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Ligand Substitution in Cubic Clusters: Surprising Isolation of the Cocrystallization Products of $Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6$ and $Cu_6[S_2P(OEt)_2]_6$

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The cluster $\{Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6\}_{0.54}\{Cu_6[S_2P(OEt)_2]_6\}_{0.46}$ (**2**) was prepared in 78% yield from the reaction of $Cu_8(Se)[Se_2P(OPr)_2]_6$ (**1**) and $NH_4S_2P(OEt)_2$ in toluene. The central selenide ion in **2** was characterized by ^{77}Se NMR at δ –976 ppm. The simulated solid-state ^{31}P NMR spectrum shows two components with an intensity ratio close to 55:45. The peak centered at 100.7 ppm is assigned to the ^{31}P nuclei in the hexanuclear copper cluster, and that at 101.1 ppm is due to the octanuclear copper cluster. The single-crystal X-ray diffraction analysis confirms the cocrystallization structures of $Cu_8(Se)[S_2P(OEt)_2]_6$ (54%) and $Cu_6[S_2P(OEt)_2]_6$ (46%) (**2**: trigonal, space group $R\bar{3}$, $a = 21.0139(13)$ Å, $c = 11.404(3)$ Å, $\gamma = 120°$, $Z = 3$). While the octanuclear copper cluster possesses a 3-fold crystallographic axis which pass through the Cu(2), Se, and Cu(2A) atoms, the six copper atoms having the S_6 point group symmetry in $Cu_6[S_2P(OEt)_2]_6$ form a compressed octahedron. The $Cu_8(\mu_8\text{-}Se)$ cubic core in $Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6$ is larger in size than the metal core in $Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6$ (**1**) although the bite distance of the Se-containing bridging ligand is larger than that of the S ligand. To understand the nature of the structure contraction of the metal core and metal–μ_8-Se interaction, molecular orbital calculations have been carried out at the B3LYP level of density functional theory. MO calculations suggest that Cu–μ_8-Se interactions are not very strong and a half bond can be formally assigned to each Cu–μ_8-Se bond. Moderate Cu···Cu repulsion exists, and it is the bridging ligands that are responsible for the observed Cu···Cu contacts. Hence, the S-ligating copper clusters have greater Cu···Cu separations because each Cu carries more positive charge in the presence of the more electronegative S-containing ligands.

Introduction

Cubic transition metal clusters of the type $M_8(\mu_4\text{-}E)_6L_8$ (M = transition metal, E = main-group element or ligand, L = two-electron terminal ligand) have been extensively studied by several research groups.[1−4] These types of molecules consist of a cubic metal core circumscribed by a concentric octahedron of μ_4-E atoms. Each metal atom occupied the site of local C_{3v} symmetry with coordination completed by a terminal ligand, L. Encapsulation of a metal atom[1b,2f−h,5,6] or a main-group atom[7] at the center of the metallic cube has also been found in several hexacapped cubic clusters. The bonding analysis of these clusters which

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correlates various numbers of metallic valence electrons (MVEs) as well as the M−M and M−E bonding has been thoroughly discussed by Saillard, Halet, and co-workers.[8] Significant metal−metal bonding exists in all these clusters.

There is another type of cubic metallic molecule whose stability of the cubic architecture is mainly due to the bridging ligands.[9] There are two categories: The first one is the cubic clusters containing edge-bridged ligands. Examples are $M_8L_6^{4-}$ (M = Cu^I, Ag^I, L = dichalcogenolato ligand), of which 12 edges of the cube are bridged by sulfur (or selenium) atoms in an array of an icosahedron.[10] Encapsulation of a closed-shell ion such as S^{2-}, Se^{2-}, Cl^-, and Br^- in the center of the cube is also known for edge-bridged cubic clusters.[11] The other category is the cubic clusters having 12 edged-bridged chalcogenolato ligands and 6 face-bridged chalcogen atoms. Examples are $Ln_8(\mu_4\text{-}E)_6(\mu\text{-}EPh)_{12}(L)_8$ (Ln = lanthanide ion; E = S, Se; L = Lewis base)[12] where the coordination sphere of the lanthanide metal is completed by a solvent molecule.

