An Ab Initio Study of Structures and Energetics of Copper Sulfide Clusters

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Abstract: The results of ab initio calculations for the sulfur-bridged copper clusters $[Cu_{2n}S_n(PR_3)_m]$ ($n = 1-4, 6$; $m = 0, 2, 4, 6, 8$; R = H, CH_3) were compared with those of theoretical investigations of the selenium-containing analogues that have been recently reported. The theoretical work was carried out in order to find a possible explanation for the experimentally observed—different—properties of both cluster types. The structural principles turned out to be independent of the chalcogen, except the necessary shortening of the copper–chalcogen atomic distance that results from the formal substitution of sulfur for selenium. Comparison of the energetics of the sulfur- and selenium-containing compounds showed that it is necessary to discuss the influence of the tertiary phosphine ligands that protect the existing clusters from reaction to give the solids Cu_2S and Cu_2Se. However the results of the calculations suggest that the different thermodynamic data of the cluster core and the Cu–P bonds—at least if PH_3 or PMe_3 are taken into account—cannot be the only cause for the differences in the experimental behaviour. The responsibility rests rather with kinetic effects, such as the steric demand of the actual ligands or the activation energy of decomposition of the ligand shell during the cluster-forming reaction.

Keywords
ab initio calculations · chalcogen compounds · copper clusters · ligand stabilisation · thermodynamics

Introduction

Comprehensive theoretical investigations of selenium-bridged copper clusters of the general formula $[Cu_{2n}Se_n(PR_3)_m]$ ($n = 1-4, 6$; $m = 0, 2, 4, 6, 8$; R = H, CH_3), with and without a ligand shell, have recently been reported.[1] From these investigations, basic principles that govern the structure and stability of such molecules were determined. These rules were confirmed for the calculated structure of the hexamer $[Cu_{12}Se_6]$ (O_h symmetry), in which the undistorted Cu–Se framework corresponds to that found in the recently synthesised compound $[Cu_{12}Se_6(PEtPh_2)_8]$, which has been characterised by X-ray crystallography.[2] The resulting tetragonal distortion of the cluster structure through the coordination of the tertiary phosphine ligands can be predicted by calculating the corresponding eightfold PH_3-substituted species. Both the calculated and the experimental results give comparable structural parameters within the limits of the methods used.[2]

The compound $[Cu_{12}Se_6(PEtPh_2)_8]$ is the smallest known Cu–Se cluster and has been up till now the only example available for a structural comparison between selenium and sulfur-containing copper clusters. Meanwhile a whole series of isostructural sulfur-bridged copper clusters of the formula $[Cu_{12}S_6(PRR'_2)_8]$ (R = Et, *n*Pr, Ph; R' = Et, Ph) has been reported.[2, 3] There is a larger number of bigger selenium-bridged clusters known, as opposed to the Cu–S clusters, of which only this single structure type has been reported as well as the formal condensation product $[Cu_{20}S_{10}(PPh_3)_8]$.[2, 4] $[Cu_{12}Se_6(PEtPh_2)_8]$ is obviously an intermediate product formed during the reaction of the formation of larger aggregates. This cluster crystallises at low temperatures from a dark brown solution in the form of light red crystals, which decompose within a few hours at room temperature. The sulfur-bridged form of "Cu_{12}" appears to be the end-product of the respective cluster-forming reaction. The compound $[Cu_{12}S_6(PEtPh_2)_8]$, in contrast to all other known chalcogen-bridged copper clusters, is not air- and water-sensitive.[5] One would therefore expect that the experimentally found sulfur-bridged hexamer would form a (meta)stable species with regard to growth into bigger clusters, while for selenium-containing clusters, ensuing uptake of further metal and chalcogen atoms—which always involves energy gain—is preferred. On the other hand, Dance et al. deduced from mass spectroscopic investigations of S- and Se-containing copper cluster ions that the range of products is independent of the chalcogen.[6]

We present here the results of calculations on sulfur-bridged copper clusters which, in conjunction with the calculations for analogous selenium-bridged species, should help to explain the experimental results. The series of ligand-free Cu–Se and Cu–S clusters has been extended with the recent calculations for the pentamer $[Cu_{10}E_5]$ and the decamer $[Cu_{20}E_{10}]$ (E = S, Se), the structures and energetics of which will be discussed here.

Methods

All the cluster structures presented were optimised within the framework of second-order Møller–Plesset-perturbation theory (MP2) [7] with analytically calculated energy gradients by means of the TURBOMOLE programme package [8]. To ascertain the minimum character, the SCF force constants of the compounds $[Cu_{2n}E_n]$

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(E = S, Se; $n \leq 6$) were calculated and the modes with wavenumbers less than 50 cm^{-1} were investigated by means of MP2 energy calculations for the structures distorted along these modes. For larger clusters, the energy minima were not characterised, but the structures of these molecules were calculated by following the structures of experimentally known species in the highest possible point group symmetry.

Effective core potentials (ECPs) were employed for all heavy atoms which described the inner shells (Cu: 18 core electrons [9a]; Se: 28 core electrons [9a]; S, P: 10 core electrons [9b]), the ECPs of Cu and Se including relativistic corrections. A decrease of the effective core of copper to 10 electrons has been discussed in ref. [10] and need not be taken into account. The basis sets (Cu: (325)/[222]; Se, S, P: (331)/[221]; C: (63)/[21]; H: (3)/[1]) were optimised for atoms and molecules [10,11].

