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Ab Initio Study of Structures and Energetics of Small Copper–Selenium Clusters

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Abstract: Structures of clusters $(Cu_2Se)_n$ and $(Cu_2Se)_n(PR_3)_m$ for $n \leq 6$ and R = H, CH_3 are presented which have been determined in ab initio calculations including dynamical electron correlation (Møller–Plesset perturbation theory and coupled cluster). Various stable isomers exist for the dimer and larger clusters. The energetic separation of the isomers is rather small, and the energy hypersurfaces are in part very shallow. A few basic structural criteria deduced from the small cluster structures turned out to be ideally fulfilled in the hexamer $Cu_{12}Se_6$ already known experimentally as a ligand-stabilized species. The bonding of phosphine ligands affects the cluster structures significantly only in cases where an ideal coordination at Cu conflicts with steric requirements. Bonding energies per monomer unit of ligand-free clusters and CuP bonding energies suggest that the clusters are energetically unstable.

Introduction

Copper selenide, Cu_2Se, forms a solid with two known modifications. It is rather ionic in character, and therefore, clusters $(Cu_2Se)_n$ are thermodynamically unstable. They are intermediates in the formation of the bulk material, and their isolation and characterization are only possible through stabilization and especially steric shielding with ligands on the surface. Fenske et al. succeeded in synthesizing a variety of clusters $(Cu_2Se)_n(PR_3)_m$ (e.g., n = 15, 18, 22, 35, 73) which were characterized by crystal structure analyses.[1] The synthesis of the smallest species so far, $Cu_{12}Se_6(PPh_2Et)_8$, was achieved only recently. Ab initio calculations performed for $Cu_{12}Se_6$ in parallel to the crystal structure analysis of $Cu_{12}Se_6(PPh_2Et)_8$ predicted the same cluster structure as found experimentally.[2]

In the present work, we extent a recent ab initio investigation of Cu_2Se and Cu_4Se_2 to larger clusters Cu_6Se_3 and Cu_8Se_4 as well as clusters stabilized by phosphine ligands. Characteristic structural features of the clusters are deduced which then help to rationalize the relative stability of various isomers. From the calculations, we especially get insight into the energetics of the clusters which is not available experimentally. In particular, we present results for the bonding energies in bare clusters from which we can assess the energetic instability toward further cluster growth. We also compute and discuss stabilization effects introduced by phosphine ligands.

Methods and Basis Sets

Methodological aspects were studied extensively in our recent work on Cu_2Se and Cu_4Se_2[3] where we applied various quantum chemical methods up to high-level treatments such as coupled cluster theory restricted to single and double excitations (CCSD)[4] and augmented by a perturbational estimate for triple excitations (CCSD(T)).[5] It turned out that inclusion of dynamic electron correlation is essential for structures, with the Møller–Plesset second-order method (MP2)[6] being already sufficiently accurate as compared to CCSD(T). The correct energetic order of isomers is also only obtained with inclusion of correlation, but the energy differences are somewhat overestimated by MP2 (Table 2). The CuCu interactions leading to relatively short CuCu distances in the range 221–261 pm were mainly attributed to dispersion effects from the d^{10} shells of the Cu(I) atoms. On the basis of these experiences, we now report results for larger clusters and the effects introduced by phosphine ligands.

The structures of Cu_2Se and its dimer have been determined on the CCSD(T) level[3] using the program system ACES II.[7] All other structures, i.e. those of larger bare clusters as well as ligand-stabilized species, have been obtained on the MP2 level with the program package TURBOMOLE.[8] We did not calculate MP2 second derivatives. To ensure that the structures are local minima on the energy surface, we calculated self-consistent field (SCF) force constants and checked normal modes with wavenumbers less than 50 cm^{-1} (or even imaginary) by single-point MP2 calculations for structures distorted along these modes. In a second cross-check, the structures of the ligand-free clusters were also optimized without using point group symmetry, starting with a structure distorted to C_1.

The basis sets used for copper and selenium are the same as in reference 3, i.e. relativistically corrected effective core potentials (ECPs) with 18 (Cu) and 28 (Se) core electrons[9] and optimized bases (325)/[222] (Cu) and (331)/[221] (Se).[3] For an economic description of the phosphine ligands, we also applied an ECP with 10 core electons at P together with the (reoptimized) basis (331)/[221][10] with a d exponent of $\eta = 0.45$. Furthermore, we used an optimized (3)/[1] single-ζ basis for H and a (63)/[21] (C), (3)/[1] (H) single-ζ basis for CH_3, optimized for CH_4.[11]

Ligand-Free Clusters $(Cu_2Se)_n$

All stable structures located so far for $(Cu_2Se)_n$, n = 1–6, are shown in Figure 1, with isomers ordered according to