Most research on cubic metal clusters has concentrated on their synthesis and structural characterization. Little attention has yet been devoted to their reactivities. Among these are the exchange of labile terminal ligands in the hexacapped cubic clusters,[13] the protonation reaction with protonic acid, and the oxidation with sulfur on the dithiolato ligands of edge-capped cubic clusters.[14] It seems that the substitution (or exchange) of capping atoms (either edge- or face-capped) on the cubic clusters has never been reported until very recently Brennan and co-workers demonstrated that chalcogenido, chalcogenolate, and neutral donors in the octametallic $Ln_8(\mu_4\text{-}E)_6(\mu\text{-}EPh)_{12}(L)_8$ clusters are chemically exchangeable to give cluster derivatives with the same octametallic core.[15]

We are interested in performing ligand substitution reactions on the cubic clusters. Herein, we report the first substitution reaction on the bridging ligands in $Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6$ with the diethyl dithiophosphato ligands (dtp). Surprisingly the single-crystal X-ray diffraction study on the product reveals the cocrystallization structures of $Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6$ and $Cu_6[S_2P(OEt)_2]_6$, which share a common $Cu_6[S_2P(OEt)_2]_6$ unit and superimpose along the C_3 axis of the trigonal crystal system. To our knowledge such a cocrystallization product is the second example next to $\{Ag_8(\mu_8\text{-}Se)[Se_2P(O^iPr)_2]_6\}_{0.5}\{Ag_6[Se_2P(O^iPr)_2]_6\}_{0.5}$.[11d] In addition, the nature of the metal−μ_8-Se interaction has been studied by density functional theory.

Experimental Section

Materials and Measurements. All chemicals were obtained from commercial sources and used as received. The ligand $NH_4S_2P(OEt)_2$ was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). Toluene was distilled from Na/K. All the reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. The starting compound, $Cu_8(\mu_8\text{-}Se)[S_2P(OPr)_2]_6$ (**1**), was prepared from a known procedure.[11f] Silica gel 60 (0.063−0.20 mm) was used for column chromatography. The elemental analyses were performed by the Taipei Instrumental Center. NMR spectra were recorded on Bruker AC-F200 and Advance-300 Fourier transform spectrometers. The $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR are referenced externally against 85% H_3PO_4 (δ = 0 ppm) and PhSeSePh (δ = 463 ppm), respectively. Solid-state ^{31}P MAS NMR measurements were performed on a Bruker AVANCE-400 spectrometer at a resonance frequency of 162.0 MHz for ^{31}P nucleus with a 4 mm rotor at a spinning speed of 10 kHz. The sample amount, all in crystalline form, inside the rotor was about 105 mg. A $\pi/4$ pulse length of 2.5 μs and a repetition time of 50 s ($T_1 \sim 20$ s) were used to obtain a quantitative spectrum. A total of 132 scans were accumulated. The spectrum was obtained using a line broadening of 30 Hz.

Preparation of $\{Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6\}_{0.54}\{Cu_6[S_2P(OEt)_2]_6\}_{0.46}$ (2). The compound $Cu_8(Se)[Se_2P(OPr)_2]_6$ (0.10 g, 0.042 mmol) was dissolved in toluene (100 mL) with stirring, and then $NH_4S_2P(OEt)_2$ (0.0515 g, 0.252 mmol) was added. The reaction mixture was refluxed under an atmosphere of dinitrogen for 24 h and allowed to cool to room temperature. The resultant yellow solution was filtered. The filtrate was then concentration to ca. 4 mL and loaded into a silica gel column. Unreacted starting compound, $\{Cu_8(Se)[Se_2P(OPr)_2]_6\}$ (**1**) (20%), was removed first from the silica gel column using dichloromethane/hexane (3:2) as eluent. Using

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Table 1. Selected Crystallographic Data for $\{Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6\}_{0.54}\{Cu_6[S_2P(OEt)_2]_6\}_{0.46}$ (**2**)

formula	$C_{24}H_{60}Cu_{7.08}O_{12}P_6S_{12}Se_{0.54}$	V, Å^3	4361(1)
fw	1603.76	Z	3
space group	$R\bar{3}$	ρ_{calcd}, g cm^{-3}	1.832
a, Å	21.0139(13)	λ(Mo Kα), Å	0.710 73
b, Å	21.0139(13)	μ, mm^{-1}	3.518
c, Å	11.404(3)	T, K	293
α, deg	90	R1[a]	0.0599
β, deg	90	wR2[b]	0.1640
γ, deg	120		

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

methanol as eluent yielded a yellow band of compound **2** (0.055 g, 78%). Anal. Calcd for $C_{24}H_{60}Cu_{7.08}O_{12}P_6S_{12}Se_{0.54}$: C, 17.97; H, 3.74; S, 23.99. Found: C, 19.13; H, 3.59; S 24.35. ^{1}H NMR ($CDCl_3$): δ 1.39 (t, 36H, CH_2CH_3, J_{HH} = 7 Hz), 4.17 (m, 24H, CH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 101 ppm. $^{77}Se\{^1H\}$ NMR($CDCl_3$): δ −976 ppm.

