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Gas phase inorganic synthesis: copper sulfide cluster anions react with phosphorus, P_4, to generate copper compounds with P_mS_n ligands

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Anions $[Cu_xS_y]^-$ reacted with P_4 (g) to form products which were formally addition of P_2 units, but are shown by density functional calculations and collisional induced dissociation to contain P_nS_m ligands co-ordinated to copper; the reactivities of the $[Cu_xS_y]^-$ ions correlate with their geometrical rather than electronic structures, according to the principles which are described.

The scope for syntheses of inorganic compounds in the gas phase is less well developed for negative ion precursors than for positive ions, partly because the lesser general reactivities of negative inorganic ions[1] have limited investigations using them. Recently we revealed[2] that metal sulfide anions are unusually reactive with S_8, H_2S and thiols, although not with oxygen homologues. We now report that $[Cu_xS_y]^-$ ($x = 1–6$, $y = 2–4$) ions also react with P_4 (g) to generate copper compounds with P_mS_n ligands ($m = 2$, $n = 1$ or 2), presaging general synthesis of more complex and significant inorganic systems,[3] and we describe the relevant principles of structure and reactivity.

Table 1 lists the products of reaction of eight $[Cu_xS_y]^-$ ions with P_4 (g), and the relative rates of reaction under the same conditions.* The ions $[CuS_2]^-$, $[CuS_3]^-$ and $[Cu_2S_3]^-$ react rapidly to add one P_2 unit, $[Cu_4S_3]^-$ rapidly adds one and then a second P_2 unit, $[Cu_2S_2]^-$ adds three P_2 units sequentially, the ions $[Cu_3S_3]^-$ and $[Cu_5S_4]^-$ add one or two P_2 units respectively but very much more slowly than the others, and $[Cu_6S_4]^-$ does not react. There is no evidence of direct addition of intact P_4, and the relative rates of reaction are clearly determined by factors other than size of the anion. This is in contrast to the rates of reaction of C_n^- ions with P_4 (g) which decrease monotonically with *n*.[4]

The structures of $[Cu_xS_y]^-$ and of the products of reaction with P_4 were investigated using density functional calculations.† The notation *x/y* and *x/y/z* is used for ions $[Cu_xS_y]^-$ and $[Cu_xS_yP_z]^-$ respectively, and isomers of each are labelled with letters **A**, **B**, **C**. The most stable isomers for the eight Cu_xS_y anions from $[CuS_2]^-$ to $[Cu_6S_4]^-$ are shown in Fig. 1. While $[CuS_2]^-$ is linear (**1/2A**), the $[Cu(S_3)]^-$ isomer **1/3A** is 150 kJ mol^{-1} more stable than the trigonal planar $[Cu(S)_3]^-$ isomer. For $[Cu_2S_3]^-$ the best connectivity is S–Cu–S–Cu–S, with the bent isomer **2/3A** only 4 kJ mol^{-1} more stable than the fully linear extended isomer: this demonstrates that linear S–Cu–S local co-ordination is a major factor while Cu–Cu interaction is a minor influence. The anion $[Cu_3S_3]^-$ is the D_{3h} isomer $Cu_3(\mu\text{-}S)_3$, while for $[Cu_4S_3]^-$ the isomer **4/3A** which allows linear local S–Cu–S co-ordination at two Cu but distortions at the other two Cu is 113 kJ mol^{-1} more stable than the next best isomer. [The S-void cubane isomer, $Cu_4(\mu_3\text{-}S)_3$, converts to **4/3A**.] The best $[Cu_5S_4]^-$ isomer is **5/4A** which allows approximately linear co-ordination at all Cu, and is effectively two fused **3/3A**. The high symmetry (T_d) isomer **6/4A** allows approximately linear S–Cu–S co-ordination at all Cu atoms.