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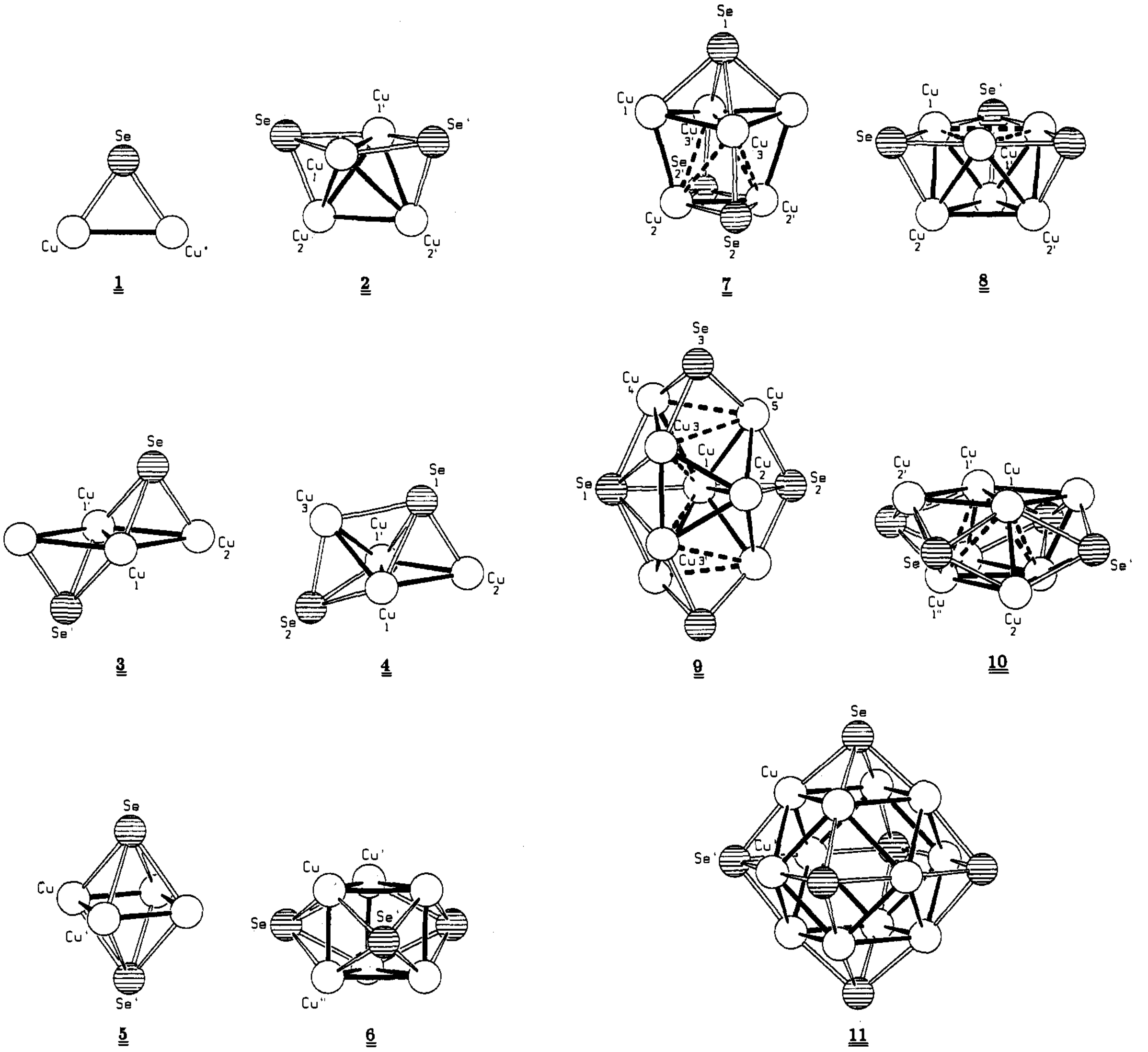

Figure 1. Computed structures of bare clusters $(Cu_2Se)_n$, $n = 1-6$. Isomers are ordered according to decreasing stability.

decreasing stability. The values of the structure parameters are collected in Table 1, while Table 2 contains total, relative, and bonding energies. The monomer and dimer structures **1**–**3** and **5** were already reported in ref 3; they are included here for completeness. One additional isomer, **4**, has been found for Cu_4Se_2. It shows C_s symmetry and can be derived from **3** by bending the molecule at the Cu1–Cu1′ axis, forming the additional bond Cu3Se1. This new isomer lies energetically between the structures **3** and **5** (Table 1). As already stated in ref 3, the energy differences between the isomers of Cu_4Se_2 are very small. The lowest (**2**) and highest (**5**) lying species are separated by 13.5 kJ/mol (CCSD(T)) only.

Three stable isomers, **6**–**8**, were found for Cu_6Se_3 with energy differences of 33.1 kJ/mol (**6**–**7**) and 14.6 kJ/mol (**7**–**8**) (MP2, Table 2). Their structures can be related to those found for the dimer in the following way. The face-capped trigonal Cu_6 prism in **6** (D_{3h} symmetry) can be regarded as an extension of the structure of **5**, and the capped trigonal antiprism in **8** (C_{3v}) can be looked at as an extension of **2**. The structure of **7** (C_{2v}), containing three highly distorted face-connected tetrahedra, can be derived from **2** by addition of a Cu_2Se monomer at the bottom. This is the way this structure has actually been found in the calculations.

Two isomers, **9** (C_s) and **10** (D_{2d}), were found for Cu_8Se_4, separated energetically by 74 kJ/mol (MP2). Both structures contain five face-connected tetrahedra, with Se atoms bridging three to five Cu sites. Two additional structures that could be generated by extension of **6** and **8**—a face-capped tetragonal Cu_8 prism (D_{4h}) and an antiprism (C_{4v}) (Figure 2)—turned out to be saddle points. The former especially relaxed to isomer **10** by deformation of the square basal faces to rhombuses with formation of a new Cu1Cu1′ contact. No such relaxation of the prism is possible in the trimer structure **6**.