Safety Note. *Selenium and its derivatives are toxic! These materials should be handled with great caution.*

X-ray Crystallographic Procedures. Single crystals of **2** were obtained directly from the reaction products. A crystal of size 0.50 × 0.40 × 0.38 mm was mounted on the tips of glass fibers with epoxy resin. Data were collected at 293 K on a P4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and were corrected for Lorentzian, polarization, and Ψ-scan absorption effects. The structure was solved by the use of direct methods, and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[16] incorporated in SHELXTL/PC V5.10.[17] A total of 2530 reflections were collected, of which 1548 were unique (R_{int} = 0.0390) and 1243 were observed with $I > 2\sigma(I)$. The site occupancies of Cu(2) and Se in special positions were initially set to one. U_{eq} of these two atoms are 0.090(1) and 0.114(2), which is nearly twice as large as the U_{eq} of other Cu and S atoms. In addition, an unreasonably high wR2 of 0.3536 was obtained. Therefore, the site occupancy factors of Cu(2) and Se were tied up and refined simultaneously. Final convergence resulted in site occupancies of 0.54. Hydrogen atoms were added to their idealized positions. The final cycle of the full-matrix least-squares refinement was based on 1548 observed reflections and 97 parameters and converged with unweighted and weighted agreement factors of R1 = 0.0599 and wR2 = 0.1812 (all data), respectively. The largest residual peak and hole are 0.915 and −1.695 e/Å^3. Selected crystal data of **2** are summarized in Table 1.

Results and Discussion

The compound $\{Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6\}_{0.54}\{Cu_6[S_2P(OEt)_2]_6\}_{0.46}$ (**2**) was prepared in ~80% yield from the reaction of $Cu_8(Se)[Se_2P(OPr)_2]_6$ (**1**) and $NH_4S_2P(OEt)_2$ in a molar ratio of 1:6 in toluene under reflux condition. The central selenide ion in **2** is unequivocally characterized by ^{77}Se NMR, whose chemical shift is centered at −976 ppm. The ^{1}H NMR spectrum exhibits chemical shifts at δ 1.39 and 4.17 ppm for the $-CH_2CH_3$ group of the ligands. The $^{31}P\{^1H\}$ NMR spectrum shows a peak at δ 101 ppm. Only one type of ligand signal was obtained probably due to the fact that the Cu−S bonds are very labile in solution and interchange, faster than the NMR time scale, between cubic and hexanuclear clusters. Thus, solid-state ^{31}P NMR was measured which is discussed below. Elemental analyses also match with the molecular formulation of **2**.

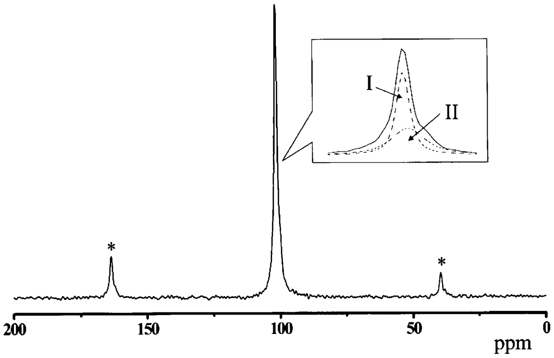

Figure 1. Solid-state ^{31}P MAS NMR spectrum of **2** acquired at a spinning speed of 10 kHz. The asterisks denote the first-order sidebands. The spectrum was deconvoluted by using two peaks in an intensity ratio close to 55:45 for two different types of phosphorus as displayed in the inset.

