁₂ cuboctahedron are capped by six dtc ligands, each of them bridging four metal centres in a (μ₂, μ₂) binding mode. As
a result, the twelve dtc sulfur atoms form a truncated tetrahe- 
dral cage. Four among the eight triangular faces of the cubo-
tahedron are capped by alkynyl groups in a μ₂-η¹ fashion. It 
follows that each of the twelve outer Cu atoms is in an 
approximately planar CuS₂Cl coordination mode (not taking 
into account bonding with X). Not considering the sub-
stituents on alkynyls, the idealized symmetry of the clusters is 
T₄d. The main-group-centered structures (2a, b, 3d, e and 
4e) are however more distorted away from this ideal symmetry 
than that with X = Cu (1a). This is exemplified by the larger 
dispersion of the Cu–Cu and X–Cu distances. All these structures 
exist in either long X–Cu distance (Table 2) but still within bonding 
contacts (see below). The Cu–(μ₂-S) bond lengths of 2a, b are in the 
range 2.561(3)–2.934(4) Å, i.e. longer but comparable to that of 
Cu–(μ₂-S) 2.402–2.870 Å in [Cu₅₁(μ₂-S)[μ₂-Br][3(S₂P(OPr)₂)₆].

The average Cu–(μ₂-Br) distance in 4e (2.977 Å) is comparable to 
the Cu–(μ₂-Br) distance (2.942 Å) observed in [Cu₅₁(μ₂-Br)[μ₂- 
Br][2(S₂P(OPr)₂)₆]. The average Cu–(μ₂-X) distance in [Cu₅₁(μ₂-
X)[2(S₂P(OPr)₂)₆] is shorter than in 3d, e and 4e (2.72 Å) (ref. 4c) and 
2.74 Å (ref. 4d) for Cl and Br, respectively. The average Cu– 
C distances in compounds 2a–b, 3d–e and 4e are larger than in 
the Cu-centered cluster 1a, the largest value corresponding to 
the bromine-centered cluster 4e, presumably owing to the larger 
size of bromine. In this particular compound, the Cu–Cu 
distance overpasses the sum of the van der Waals radii and it 
can be anticipated that the entrapment of anions larger than 
bromide into the Cu₁₂ cage would destabilize the structure. For 
all the structures reported in Table 2, the Cu–S(dtc) Cu–C and 
C=C bond distances (Table 2) are in the normal range and vary 
little across the series. The highest coordination number found 
in the literature is 8 for chloride and 9 for bromide. Thus, to the 
best of our knowledge, compounds 3d–e and 4e are the first 
isolated examples of μ₂₃-chloride and μ₂₃-bromide encapsulated 
in molecular compounds. In these clusters, as well as in the 
copper- and sulfide-centered species, the central atom plays 
a template role in the formation of this large cluster. This 
cuboctahedral configuration represents a marked contrast with 
the centered icosahedral geometry observed in the core unit of 
[Ag₂₀[Cr₂P(OPr)₃]₁₂] (E = S, Se) and [Ag₂₁(S₂P(OPr)₃)₁₂]. It is 
worth mentioning that no guest element exists in the 
dodecahedral structures of [Cu₁₂S₄]₄⁻, [Cu₁₂(NPh)₈]₄⁻, [Bu₄-
SiP]₈Cu₁₂], and [Cu₁₂E₈(PR₃)₈] (E = S, Se, Te). Whereas a couple of 
examples of Au₁₂ and Ag₁₂ dodecahedra encapsulating 
a sodium or silver atom, respectively, are known, compounds 
1–5 are the first examples of a copper cuboctahedra 
encapsulating another atom (except for Lang's compound of ref. 4h).

In the case of 1a, the metallic core is, to the best of our knowledge, 
the first example of a copper-centred Cu₁₃ cuboctahedron, 
identical to that observed in the fcc structure of bulk copper.