As the cluster size increases, the number of possible minima on the energy surface grows rapidly, as does the computational effort for their determination. Although a careful investigation of the most probable structures has been carried out, we cannot be certain that all local minima have been found, especially for $n \geq 3$.

For a qualitative understanding of the relative stabilities of the isomers of a given cluster size, three criteria turned out to be helpful:

(1) Each Se ideally bridges three or four Cu atoms. The CuSe distances are longer the more loaded the Se and Cu atoms are with bond partners. The shortest CuSe distance is thus found in **1** with 222.4 pm (CCSD(T), Table 1).

(2) There should be as many CuCu contacts as possible. This normally leads to more or less distorted polyhedral substructures. For the threshold for the distance of Cu atoms to be considered "in contact", we found $r < 265$ pm as a reasonable criterion.

(3) Large SeCuSe angles are preferred, ideally 180°. In cases where two Se atoms are bridging the same two Cu atoms (as,

Table 1. Computed MP2 Structure Parameters for Ligand-Free Clusters $(Cu_2Se)_n$[a]

species[b]	symmetry	distances (pm) and angles (deg)
1[c]	C_{2v}	CuCu′ = 252.1 (251.8), CuSe = 220.0 (222.4)
2[c]	C_{2v}	Cu1Cu1′ = 221.6 (226.1), Cu1Cu2 = 260.2 (263.9), Cu2Cu2′ = 261.2 (256.7), Cu2Se = 222.8 (225.1), Cu1Se = 237.0 (240.5), SeCu1Se′ = 123.9 (123.8)
3[c]	C_{2h}	Cu1Cu1′ = 221.2 (225.8), Cu1Cu2 = 258.8 (259.8), Cu2Se = 223.4 (225.5), Cu1Se = 236.6 (240.1), SeCu1Se′ = 124.3 (123.9)
4	C_s	Cu1Cu3 = 233.2 (234.8), Cu1Cu1′ = 235.3 (242.8), Cu1Cu2 = 247.9 (246.8), Cu2Se1 = 224.3 (226.6), Cu1Se2 = 233.8 (236.5), Cu3Se2 = 235.5 (238.7), Cu1Se1 = 248.8 (254.9), Cu3Se1 = 250.4 (252.0), Se1Cu1Se2 = 112.4 (111.9), Se1Cu3Se2 = 111.2 (112.1)
5[c]	D_{4h}	CuCu′ = 222.8 (224.6), CuSe = 245.8 (249.1), SeCuSe′ = 100.3 (100.8)
6	D_{3h}	CuCu″ = 220.2, CuCu′ = 249.0, CuSe = 240.4, SeCuSe′ = 124.4
7	C_{2v}	Cu2Cu2′ = 223.0, Cu1Cu3 = 233.2, Cu1Cu2 = 244.8, Cu2Cu3 = 275.2, Cu3Cu3′ = 284.1, Cu3Se2 = 223.1, Cu3Se1 = 233.5, Cu2Se2 = 236.6, Cu1Se1 = 242.3, Se1Cu3Se2 = 159.9, Se2Cu2Se2′ = 123.7
8	C_{3v}	Cu1Cu2 = 248.6, Cu2Cu2′ = 258.4, Cu1Cu1′ = 268.1, Cu2Se = 228.0, Cu1Se = 229.5, SeCu1Se′ = 168.5
9	C_s	Cu3Cu4 = 224.8, Cu2Cu5 = 232.2, Cu3Cu3′ = 247.1, Cu2Cu3 = 247.9, Cu1Cu5 = 253.2, Cu1Cu4 = 255.7, Cu1Cu2 = 260.6, Cu4Cu5 = 267.1, Cu3Cu5 = 274.9, Cu1Cu3 = 275.7, Cu5Se3 = 225.3, Cu3Se3 = 230.0, Cu5Se2 = 231.1, Cu1Se1 = 232.1, Cu1Se2 = 233.3, Cu4Se3 = 236.6, Cu3Se1 = 243.6, Cu4Se1 = 251.5, Cu2Se2 = 254.5, Se2Cu5Se3 = 164.0, Se1Cu1Se2 = 163.7, Se1Cu3Se3 = 127.5, Se1Cu4Se3 = 120.9
10	D_{2d}	Cu1Cu2 = 223.7, Cu1Cu2′ = 260.1, Cu1Cu1′ = 262.6, Cu1Cu1″ = 275.4, Cu2Se = 233.1, Cu1Se = 245.2, SeCu2Se′ = 127.6, SeCu1Se′ = 117.1
11[d]	O_h	CuCu′ = 252.0, CuSe = 233.3, SeCuSe′ = 170.4

[a] Values given in parentheses have been obtained on the CCSD(T) level. [b] As in Figure 1. [c] Reference 3. [d] Reference 2.