Solid-State ^{31}P NMR. The obviously different bridging patterns for the dtp ligands (vide infra) suggest that the chemical shifts of the phosphorus nuclei between two clusters $\{Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6\}$ and $\{Cu_6[S_2P(OEt)_2]_6$ should be different. Thus, the solid-state ^{31}P magic angle spinning (MAS) NMR is performed. A peak at 101.1 ppm with its sidebands is displayed in Figure 1. A close examination of the expanded spectrum, which is shown in the inset, indicates that the peak at 101.1 ppm is asymmetrical and is associated with an upfield shoulder centered at 100.7 ppm. The presence of the shoulder is also evidenced in its downfield first-order sidebands. Thus, the spectrum is satisfactorily simulated with two components (site I and II) with the integration ratio close to 55:45. It is also of interest to note that the line width of site II (440 Hz) is significantly larger than that of site I (170 Hz). The peak centered at 100.7 ppm for site II can be reasonably assigned to the ^{31}P nuclei in the hexanuclear cluster, which is close to the previously reported one.[11a] Therefore, the site I at 101.1 ppm is likely ascribed to the octanuclear cluster. Besides, their intensity ratio is nearly consistent with the single-crystal X-ray diffraction results.

Crystal Structure and DFT Calculation. The single-crystal X-ray diffraction analysis confirms that the cluster **2** indeed contains the cocrystallization structures of $Cu_8(Se)[S_2P(OEt)_2]_6$ (54%) and $Cu_6[S_2P(OEt)_2]_6$ (46%) superimposing along the C_3 axis of the trigonal crystal system. Selected bond lengths and angles are given in Table 2. As shown in Figure 2 the major difference between the two structures is the linear "Cu_2Se" unit on the 3-fold crystallographic axis which pass through the Cu(2), Se, and Cu(2A) atoms. While the hexanuclear copper cluster $Cu_6[S_2P(OEt)_2]_6$,[11a] whose six copper atoms form a compressed octahedron, has been reported before to have the S_6 point group symmetry and each dtp ligand adopts a trimetallic triconnective coordination mode (μ_2, μ_1), the $Cu_8(Se)[S_2P(OEt)_2]_6$ is the first selenide-centered Cu^I_8 cubic cluster surrounded by the dithiophosphato ligands in a tetrametallic tetraconnective coordination pattern

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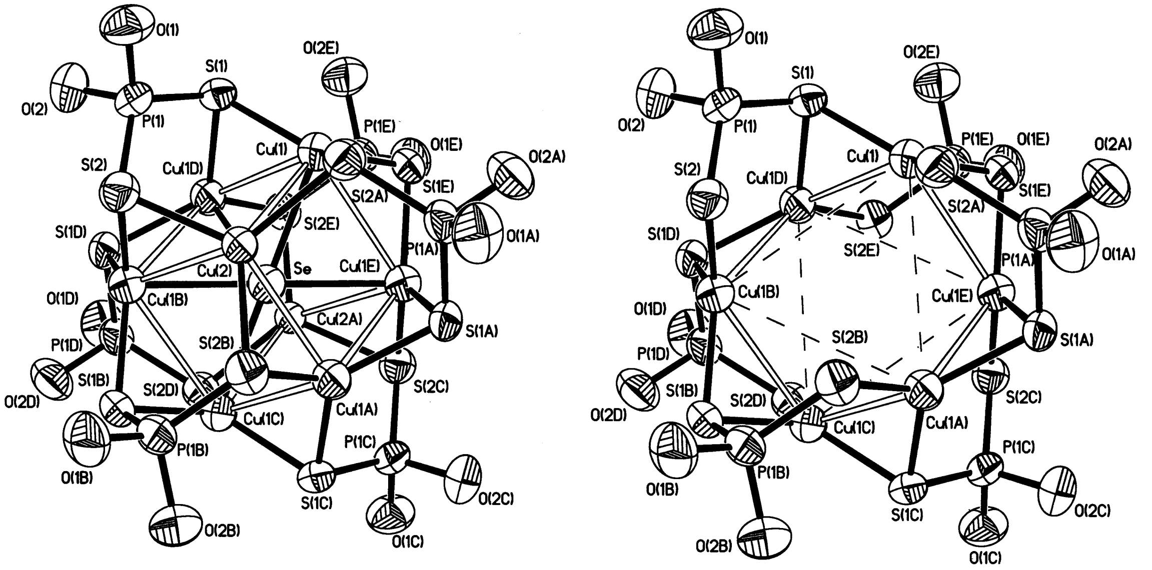

Figure 2. Thermal ellipsoid drawing (50% probability) of **2** with ethyl groups omitted for clarity: (left) $Cu_8(\mu_8\text{-Se})[S_2P(OEt)_2]_6$; (right) $Cu_6[S_2P(OEt)_2]_6$.