Results and Discussion

Structures: The structures of the calculated ligand-free clusters $[Cu_{2n}S_n]$ ($n = 1-6$, 10), with the isomers listed in order of decreasing stability, are shown in Figure 1. This sequence is identical, with the exception of species **7** and **8**, for both S and Se bridging ligands (see Table 3). The most important atom distances and angles are given in Table 1. The numbers in parentheses in both the table and in the following text refer to the values of the analogous Se-bridged structures.[1,12]

The topology of the various cluster structures, with the exception of the pentamer and decamer, have been discussed in detail in ref. [1], therefore only the pentamer and the decamer will be described here. The molecular structure of $[Cu_{10}E_5]$ (E = S: **11a**; E = Se: **11b**) with D_{3h} symmetry can be derived from the structure of the tetramer $[Cu_8E_4]$ with C_s symmetry (E = S: **9**) in the following way: a further Cu_2S unit can be formally added in the mirror plane of **9**, so that in **11a** a Cu_3S_3 heterocycle (Cu2, S1 and their symmetry equivalents) surrounds a central copper atom. In **9** the two Cu_3 triangles, situated above and below this plane, lean towards each other, thus facilitating an additional short Cu3–Cu3′ contact of 250.7 pm (247.1 pm). As a result of the inclusion of three further atoms in **11a**, this Cu–Cu contact is no longer possible, and both the Cu_3 triangles lie parallel to each other. The distance from the central copper atom (Cu1) to the surrounding copper atoms in the Cu_4S_3 plane, in **11a**, is 214.2 pm (215.4 pm in **11b**), which is the shortest Cu–Cu distance found up till now in investigations of sulfur and selenium-bridged copper clusters. Nevertheless there does not appear to be a strong covalent binding force between the copper atoms. A population analysis of the SCF wavefunction after Ahlrichs and Ehrhardt[13] results in a shared electron number (s.e.n.) of only 0.25 for Cu1 and Cu2 in **11b**, as in Cu_2Se, and thereby indicates a very weak covalent contribution to the bonding[10] (for comparison: in Cu_2, one has a s.e.n. of 1.2 in the equilibrium (222 pm) and a s.e.n. of 1.1 for a Cu–Cu distance of 252 pm). The dispersion-like interaction of the d^{10} shells causes only a weak interaction between the copper atoms. The grip of the surrounding chalcogen framework is the main cause of the shortest Cu–Cu distances (below 230 pm).

The structure optimisation for the decamer $[Cu_{20}E_{10}]$ (E = S: **13a**; E = Se: **13b**) in D_{4h} symmetry has been started with the structural parameters of the experimentally found molecule $[Cu_{20}S_{10}(PPh_3)_8]$.[2] Again, as previously discussed in ref. [2], the resulting cluster framework can be derived from the hexamer $[Cu_{12}E_6]$ through formal condensation.

Further consideration will be restricted to the comparison of sulfur and selenium-bridged copper clusters. Correlated to the smaller atom radius of sulfur to selenium (104 vs. 117 pm),[14] the Cu–S distances are all smaller than the corresponding Cu–Se distances. The difference ranges from 8 (in **9**) to 19 pm (in **13a**). One finds shorter as well as longer Cu–Cu distances when making the comparison with the selenium analogues. The

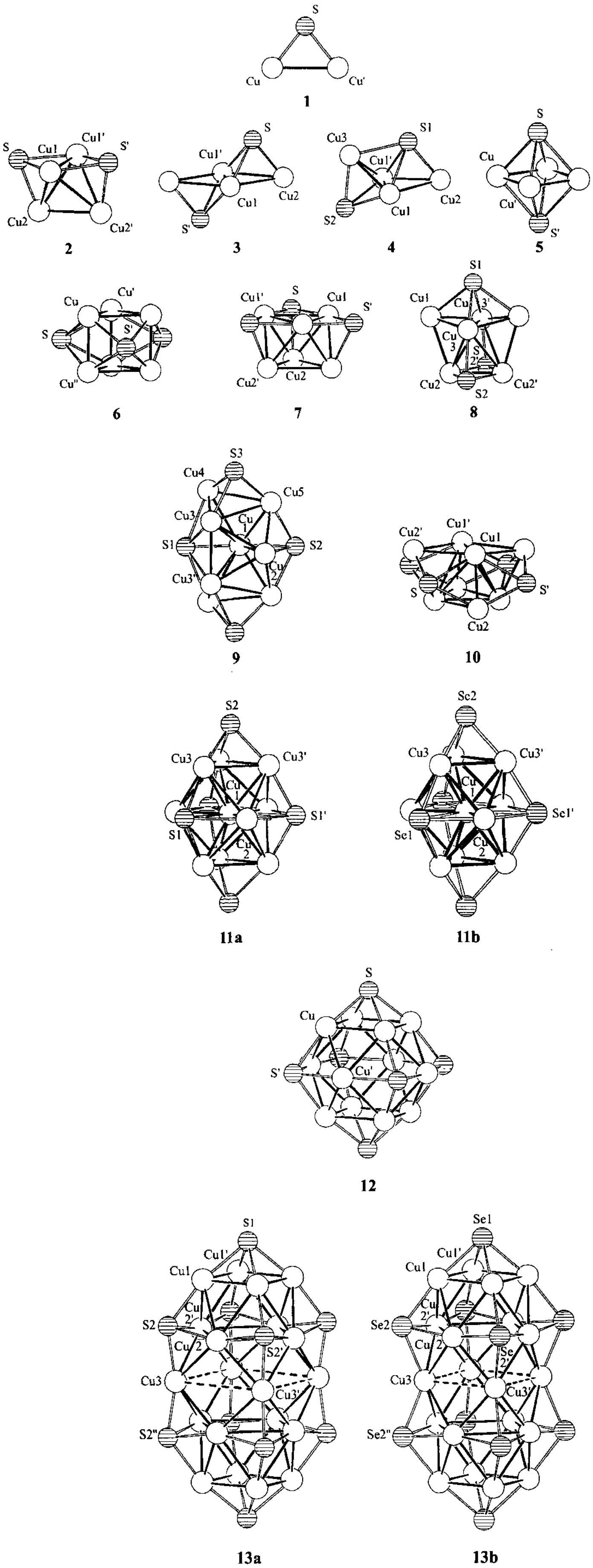

Fig. 1. Calculated structures of the ligand-free clusters **1–13**.

