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A novel nonacoordinate bridging selenido ligand in a tricapped trigonal-prismatic geometry. X-Ray structure of $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OPr^i)_2]_6$

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The first nonacoordinate bridging selenido ligand in a tricapped trigonal prismatic geometry, $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OPr^i)_2]_6$, is prepared along with closed-shell ion-centered $Cu^I{}_8$ cubes, $Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6$ and $Cu_8(\mu_8\text{-}Br)[Se_2P(OPr^i)_2]_6(PF_6)$, from the reaction of $NH_4Se_2P(OPr^i)_2$, $Cu(CH_3CN)_4PF_6$, and Bu_4NBr in CH_2Br_2 at 0 °C.

One of the most commonly observed coordination geometries for a central atom which is surrounded by nine outer or ligand atoms is a tricapped trigonal prism.[1] Notable examples are lanthanide complexes,[2] $[ReH_9]^{2-}$ and its derivatives.[3] To the best of our knowledge this geometry has never been observed in any main group elements, though a main-group element in the cavity of a monocapped square antiprism is known in a couple of metal carbonyls.[4]

Molecular cubic clusters encapsulating main-group elements are particularly interesting from the general point of view of bonding.[5] To date two types of main-group element-centered transitional metal cubic clusters which include face-capped and edge-capped cubes have been characterized. While $Ni_8(\mu_8\text{-}As)(\mu_4\text{-}As)_6(PPh_3)_8$ is the only face-capped cube,[6] several edge-capped $Cu^I{}_8$ cubes centered by S^{2-},[7] Cl^- and Br^- [8] are known for dithiophosphate ligands. An unusual sulfide-centered, edge-capped mixed-metal cube, $[Mn_4Cu_4S(SPr^i)_{12}]^{2-}$, which is defined by two interpenetrating copper and manganese tetrahedra, is also accessible by reaction of $[Mn_2(SPr^i)_6]^{2-}$ with CuCl.[9] With the dialkyl diselenophosphate ligands (dsep), we uncovered the first selenide-centered edge-capped $Cu^I{}_8$ cubes.[10] Subsequently an exceptional co-crystallization with clusters, $Ag_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_6$ and $Ag_6[Se_2P(OR)_2]_6$, superimposing on a trigonal lattice, was observed.[11] To extend our research efforts in centered cubic cluster synthesis, we focus on the halide ion and uncovered, besides selenide-centered $Cu^I{}_8$ cubes, **1**, a halide-centered $Cu^I{}_8$ cube, **3**, and a remarkable, undecanuclear copper cluster containing a selenide ion in the center of a pentacapped trigonal prism, $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}X)_3\text{-}[Se_2P(OPr^i)_2]_6$, **2**. Cluster **2** is a novel example possessing not only a 3,3,4,4,4-pentacapped trigonal prismatic copper framework but also a nonacoordinate bridging selenido ligand in a tricapped trigonal prismatic geometry.

At least three clusters are produced from the reaction of $NH_4Se_2P(OPr^i)_2$ (1.2 g, 3.69 mmol), $Cu(CH_3CN)_4PF_6$ (0.917 g, 2.46 mmol) and Bu_4NBr (0.793 g, 2.46 mmol) in CH_2Br_2 (50 mL) at 0 °C for 24 hours. Both yellow clusters **1** and **2** dissolved in n-hexane are separated by column chromatography (eluent: ethyl acetate/hexane = 3/4) whereas the cationic species **3** is insoluble.† The formulation of **2** was confirmed by elemental analyses, positive FAB mass spectroscopy, ^1H and ^{31}P NMR spectroscopy. In the positive FAB mass spectrum of **2**, three major peaks which correspond to the intact molecule, an intact molecule with the loss of a bromide ion, $\{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_2[Se_2P(OPr^i)_2]_6\}^+$, and an intact molecule with the loss of a dsep ligand, $\{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OPr^i)_2]_5\}^+$, respectively, were identified. These observed peaks are in agreement with the results of their respective, simulated isotopic patterns.

