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Gas phase coordination chemistry: copper sulfide cluster anions reacting with tertiary phosphine ligands in the gas phase

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Abstract—The reactions of $[Cu_xS_y]^-$ cluster anions with triphenylphosphine and 1,3,5-triaza-7-phosphaadamantane have been studied by Fourier transform ion cyclotron resonance mass spectrometry. Ions $[CuS_2]^-$, $[Cu_2S_2]^-$, $[Cu_2S_3]^-$ and $[Cu_4S_3]^-$ react, while $[Cu_3S_3]^-$, $[Cu_5S_4]^-$ and $[Cu_6S_4]^-$ are much less reactive. The reactions are addition of one phosphine, with exceptional abstraction of Ph from Ph_3P by $[Cu_2S_2]^-$. The reactivities with phosphines correlate with the geometrical structures of $[Cu_xS_y]^-$. Termination of $[Cu_xS_y]^-$ clusters with phosphines provides the link between the gas-phase and condensed-phase coordination chemistry of copper chalcogenide clusters. © 1997 Elsevier Science Ltd

Keywords: copper; sulfide; cluster; phosphine; gas-phase; addition; mass spectrometry.

In a recent paper [1] we surveyed the generation, compositions, stabilities and reactivities of metal sulfide cluster anions, and using $[Cu_xS_y]^-$ ions as examples we outlined relationships between stability, reactivity and geometrical structure. Initially the reactivity studies were carried out with sulfur compounds S_8, H_2S and thiols, using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Subsequently we have shown that these $[Cu_xS_y]^-$ ions react also with P_4 and described relationships between the structures of the clusters (obtained by density functional calculations), their reactivity and the structures of the products [2].

In this article we report that $[Cu_xS_y]^-$ ions react with tertiary phosphines. This is significant for two reasons. One is that metal sulfide anions in the gas phase are generally unreactive (relative to inorganic cations) with common reagents such as the O_2, N_2O, CO, acetone and alcohols [1] and so reaction with tertiary phosphines extends the scope of reactivity. The second reason is that tertiary phosphines are common terminating ligands in inorganic and organometallic chemistry and, therefore, are able to stabilize the gas phase clusters in attempts to synthesize them in the condensed phase. Fenske *et al.* [3–10] have described a remarkable range of small and large copper chalcogenide clusters terminated with phosphine ligands and so the compounds described in this report make the connection between the condensed-phase chemistry and the gas-phase chemistry of copper sulfide clusters.

One arylphosphine and one alkylphosphine are used here, namely triphenylphosphine and 1,3,5-triaza-7-phosphaadamantane (PTA). Triphenylphosphine is widely used in condensed phase chemistry, but to our knowledge it has not been used previously in gas-phase inorganic chemistry, due to low volatility. PTA is a small aliphatic phosphine which also has not been used in gas phase studies: it is a cage-type ligand with a small cone angle (102°) [11–13] which has been shown to coordinate to metals through the phosphorus atom [14–17].

Only three previous investigations have involved the interactions of metal ions with phosphines in the gas phase. Schwarz *et al.* studied the reaction of bare Fe^+ ions with phosphaalkynes [18], Bjarnason [19] recently studied the reaction of Ti^+ with methylphosphine and we have studied ions produced by laser ablation of some metals with an involatile aliphatic phosphine $P(CH_2CH_2CN)_3$ (TCP) [20].

EXPERIMENTAL

Laser ablation of copper sulfide, Cu_2S, by a laser pulse from a Nd-YAG laser at 1064 nm, was used to

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produce $[Cu_xS_y]^-$ anions [1,21]. These anions were trapped in the cell of a FTICR mass spectrometer where the reactions took place. Details of the sample preparation, the FTICR, the cell and the production of spectra have been previously described [1,20].

After ablation the selection and isolation of specific anions in the ion trap was accomplished using a rf chirp pulse to eject all unwanted ions from the cell; this was carried out in the presence of the phosphine and the reactions were allowed to take place for measured time periods before monitoring the products.

The volatility of Ph_3P was very low and so a surface of the probe tip (containing the Cu_2S) which was not in the laser irradiation area was coated with a thin film of Ph_3P. This gave $Ph_3P(g)$ at an uncorrected pressure of 5×10^{-6} Pa, which was sufficient to measure the reactions with some of the $[Cu_xS_y]^-$ anions.

The volatility of PTA was greater than that of Ph_3P and similar to that of S_8 [22]. In this case PTA was placed in a melting point tube which was attached to the probe tip, producing a pressure of 1×10^{-5} Pa.