Table 1. Calculated distances and angles in the ligand-free clusters **1**–**13**; values given in parentheses are for the corresponding selenium-bridged clusters [1].

n	Structures [a]	Symmetry	Distances [pm] and angles [°]
1	**1**	C_{2v}	Cu–Cu′ = 251.6 (252.1), Cu–S = 208.7 (220.0)
2	**2**	C_{2v}	Cu1–Cu1′ = 218.5 (221.6), Cu1–Cu2 = 260.8 (260.2), Cu2–Cu2′ = 272.9 (261.2), Cu2–S = 211.8 (222.8), Cu1–S = 226.4 (237.0), S-Cu1-S′ = 122.1 (123.9)
	3	C_{2h}	Cu1–Cu1′ = 217.2 (221.2), Cu1–Cu2 = 265.1 (258.8), Cu2–S = 211.4 (223.4), Cu1–S = 226.3 (236.6), S-Cu1-S′ = 122.7 (124.3)
	4	C_s	Cu1–Cu1′ = 229.4 (235.3), Cu1–Cu3 = 232.3 (233.2), Cu1–Cu2 = 252.8 (247.9), Cu2–S1 = 212.2 (224.3), Cu3–S2 = 223.6 (235.5), Cu1–S2 = 223.9 (233.8), Cu1–S1 = 236.6 (248.8), Cu3–S1 = 247.4 (250.4), S1-Cu1-S2 = 110.8 (112.4), S1-Cu3-S2 = 107.1 (111.2)
	5	D_{4h}	Cu–Cu′ = 221.3 (222.8), Cu–S = 136.3 (245.8), S-Cu-S′ = 97.1 (100.3)
3	**6**	D_{3h}	Cu–Cu″ = 217.7 (220.2), Cu–Cu′ = 248.5 (249.0), Cu–S = 230.5 (240.4), S-Cu-S′ = 121.7 (124.4)
	7	C_{3v}	Cu1–Cu2 = 248.3 (248.6), Cu2–Cu2′ = 265.2 (258.4), Cu1–Cu1′ = 265.5 (268.1), Cu2–S = 217.6 (228.0), Cu1–S = 218.6 (229.5), S-Cu1-S′ = 165.2 (168.5)
	8	C_{2v}	Cu2–Cu2′ = 219.7 (223.2), Cu1–Cu3 = 233.4 (233.2), Cu1–Cu2 = 249.2 (244.8), Cu2–Cu3 = 270.1 (275.2), Cu3–Cu3′ = 278.9 (284.1), Cu2–S2 = 212.4 (223.1), Cu3–S1 = 223.4 (233.5), Cu2–S2 = 226.2 (236.6), Cu1–S1 = 231.4 (242.3), S1-Cu3-S2 = 157.3 (159.9), S2-Cu2-S2′ = 121.9 (123.7)
4	**9**	C_s	Cu3–Cu4 = 222.3 (224.8), Cu2–Cu5 = 231.7 (232.2), Cu1–Cu5 = 249.37 (253.2), Cu2–Cu3 = 250.7 (247.9), Cu3–Cu3′ = 250.7 (247.1), Cu1–Cu4 = 257.0 (255.7), Cu1–Cu2 = 264.4 (260.6), Cu3–Cu5 = 268.1 (274.9), Cu4–Cu5 = 271.1 (267.1), Cu1–Cu3 = 272.5 (275.7), Cu5–S3 = 214.9 (225.3), Cu3–S3 = 220.3 (230.0), Cu5–S2 = 221.7 (231.1), Cu1–S1 = 221.7 (232.1), Cu1–S2 = 223.2 (233.3), Cu4–S3 = 225.2 (236.6), Cu3–S1 = 233.3 (243.6), Cu4–S1 = 243.2 (251.1), Cu2–S2 = 240.9 (254.5), S2-Cu5-S3 = 161.4 (164.0), S1-Cu1-S2 = 159.0 (163.7), S1-Cu3-S3 = 125.6 (127.5), S1-Cu4-S3 = 118.9 (120.9)
	10	D_{2d}	Cu1–Cu2 = 220.6 (223.7), Cu1–Cu2′ = 260.4 (260.1), Cu1–Cu1′ = 264.8 (262.2), Cu1–Cu1″ = 278.0 (275.4), Cu2–S = 223.4 (233.1), Cu1–S = 234.0 (245.2), S-Cu2-S′ = 126.3 (127.6), S-Cu1-S′ = 116.8 (117.1)
5	**11a (11b)**	D_{3h}	Cu1–Cu2 = 214.2 (215.4), Cu1–Cu3 = 242.6 (245.6), Cu3–Cu3′ = 262.8 (262.9), Cu2–Cu3 = 268.7 (272.1), Cu3–S2 = 217.4 (227.1), Cu3–S1 = 219.0 (228.7), Cu2–S1 = 241.6 (250.2), Cu1–S1 = 261.9 (274.4), S1-Cu3-S2 = 165.9 (170.6), S1-Cu2-S1′ = 139.7 (143.6)
6	**12**	O_h	Cu–Cu′ = 249.3 (252.0), Cu–S = 223.4 (233.3), S-Cu-S′ = 165.8 (170.4)
10	**13a (13b)**	D_{4h}	Cu1–Cu1′ = 245.9 (251.2), Cu1–Cu2 = 258.5 (256.9), Cu2–Cu3 = 264.4 (256.9), Cu2–Cu2′ = 297.3 (301.5), Cu3–Cu3′ = 391.8 (326.0), Cu3–S2 = 215.6 (234.9), Cu1–S2 = 219.7 (232.0), Cu2–S2 = 221.3 (229.2), Cu1–S1 = 223.4 (233.5), S1-Cu1-S2 = 166.7 (168.9), S2-Cu3-S2″ = 163.2 (134.4), S2-Cu2-S2′ = 160.7 (165.8)

