First selenide-centered Cu^I_8 cubic clusters containing dialkyl diselenophosphate ligands. X-Ray structure of $\{Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6\}$

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$[Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6\}$, the first discrete Cu^I_8 cubane in which each face of the cube is bridged by a diselenophosphate ligand and has an interstitial selenide ion (Se^{2-}), is reported.

The interests in combining transition metals and main group elements in clusters stem from two possibilities that these compounds could be useful precursors for the synthesis of new materials and provide a search for new coordinations and geometries.[1] We are interested in the synthesis of molecular cubic clusters having an interstitial main-group atom because they are not only extremely rare[2] but also particularly interesting in view of their unusual bonding characteristics.[3] Although there are several examples of metal carbonyls having μ_8-E (E = C,[4] Si,[5] P,[6] S[7] and As[8]) bridges, the metallic frameworks surrounding the interstitial atom are largely tetragonal (square) antiprisms.

In 1990, Fenske and Krautscheid reported a beautiful mega cluster, $Cu_{20}(\mu_8\text{-}Se)Se_{12}(PEt_3)_{12}$ **1**,[9] which consists of an undistorted, selenide centered Cu_8 cube, each of whose edges is bridged by a peripheral copper atom. The resulting 20 copper atom polyhedron is surrounded by twelve selenium ligands which are arranged in such a fashion as to form a near regular icosahedron. The peripheral copper atom is further coordinated by a PEt_3 ligand. The average formal oxidation state of each copper atom of the cluster is 1.3. In 1995, a sulfide centered Cu^I_8 cube, $\{Cu_8(\mu_8\text{-}S)[S_2P(OPr^i)_2]_6\}$ **2**, whose core geometry is analogous to the central portion of Fenske's compound was reported by Fackler.[1] Unlike compound **1** in which each edge of the cube is bridged by a copper atom, **2** is bridged by a sulfur atom of the dithiophosphate ligand. This brings to our attention as to whether a discrete Cu_8 cube with a selenium atom in its center can be isolated.

In order to synthesize a molecule having a selenide centered Cu^I_8 cube, we focused our attention on the ligand dialkyl diselenophosphate, $Se_2P(OR)_2^-$ (dsep). In sharp contrast to many studies on compositions and structures of phosphor-1,1-dithiolato metal complexes,[10] the chemistry of phosphor-1,1-diselenolato metal compounds has received scant attention. Consequently, there are very few papers referring to this ligand.[11] Among these, are the preparation of various dialkyl diselenophosphates and investigations of the spectroscopic properties of several main group and transition metal complexes. Powder X-ray patterns of some of the compounds are also included. Herein, we report the first discrete Cu^I_8 cubane encapsulating a selenide ion (Se^{2-}), $\{Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6\}$ **3**. To our surprise this is also the first phosphor-1,1-diselenolato complex of any element studied by single crystal X-ray diffraction.

Treatment of $NH_4Se_2P(OPr^i)_2$ and $Cu(MeCN)_4PF_6$ in a 2 : 1 ratio in diethyl ether at 0 °C for 4 h results in a pale yellow solution. After chromatographic work-up (silica gel, eluent CH_2Cl_2–hexane = 3 : 2), a yellow material identified as **3** can be isolated in 40% yield. Compound **3** was fully characterized by positive FAB mass spectrometry, NMR† (^1H, ^{31}P) and X-ray diffraction.‡ In the positive FAB mass spectrum, a peak at *m/z* 2429 corresponds to the intact selenide-centered diselenolate Cu^I cluster. Also appearing in the mass spectrum is a peak at *m/z* 2122 which can be attributed to loss of a dsep ligand giving $\{Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_5\}^+$. The ^{31}P NMR spectrum displays a singlet with satellites (J_{PSe} 671 Hz) at δ 73. This clearly implies all dsep ligands of **3** are equivalent in solution.