RESULTS

The $[Cu_xS_y]^-$ anions were individually selected and trapped in the spectrometer and allowed to react with the two phosphines for periods up to 50 s and in some cases up to 100 s. The reactants, products and reaction timescales are listed in Table 1. Figure 1 shows the composition of the reaction mixture of $[Cu_2S_2]^-$ with Ph_3P after 20 s. Figure 2 shows the spectrum of the $[Cu_4S_3]^-$ plus Ph_3P reaction after 4 s. Figure 3 shows the reaction of PTA with $[Cu_4S_3]^-$ after 2 s and Fig. 4 the reaction of PTA with $[Cu_5S_4]^-$ after 10 s. The table and the spectra indicate that only monoaddition products of $[Cu_xS_y]^-$ and phosphine were observed, except for $[Cu_2S_2]^-$ which with Ph_3P also forms an ion corresponding to the formula $[Cu_2S_2Ph(Ph_3P)]^-$. The formation of the $[Cu_2S_2(Ph_3P)]^-$ ion is fast, while the formation of $[Cu_2S_2Ph(Ph_3P)]^-$ is much slower and appears to be from $[Cu_2S_2(Ph_3P)]^-$. $[Cu_2S_3]^-$ could not be isolated in the presence of PTA, which may be due to its very rapid complete reaction with PTA before ion selection was made.

The ion $[Cu_3S_3]^-$ does not react with either phosphine, while $[Cu_6S_4]^-$ reacts very slowly with Ph_3P and not detectably with PTA.

DISCUSSION

We have provided examples of basic gas-phase coordination chemistry involving ligands used in condensed-phase chemistry. While the bare $[Cu_xS_y]^-$ ions might be expected to have limited stability in a condensed phase environment (or even in a more dense gas phase), with protecting ligands such as phosphines this gas-phase chemistry is now approaching the condensed-phase cluster chemistry exemplified by the work of Fenske [3–10]. Copper sulfide anions are of low reactivity and even though the concentrations of the ligands are extremely low ($\sim 10^{-11}$ molar), these anions react with sulfur and phosphine donors but are inert to oxygen donors and notions of hard and soft acids and bases are evident. The variations in reactivity of the $[Cu_xS_y]^-$ ions with phosphines are similar to those with the sulfur donors [1], and also to reactions with P_4 [2], and are ascribed to differences in geometrical structure in the $[Cu_xS_y]^-$ ions. In general $[Cu_3S_3]^-$, $[Cu_5S_4]^-$ and $[Cu_6S_4]^-$ have low or very low reactivity, while $[CuS_2]^-$, $[Cu_2S_2]^-$, $[Cu_2S_3]^-$ and $[Cu_4S_3]^-$ are reactive. $[Cu_2S_2]^-$ is the only ion which is able to abstract Ph from Ph_3P.

There are some differences between the reactivity of the two phosphines. PTA reacts relatively rapidly with all anions except $[Cu_3S_3]^-$ and $[Cu_6S_4]^-$, and reacts much faster than Ph_3P with $[CuS_2]^-$ and $[Cu_5S_4]^-$. There is a clear contrary result with $[Cu_2S_2]^-$, which adds Ph_3P faster than it adds PTA, and is then able to abstract Ph which presumably becomes bound to S forming a PhS^- ligand in the product. PTA reacts speedily with all the anions except $[Cu_6S_4]^-$ and $[Cu_3S_3]^-$. The anomalously slow reaction of $[CuS_2]^-$ with Ph_3P could be due to the larger cone angle affecting the bending of linear $[CuS_2]^-$ to trigonal $[Ph_3PCuS_2]^-$.

We have shown [1,23] that stability and unreactivity in $[Cu_xS_y]^-$ ions correlates with a geometrical (rather than electronic [23]) property, namely the occurrence

Table 1. Products and their relative formation rates for reactions of $[Cu_xS_y]^-$ with Ph_3P and PTA

	Reaction with Ph_3P (L)		Reaction with PTA (L′)	
Ion $[Cu_xS_y]^-$	Product	Reaction time[a]	Product	Reaction time[a]
$[CuS_2]^-$	$[CuS_2L]^-$	>100	$[CuS_2L']^-$	5
$[Cu_2S_2]^-$	$[Cu_2S_2L]^-$	2	$[Cu_2S_2L']^-$	10
	$[Cu_2S_2LC_6H_5]^-$	~50		
$[Cu_2S_3]^-$	$[Cu_2S_3L]^-$	>100	—	
$[Cu_3S_3]^-$	No reaction	—	No reaction	—
$[Cu_4S_3]^-$	$[Cu_4S_3L]^-$	3	$[Cu_4S_3L']^-$	3
$[Cu_5S_4]^-$	$[Cu_5S_4L]^-$	>100	$[Cu_5S_4L']^-$	7
$[Cu_6S_4]^-$	$[Cu_6S_4L]^-$	>100	No reaction	—

[a] Time in s for the product ion to attain 50% relative intensity.