The X-ray structure of 5a (Fig. 5 and Table 2) can be derived 
from that of 3 by replacing one of the four μ₁-alkynyl moieties by 
an isosolob μ₁-Cl ligand, which lowers the cluster ideal 
symmetry from T₄d to C₂v. Apart from this substitution, the 
structure of 5a is similar to that of clusters 3. Not considering 
bonding with the encapsulated chloride, three among 
the twelve copper atoms are in the Cu₃S₃Cl coordination, leaving 
ine other metals in a Cu₃S₃ coordination. 5a exhibits a broad 
range of Cu–Cu distances (2.563–3.245 Å). The corresponding 
average value (2.781 Å) is shorter than that observed in 3d (2.844 Å).

The average Cu–(μ₂-Cl) distance in 5a (2.778 Å) is substantially 
larger than that corresponding to the Cu–(μ₂-Cl) distance 
(2.321 Å). Interestingly, the C=C distances of 5a (avg. 1.134 Å) 
are significantly shorter than that of the tetra-alkynyl sulfur species 
reported in Table 2 (avg. 1.19–1.22 Å).

### Optical properties

It is fascinating that a single atom alteration between clusters 1– 
3 can lead to diverse variations in their UV-vis spectra (Fig. 6).
The homo-nuclear Cu₃₃ cluster (1a) looks pinkish to the naked 
eye, whereas the sulfide- (2a) and chloride- (3a) centred 
clusters appear to be orange. The UV-vis spectrum of 1a shows 
broad multiband optical absorption (at 337, 513, 540, 571 nm) 
and an intense absorption band at 287 nm, whereas the inverse 
co-ordination clusters 2a (317, 450 nm) and 3a (312 nm) show 
different patterns in their UV-vis spectrum. Substitution of the 
central metal atom (Cu) in 1 with main-group elements like 
sulfur and halogen increases the intensity of photoemission. At 
77 K clusters 2a and 3a exhibit a structureless emission band, 
centred at 562 and 585 nm, respectively (Fig. S13†). On the 
other hand, the compound 1a is almost non-emissive.

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**Table 2** Selected bond lengths (Å) for 1a, 2a–b, 3d–e, 4e and 5a

|          | X_{cent} | X_{cent}-Cu | Cu–Cu | C≡C | Cu_{cube}–Cu | Cu_{cube}–S |
|----------|----------|-------------|-------|-----|--------------|-------------|
| 1a⁴      | Cu       | 2.605–2.669 | 2.522–2.786 | 1.187–1.213 | 2.001–2.076 | 2.257–2.320 |
| Avg.     | 2.636    | Avg. 2.636  | Avg. 2.636 | Avg. 1.202 | Avg. 2.035   | Avg. 2.289  |
| 2a       | S        | 2.589–2.934 | 2.521–3.091 | 1.179–1.220 | 1.993–2.241 | 2.256–2.328 |
| Avg.     | 2.706    | Avg. 2.709  | Avg. 2.709 | Avg. 1.201 | Avg. 2.094   | Avg. 2.295  |
| 2b       | S        | 2.561–2.892 | 2.549–3.128 | 1.143–1.200 | 2.002–2.203 | 2.264–2.359 |
| Avg.     | 2.713    | Avg. 2.717  | Avg. 2.717 | Avg. 1.178 | Avg. 2.092   | Avg. 2.302  |
| 3d       | Cl       | 2.694–2.957 | 2.495–3.226 | 1.222–1.223 | 1.982–2.095 | 2.206–2.332 |
| Avg.     | 2.831    | Avg. 2.844  | Avg. 2.844 | Avg. 1.223 | Avg. 2.019   | Avg. 2.274  |
| 3e       | Cl       | 2.807–3.035 | 2.527–3.212 | 1.205–1.257 | 1.956–2.075 | 2.243–2.291 |
| Avg.     | 2.926    | Avg. 2.884  | Avg. 2.884 | Avg. 1.225 | Avg. 2.025   | Avg. 2.267  |
| 4e       | Br       | 2.881–3.072 | 2.563–3.306 | 1.196–1.217 | 1.943–2.100 | 2.238–2.311 |
| Avg.     | 2.977    | Avg. 2.975  | Avg. 2.975 | Avg. 1.190 | Avg. 2.029   | Avg. 2.629  |
| 5a       | Cl       | 2.635–2.911 | 2.563–3.245 | 1.059–1.174 | 1.985–2.173 | 2.249–2.316 |
| Avg.     | 2.778    | Avg. 2.781  | Avg. 2.781 | Avg. 1.134 | Avg. 2.084   | Avg. 2.279  |
Fig. 5 Single crystal structure of the cluster cation 5a with 30% thermal probability ellipsoids. All N£Bu₂ and C(O)OCH₃ moieties are omitted for clarity.