Table 2. Selected Bond Distances (Å) and Angels (deg) for **2** with Esds in the Parentheses

Se−Cu(1)	2.624.1	P(1)−O(2)	1.594(6)
Se−Cu(2)	2.539(3)	S···S (bite)	3.478
Cu(1)−S(1)	2.285(2)	Cu(1)−Se−Cu(2)	69.68(2)
Cu(1)−S(1E)	2.310(2)	Cu(1)−Se−Cu(1E)	71.39(2)
Cu(1)−S(2A)	2.275(2)	Cu(1)−S(1)−Cu(1D)	83.57(6)
Cu(2)−S(2)	2.342(2)	Cu(2)−S(2)−Cu(1B)	79.42(8)
Cu(2)−S(2B)	2.342(2)	S(1)−Cu(1)−S(1E)	117.31(5)
Cu(1)−Cu(2)	2.950(2)	S(1)−Cu(1)−S(2A)	122.47(8)
Cu(1A)−Cu(1C)	3.062(2)	S(1E)−Cu(1)−S(2A)	116.70(7)
P(1)−S(1)	2.005(3)	S(2)−Cu(2)−S(2A)	118.18(4)
P(1)−S(2)	2.005(3)	S(1)−P(1)−S(2)	120.24(10)
P(1)−O(1)	1.564(5)		

(μ_2, μ_2).[18] The latter structure clearly suggests that it is the product of a metathesis reaction of $Cu_8(Se)[Se_2P(OPr)_2]_6$ with the sulfur-donor ligands. Furthermore it is interesting to realize that the reported[11a] hexacopper cluster indeed has two water molecules which appeared to be H-bonded in a distorted fashion to the nonbridging S atoms and sit on the 3-fold crystallographic axis. Thus, a void does exist in the present hexanuclear copper cluster. The mean plane distance between two uncapped Cu_3 triangles through which the 3-fold axis passes is 1.822(3) Å, and the diagonal distance of the compressed octahedron is 5.247 Å in $Cu_6[S_2P(OEt)_2]_6$.

The compound **2** crystallizes in the $R\bar{3}$ space group with one dtp ligand in the asymmetric unit. Two types of Cu−Se distances, 2.624(1) and 2.539(3) Å, are observed in the novel octanuclear copper cluster with the shorter ones exhibited along the 3-fold rotational axis. This in turn results in two types of Cu−Cu distances of 2.950(2) and 3.062(2) Å and two types of Cu−Se−Cu angles, 71.39(2) and 69.68(2)° (70.53° is required for an idealized cubic arrangement).[19] Each edge of the metallic cube is further bridged by a sulfur atom of the dtp ligand having Cu−S bond lengths in the range of 2.275(2) and 2.342(2)Å. The ligand "bite" distance, the distance between two sulfur atoms of dtp, is 3.478 Å. Careful examination of the Cu_8Se core in $Cu_8(\mu_8\text{-Se})[S_2P(OEt)_2]_6$ by comparison with $Cu_8(\mu_8\text{-Se})[Se_2P(OPr)_2]_6$ (**1**), whose Cu−Se and Cu−Cu distances are in the range of 2.504(2)−2.520(1) and 2.899(2)−2.912(2) Å, respectively,[11f] suggests that there is greater contraction in size of the Cu_8-Se cube where bridging selenium donor lignads are present (**1**). This is particularly surprising because the ligand bite distance in **1** (3.776 Å) is much larger than that in **2** (3.478 Å) and normally we will expect that the volume of the cube core in **1** should be larger.

To understand the nature of the structure contraction of the metal core and metal−μ_8-Se interaction, molecular orbital calculations of the model clusters $Cu_8(\mu_8\text{-Se})[Se_2P(OH)_2]_6$ and $Cu_8(\mu_8\text{-Se})[S_2P(OH)_2]_6$ have been carried out at the B3LYP level of density functional theory.[20] The orbital patterns for the clusters are very similar to each other. Careful examination of the molecular orbitals obtained from the B3LYP calculations indicates that for each cluster the three p orbitals of μ_8-Se make the major contribution to the highest occupied molecular orbitals (HOMOs). The results here are quite different from the ones reported previously in which the HOMOs were found to have mainly the Cu's metal d orbitals.[9a] Different results apparently are due to the different

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(18) Haiduc, H.; Snowerby, D. B.; Lu, S.-F. *Polyhedron* **1995**, *14*, 3389.