Table 2. Total Energies (au) and Relative and Bonding Energies (kJ/mol) for Bare Clusters $(Cu_2Se)_n$ Obtained on the MP2 and CCSD(T) Levels at the Respective Equilibrium Structures

		E_{tot}		ΔE[b]		E_B[c]	
n	species[a]	MP2	CCSD(T)	MP2	CCSD(T)	MP2	CCSD(T)
1	**1**[d]	−110.420 193	−110.398 988				
2	**2**[d]	−220.962 573	−220.912 470	0.0	0.0	160.4	150.3
	3[d]	−220.960 041	−220.910 619	6.6	4.9	157.1	147.9
	4	−220.958 665	−220.910 064	10.3	6.3	155.3	147.1
	5[d]	−220.953 545	−220.907 318	23.7	13.5	148.5	143.5
3	**6**	−331.573 070		0.0		273.5	
	7	−331.560 456		33.1		262.4	
	8	−331.554 889		47.7		257.6	
4	**9**	−442.169 569		0.0		320.8	
	10	−442.141 384		74.0		302.3	
6	**11**[e]	−663.497 772				427.3	

[a] As in Figure 1. [b] Energy relative to the most stable isomer. [c] $E_B = E[Cu_2Se] - (1/n)E$. [d] Reference 3. [e] Reference 2.

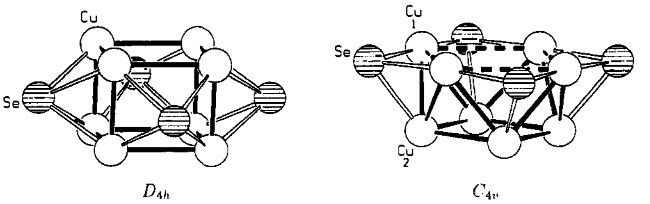

Figure 2. Two saddle points on the Cu_8Se_4 energy surface (MP2), labeled with the corresponding point group symmetry.

for example in **2**), the SeCuSe angle is close to 120°. Angles of this type will be named bridge angles in the following. Most of the SeCuSe angles fall in these two categories; there are no angles between 130° and 160°. Angles significantly below 120° are found only in less stable structures, e.g. **5**.

The last point reflects the well-known tendency of the coinage metals in oxidation state +I to form linear arrangements of bond partners.[12] The copper–selenium clusters show this feature especially in the bonding of stabilizing phosphine ligands, as will be discussed in the next section.

In Table 3, we have collected the number of CuSe bonds, CuCu contacts, and SeCuSe angles (grouped in three categories) for the $(Cu_2Se)_n$ structures. In the following we try a rationalization of the relative stability of isomers based on this information and the structural data in Table 1. Values given for structure parameters as well as relative energies refer to CCSD(T) calculations for Cu_2Se and Cu_4Se_2 and MP2 calculations for larger clusters.

The case of Cu_2Se is trivial since only a single stable structure exists. As already mentioned above, the energy differences between the four isomers of Cu_4Se_2 are small, so the underlying structural effects can be expected to be subtle. **2** and **3** have in

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Table 3. Number of CuSe Bonds, CuCu Contacts (r < 265 pm), and Certain Types of SeCuSe Angles Found in $(Cu_2Se)_n$ Clusters

n	species[a]	no. of CuSe	no. of CuCu	no. of ∠SeCuSe <120°	120°–130°	160°–180°
1	**1**	2	1			
2	**2**	6	6		2	
	3	6	5		2	
	4	7	5	3		
	5	8	4	4		
3	**6**	12	9		6	
	7	10	7		2	2
	8	9	9			3
4	**9**	15	12		4	3
	10	16	10	4	4	
6	**11**	24	24			24

[a] As in Figure 1.

most details the same topology, as can be verified by comparison of the structural data in Table 1. The only difference is the additional Cu2Cu2′ contact in **2**, which introduces two additional contributions to the total energy: Coulomb repulsion between the positively charged Cu atoms (charges are about +0.3[3]) and a CuCu attraction due to dispersion interaction of the d^{10} shells. The latter obviously dominates, and the additional CuCu contact stabilizes **2** by 4.9 kJ/mol. Since dispersion effects can only be covered in treatments including electron correlation, it is thus not surprising that an SCF treatment gives the opposite energetic order of **2** and **3**.[3]

In going from **3** to **4**, the structure bends around the Cu1–Cu1′ axis and Cu3 (in **4**) approaches Se1 to form a new CuSe bond. However, this bending also decreases the Se1Cu1Se2 angle to 111.9° and opens the short Cu1Cu1′ contact by 17 pm. The energetic effects virtually cancel, and **3** appears to be only 1.5 kJ/mol more stable than **4**.

The formation of the largest number of CuSe bonds, achieved in **5**, is only possible by the complete opening of the Cu1Cu1′ connection in **4**, resulting in a Cu square with Se above and below the plane. The remaining four CuCu contacts are very short (224.6 pm), but nevertheless, the extremely small SeCuSe angles of 100.8° are unfavorable. This allows us to rationalize that **5** is 7.2 kJ/mol higher in energy than **4**.

The most stable trimer, **6**, shows nine close CuCu contacts, three of them, CuCu″ = 220.2 pm, being the shortest CuCu distances found in this work in copper–selenium clusters. Isomer **7** seems to have more CuCu contacts than **6** at first sight, since its Cu substructure consists of three (though highly distorted) face-connected tetrahedra. However, five of the CuCu distances are larger than 275 pm (drawn with dashed lines in Figure 1), so only seven CuCu contacts are actually present. Furthermore, **7** has two CuSe bonds less than **6**. This helps to rationalize why **7** is less stable than **6**. The energy difference of 33.1 kJ/mol obtained with the MP2 method is probably too large, as has been found for the relative stabilities of the dimers by comparison with CCSD(T) results (Table 2).[3] The third trimeric isomer, **8**, is another 14.6 kJ/mol higher in energy than **7**, although in this structure three favorable angles SeCu1Se′ of 168.5° are found and nine CuCu distances are below the threshold. Nevertheless, there are no CuCu distances as short as in the other isomers; the shortest one is Cu1Cu2 with 248.6 pm.