Theoretical investigations

In order to shed some light on the bonding and properties of the reported inverse-coordinated clusters, density functional theory (DFT) calculations were performed on various model clusters. The simplest homologs of compounds 1–4, namely 1′–4′, were built with S₂CN₅₂ = S₂CNH₂ and CCR’ = CCH. Relevant computed data are given in Table 3. The optimized geometries of 1′–4′ were all found to be of exact T₄d symmetry (no imaginary vibrational frequency). Their metrical parameters are in good agreement with the averaged experimental values of compounds 1–4 (Table 2). Unsurprisingly, the computed natural atomic orbital (NAO) charges are consistent with the formal oxidation state of the encapsulated element X being Cu⁺, S²⁻, Cl⁻ and Br⁻ in clusters 1′ to 4′, respectively, whereas those of the 12 cuboctahedral metals always indicate the Cu⁺ state. However, the differences between the computed and formal charges of X vary with its nature, indicating that the covalent component of the host–guest interaction decreases as Cu > S > Br ≈ Cl. The Cu–X Wiberg indices (Table 3) are also consistent with this view. Thus 1′ (X = Cu) is substantially more covalent than 3′ (X = Cl). The simplified interaction diagrams of Fig. 7 illustrate this situation. Considering that each approximately planar tricoordinated Cu¹ cuboctahedral vertex has a 4p vacant orbital pointing toward the middle of the cage, one is left with 12 vacant combinations (a1 + e + t₁ + 2 t₂) for the whole empty cage, of which the lowest ones (a1 + t₁) constitute a nice set of accepting orbitals. In the case of X = Cu, the occupied 4s orbital of the encapsulated formally Cu¹⁻ metal and the a₁ accepting orbital of the cage interact strongly, because of their proximity in energy. The resulting bonding a₁ MO is substantially delocalized on the 13 copper atoms and therefore both Cu_{cent}–Cu_{cage} and Cu_{cage}–Cu_{cage} bonding arise. This MO can be identified as the 1S jellium orbital containing the 2 electrons of the superatom 1′. In the case of X = Cl, the occupied halide

![Fig. 6](image)

(a) Experimental UV-vis absorption spectra of the clusters 1–3. (b) TDDFT-simulated UV-vis absorption spectra of the clusters 1″–3″.