[a] See Figure 1.

relatively loose copper substructures (compare the Cu–Cu force constant of 23 N m^{-1} in Cu_2Se)[10] are easily deformed and follow the changes of the chalcogen framework. For doubly bridged Cu–Cu contacts the metal–metal distances found in the S-bridged clusters are always shorter (a maximum of 6 pm in **4**). With only one or no bridges the Cu–Cu contacts are, in general, longer (a maximum of 12 pm in **2**) than those found in the corresponding Cu–Se clusters. The biggest difference is found for $Cu_{20}E_{10}$ (**13a**, **13b**). The Cu3–Cu3′ distance is 66 pm larger in **13a** than in **13b**; this can be explained in the following manner: in **13a** the four equatorial copper atoms (Cu3 and its symmetry equivalents) are forced further out by the shortened copper–chalcogen bond Cu3–S2 (19 pm shorter than Cu3–Se2 in **13b**). No bridging chalcogen atoms that would stabilise shorter Cu–Cu distances exist around Cu3. At the same time, this enlargement of the equatorial Cu_4 ring in **13a** causes an increase in the S2-Cu3-S2′ angle of 29° with respect to the Se2-Cu3-Se2′ angle in **13b**. All other S-Cu-S angles in the Cu–S clusters discussed are smaller than those found in the analogous selenium-bridged species. The sulfur atoms are therefore more closely packed around the copper framework than the selenium atoms in the corresponding structures, so the volumes of the sulfur-bridged clusters are smaller.

As the isolated clusters always appear as ligand-protected molecules, it is necessary to discuss the influence of the phosphine ligands as the deciding parameter for the structure of copper clusters. The influence of differently substituted tertiary phosphines can be seen from many experimental examples of copper selenide clusters.[4] Calculations for copper selenide clusters also show the typical deformation as soon as PR_3 groups coordinate to the copper atoms: the copper atoms affected are forced to move slightly out of the polyhedron, while the ligand-free copper atoms move towards the centre of the cluster. The Cu–Se bond lengths remain almost unchanged with respect to the "naked" clusters.[1]

The structures of the sulfur-containing molecules with PH_3 ligands for which calculations were carried out are shown in Figure 2. The structure parameters are given in Table 2—again the values in parentheses are for the corresponding selenium clusters.[15a] For the ligand-coated species of the sulfur and selenium-bridged copper clusters, qualitatively identical structures with a corresponding order of energy were obtained. The above-mentioned changes in structure, based on the binding of PH_3 groups, affect both sulfur and selenium-containing structures in the same way.[15b]

Energetics: By considering the calculated stabilisation energies per Cu_2E monomeric unit [Eq. (1)], it is possible to make a

$$E_n = 1/n\,E(Cu_{2n}E_n) - E(Cu_2E) \qquad (1)$$

comparison of the relative stabilities of sulfur- and selenium-bridged clusters. Table 3 shows the total energies, E, calculated with the MP2 method, the relative energies of different isomers ΔE_{rel} and the stabilisation energies per monomeric unit, E_n, for the "naked" clusters. The change in the stabilisation energy per monomeric unit for the most stable Cu–S and Cu–Se cluster isomers is shown in Figure 3. For clusters up to $n \leq 5$, the difference in stabilisation energy of the respective species of both cluster types is not large, with a maximum of ± 5 kJ mol^{-1} within the expected errors of the method. It is only from $n = 6$ that a trend to higher binding energies in the sulfur-bridged clusters can clearly be seen, which is expected when one considers the higher enthalpy of formation of solid Cu_2S (-83.4 kJ mol^{-1}[16]) as compared with that of solid Cu_2Se

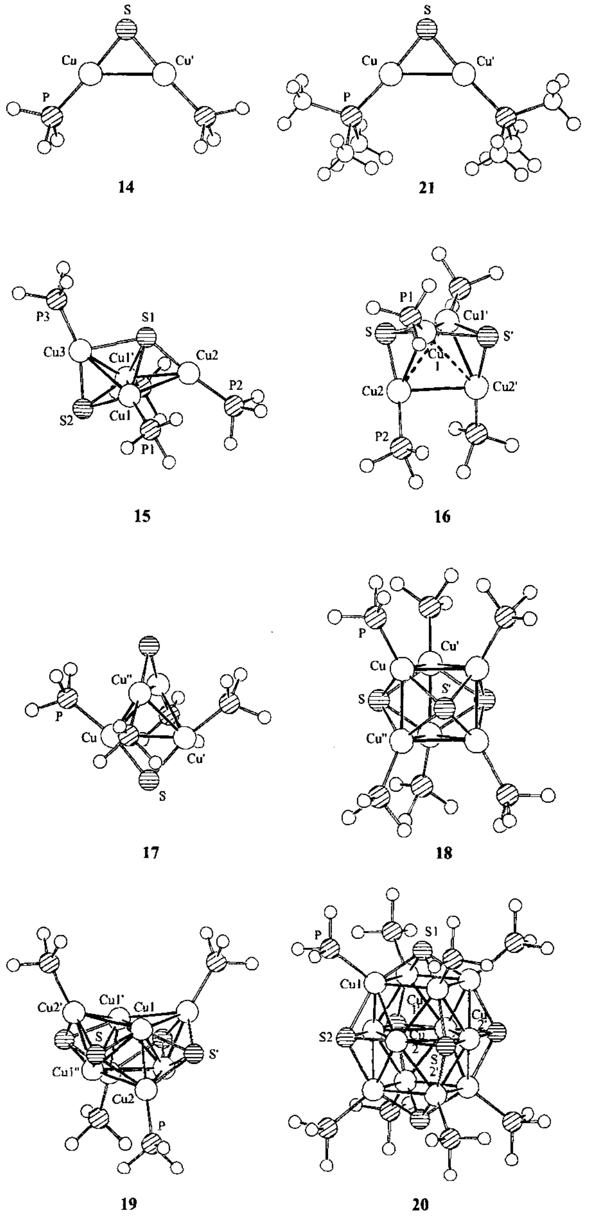

Fig. 2. Calculated structures of the ligand-containing clusters **14**–**21**.