A rationalization for the energetic order of the two Cu_8Se_4 isomers might be found mainly in the SeCuSe bond angles. **9** contains three angles larger than 160° and another four between 120° and 130°. In **10** all angles are of the bridge type, with four of them being even smaller than 120°.

With the above stability criteria in mind, the structure **11** (Figure 1) found for the hexamer $Cu_{12}Se_6$[2] appears ideal. In this cluster, the Se atoms cap all square faces of a regular Cu cubooctahedron. The cluster contains 24 CuSe bonds (distance 233.3 pm) and also 24 CuCu contacts (distance 252 pm). All 12 Cu atoms are almost linearly coordinated by two Se atoms with angles of 170.4°. This structure thus represents an ideal arrangement (in the above sense) of 12 Cu and six Se atoms.

The clusters are thermodynamically not stable, at least at low temperatures where entropy effects are less important. This is immediately clear as bonding energies per monomer unit

$$E_B = E[Cu_2Se] - (1/n)E[(Cu_2Se)_n]$$

are considered for clusters of increasing size (Table 2). E_B grows with the cluster size, with the relative changes becoming smaller for the larger systems. This reflects the tendency of the clusters to add further monomers until the bulk material is formed. In the asymptotical limit of the solid, the bonding energy should be related to the lattice energy,[13] but the clusters presented here are still too small to allow for an extrapolation.

Ligand-Stabilized Clusters $(Cu_2Se)_n(PR_3)_m$

In Figure 3, we present the calculated structures of clusters with PH_3 ligands. The ligands normally contain bulky organic substituents providing large steric demand (kinetic stabilization) and also a better bonding capability (thermodynamic stabilization). We used PH_3 as a model ligand in order to reduce the computational effort. To check the effects of larger substituents, we also employed $P(CH_3)_3$ for the clusters **1**, **2**, and **5**, resulting in structures **19** and **20** (Figure 4). Table 4 contains the structure parameters for the ligand-clad clusters. Computed total energies, relative energies of isomers, and especially bonding energies for the ligands are displayed in Table 5.

Most of the important features of the ligand-stabilized cluster structures are already present in the smallest member **12** (Figure 3). The PH_3 ligands are bound to the Cu atoms with a SeCuP angle of 176.3°. This angle is very close to the ideal value of 180° for a linear coordination at Cu. As already mentioned in the last section, such a bonding situation is preferred by Cu(I), Ag(I), and Au(I). The common explanation is based on an sd-type hybridization at the coinage metal atom.[12] Analogous structures are known for the Au(I) compounds $Au_2Se(PPh_3)_2$[14] and $Au_2Se(PH_3)_2$,[15] the former showing SeAuP angles of 175°.

The CuSe bond remains virtually unaffected by the bonding of the ligand; the bond length is only 0.3 pm larger in **12** than in **1** (MP2). Significant structural changes are only found for the CuCu distance, which is about 17 pm longer in **12**. The partial donation of an electron pair from the ligand to Cu leads to a considerable lengthening of the CuCu contact, especially in combination with the small CuCu force constant of 23 N/m.[3] Although this effect is intuitively not unexpected, we have not been able to discern a quantitative explanation from, for example, population analyses.

The CuP bond length is 214.5 pm, and the CuP bonding energy

$$E_B[CuP] = (1/m)E[(Cu_2Se)_n] + E[PR_3] - (1/m)E[(Cu_2Se)_n(PR_3)_m]$$

amounts to 133 kJ/mol (Table 5). In changing the ligand from PH_3 to $P(CH_3)_3$, the cluster structure remains almost unaffected, with the exception of the CuP bond which is lengthened by