Table 3 Selected computed data

| X   | HOMO–LUMO gap (eV) | Cu–X average [range] [Å] | WI(Cu–X) average [range] | Cu–Cu average [range] [Å] | WI(Cu–Cu) range [Å] | q(X)[d] | q(Cu)[d] |
|-----|-------------------|-------------------------|--------------------------|---------------------------|---------------------|-------|--------|
| 1'  | (T₄d) Cu          | 3.08                    | 2.666                    | 0.061                     | 2.595–2.725         | 0.047–0.050     | –0.54  | +0.69  |
| 1'' | (C₁) Cu           | 3.08                    | 2.675 [2.637–2.722]      | [0.047–0.074]            | 2.556–2.795         | 0.038–0.053     | –0.53  | +0.70  |
| 2'  | (T₄d) S           | 3.56                    | 2.674                    | 0.047                     | 2.619–2.728         | 0.033–0.034     | –1.61  | +0.74  |
| 2'' | (C₁) S            | 3.53                    | 2.747 [2.371–3.018]      | 0.049 [0.014–0.104]      | 2.532–3.276         | 0.008–0.048     | –1.59  | +0.75  |
| 3'  | (T₄d) Cl          | 3.84                    | 2.899                    | 0.023                     | 2.707–3.083         | 0.019–0.036     | –0.82  | +0.75  |
| 3'' | (C₁) Cl           | 3.73                    | 2.967 [2.721–3.271]      | 0.023 [0.012–0.049]      | 2.522–3.379         | 0.007–0.057     | –0.81  | +0.76  |
| 4'  | (T₄d) Br          | 3.82                    | 2.942                    | 0.026                     | 2.708–3.168         | 0.015–0.036     | –0.81  | +0.75  |
| 4'' | (C₁) Br           | 3.72                    | 2.931 [2.791–3.071]      | 0.024 [0.017–0.036]      | 2.719–3.133         | 0.012–0.040     | –0.81  | +0.74  |
| 5'  | (T₄d) Cl          | 4.07                    | 2.971                    | 0.026                     | 2.829–3.111         | 0.039–0.054     | –0.80  | +0.70  |

a Cu from the Cu₃ known cuboctahedron. b In the T₄d symmetry, there are two symmetry-independent cuboctahedral Cu–Cu edges. c WI: Wiberg index. d q: Natural atomic charge.
homologs (Fig. 6b), the latter being thus closer to the experimental ones (Fig. 6a). The low-energy band observed for 1a at 540 nm is computed at 538 nm for 1' and corresponds to a HOMO (a1)→LUMO (t2) transition, a mixture of MMCT and MLCT (L = dtc) characters. As illustrated above in Fig. 7, the 1S HOMO present in 1' does not exist in the halide- or chalcogenide-centered species. Consequently, the latter cannot exhibit the same low-energy band. The band observed for 2a at 450 nm corresponds to a HOMO (t2) → LUMO (t2) transition computed at 446 nm for 2'. It is of MLCT (L = dtc) nature. A similar low-energy MLCT transition is computed at 390 nm for 3'. For the three models, the major transitions of higher energy are mainly of MLCT character.

Conclusions
In summary, we have isolated and fully characterized \([\text{Cu}_{12}(\text{alkynyl})]_{4}(\text{dtc})_{6}[\text{PF}_6]\) clusters, the first copper-centred cuboctahedral copper NCs, a miniature of the bulk copper fcc structure, with partial Cu(0) character confirmed by XANES. Furthermore, they have been reacted to synthesize novel chalcogen- and halogen-centered cuboctahedral copper clusters \([\text{Cu}_{12}(\mu_{12}-\text{X})](\text{dtc})_{6}[\text{Cl}]_{2}^{+}\) (E = Cl, Br, S). These clusters are the first examples of compounds in which a sulfide, chloride or bromide ion holds a so large coordination number (12). Prior to this report, the highest coordination number for sulfur and bromine was nine, and eight for chlorine. Bonding interactions between the Cu\(_{12}\) cuboctahedral cage and the encapsulated element (X), rationalized by DFT calculations, indicate that the covalent component of the host–guest bonding interaction decreases as Cu > S > Br = Cl. While the nature of the low-energy band observed for 1a can be reasonably assigned as a mixture of MMCT and MLCT (L = dtc) characters, it is primarily MLCT transition (L = dtc) for 2 and 3. Strikingly, new compounds have been prepared via replacing alkynyl with chloride. This synthetic methodology may open an avenue for the rational synthesis of organometallic compounds other than the spontaneous self-assembly. The new compounds synthesized are well characterized and the physical properties are explained by both theory and experimental methods.

