

# 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  $P_mS_n$  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.

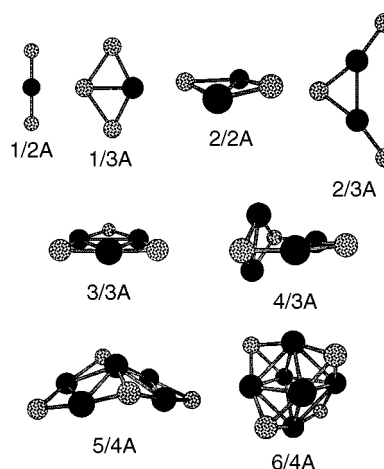
The scope for syntheses of inorganic compounds in the gas phase is less well developed for negative ion precursors than for positive ions, partly because the lesser general reactivities of negative inorganic ions<sup>1</sup> have limited investigations using them. Recently we revealed<sup>2</sup> that 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,<sup>3</sup> 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  $[Cu_2S_2]^-$  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  $n$ .<sup>4</sup>

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<sup>-1</sup> more stable than the trigonal planar  $[Cu(S_3)]^-$  isomer. For  $[Cu_2S_2]^-$  the best connectivity is S-Cu-S-Cu-S, with the bent isomer 2/3A only 4 kJ mol<sup>-1</sup> 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  $Cu_3(\mu-S)_3$ , 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<sup>-1</sup> more stable than the next best isomer. [The S-

void cubane isomer,  $Cu_4(\mu_3-S)_3$ , 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) undercoordinated 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

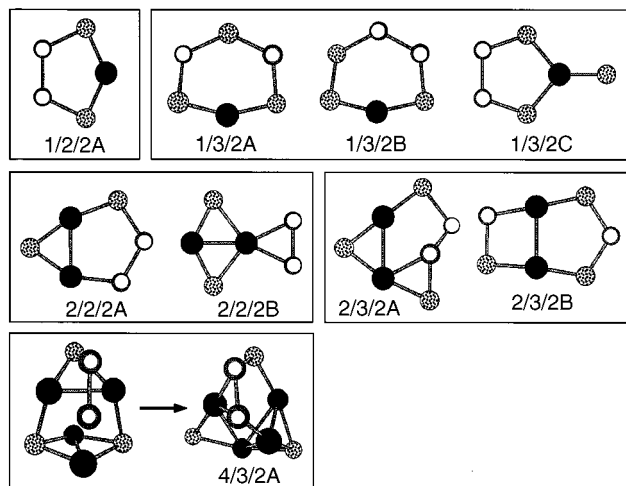
**Table 1** Products and relative time-scales for the reactions  $[Cu_xS_y]^- + P_4$  (g)

$[Cu_xS_y]^-$	Product	Relative rate*	
		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	
	$[Cu_2S_2P_8]^-$	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),  $1 \times 10^{-5}$  Pa.

\* The uncorrected gauge pressure of  $P_4$  (g) was  $1 \times 10^{-5}$  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.<sup>2</sup>

† 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  $[\text{Cu}_x\text{S}_y\text{P}_z]^-$ , labelled  $x/y/z$ : Cu black, S stippled, P white. Relative energies ( $\text{kJ mol}^{-1}$ ) 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  $[\text{Cu}_x\text{S}_y]^- + \text{P}_4$  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  $\text{P}_2$  units are most stably bound not as additional ligands to underco-ordinated Cu atoms, but  $\text{P}_m\text{S}_n$  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  $96 \text{ kJ mol}^{-1}$  more stable than any  $[\text{CuS}_2\text{P}_2]^-$  isomer with  $\text{Cu}-\eta^2\text{-P}_2$  co-ordination; (2) isomer **2/2/2A** with SPP chelation is the barrierless rearrangement product of addition of  $\text{P}_2$  across the face of **2/2A**, and is  $70 \text{ kJ mol}^{-1}$  more stable than **2/2/2B**; (3) isomer **2/3/2A**, the most stable of four investigated, results from addition of  $\text{P}_2$  to the mouth of **2/3A**; (4) addition of  $\text{P}_2$  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  $\text{P}_m\text{S}_n$  ligands co-ordinate Cu is not surprising since the S atoms in the anions are negatively charged (calculated atomic charges are  $\text{Cu}^{0.05}$  to  $0.15$ ,  $\text{S}^{-0.35}$  to  $-0.6$ , with terminal S atoms more negative) and a  $\text{P}_2$  moiety separating from  $\text{P}_4$  would be electrophilic. In order to confirm these predictions of  $\text{P}_m\text{S}_n$  ligand formation we have investigated by collisional induced dissociation (CID, with Ar) the more abundant products  $[\text{Cu}_2\text{S}_2\text{P}_2]^-$  and  $[\text{Cu}_2\text{S}_3\text{P}_2]^-$ . The anion  $[\text{Cu}_2\text{S}_2\text{P}_2]^-$  yields  $\text{P}_2\text{S}^-$ , and  $[\text{Cu}_2\text{S}_3\text{P}_2]^-$  yields  $\text{P}_2\text{S}^-$  and  $\text{PS}_2^-$ . 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  $\text{P}_2\text{S}^-$  and  $\text{PS}_2^-$

anions are formed during CID of the adducts but similar CID experiments with nickel sulfide adducts  $[\text{Ni}_2\text{S}_2\text{P}_4]^-$  and  $[\text{Ni}_2\text{S}_2\text{P}_8]^-$  involve only loss of  $\text{P}_2$  and  $\text{P}_4$  units and no  $\text{P}_x\text{S}_y^-$  anions are observed.<sup>5</sup>

The insight provided by this work can be summarised as: (1) reactivity for  $[\text{Cu}_x\text{S}_y]^-$  correlates with geometrical characteristics more than electronic structure, and specifically with Cu atoms without pseudo-linear S–Cu–S co-ordination; (2) reactions of  $[\text{Cu}_x\text{S}_y]^-$  with  $\text{P}_4$  yield new species with  $\text{P}_m\text{S}_n$  ligands enveloping clustered Cu atoms;<sup>‡</sup> (3) metal sulfide anions are reactive in the gas phase. Metal compounds with co-ordinated  $\text{P}_m\text{S}_n$  fragments have significance as lameller hosts (containing  $\text{P}_2\text{S}_6^{4-}$ ),<sup>8–10</sup> and as electronic materials, and are generally prepared by moderate temperature elemental reactions<sup>10</sup> and in fluxes,<sup>11</sup> or by organometallic reactions.<sup>12,13</sup> We expect that the compounds and elementary reactions reported here will permit elaboration of these systems.§

## Acknowledgements

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<sup>‡</sup> There is analogy between the reaction of  $\text{P}_4$  with  $[\text{Cu}_x\text{S}_y]^-$  anions and the recently reported reaction of  $\text{P}_4$  with the anionic nucleophile  $\text{Me}_3\text{SiCN}_2^-$  to form a 1,2,3,4-diazadiphosphole ring.<sup>6</sup> The anion  $\text{PS}_3^-$  (g) has also been described.<sup>7</sup>

<sup>§</sup> We have also observed the addition of  $\text{Ph}_3\text{P}$  as a capping ligand to  $[\text{Cu}_x\text{S}_y]^-$ , a reaction which is expected to stabilise the new clusters.<sup>14</sup>

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