(– 59.3 kJ mol^{-1} [16]). With reference to the stabilisation energies E_n of the Cu–S clusters, the differences in stabilisation energy that result from the chalcogen substitution amount to less than 5% for the clusters investigated here. It is therefore understandable that Dance et al. observe basically chalcogen-independent mass spectra from the laser ablation of the cluster ions from the respective solids.[6]

As previously mentioned, the sulfur-bridged copper clusters known up till now have only been isolated in the form of the hexamer and the formal condensation product, which distinguishes them from the generally bigger selenium-bridged compounds. The energetics of the "naked" clusters offer no explanation for this; although the stabilisation energies E_n of clusters with $n > 10$ would be necessary in order to be able to interpret the course of the graph in Figure 2 with more certainty, it can still be clearly discerned that $[Cu_{12}S_6]$ does not have a substantially higher stability than $[Cu_{12}Se_6]$.

In order to find a relationship to the real cluster systems, one should consider the energetics of the PH_3-coordinated species.

Table 2. Calculated distances and angles in the ligand-free clusters **14**–**21**; values given in parentheses are for the corresponding selenium-bridged clusters [1].

n	Structure [a]	Symmetry	Distances [pm] and angles [°]
1	**14**	C_{2v}	Cu–Cu′ = 268.7 (269.5), Cu–S = 209.1 (220.3), Cu–P = 213.6 (214.5), S-Cu-P = 176.6 (176.3)
2	**15**	C_s	Cu1–Cu1′ = 256.5 (258.2), Cu1–Cu3 = 261.5 (258.1), Cu1–Cu2 = 266.8 (261.8), Cu2–S1 = 210.7 (223.0), Cu3–S2 = 218.8 (232.0), Cu1–S2 = 225.5 (234.9), Cu1–S1 = 235.1 (247.2), Cu3–S1 = 250.6 (251.4), Cu1–P1 = 213.7 (215.5), Cu2–P2 = 213.7 (215.1), Cu3–P3 = 213.9 (215.3), S1-Cu1-S2 = 100.1 (103.8), S1-Cu3-S2 = 97.3 (103.3), S1-Cu2-P2 = 175.4 (174.0), S2-Cu3-P3 = 158.6 (147.8), S1-Cu1-P1 = 132.81 (129.7), S2-Cu1-P1 = 127.1 (126.4), S1-Cu3-P3 = 104.1 (108.9)
	16	C_2	Cu1–Cu1′ = 247.9 (244.4), Cu1–Cu2 = 256.6 (251.0), Cu2–Cu2′ = 274.9 (260.4), Cu1–Cu2′ = 313.0 (323.9), Cu2–S = 210.5 (222.7), Cu1′–S = 227.5 (237.7), Cu1–S = 231.7 (244.3), Cu2–P2 = 214.3 (216.0), Cu1–P1 = 217.6 (218.3), S-Cu1-S′ = 112.3 (112.8), S-Cu2-P2 = 166.4 (172.1), S-Cu1-P1 = 129.3 (126.7), S′-Cu1-P1 = 117.6 (120.3)
	17	D_{2d}	Cu–Cu″ = 262.9 (259.3), Cu–Cu′ = 279.3 (284.4), Cu–S = 211.2 (222.3), Cu–P = 217.3 (218.3), S-Cu-P = 168.9 (166.2)
3	**18**	D_3	Cu–Cu″ = 248.7 (248.9), Cu–Cu′ = 265.6 (267.0), Cu′–S = 229.1 (239.2), Cu–S = 230.3 (240.5), Cu–P = 218.7 (229.1), S-Cu-S′ = 109.8 (114.3), S′-Cu-P = 128.1 (125.7), S-Cu-P = 120 6 (118.0)
4	**19**	D_{2d}	Cu1–Cu2 = 231.6 (234.7), Cu1–Cu1″ = 263.6 (260.5), Cu1–Cu2′ = 271.9 (271.2), Cu1–Cu1′ = 286.0 (280.4), Cu1–S = 220.4 (232.2), Cu2–S = 238.3 (246.5), Cu2–P = 217.4 (219.0), S-Cu1-S′ = 126.0 (125.1), S-Cu2-S′ = 111.1 (113.4), S-Cu2-P = 122.7 (120.7)
6	**20**	D_{4h}	Cu1–Cu2 = 255.4 (256.5), Cu1–Cu1′ = 169.9 (275.2), Cu2–Cu2′ = 291.5 (283.4), Cu2–S2 = 215.7 (227.6), Cu1–S1 = 224.8 (234.5), Cu1–S2 = 234.4 (242.1), Cu1–P = 230.5 (232.6), S2-Cu2-S2′ = 175.0 (167.0), S1-Cu1-S2 = 151.0 (155.1), S1-Cu1-P = 110.8 (107.2), S2-Cu1-P = 98.3 (97.7)
1	**21**	C_{2v}	Cu–Cu′ = 268.0 (269.0), Cu–S = 209.8 (221.2), Cu–P = 215.6 (216.3), S-Cu-P = 176.0 (176.0)

[a] See Figure 2.