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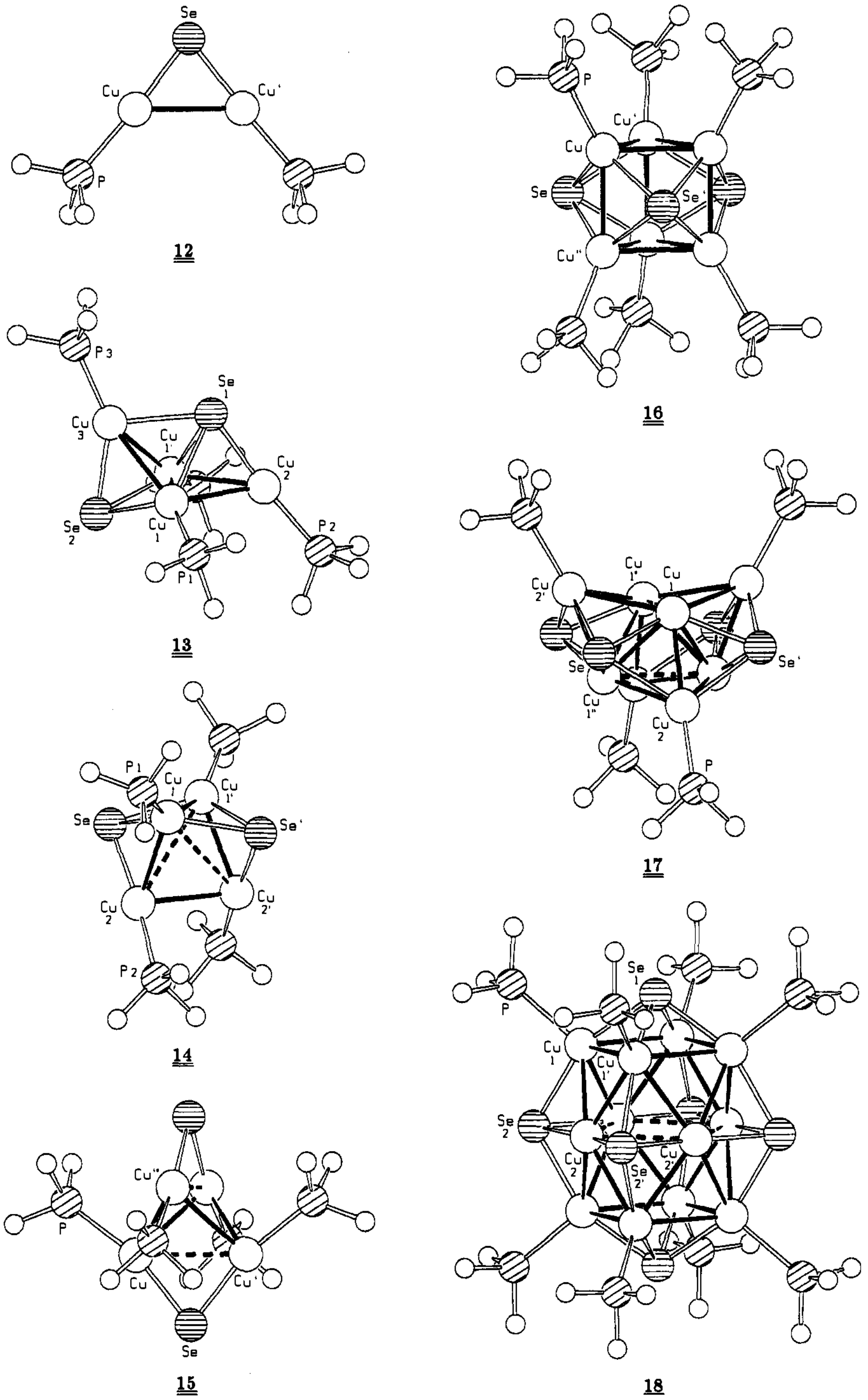
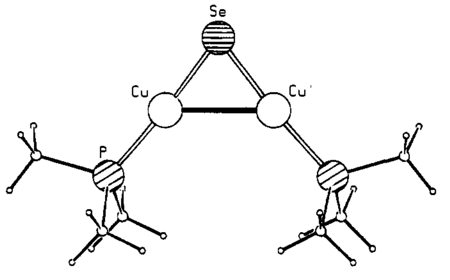


Figure 3. Computed structures of ligand-stabilized clusters $(Cu_2Se)_n(PR_3)_m$, R = H. Isomers are ordered according to decreasing stability.

about 2 pm (Table 4, Figure 4). The change in the CuP bonding energy is more significant. For **19**, we obtain E_B[CuP] = 190 kJ/mol, which is about 40% larger than for **12**. This reflects the better bonding capability of ligands with organic groups.

For the four cluster dimers **2**–**5**, we found only three ligand-stabilized structures, **13**–**15** (Figure 3). No energy minimum associated to isomer **3** could be located; addition of PH_3 leads to **13** (as for **4**). The reason may be the steric demand of the two ligands containing P1 and P1′ (in **13**) which enforces the bending of the cluster structure around the Cu1–Cu1′ axis. As found for the monomer, the CuSe bond lengths in **13** and **4** differ only slightly, but the CuCu distances are up to 25 pm larger in **13**. There is only a single almost linear SeCuP arrangement (∠Se1Cu2P2 = 174.0°) since all other Cu atoms are coordinated by two Se atoms. For the naked clusters, we have found that an arrangement with two Se atoms bound symmetrically to the same Cu atom leads to a bond angle of about 120°. An additional PH_3 ligand now tends to complete a trigonal planar coordination sphere at that Cu atom. This is found in **13** for the fragment Cu1Se1Se2P1. The SeCu1P1 angles of 126.4° and 129.7° are only slightly larger than 120°; the Se1Cu1Se2 angle of 103.8° is then necessarily smaller. The situation at atom Cu3 is in between those of Cu1 and Cu2. Since the Cu3Se1 bond is weak and rather long, the largest angle found at Cu3 is the one formed by the most strongly bond ligands Se2 and P3 with 147.8°.

The ligand-clad derivative of dimer **2**, i.e. structure **14** in Figure 3, is higher in energy than **13** by 23.3 kJ/mol, although the corresponding naked clusters **2** and **4** are in the reverse energetic order. The reason may be seen in the steric repulsion



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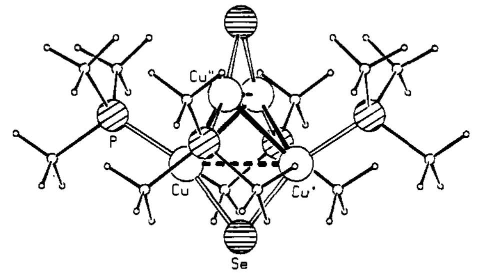

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Figure 4. Computed structures of ligand-stabilized clusters $(Cu_2Se)_n(PR_3)_m$, R = CH_3.