(19) Schugar, H. J.; Ou, C.-C.; Thich, J. A.; Lalancette, R. A.; Furey, W. Jr. *J. Am. Chem. Soc.* **1976**, *98*, 3047.

(20) Density functional calculations at the B3LYP level were performed on the model clusters $Cu_8(\mu_8\text{-Se})[Se_2P(OH)_2]_6$ and $Cu_8(\mu_8\text{-Se})[S_2P(OH)_2]_6$ on the basis of the experimentally determined structures. The basis set used for O and H atoms was 6-31G while an effective core potential with a LanL2DZ basis set was employed for Cu, P, and Se. The DFT calculations were performed with the use of the Gaussian 98 package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgpmery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomeperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

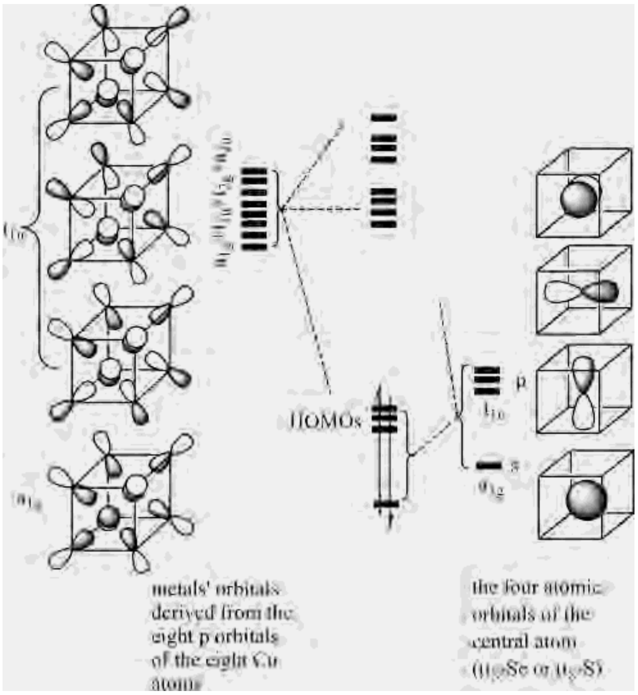

Figure 3. Schematic diagram illustrating the orbital interactions between eight copper orbitals and atomic orbitals of the central μ_8-Se in a cubic point group.

methods used in the calculations. The ones reported previously were based on the extended Hückel calculations while the results reported here are derived from density functional calculations. The qualitative bonding discussion presented here and the one reported previously[9a] are valid although the results are different regarding the characteristics of the highest occupied molecular orbitals. In our calculations, the natural bond order (NBO) analyses[21] show appreciable Cu−μ_8-Se bonding interactions. In view of these results as well as for the easiness of understanding, a schematic diagram illustrating the orbital interactions between the metals' orbitals and the atomic orbitals of the central atom is given in Figure 3.

Examining the local coordination of each copper center in the two clusters, we find that three Se or S atoms from the $Se_2P(OR)_2$ or $S_2P(OR)_2$ ligands are coordinated to each metal center and are approximately coplanar with the metal center. In such a coordination mode, the p orbital perpendicular to the plane of each metal center becomes available for bonding interaction with the central μ_8-Se. In a cubic arrangement, linear combinations of the eight such orbitals (from the eight coppers) give $a_{1g} + t_{1u} + t_{2g} + a_{2u}$ orbitals, shown in the left of Figure 3. The atomic orbitals of the central μ_8-Se transform as $a_{1g} + t_{1u}$ in the assumed cubic point group. The orbital interactions between the two sets of orbitals lead to the resulting schematic diagram shown in Figure 3. The formal oxidation state of each copper in the two clusters is +1 with a $3d^{10}$ electronic configuration. It is expected that the d orbitals are not the major contribution for the metal−ligand bonding. A similar orbital interaction diagram was proposed previously by Saillard, Halet, and coworkers on the basis of extended Hückel calculations of $Cu_8(\mu_8\text{-}S)[S_2P(OPr)_2]_6$.[9a]

Table 3. Results of Natural Bond Order and Population Analyses[a]

	Wiberg bond index		natural charge		
cluster	Cu−μ_8-Se	Cu−E (terminal)	Cu	μ_8-Se	E (terminal)
$Cu_8(\mu_8\text{-}Se)[Se_2P(OEt)_2]_6$[b]	0.09	0.19	+0.63	−1.49	−0.54
$Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6$[b]	0.09	0.19	+0.63	−1.49	−0.56
$Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6$[b]	0.08	0.17	+0.69	−1.55	−0.70

[a] E = Se or S. [b] The alkyl groups were replaced with hydrogen atoms in the model calculations.