Table 3. Total energies E, relative energies of isomers ΔE_{rel} and stabilisation energies E_n [c], calculated on the MP2 level for $[Cu_{2n}S_n]$, $[Cu_{10}Se_5]$ and $[Cu_{20}Se_{10}]$; values given in parentheses are for the corresponding selenium-bridged clusters [1].

n	Structure [a]	Symmetry	E [hartree]	ΔE_{rel} [b] [kJ mol^{-1}]	E_n [kJ mol^{-1}] [c]
1	**1**	C_{2v}	−111.173642	–	0.0 (0.0)
2	**2**	C_{2v}	−222.469127	0.0 (0.0)	159.9 (160.4)
	3	C_{2h}	−222.466426	7.1 (6.6)	156.4 (157.1)
	4	C_s	−222.460446	22.8 (10.3)	148.6 (155.3)
	5	D_{4h}	−222.449398	51.8 (23.7)	134.0 (148.5)
3	**6**	D_{3h}	−333.828105	0.0 (0.0)	268.8 (273.5)
	7	C_{3v}	−333.823907	11.0 (47.7)	265.1 (257.6)
	8	C_{2v}	−333.821597	17.1 (33.1)	263.1 (262.4)
4	**9**	C_s	−445.184457	0.0 (0.0)	321.5 (320.8)
	10	D_{2d}	−445.157056	72.0 (74.0)	303.6 (302.3)
5	**11a (11b)**	D_{3h}	−556.630481 [d]	–	400.3 (396.4)
6	**12**	O_h	−668.040254	–	436.9 (427.3)
10	**13a (13b)**	D_{4h}	−1113.492820 [d]	–	461.1 (442.0)

[a] See Figure 1. [b] Energy relative to the most stable isomer. [c] $E_n = 1/n\,E(Cu_{2n}S_n) - E(Cu_2S)$. [d] E for **11b**: −552.855945 hartree, for **13b**: −1105.885435 hartree.

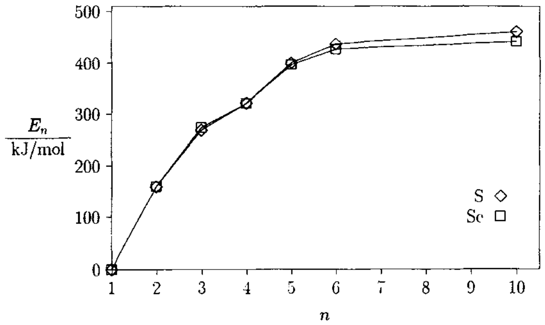

Fig. 3. Calculated MP2 stabilisation energies E_n [Eq. (1)] against increasing cluster size n for $[Cu_{2n}E_n]$ (E = S, Se).

It is helpful when comparing the energies of the sulfur and selenium-bridged clusters to consider the calculated average Cu–P binding energies in Equation (2), which show the energy

$$E_B = 1/m E(Cu_{2n}E_n(PR_3)_m) - 1/m E(Cu_{2n}E_n) - E(PR_3)^{[17]} \quad (2)$$

gain per Cu–P bond of the ligand-coated clusters as opposed to the unprotected species. Table 4 lists the total energies E calculated by the MP2 method, the relative energies of the different isomers ΔE_{rel} and the binding energies of the Cu–P bonds E_B. Figure 4 shows the graph of E_B against increasing number of monomeric units, n, for the most stable calculated PH_3-protected isomers.

Table 4. Total energies E, relative energies of the different isomers ΔE_{rel} and Cu–P bonding energies E_B [c], calculated on the MP2 level for $[Cu_{2n}S_n(PR_3)_m]$ (R = H for **14–20**, R = CH_3 for **21**); values given in parentheses are for the corresponding selenium-bridged clusters [1].

n	m	Structure [a]	Symmetry	E [hartree]	ΔE_{rel} [b] [kJ mol^{-1}]	E_B [c] [kJ mol^{-1}]
1	2	**14**	C_{2v}	−127.566686	–	140.2 (132.8)
2	4	**15**	C_s	−255.215176	0.0 (0.0)	115.6 (111.1)
	4	**16**	C_2	−255.205241	26.1 (23.3)	106.0 (102.8)
	4	**17**	D_{2d}	−255.196914	48.0 (47.1)	100.6 (96.8)
3	6	**18**	D_3	−382.899314	–	91.6 (86.0)
4	4	**19**	D_{2d}	−477.887154	–	102.1 (98.3)
6	8	**20**	D_{4h}	−733.356533	–	54.9 (50.0)
1	2	**21**	C_{2v}	−361.656238	–	195.4 (189.9)

[a] See Figure 2. [b] Energy relative to the most stable isomer. [c] $E_B = 1/m E(Cu_{2n}S_n(PR_3)_m) - 1/m E(Cu_{2n}S_n) - E(PR_3)$ [d]. [d] $E(PH_3) = -8.143141$ hartree (MP2); $E(P(CH_3)_3) = -125.166886$ hartree (MP2).

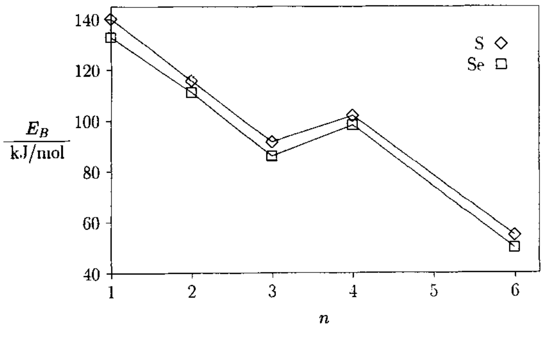

Fig. 4. Calculated Cu–P binding energies E_B [Eq. (2)] against increasing cluster size n for $[Cu_{2n}Se_n(PR_3)_m]$ (see text and Table 4).