Experimental section
General procedures and instrumentation
All chemicals were purchased from commercial sources and used as received. Solvents were purified following standard protocols. All reactions were performed in oven-dried Schlenk glassware using standard inert atmosphere techniques. All reactions were carried out in a N\(_2\) atmosphere by using standard Schlenk techniques. \([\text{Cu}_{28}\text{H}_{15}(\text{S}_{2}CN\text{Bu}_{3})]_{2}[\text{PF}_6]\) was prepared by a slightly modified procedure reported previously in the literature and characterized.\(^{19}\) NMR spectra were recorded on a Bruker Advance DPX300 FT-NMR spectrometer operating at 300 MHz. The chemical shift (\(\delta\)) and coupling constant (\(J\)) are reported in ppm and Hz, respectively. \(^{31}\)P NMR spectra were referenced to external 85\% H\(_3\)PO\(_4\) at \(\delta\) 0.00. The ESI-mass spectrum was recorded on a Fison Quattro Bio-Q (Fisons...
In a flame-dried Schlenk tube, \([\text{Cu}_{12}(\text{S}_2\text{CN}R_2)_6(\text{Cu})]PF_6\) (0.1 mmol) was suspended in THF (5 cm³) along with the terminal alkyn (1 mmol) and the resulting mixture was stirred at 30 °C for 24 h. The solvent was evaporated under vacuum and the residue was washed with diethyl ether (3 × 5 mL) to remove impurities from the ligand and the dark red residue was extracted in methanol. Finally, the solvent was evaporated to dryness under vacuum to get 1 as a pure powder in 40–70% yields. In this reaction, the corresponding alkene and \([\text{Cu}_n\text{H}(\text{S}_2\text{CR}_2)_3]PF_6\) were produced as by-products.

\[\text{[Cu}_1\text{S}_2\text{CN}R_2\text{Bu}_3][\text{C} \equiv \text{CCOOEt}]\text{PF}_6\] (1b). (0.150 g, 42%, based on Cu): ESI-MS: \(m/z\) 248.36 (M⁺). 1H NMR (300 MHz, CDCl₃): 2.03 (t, 24H, CH₂), 1.38 (br, 24H, CH₂), 1.23 (t, 12H, OCH₂CH₃), 0.94 (t, CH₃) ppm; 13C NMR (300 MHz, CDCl₃): 203.8, 152.6, 78.5, 62.7, 51.9, 28.9, 14.4, 13.5; FT-IR data in KBr pellet: 2962.2, 1503.1, 942.4, 835.3, 719.8, 557.2.

\[\text{[Cu}_{12}\text{S}_2\text{CN}R_2\text{Bu}_3][\text{C} \equiv \text{CCOOEt}]\text{PF}_6\] (1a). (0.150 g, 65%, based on Cu): ESI-MS: \(m/z\) 2239.0 (M⁺). 1H NMR (300 MHz, CDCl₃): 5.92 (br, 6H, NCH), 4.10 (br, 6H, NCH), 3.92 (br, 8H, OCH₂), 1.63 (br, 24H, CH₂), 1.31 (br, 36H, C), 1.29 (t, 12H, OCH₂CH₃) ppm; 13C NMR (300 MHz, CDCl₃): 201.2, 152.5, 78.5, 74.8, 62.8, 25.2, 20.1, 14.2, 13.7; 31P NMR (300 MHz, CDCl₃): –143.5 ppm; FT-IR data in KBr pellet (cm⁻¹): 2961.1, 2937.2, 2872.7, 2009.1, 1594.0, 1498.4, 1233.3, 1143.2, 1080.0, 1027.5, 941.4, 833.3, 719.8, 557.2.