The reactivity of the $[Cu_xS_y]^-$ ions with P_4 correlates with the geometrical structure of $[Cu_xS_y]^-$, specifically higher reactivity correlates with the occurrence of either (1) terminal CuS co-ordination (*e.g.* **1/2A** or **2/3A**), or (2) Cu atoms without linear SCuS co-ordination (*e.g.* **2/2A** or **4/3A**), or (3) underco-ordinated Cu atoms (*e.g.* **1/3A**): the most unreactive ions **3/3A**, **5/4A** and **6/4A** do not possess these features. The reactivity does *not* correlate with electronic structure, in that open configurations in the highest occupied molecular orbitals occur in

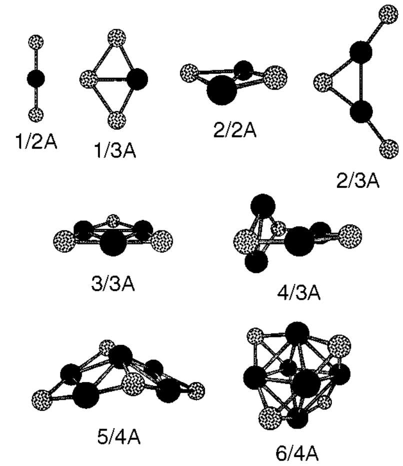

Fig. 1 Optimised structures of the most stable isomers for the eight $[Cu_xS_y]^-$ ions investigated here: the labels are *x/y*. Copper black, S stippled: Cu–Cu bonds are drawn where the distance is less than 2.7 Å

Table 1 Products and relative time-scales for the reactions $[Cu_xS_y]^-$ + P_4(g)

		Relative rate*	
$[Cu_xS_y]^-$	Product	Time for half conversion/s	Time for intermediate maximisation/s
$[CuS_2]^-$	$[CuS_2P_2]^-$	4	
$[CuS_3]^-$	$[CuS_3P_2]^-$	4	
$[Cu_2S_2]^-$	$[Cu_2S_2P_2]^-$		10
	$[Cu_2S_2P_4]^-$		20
	$[Cu_2S_2P_6]^-$	70	
$[Cu_2S_3]^-$	$[Cu_2S_3P_2]^-$	2.5	
$[Cu_3S_3]^-$	$[Cu_3S_3P_2]^-$	>100	
$[Cu_4S_3]^-$	$[Cu_4S_3P_2]^-$		5
	$[Cu_4S_3P_4]^-$	10	
$[Cu_5S_4]^-$	$[Cu_5S_4P_2]^-$		
	$[Cu_5S_4P_4]^-$	>100	
$[Cu_6S_4]^-$	No reaction	—	

* All reactions at the same pressure of P_4 (g), 1×10^{-5} Pa.

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* The uncorrected gauge pressure of P_4 (g) was 1×10^{-5} Pa. The $[Cu_xS_y]^-$ ions were generated by laser ablation of Cu_2S, and the reactions investigated by Fourier-transform ion cyclotron resonance mass spectrometry, following procedures previously described.[2]

† The Becke–Lee–Yang–Parr functional was used, with numerical basis sets; program DMol, MSI, San Diego, CA, USA.

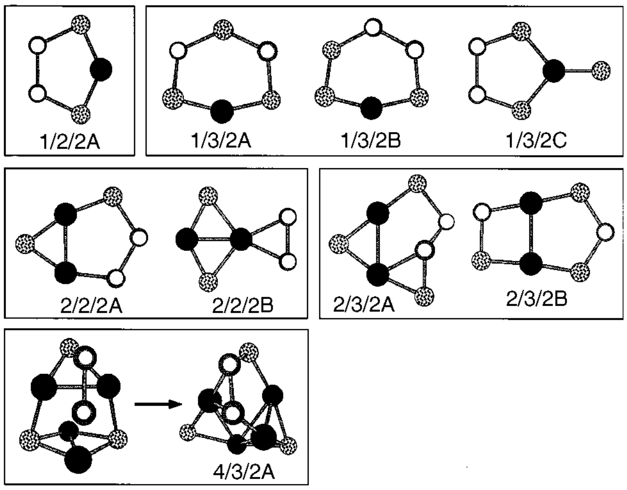

Fig. 2 Optimised structures of the more stable isomers of $[Cu_xS_yP_z]^-$, labelled ***x/y/z***: Cu black, S stippled, P white. Relative energies (kJ mol^{-1}) are: 0, +0.8, +35 for **1/3/2A,B,C** respectively; 0, +70 for **2/2/2A,B**; 0, +16 for **2/3/2A,B**

both reactive (**1/2A**) and unreactive (**3/3A**) ions, and reactive ions (such as **1/3A**) possess closed configurations with large HOMO–LUMO gaps.