The qualitative course of E_B is in agreement for both the copper sulfide and the copper selenide clusters. The binding energy for each PH_3 ligand decreases with increasing cluster size. At the same time the Cu–P bond length increases steadily from 213.6 (in **14**) to 230.5 pm (in **20**) (see Table 3). From an extrapolation of the initial almost linear drop of E_B against n, it can be seen that around the tetramer, the coordination of $2n$ PH_3 molecules to $[Cu_2E]_n$ would be unfavourable, because of the low binding energy. From this it can be predicted that less than $2n$ PH_3 ligands will bind to the Cu–E framework. Another reason for the coordination of fewer phosphine ligands is the decreasing surface-to-volume ratio with increasing cluster size, as far as one considers spherical clusters. So far, all crystallographically characterised Cu–S and Cu–Se clusters exhibit (not least because of the location of copper atoms within the central part of the molecule) Cu to P ratios of >1 (1.5–4.9[2, 4]). This ratio increases with growing cluster size, in agreement with the theoretical results.

The average Cu–P binding energies, E_B, are about 4–7 kJ mol^{-1} higher for all the sulfur-containing clusters than in those with selenium; this agrees with the aforementioned shorter Cu–P bond lengths. Figure 5 shows a simplified reaction scheme in which the calculated total binding energies, $m \times E_B$, and the energy values for the concurrent reaction of the formal uptake of further monomeric units are given. As with the selenium-containing analogues, one can determine that the cluster growth without ligands (with the exception of the trimer) is favoured with regard to the coordination of a ligand shell, so that these compounds—at least with PH_3 as ligand—can at best contribute to the kinetic stabilisation of the cluster compound. Tertiary phosphines—for example $P(CH_3)_3$ in **21**—result in larger binding energies here as well as in the Cu–Se compounds and can also contribute to energetic stabilisation, at least for $[Cu_2S(P(CH_3)_3)_2]$ (**21**). The increase in the Cu–P binding ener-

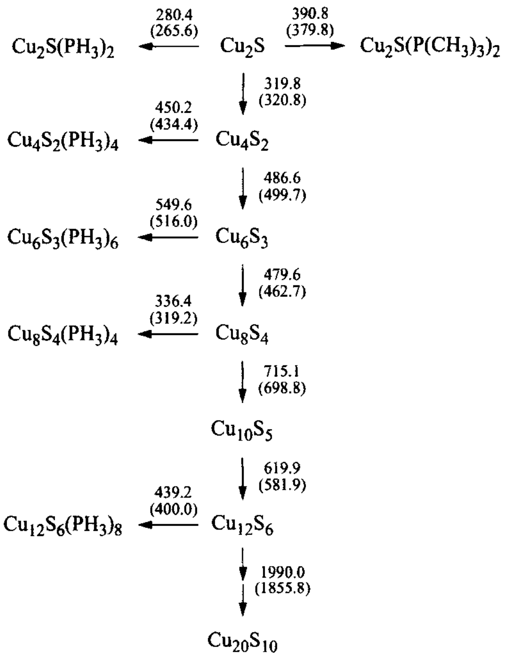

Fig. 5. Simplified reaction scheme for both cluster-growth and ligand-coordination reactions starting from Cu_2S. Values given for the reaction energies (see Tables 3 and 4) in kJ mol^{-1} correspond to the formation of the most stable isomers; if necessary, isomerisation has been assumed. Values given in brackets are for the corresponding selenium-bridged clusters [1].

gy when R is changed from H to CH_3 of 55 vs. 57 kJ mol^{-1} is nearly the same for both sulfur and selenium-containing monomers.[1, 12] If one considers the Cu–P binding energies of the ligand-protected Cu–S and Cu–Se clusters as determined from MP2 calculations as well as the stabilisation energies of both types of clusters, one can ascertain that for the PH_3-containing Cu–S clusters, the apparent energy advantages (ca. 4–9% with regard to the binding energies for E = S) are somewhat bigger than the apparent energy advantages for $n \geq 4$ for the "naked" sulfur-containing copper clusters (ca. 0.5–6.5% with regard to the stabilisation energies for E = S). This makes it easier to understand the discrepancy between the experimental result of Dance concerning ligand-free clusters and the experimentally found range of products and properties of PR_3-protected clusters. However, comparison of the calculated Cu–P binding energies of both cluster types does not show the PH_3-coated sulfur-containing hexamer to be much more thermodynamically favoured than the selenium-containing one, which does not agree with the expectations based on the experimental experience mentioned above. Nevertheless, the biggest E_B difference (9% with regard to the binding energies for E = S) does in fact appear in $[Cu_{12}E_6(PH_3)_8]$.[2]

All theoretical investigations that have been carried out up till now suggest that the experimentally found significant "island of stability" is caused mainly by a kinetic effect: the different ranges of products which are obtained when reacting complexes of Cu(I) salt and tertiary phosphines with sulfur- or selenium-containing compounds are caused by different steric effects of the more or less tailor-made ligand shell that surrounds each cluster compound. The copper selenide framework of "$Cu_{12}Se_6$" seems to be protected effectively only by the bulky $PEtPh_2$ ligand, while sterically less effective substituents allow the further uptake of metal and chalcogen atoms. In contrast, as the Cu–S cluster cores have smaller volumes than the Cu–Se cluster cores because of the shortened Cu–E distances, even less bulky phosphine ligands (e.g., PEt_3, PEt_2Ph) protect the sulfur-containing hexamer from cluster growth. If one reacts tertiary phosphines that are larger than $PEtPh_2$, the ligand shell will be forced to move away from the copper chalcogenide cluster core, which causes breakage of the weak Cu–P bonds, permitting the formation of bigger aggregates. The only example known up till now for the case of Cu–S clusters is $[Cu_{20}S_{10}(PPh_3)_8]$.[2]

In addition, another kinetic effect might be responsible for the phenomenon: since all differences in the Cu–P binding energies between ligand-coated Cu–S and Cu–Se clusters turn out to be approximately 5 kJ mol^{-1}, one could imagine that the activation energies required to break the Cu–P bond of sulfur- or selenium-bridged copper clusters differ from each other by about the same amount. Thus, from the Arrhenius equation[18] [Eq. (3)], the increase in activation energy E_a corresponds to a

$$k = A\,e^{-E_a/RT} \qquad (3)$$

decrease in the reaction rates. At a temperature of 250 K (typical for the cluster formation), an additional 5 kJ mol^{-1} is sufficient to decrease reaction rates for the hypothetical detachment of the ligand shell to one tenth of those for the Cu–Se cluster.