General synthetic method for the isolation of 1

In a flame-dried Schlenk tube, \([\text{Cu}_{13}(\text{S}_2\text{CN}R_2)_6(\text{C} \equiv \text{CCOOEt})]\text{PF}_6\) (0.1 mmol) was suspended in CH₂Cl₂ (5 cm³) along with the terminal alkyn (1 mmol) and the resulting mixture was stirred at 30 °C for 24 h. The solvent was evaporated to dryness under vacuum to get 1 as a pure powder in 40–70% yields. In this reaction, the corresponding alkene and \([\text{Cu}_n\text{H}(\text{S}_2\text{CN}R_2)_3]PF_6\) were produced as by-products.

\[\text{[Cu}_{13}\text{S}_2\text{CN}R_2\text{Bu}_3][\text{C} \equiv \text{CCOOEt}]\text{PF}_6\] (1c). (0.150 g, 65%, based on Cu): ESI-MS: \(m/z\) 2239.0 (M⁺). 1H NMR (300 MHz, CDCl₃): 5.92 (br, 6H, NCH), 4.10 (br, 6H, NCH), 3.92 (br, 8H, OCH₂), 1.63 (br, 24H, CH₂), 1.31 (br, 36H, C), 1.29 (t, 12H, OCH₂CH₃) ppm; 13C NMR (300 MHz, CDCl₃): 201.2, 152.5, 78.5, 74.8, 62.8, 25.2, 20.1, 14.2, 13.7; 31P NMR (300 MHz, CDCl₃): –143.5 ppm; FT-IR data in KBr pellet (cm⁻¹): 2961.1, 2937.2, 2872.7, 2009.1, 1594.0, 1498.4, 1233.3, 1143.2, 1080.0, 1027.5, 941.4, 833.3, 719.8, 557.2.

General synthetic method for the isolation of 3

In a flame-dried Schlenk tube, \([\text{Cu}_{13}(\text{S}_2\text{CN}R_2)_6(\text{C} \equiv \text{CR}')\text{PF}_6\] (0.1 mmol) was suspended in CH₂Cl₂ (5 cm³) along with the terminal alkyn (1 mmol) and the resulting mixture was stirred at room temperature for 3 days. The solvent was evaporated under vacuum and the residue was washed with hexane, diethyl ether and methanol and the yellow residue was extracted in CH₂Cl₂. Finally, the solvent was evaporated to dryness and subjected to column chromatography to get 3 as a pure powder in 11–30% yields. Compound 5a was isolated as a byproduct in 5% yield.

Alternative method for the synthesis of 3e and 4e

In a flame-dried Schlenk tube, \([\text{Cu}(\text{CH₃CN})_4]\text{PF}_6\) (0.27 mmol) and K[S₂CNBu₂] (0.12 mmol) were suspended in 15 mL THF solvent. To this suspension HC≡CPh (0.08 mmol) and few drops of triethylamine were added and the reaction mixture was stirred at 0 °C for 10 minutes. To the reaction mixture, Bu₄NX (0.02 mmol) was added and stirred for 12 hours. The solvent was evaporated and the residue was washed with hexane, ether and methanol. The yellow residue was extracted in dichloromethane and purified by passing through alumina, which yielded 3e and 4e in 45 and 52% yields respectively.

\[\text{[Cu}_{12}\text{Cl}][\text{S}_2\text{CN}R_2\text{Bu}_3][\text{C} \equiv \text{CCOOEt}]\text{PF}_6\] (3a). ESI-MS: \(m/z\) 2354.8 (M⁺). 1H NMR (300 MHz, CDCl₃): 4.04 (t, 24H, NCH₂), 3.71 (s, 12H, OCH₃), 1.79 (br, 24H, CH₂), 1.49 (br, 24H, CH₂CH₃), 0.98 (t, 36H, CH₃) ppm; 13C NMR (300 MHz, CDCl₃): 203.7, 150.2, 98.2, 81.8, 51.7, 53.0, 29.2, 21.1, 13.4; 31P NMR (300 MHz, CDCl₃): –143.5 ppm; FT-IR data in KBr pellet (cm⁻¹): 2960.2, 2937.0, 2873.5, 2017.5, 1690.4, 1498.2, 1292.4, 1220.6, 928.5, 844.6.