X-Ray analysis‡ of **2** reveals a $Cu_{11}Se$ core, stabilized by three bromide and six dsep ligands. The central core adopts a slightly distorted, fivefold capped trigonal prismatic copper framework, with an encapsulated selenium ion. Shown in Fig. 1 is the $SeCu_{11}$ core which displays an idealized D_{3h} symmetry. Both Cu(1) and Cu(2), each capping the triangular face of the prism, are located on the pseudo-three-fold axis, as is the encapsulated selenium ion Se(01). The Cu–Se(01) bond distances are noteworthy. Whereas two on the C_3 axis, 3.480 and 3.574 Å, are extremely long, the rest are in the range 2.519(2)–2.748(2) Å and are within the limits reported by Fenske and coworkers.[12] Consequently a novel nonacoordinate bridging selenido ligand in a tricapped trigonal primastic geometry is revealed in the title compound. The edges of the trigonal prism are in the range 3.431–3.588 Å while the heights (Cu7–Cu8, Cu6–Cu9, and Cu10–Cu11) are on average 3.103(2) Å. There exist a total of nine Cu_4 butterflies where the wing-tip positions are represented by five capping copper atoms with each edge and height of the trigonal prism being the hinges. Those Cu_4 butterflies comprising a copper atom on the C_3 axis are each connected by a dsep ligand having a tetrametallic

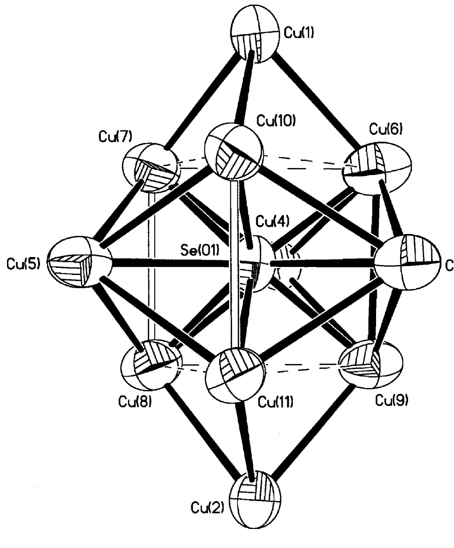

Fig. 1 The $Cu_{11}Se$ core in **2**. Selected bond lengths [Å]: Se(01)–Cu(3) 2.748(2), Se(01)–Cu(4) 2.739(2), Se(01)–Cu(5) 2.736(2), Se(01)–Cu(6) 2.568(2), Se(01)–Cu(7) 2.576(2), Se(01)–Cu(8) 2.580(2), Se(01)–Cu(9) 2.519(2), Se(01)–Cu(10) 2.551(2), Se(01)–Cu(11) 2.552(2), Cu(1)–Cu(10) 2.804(2), Cu(1)–Cu(7) 2.851(2), Cu(1)–Cu(6) 2.869(2), Cu(2)–Cu(9) 2.787(2), Cu(2)–Cu(8) 2.842(2), Cu(2)–Cu(11) 2.861(2), Cu(3)–Cu(9) 2.883(2), Cu(3)–Cu(6) 2.886(2), Cu(3)–Cu(11) 2.919(2), Cu(3)–Cu(10) 2.925(2), Cu(4)–Cu(6) 2.860(2), Cu(4)–Cu(9) 2.877(2), Cu(4)–Cu(7) 2.936(2), Cu(4)–Cu(8) 2.970(2), Cu(5)–Cu(10) 2.897(2), Cu(5)–Cu(7) 2.916(2), Cu(5)–Cu(8) 2.932(2), Cu(5)–Cu(11) 2.947(2), Cu(6)–Cu(9) 3.052(2), Cu(7)–Cu(8) 3.134(2), Cu(10)–Cu(11) 3.124(2).