Conclusion

The structures and energetics of sulfur-bridged copper clusters with and without ligand shells, $[Cu_{2n}S_n(PR_3)_m]$ ($n = 1$–6, 10; $m = 0, 2, 4, 6, 8$; R = H, CH_3), were investigated by ab initio methods. The results were then compared with the selenium-containing analogues.[1, 2, 9] Furthermore, the series of the calculated Cu–Se cluster structures was extended with the addition of the $Cu_{10}Se_5$ and $Cu_{20}Se_{10}$ species.

The structure parameters of both cluster types are qualitatively identical. Differences in bond lengths and angles are all understandable given the smaller atomic radius of sulfur with regard to selenium. The shorter Cu–P distances that are found for the PH_3-coated Cu–S molecules can be reconciled with the somewhat larger electronegativity of sulfur as opposed to selenium and thus the slightly stronger polarisation of the affected copper atoms.

The calculated stabilisation energy per monomeric unit of the "naked" copper sulfide clusters is similar to that of the selenium-bridged species up to $n = 5$. From $[Cu_{12}S_6]$ a trend to higher binding energies in the Cu–S clusters can be seen that corresponds with the enthalpy data of the solids Cu_2S and Cu_2Se. The calculated average Cu–P binding energies of the PH_3-containing compounds were found to amount to 4–7 kJ mol^{-1} more in all the sulfur-bridged clusters. There is thus no indication from the binding energies of a special preference for the formation of the hexamer in the series of sulfur-bridged copper clusters in comparison to the selenium-bridged species.

A probable cause for the difference in the chemistry in the two families of chalcogen-bridged clusters lies rather in the different "atom densities" of the cluster cores found for the two chalcogens. Thus it follows that the spatial requirements of the ligand shells, which stabilise the clusters kinetically, play an important role. For the more "compact" Cu–S clusters, less sterically demanding PR_3 ligands can provide effective protection for the hexamer core from further cluster growth, whereas in the selenium-containing compounds, there is only one example (with $PEtPh_2$) in which the optimal shell is achieved.

Another reason that follows from a kinetic effect concerning the already formed hexameric cluster might be the activation energy for the detachment of the ligand shell, which is necessary for the uptake of further copper and chalcogen atoms. If the activation energies for this hypothetical breaking of one Cu–P bond were about 5 kJ mol^{-1} higher for the Cu–S clusters than the Cu–Se clusters—corresponding to the Cu–P binding energy differences—one would expect reaction rates for the detachment of the ligand shell of one tenth of the rate for selenium-bridged copper clusters at typical reaction temperatures.

In order to be able to interpret the experimental observations better, it is necessary to continue the investigations with calculations for larger cluster compounds, with and without the ligand shell and, where applicable, to include the actual ligands used. This might show the larger sulfur-bridged clusters to be at an energy disadvantage, which could be more marked than the gradual advantages of the smaller Cu–S clusters that can be inferred from the present calculations. However, the corresponding investigations at the necessary level cannot be carried out at the moment because of the huge computational expenditure.

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[15] a) The structural parameters of $[Cu_{12}S_6(PH_3)_8]$ (**20**) correspond to those obtained in the experimental structure of $[Cu_{12}S_6(P\mathit{n}PrPh_2)_8]$ [3], which has the least distorted Cu–S cluster core. The differences in the Cu–Cu bond distances between the calculated and the experimental structures are very small for the Cu–S and the Cu–P bond lengths (0–4 pm) and bigger for most of the (nonbonding) Cu–Cu distances (3–22 pm). However, one should notice that Cu–Cu distances that are equivalent in **21** differ by up to 15 pm in the experimental structure. b) As with the ligand-free clusters, the range of Cu–E and Cu–Cu distances is bigger in the case of sulfur-containing compounds than for those containing selenium. Likewise one finds that through the substitution of sulfur for selenium, a significant decrease of Cu–E distances—13 pm (in **15**) to 8 pm (in **19**)—is observed. However, in one case, there is almost no change (Cu3–S1 in **15**). At 250.6 pm (251.4 pm), this metal–chalcogen bond is the longest found in these investigations. Also the metal–metal distances are for the most part shorter in the sulfur-containing clusters. The deviation of ±5 pm compared with the copper selenide clusters is small, in fact there are bigger differences to be found in some cases when comparing with the "naked" clusters; the Cu–Cu contacts with a maximum of one sulfur bridge are particularly affected (e.g., **20**: Cu2–Cu2′) as well as those which exhibit large metal-atom distances in both cluster types (e.g., **16**: Cu2–Cu2′). The comparison of S-Cu-S angles with the corresponding Se-Cu-Se angles gives the same result as for the ligand-free clusters (except the S-Cu1-S′ angle in **19**, +0.9°). The Cu–P bond lengths are up to 2 pm shorter in the sulfur-bridged clusters than in the selenium analogues. This might be put down to the slightly larger electronegativity of sulfur (2.58) [19] than selenium (2.55) [19] and therefore the associated somewhat stronger polarisation of the copper atoms.

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