of the two ligands containing P2 (in **14**) which is inevitable if the favorable linear SeCu2P2 arrangement is formed. The cluster gives way to this strain by lengthening the Cu1Cu2′ distance to more than 320 pm. The Cu2Cu2′ contact remains almost unaffected, and the relaxation of the structure may be described as a twist around the Cu2–Cu2′ axis. With the much larger $P(CH_3)_3$ ligands, this distortion should be still more drastic. In fact, with $P(CH_3)_3$, we did not even find a local minimum analogous to **14**. The Cu1Se bond, which is already lengthened by about 7 pm in **14** (as compared to **2**), gets completely broken, resulting in structure **20** (Figure 4). It is remarkable that the norm of the molecular energy gradient has been less than 10^{-3} au at intermediate stages of the structure relaxation, thus again demonstrating the shallowness of the energy hypersurfaces of the clusters. **20** and the analogous PH_3 species **15** are ligand-covered derivatives of the least stable dimer **5**. **15** is also the least stable of the PH_3-stabilized dimers, but with larger ligands this isomer becomes more favorable.

The surface to volume ratio of the clusters decreases with increasing cluster size. This might lead to an unfavorable crowding of ligands on the surface if all Cu sites were occupied. Therefore it normally cannot be predicted a priori how many ligands a cluster will ideally bind. This also depends on the size of the ligands, of course. A systematic investigation of all possible ligand-stabilized species would thus be a very laborious task and would require enormous computational resources. We concentrate here on three examples, i.e. ligand-covered derivatives of the trimer **6**, the tetramer **10**, and the hexamer **11**, respectively.

Structure **16** (Figure 3) shows the expected arrangement of six PH_3 ligands added to **6**. Each Cu atom is coordinated by two Se atoms and one P with an out-of-plane angle of 13.3° for the CuP bond. The CuSe distances are again almost the same as in the ligand-free cluster while the CuCu contacts are considerably lengthened (cp. Tables 1 and 4).

In structure **17**, only one-half of the Cu sites (Cu2) are occupied by PH_3. These four Cu atoms are already in an exposed position in the naked cluster, **10**, and should therefore be ideal for binding ligands. Due to the additional CuP bond, the Cu2 atoms are moved outward in **17** to approach a near planar configuration (the out-of-plane angle for the CuP bond is 21.5°).

In the hexamer **18**, the phosphine ligands again complete a trigonal planar arrangement of bond partners at Cu. The Cu1 atoms are therefore moved outward compared to those in **11**, resulting in a smaller Se1Cu1Se2 angle of 155.1°.[2]

Finally, we consider the amount of energetic stabilization introduced by ligand bonding. Figure 5 shows a simplified reaction scheme for the cluster growth and the addition of

Table 4. Computed MP2 Structure Parameters for Ligand-Covered Clusters $(Cu_2Se)_n(PR_3)_m$, with R = H for Structures **12**–**17** and R = CH_3 for **19** and **20**

species[a]	symmetry	distances (pm) and angles (deg)
12	C_{2v}	CuCu′ = 269.5, CuSe = 220.3, CuP = 214.5, SeCuP = 176.3
13	C_s	Cu1Cu3 = 258.1, Cu1Cu1′ = 258.2, Cu1Cu2 = 261.8, Cu2Se1 = 223.0, Cu3Se2 = 232.0, Cu1Se2 = 234.9, Cu1Se1 = 247.2, Cu3Se1 = 251.4, Cu2P2 = 215.1, Cu3P3 = 215.3, Cu1P1 = 215.5, Se1Cu1Se2 = 103.8, Se1Cu3Se2 = 103.3, Se1Cu2P2 = 174.0, Se2Cu3P3 = 147.8, Se1Cu1P1 = 129.7, Se2Cu1P1 = 126.4, Se1Cu3P3 = 108.9
14	C_2	Cu1Cu1′ = 244.4, Cu1Cu2 = 251.0, Cu2Cu2′ = 260.4, Cu1Cu2′ = 323.9, Cu2Se = 222.7, Cu1Se′ = 237.7, Cu1Se = 244.3, Cu2P2 = 216.0, Cu1P1 = 218.3, SeCu1Se′ = 112.8, SeCu2P2 = 172.1, SeCu1P1 = 126.7, Se′Cu1P1 = 120.3
15	D_{2d}	CuCu″ = 259.3, CuCu′ = 284.4, CuSe = 222.3, CuP = 218.3, SeCuP = 166.2
16	D_3	CuCu″ = 248.9, CuCu′ = 267.0, Cu′Se = 239.2, CuSe = 240.5, CuP = 218.7, SeCu1Se′ = 114.3, Se′CuP = 125.7, SeCuP = 118.0
17	D_{2d}	Cu1Cu2 = 234.7, Cu1Cu1″ = 260.5, Cu1Cu2′ = 271.2, Cu1Cu1′ = 280.4, Cu1Se = 232.2, Cu2Se = 246.5, Cu2P = 219.0, SeCu1Se′ = 125.1, SeCu2Se′ = 113.4, SeCu2P = 120.7
18[b]	D_{4h}	Cu1Cu2 = 256.5, Cu1Cu1′ = 275.2, Cu2Cu2′ = 283.4, Cu2Se2 = 227.6, Cu1Se1 = 234.5, Cu1Se2 = 242.1, Cu1P = 232.6, Se1Cu1Se2 = 155.1, Se2Cu2Se2′ = 167.0, Se1Cu1P = 107.2, Se2Cu1P = 97.7
19	C_{2v}	CuCu′ = 269.0, CuSe = 221.2, CuP = 216.3, SeCuP = 176.0
20	D_{2d}	CuCu″ = 258.6, CuCu′ = 278.6, CuSe = 224.0, CuP = 219.7, SeCuP = 160.6

[a] As in Figures 3 and 4. [b] Reference 2.