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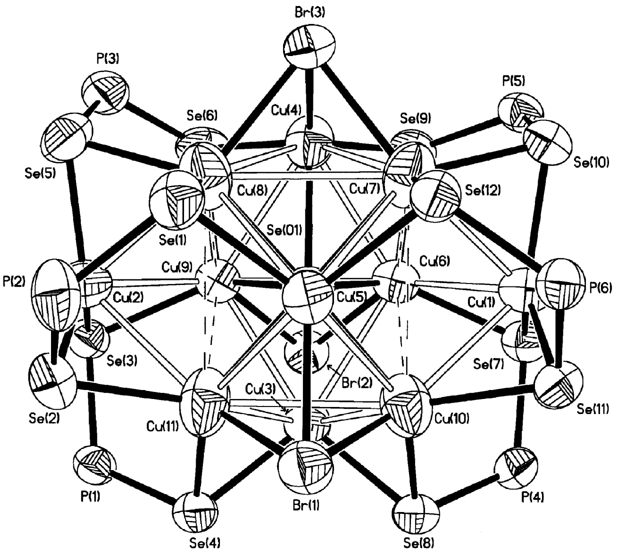

Fig. 2 The thermal ellipsoid drawing (50% probability) of **2**. The isopropoxy groups have been omitted for clarity. Selected bond lengths [Å]: Br(1)–Cu(5) 2.452(2), Br(1)–Cu(10) 2.565(2), Br(1)–Cu(11) 2.627(2), Br(2)–Cu(3) 2.451(2), Br(2)–Cu(6) 2.564(2), Br(2)–Cu(9) 2.622(2), Br(3)–Cu(4) 2.453(2), Br(3)–Cu(7) 2.539(2), Br(3)–Cu(8) 2.595(2), Cu–Se 2.350(2)–2.502(2).

tetraconnective (μ_2,μ_2)[13] coordination pattern (Fig. 2) The remaining three, where hinge positions are the heights of the prism, are each occupied by a triply bridging bromide atom over an alternating set of three of the six triangular faces. The Cu–Br bond distances are on average 2.541(2) Å. Two distinct coordination environments around copper atoms of the cluster are observed: two on the C_3 axis are coordinated by three selenium atoms of three different dsep ligands and the rest are surrounded by three selenium atoms and one bromine atom. Overall, owing to the existence of three, alternating triply bridging bromides, the D_{3h} symmetry depicted in Fig. 1 has been lowered to C_{3h}.

Compound **3** forms colorless crystals in the monoclinic space group $C2/c$ and reveals a bromide-centered Cu^I_8 cube of which each edge of the cube is bridged by a selenium atom of the dsep ligand (Fig. 3). The averaged Cu–Cu bond length of 3.179(4) Å is about 0.25 Å longer than the corresponding Cu–Cu distance in the selenide-centered Cu^I_8 cube.[10] The averaged Cu–Br distance of 2.754(1) Å is comparable with those previously reported in $[Cu_8(\mu_8\text{-}Br)(S_2P(OPr^i)_2)_6][PF_6]$[8] and significantly longer than those in **2**.

In summary, the first selenium atom surrounded by nine copper atoms in a tricapped trigonal prismatic geometry is identified along with a halide-centered Cu^I_8 cube containing dsep ligands during the preparation of closed-shell ion-centered cubic clusters. The silver analogues of **2** and **3** have been characterized structurally and details will be reported soon. This research was supported by the National Science Council of Taiwan (NSC 89-2113-M-033-004).