Such a simple bonding model suggests that there are only four bonding molecular orbitals for the eight Cu−Se bonds between the eight coppers and the central μ_8-Se. Formally, one can suggest a half bond between each Cu and the central μ_8-Se when compared to the bonds between Cu and Se from the $Se_2P(OR)_2$ (or $S_2P(OR)_2$) ligands. Interestingly, the NBO analyses (Table 3) from the molecular orbital calculations indeed show that the Wiberg bond indices (also called bond order)[22] of Cu−μ_8-Se are approximately half of the terminal Cu−Se or Cu−S bonds. The X-ray data also give longer Cu−μ_8-Se distances (by ca. 0.05 Å) in comparison with the Cu−Se distances between Cu and the terminal $Se_2P(OR)_2$ ligands, supporting the formal bond order assignment.

All the cubic clusters having the $Cu_8(\mu_8\text{-}Se)[E_2P(OR)_2]_6$ (E = S or Se) formula adopt similar structural topologies. However, it is interesting that the $Cu_8(\mu_8\text{-}Se)$ cubic core in $Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6$ is larger in size than the $Cu_8(\mu_8\text{-}Se)$ cores in $Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6$. The trend in the core sizes is quite unexpected because the ligand bite distance is smaller for ligands having S in comparison to those having Se. The discussion above based on the MO calculations performed suggests that Cu−μ_8-Se interactions are not very strong and a half bond can be formally assigned to each Cu−μ_8-Se bond. In addition, Cu···Cu interactions are believed to be even weaker in view of the fact that there are no valence electrons available for Cu−Cu bonding. As noted before,[9] the bridging ligands play important roles in bringing all the metal centers together. With these considerations, we expect that moderate Cu···Cu repulsion exists and it is the bridging ligands that are responsible for the observed Cu···Cu contacts. Therefore, we would expect that the S-ligating copper clusters have greater Cu···Cu separations because each Cu carries more positive charge in the presence of the more electronegative S-containing ligands. Thus, we observe that the S-ligating cluster has a larger cubic metal core when compared to that having the Se-containing ligands. The natural population analyses (NPA) in Table 3, although they are only approximately, nicely show that Cu carries greater charge in $Cu_8(\mu_8\text{-}Se)[S_2P(OH)_2]_6$ than in $Cu_8(\mu_8\text{-}Se)[Se_2P(OH)_2]_6$.

It should be noted that the structural contraction of metal cores has also been found in $Cu_8(\mu_8\text{-}Cl)$ cubic clusters.[11h] For example, the structure type $\{Cu_8(\mu_8\text{-}Cl)[Se_2P(OR)_2]_6\}^+$ has a smaller metal core than that in $\{Cu_8(\mu_8\text{-}Cl)[S_2P\text{-}$

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[21] Reed, A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

[22] Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083. The Wiberg bond indices (bond orders) are a measure of bond strength.

$(OEt)_2]_6\}^+$. Again, the charge argument given above can be used to explain the contraction phenomenon.

Conclusion

Two different clusters, with different stoichiometries, with and without an interstitial atom and with different metal cores occupying nearly the same sites in the crystal structure of **2**, though uncommon, are unequivocally confirmed by both the MAS ^{31}P NMR and X-ray diffraction. In addition, MO calculations suggest that each Cu carries more positive charge in the presence of the more electronegative S-containing ligands, leading to that the $Cu_8(\mu_8\text{-}Se)$ cubic core in $Cu_8(\mu_8\text{-}Se)[S_2P(OEt)_2]_6$ is larger in size than the $Cu_8(\mu_8\text{-}Se)$ core in $Cu_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_6$, which is in good agreement with the X-ray structure analysis. Finally, the successful ligand substitution reaction on edge-capped Cu^I_8 cubic clusters with sulfur-donor ligands shows potential for the construction of larger clusters.

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Supporting Information Available: X-ray crystallographic files in CIF format for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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