One and a half molecules of **3** exist in the asymmetric unit with the Se(02) atom located at a crystallographic inversion center. Fig. 1 shows a thermal ellipsoid drawing of one of the two independent molecules of **3**. The copper atoms are arranged at the corners of an almost regular cube. Each selenium atom of the dsep ligand bridges two copper atoms. Thus dsep exhibits a 'tetrametallic tetraconnective'[10f] (μ_2, μ_2) coordination pattern and each occupies a square face of the cube. The average 'bite distance' is 3.784(2) Å, which is *ca.* 0.2 Å longer than that observed for the sulfur analogue.[2a] Each copper atom of the cube is coordinated to three selenium atoms of three different ligands. The averaged Cu–Se(dsep) bond length is 2.447 Å and the Se–Cu–Se bond angles range from 113.15(11) to 118.09(11)°. In addition to the distorted trigonal planar geometry around the copper atom, there is a strong interaction to the central selenium atom. The average Cu–Cu distance of **3** is 2.928 Å, which is *ca.* 0.08 Å shorter than that observed for Fenske's compound. Consequently, the bond length between

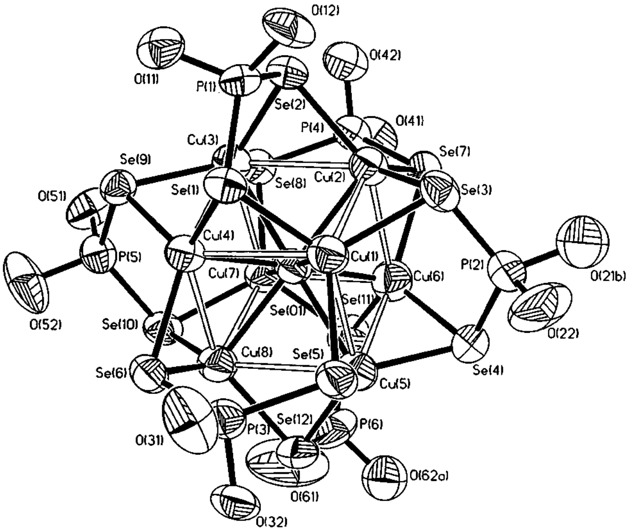

Fig. 1 The thermal ellipsoid drawing (50% probability) of one of the two independent molecules of **3**. The isopropyl groups are omitted for clarity. Selected bond lengths (Å): Se(01)–Cu(1) 2.550(3), Se(01)–Cu(2) 2.524(3), Se(01)–Cu(3) 2.577(3), Se(01)–Cu(4) 2.520(3), Se(01)–Cu(5) 2.546(4), Se(01)–Cu(6) 2.506(3), Se(01)–Cu(7) 2.532(3), Se(01)–Cu(8) 2.532(3), Cu(1)–Cu(2) 2.919(3), Cu(1)–Cu(4) 2.929(3), Cu(1)–Cu(5) 2.921(3), Cu(2)–Cu(6) 2.917(3), Cu(2)–Cu(3) 2.941(3), Cu(3)–Cu(4) 2.974(3), Cu(3)–Cu(7) 2.955(3), Cu(4)–Cu(8) 2.859(3), Cu(5)–Cu(6) 2.920(4), Cu(5)–Cu(8) 2.966(4), Cu(6)–Cu(7) 2.875(4), Cu(7)–Cu(8) 2.966(4).

the central selenide and the peripheral copper atoms ranges from 2.506(3) to 2.577(3) Å and is slightly shorter than that of $[Cu_{20}Se_{13}(PEt_3)_{12}]$, [2.605(3) Å]. Astonishingly the averaged $Cu–Se_{cen}$ bond length, (2.535 Å), in **3** is even shorter than that of the corresponding sulfide analogues (2.694[2a] and 2.585 Å[2b]). Overall owing to the lack of fourfold symmetry, molecule **3** has an idealized T_h point group symmetry. The central selenide atom in conjunction with the twelve selenium atoms of the ligands forms a body-centered icosahedron. Previously this type of geometry has only been observed upon two occasions, for **1** and $Cu_{26}Se_{13}(PEt_2Ph)_{14}$.[12]