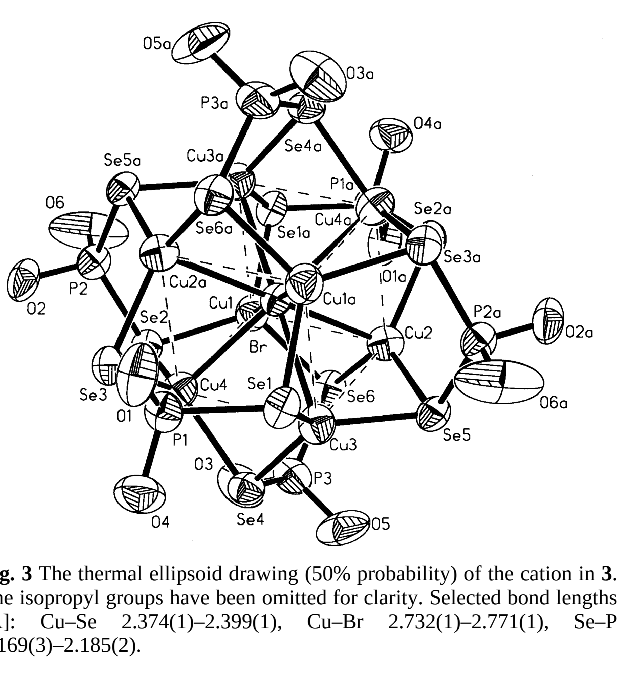

Fig. 3 The thermal ellipsoid drawing (50% probability) of the cation in **3**. The isopropyl groups have been omitted for clarity. Selected bond lengths [Å]: Cu–Se 2.374(1)–2.399(1), Cu–Br 2.732(1)–2.771(1), Se–P 2.169(3)–2.185(2).

Notes and references

† *Characterization* of **2**: ^{1}H NMR ($CDCl_3$) δ 1.34 (d, J = 6 Hz, 36H, CH_3), 1.37 (d, J = 6 Hz, 36H, CH_3), 4.75 (m, 6H, CH), 5.17 (m, 6H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 74.8 (J_{SeP} 647, 668 Hz); positive ion FAB-MS: *m/z*: 2859.4 (M)$^+$, 2779.3 (M − Br)$^+$, 2552.1 (M − dsep)$^+$. Anal. calcd. for $C_{36}H_{84}O_{12}P_6Se_{13}Br_3Cu_{11}\cdot 1/2C_6H_{14}$: C, 16.13; H, 3.13; found: C, 16.15; H, 3.25%; **3**: ^{1}H NMR ($CDCl_3$) δ 1.41 (d, J = 6 Hz, 72H, CH_3), 4.81 (m, 12H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 68.2 (J_{SeP} 648 Hz); positive ion FAB-MS: *m/z*: 2430.5 (M)$^+$. Anal. calcd. for $C_{36}H_{84}F_6O_{12}P_7Se_{12}BrCu_8$: C, 16.79; H, 3.29; found: C, 16.75 ; H, 3.20%.

‡ *Crystal data* for **2**: $C_{36}H_{84}O_{12}P_6Se_{13}Br_3Cu_{11}$, M = 2860.00, triclinic, $P\bar{1}$, a = 15.2820(8), b = 15.5376(8), c = 20.4796 (11) Å, α = 93.011(1), β = 106.941(1), γ = 108.216(1)°, V = 4363.1(4) Å^3, T = 298(2) K, Z = 2, μ(Mo-Kα) = 9.568 mm^{-1}, 20983 reflections measured, 14482 unique [R(int) = 0.0398] which were used in the calculations. The final $R1$ = 0.0639, $wR2$ = 0.1397 and for all data $R1$ = 0.0851, $wR2$ = 0.1535.

3: $C_{36}H_{84}F_6O_{12}P_7Se_{12}BrCu_8$, M = 2575.57, monoclinic, $C2/c$, a = 24.345(5), b = 13.151(3), c = 24.991(5) Å, β = 91.34(3)°, V = 7999(3) Å^3, T = 293(2) K, Z = 4, μ(Mo-Kα) = 8.241 mm^{-1}, 11231 reflections measured, 6703 unique [R(int) = 0.0356] which were used in the calculations. The final $R1$ = 0.0502, $wR2$ = 0.1096 and for all data $R1$ = 0.0647, $wR2$ = 0.1189.

CCDC 182/1763. See http://www.rsc.org/suppdata/cc/b0/b005366j/ for crystallographic files in .cif format.

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