\[\text{[Cu}_{12}\text{Cl}][\text{S}_2\text{CN}R_2\text{Bu}_3][\text{C} \equiv \text{CCOOEt}]\text{PF}_6\] (3b). (0.150 g, 42%, based on Cu): ESI-MS: \(m/z\) 2410.7 (M⁺). 1H NMR (300 MHz,
The single crystals were mounted on the tip of the microscope, and data were collected using a Bruker Apex II CCD diffractometer. Absorption corrections were applied to the data. The structure was solved by direct methods and refined by least-squares against $F^2$ using the SHELXL-2018/3 package, incorporated in SHELXTL/PC V6.14. All non-hydrogen atoms were refined anisotropically. Geometric restraints for the sp^3 carbon bond of these atoms were applied. In the crystal of 2a, the C(O)OMe motifs on two of four methyl propiolate groups were disordered over two positions with equal occupancy. Structures 2b, 3e and 4e contain large solvent-accessible voids, with substantial peaks of electron density visible inside these voids which could be due to the loss of solvent while mounting a single crystal at ambient temperature. In 3d, the co-crystallization of [Cl@Cu$_{12}$(S$_2$CN)$_2$Pr$_6$]$_2$(C$_6$H$_5$(CF$_3$)$_2$)$_2$PF$_6$ and [Cu@Cu$_{12}$(S$_2$CN)$_2$Pr$_6$]$_2$(C$_6$H$_5$(CF$_3$)$_2$)$_2$PF$_6$ was found. The central atom in the Cu$_{12}$ cuboctahedral cage was refined with 70% Cl and 30% Cu, Cu1 and Cu1B are refined with occupancy 0.7 ± 0.3. Thus, the composition in crystal 3d is [Cl@Cu$_{12}$(S$_2$CN)$_2$Pr$_6$]$_2$(C$_6$H$_5$(CF$_3$)$_2$)$_2$PF$_6$ and [Cu@Cu$_{12}$(S$_2$CN)$_2$Pr$_6$]$_2$(C$_6$H$_5$(CF$_3$)$_2$)$_2$PF$_6$. In 5a, eight cationic [Cu$_{12}$(S$_2$CN)$_2$Pr$_6$](µ-Cl)$(S$_2$CNBu)$_2$(COCOMe)$_2$ molecules, four PF$_6^-$ anions, and four Cl$^-$ anions were found in one unit cell. The chloride atom was further disordered at multiple positions. Thus, the composition in crystal 5a is [Cu$_{12}$(S$_2$CN)$_2$Pr$_6$](µ-Cl)$(S$_2$CNBu)$_2$(COCOMe)$_2$PF$_6$. Additional crystallographic data for this paper.