Table 5. Total Energies (au), Relative Energies of Isomers, and CuP Bonding Energies (kJ/mol) Obtained on the MP2 Level for Ligand-Covered Clusters $(Cu_2Se)_n(PR_3)_m$, with R = H for Structures **12**–**17** and R = CH_3 for **19** and **20**

n	m	species[a]	E_{tot}	ΔE[b]	E_B[c]
1	2	**12**	−126.808 601		132.8
2	4	**13**	−253.702 577		111.2
2	4	**14**	−253.693 704	23.3	102.8
2	4	**15**	−253.684 642	47.1	102.7
3	6	**16**	−380.631 513		86.0
4	4	**17**	−474.865 664		98.3
6	8	**18**[d]	−728.799 384		50.0
1	2	**19**	−360.898 641		189.9
2	4	**20**	−721.874 179		166.1

[a] As in Figures 3 and 4. [b] Energy relative to the most stable isomer. [c] $E_B[CuP] = (1/m)E[(Cu_2Se)_n] + E[PR_3] - (1/m)E[(Cu_2Se)_n(PR_3)_m]$. [d] Reference 2.

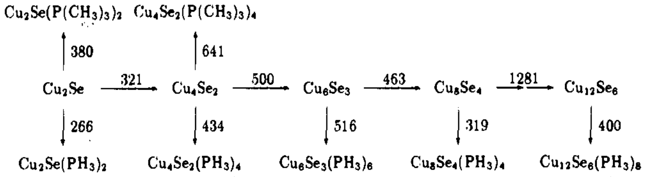

Figure 5. Simplified reaction scheme for the cluster growth and addition of ligands. Reaction energies have been obtained from MP2 calculations for the most stable localized isomers, respectively, and are given as absolute values in kJ/mol.

ligands. Reaction energies are given with respect to the most stable isomers, which implies that always the most stable structure is formed, possibly via isomerization processes. The result is straightforward: with PH_3 as the ligand, the cluster growth is always favored or at least competitive to the stabilization reaction. Larger ligands such as $P(CH_3)_3$ give larger bonding energies and are therefore capable of energetic stabilization. However, the reactions in Figure 5 are idealized cases. The species involved in the cluster growth are likely to be already partially covered with ligands, so the energetic stabilization attainable by complete saturation might not be competitive. Furthermore, entropy effects are important at finite temperatures which are not considered here.

Conclusions

We have discussed structures of bare clusters $(Cu_2Se)_n$ as well as ligand-covered species $(Cu_2Se)_n(PR_3)_m$ for $n = 1-6$, calculated on the MP2 and, for Cu_2Se and Cu_4Se_2, on the CCSD(T) levels. Several isomers have been found, especially for the dimer Cu_4Se_2. The energetic order of the isomers has been rationalized with the help of some basic structure principles: structures with as many "short" CuCu contacts as possible are favored, while three or four CuSe bonds are formed per Se atom. In case of two bond partners at Cu (Se−Cu−Se or Se−Cu−P), a linear arrangement is preferred, which is a well-known feature of the coinage metals in oxidation state +I. Three bond partners ideally result in trigonal planar coordination. These criteria strongly suggest the structures of $Cu_{12}Se_6$ (**11**) and $Cu_{12}Se_6(PH_3)_8$ (**18**) as found for $Cu_{12}Se_6(PR_3)_8$ experimentally and in ab initio calculations.[2] From the bonding energies per monomer unit, it is clear that the $(Cu_2Se)_n$ clusters are energetically not stable toward formation of the solid.

The coverage of the cluster surface with ligands clearly provides kinetical stabilization due to steric shielding. On the other hand, it has turned out that even the species saturated with ligands may be energetically unstable. Especially for PH_3 ligands, the amount of energy gained by ligand bonding can hardly compete with the cluster growth. Ligands with organic groups, e.g. $P(CH_3)_3$, form stronger bonds to the cluster core, and the formation of the fully covered species is favored compared to the reaction of the bare cluster with another monomer unit. However, naked clusters are usually not present in reaction solutions and also completely covered species are unlikely because of ligand exchange and mobility, at least at sufficiently high temperatures. But clusters covered only partly with ligands might rather tend to add another monomer than to complete the ligand sphere. Nevertheless, there can be kinetic stabilization due to steric effects already in the partly covered clusters, depending on the ligand. It should therefore be expected that the isolation of the small clusters requires ligands with large organic groups for effective steric shielding, and perhaps cooling to reduce ligand mobility.

The bonding of ligands affects the cluster structures significantly in cases where the aspired linear or trigonal planar coordination of the Cu atoms leads to steric repulsion of the ligands. The clusters give way to this strain by relaxation along weak modes in the cluster core which involve mainly the CuCu contacts. Steric interactions in the ligand sphere can change the energetic order of isomers compared to the naked clusters or may even make an isomer impossible, as has been found for $Cu_4Se_2(PH_3)_4$. In cases where steric repulsion is marginal (as in **12**), the main effect introduced by the ligands is the partial electron transfer to the Cu atoms, leading to larger CuCu distances.

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