The likely structures of the products of the $[Cu_xS_y]^-$ + P_4 reactions have also been explored, and some of the most energetically favoured of the 35 optimised structures are presented in Fig. 2. In general the P_2 units are most stably bound not as additional ligands to underco-ordinated Cu atoms, but P_mS_n units co-ordinated to Cu. This conclusion is exemplified by the following results (see also relative energies listed in the caption to Fig. 2): (1) isomer **1/2/2A** with SPPS chelation is 96 kJ mol^{-1} more stable than any $[CuS_2P_2]^-$ isomer with Cu–η^2-P_2 co-ordination; (2) isomer **2/2/2A** with SPP chelation is the barrierless rearrangement product of addition of P_2 across the face of **2/2A**, and is 70 kJ mol^{-1} more stable than **2/2/2B**; (3) isomer **2/3/2A**, the most stable of four investigated, results from addition of P_2 to the mouth of **2/3A**; (4) addition of P_2 to the face of **4/3A** as shown in Fig. 2 generates the most stable isomer **4/3/2A**.

The formation of P–S bonds and structures in which P_mS_n ligands co-ordinate Cu is not surprising since the S atoms in the anions are negatively charged (calculated atomic charges are $Cu^{0.05\text{ to }0.15}$, $S^{-0.35\text{ to }-0.6}$, with terminal S atoms more negative) and a P_2 moiety separating from P_4 would be electrophilic. In order to confirm these predictions of P_mS_n ligand formation we have investigated by collisional induced dissociation (CID, with Ar) the more abundant products $[Cu_2S_2P_2]^-$ and $[Cu_2S_3P_2]^-$. The anion $[Cu_2S_2P_2]^-$ yields P_2S^-, and $[Cu_2S_3P_2]^-$ yields P_2S^- and PS_2^-. These CID results are consistent with the structures **2/2/2A**, **2/3/2A** and **2/3/2B** which were calculated to be most stable, and thereby support strongly the other predictions of stable structures in Fig. 2. It is possible that the P_2S^- and PS_2^- anions are formed during CID of the adducts but similar CID experiments with nickel sulfide adducts $[Ni_2S_2P_4]^-$ and $[Ni_2S_2P_8]^-$ involve only loss of P_2 and P_4 units and no $P_xS_y^-$ anions are observed.[5]

The insight provided by this work can be summarised as: (1) reactivity for $[Cu_xS_y]^-$ correlates with geometrical characteristics more than electronic structure, and specifically with Cu atoms without pseudo-linear S–Cu–S co-ordination; (2) reactions of $[Cu_xS_y]^-$ with P_4 yield new species with P_mS_n ligands enveloping clustered Cu atoms;‡ (3) metal sulfide anions are reactive in the gas phase. Metal compounds with co-ordinated P_mS_n fragments have significance as lameller hosts (containing $P_2S_6^{4-}$),[8–10] and as electronic materials, and are generally prepared by moderate temperature elemental reactions[10] and in fluxes,[11] or by organometallic reactions.[12,13] We expect that the compounds and elementary reactions reported here will permit elaboration of these systems.§

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‡ There is analogy between the reaction of P_4 with $[Cu_xS_y]^-$ anions and the recently reported reaction of P_4 with the anionic nucleophile $Me_3SiCN_2^-$ to form a 1,2,3,4-diazadiphosphole ring.[6] The anion PS_3^- (g) has also been described.[7]

§ We have also observed the addition of Ph_3P as a capping ligand to $[Cu_xS_y]^-$, a reaction which is expected to stabilise the new clusters.[14]

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