Crystalline structures of 2a: C$_2$h$_{112}$Cu$_{12}$N$_2$O$_{13}$S$_{13}$, orthorhombic, P2$_1$2$_1$2$_1$, $a = 18.2449(13)$ Å, $b = 23.2801(15)$ Å, $c = 33.8417(17)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. V = 9005.7(12) Å$^3$, $Z = 4$, $\rho$ calc = 1.578 cm$^{-3}$, $\mu$ = 2.840 mm$^{-1}$, 56 212 measured reflections, 17 421 independent reflections ($R_{int} = 0.0477$), $R_1 = 0.4971$ [I > 2σ(I)], $wR_2 = 0.2124$ (all data), flack parameter: 0.006(4), goodness-of-fit on $F^2$: 1.043. Crystallographic data of 2b: C$_{74}$H$_{128}$Cu$_{12}$N$_6$O$_{8}$S$_{13}$, orthorhombic, P2$_1$2$_1$2$_1$, $a = 19.1032(9)$ Å, $b = 23.2801(11)$ Å, $c = 24.7421(12)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. V = 11 577.9(7) Å$^3$, $Z = 4$, $\rho$ calc = 1.434 cm$^{-3}$, $\mu$ = 2.523 mm$^{-1}$, 125 549 measured reflections, 19759 independent reflections ($R_{int} = 0.0374$), $R_1 = 0.4940$ [I > 2σ(I)], $wR_2 = 0.1122$ (all data), flack parameter: $-0.004(4)$, goodness-of-fit on $F^2$: 1.054. Crystallographic data of 3d: C$_{93}$H$_{152}$Cl$_{4}$Cu$_{12}$Pr$_6$N$_{13}$O$_{12}$S$_{12}$, orthorhombic, Pmna, $a = 21.8103(5)$ Å, $b = 22.9770(6)$ Å, $c = 22.0359(6)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. V = 11 044.8(5) Å$^3$, $Z = 4$, $\rho$ calc = 1.814 cm$^{-3}$, $\mu$ = 2.670 mm$^{-1}$, 90 620 measured reflections, 9730 independent reflections ($R_{int} = 0.0303$), $R_1 = 0.0450$ [I > 2σ(I)], $wR_2 = 0.1122$ (all data), goodness-of-fit-on $F^2$: 1.099. Crystallographic data of 3e: C$_{17}$H$_{26}$Cl$_{4}$Cu$_{12}$F$_{13}$N$_{13}$O$_{12}$P$_{12}$S$_{24}$, triglicine, Pnma, $a = 17.6501(6)$ Å, $b = 19.8146(6)$ Å, $c = 32.2844(11)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. V = 11 144.6(6) Å$^3$, $Z = 2$, $\rho$ calc = 1.555 cm$^{-3}$, $\mu$ = 2.561 mm$^{-1}$, 83 631 measured reflections, 39 024 independent reflections ($R_{int} = 0.0260$), $R_1 = 0.0664$ [I > 2σ(I)], $wR_2 = 0.1885$ (all data), goodness-of-fit-on $F^2$: 1.107. Crystallographic data of 4c: C$_{68}$H$_{125}$BrCu$_{12}$F$_{13}$N$_{13}$O$_{12}$P$_{12}$S$_{24}$, triglicine, Pnma, $a = 17.7551(15)$ Å, $b = 19.6625(17)$ Å, $c = 32.7673(3)$ Å, $\alpha = 85.8425(17)$, $\beta = 85.6900(17)$, $\gamma = 76.1059(16)$. V = 11 055.9(16) Å$^3$, $Z = 4$, $\rho$ calc = 1.573 cm$^{-3}$, $\mu$ = 2.911 mm$^{-1}$, 63 677 measured reflections, 38 372 independent reflections ($R_{int} = 0.0533$), $R_1 =$...
0.0806 [I > 2σ(I)], wR2 = 0.2652 (all data), goodness-of-fit on F2: 1.047. Crystallographic data of 5a: C102H124Cl2Cu34F6N12O13, PS24, monoclinic, C2/c, a = 31.396(3) Å, b = 19.8294(17) Å, c = 33.181(3) Å, α = 90°, β = 97.826(17)°, γ = 90°. V = 20 465(3) Å3, Z = 4, ρ calc = 1.557 cm−1, μ = 2.804 mm−1, 56 963 measured reflections, 17 941 independent reflections (Rint = 0.0445), R1 = 0.0997 [I > 2σ(I)], wR2 = 0.2334 (all data), goodness-of-fit on F2: 1.015.

Computational details

Geometry optimizations were performed using DFT calculations with the Gaussian 09 package,24 using the PBE0 functional25 and the all-electron Def2-TZVP set from EMSL Basis Set Exchange Library.26 All the optimized geometries were characterized as true minima on their potential energy surface by harmonic vibrational analysis. The Wiberg bond indices were computed with the NBO 5.0 program.27 The UV-visible transitions were calculated by means of TD-DFT calculations,28 at the PBE0/Def2-TZVP level. Only singlet-singlet, i.e. spin-allowed, transitions were computed. The UV-visible spectra were simulated from the computed TD-DFT transitions and their oscillator strengths by using the SWizard program,29 each transition being associated with a Gaussian function of half-height full width equal to 1500 cm⁻¹. The compositions of the molecular orbitals were calculated using the AOMix program.30

Conflicts of interest

There are no conflicts to declare.

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