Besides Fenske's cluster **1**, compound **3** is the only coordination complex possessing a μ_8-Se bridge. Nevertheless, μ_8-Se bridges do exist in several solid state materials of the type A_2Se (A = Li, Na, and K) with antifluorite structure.[13] It is worth noting that a metal atom in the center of a metallic cube is known for Ni[14] and Pd[15] and a remarkable solid state material, $K_4Cu_8Te_{11}$, in which a potassium ion is encapsulated in the center of a cubic Cu_8 core has also been reported.[16]

The P–Se distances of **3**, [2.144(7)–2.177(6) Å], are slightly shorter than those observed for bridging PSe_2 fragments in the solid state compounds $A_2AuP_2Se_6$ (A = K, Rb) [2.197(6)–2.258(6) Å],[17] $[Cs_2Cu_2P_2Se_6]$ [2.186(4)–2.202(5) Å],[18] and the molecular complexes $[Hg_4(Se_2)_2(PSe_4)_4]^{8-}$ [2.221(5)–2.237(5) Å][19] and $[Fe_2(CO)_4(PSe_5)_2]^{2-}$ [2.214(6)–2.216(6) Å.[20] Observation of a μ_2, μ_2 bridging mode in **3** is unusual and unprecedented for selenophosphate complexes. Three new clusters containing dsep ligands, $Ag_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6$, $Ag_9(\mu_7\text{-}Se)[Se_2P(OPr^i)_2]_8$ and $Ag_{10}(\mu_7\text{-}Se)[Se_2P(OPr^i)_2]_8$ have also been characterized and details will be reported in due course.

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Notes and References

† $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 73 (J_{SeP} 671 Hz); ^1H NMR ($CDCl_3$), δ 1.37 [d, 72H, $CH(CH_3)_2$], 4.88 [m, 12H, $CH(CH_3)_2$]; $^{77}Se\{^1H\}$ NMR ($CDCl_3$), δ −59 (J_{SeP} 671 Hz). Unfortunately we were unable to detect the resonance frequency of the central selenide ion in the ^{77}Se NMR which might be caused by the long T_1 value. FAB MS, m/z 2429 (M^+), 2122 (M − dsep); Anal. Calc. for $C_{36}H_{84}Cu_8O_{12}P_6Se_{13}$: C, 17.80; H, 3.46. Found: C, 17.66; H, 3.34%.

‡ *Crystal data*: $C_{36}H_{84}Cu_8O_{12}P_6Se_{13}$, M = 2429.65; monoclinic, space group $P2_1/n$, a = 13.8341(8), b = 36.969(2), c = 21.9728(12) Å, β = 93.2630(10)°, V = 11219.3(11) Å^3, Z = 6, D_c = 2.158 Mg m^{-3}, $F(000)$ = 6960, T = 298(2) K.

An orange crystal with dimensions 0.20 × 0.20 × 0.40 mm was used for X-ray structural analysis. Intensity data were collected over one quadrant using the ω scan mode on a Siemens SMART CCD diffractometer equipped with graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å). A total of 11 805 unique reflections were measured. The structure was solved by direct methods using SHELXTL-PLUS software package.[21] All Cu and Se atom positions were revealed on the first refinement. Other non-hydrogen atoms were located from subsequent difference Fourier syntheses. Parts of oxygen and carbon atoms of the isopropyl groups (7 out of 18) were found disordered. These disordered atoms were treated in an equal population model. Bond distances were constrained for disordered atoms and atoms connected to the disordered atoms during the structure refinement. These constraints were: P–O = 1.600 Å, O–C = 1.500 Å and C–C = 1.550 Å. The structure was refined by full-matrix least-squares method on F^2. All but disordered atoms and atoms attached to them were refined anisotropically. H-atoms were not included. Refinement converged to $R1$ = 0.0748 [$I > 2\sigma(I)$], $wR2$ = 0.1664 (all data) and S = 1.143 based on 940 variables, 43 restraints, and 11 805 reflections. CCDC 182/947.

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