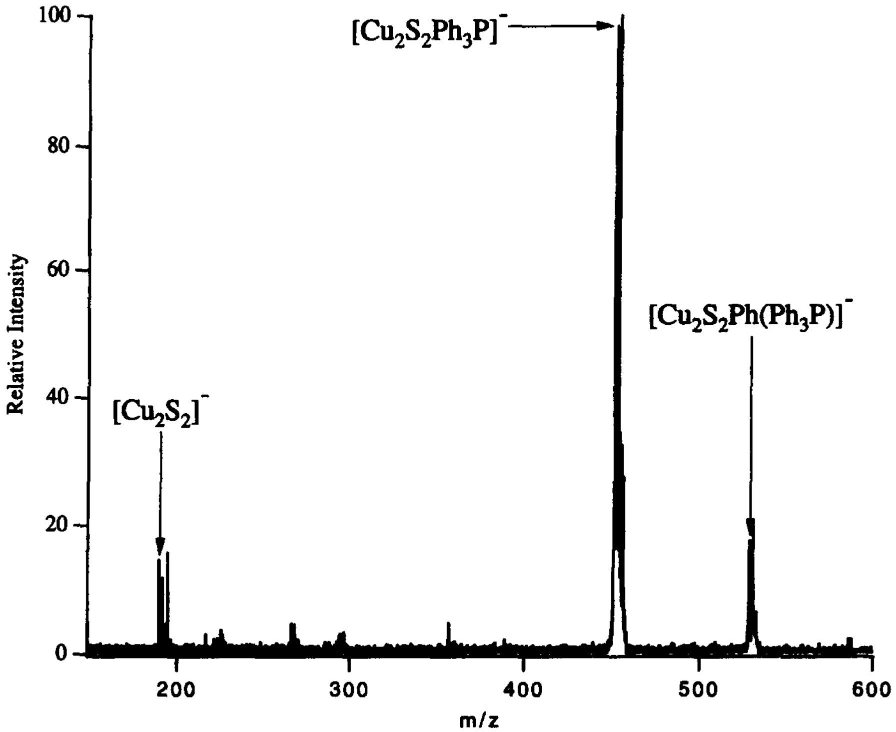

Fig. 1. Negative ion mass spectrum of the mixture $[Cu_2S_2]^-$ plus Ph_3P after reaction for 20 s.

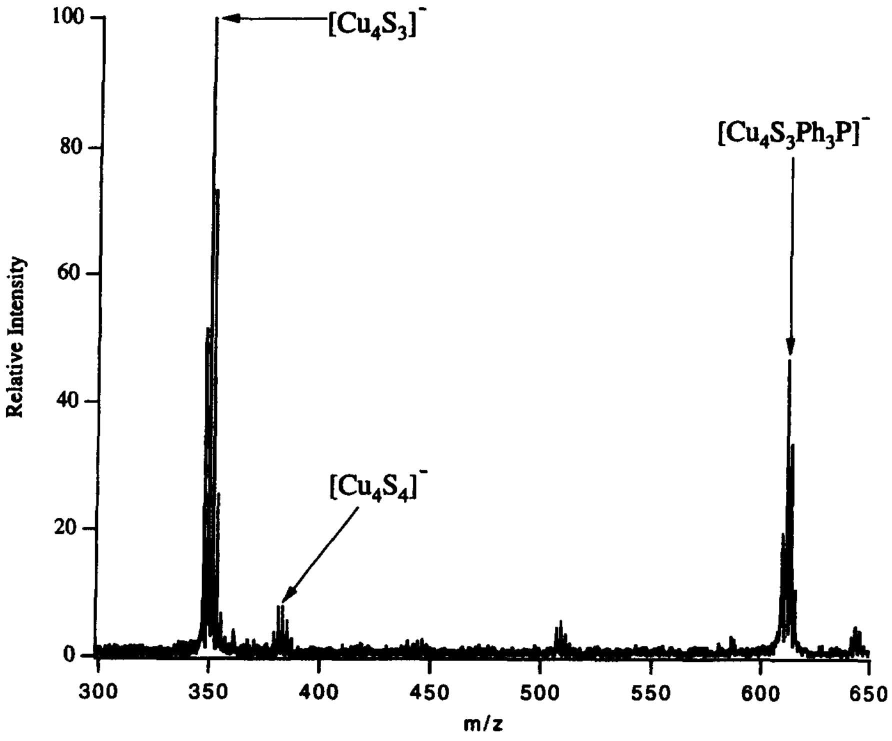

Fig. 2. Negative ion mass spectrum of the mixture $[Cu_4S_3]^-$ plus Ph_3P after reaction for 4 s.

of Cu atoms with pseudo-linear S—Cu—S local coordination in the cluster. This occurs in the clusters $[Cu_3S_3]^-$, $[Cu_5S_4]^-$ and $[Cu_6S_4]^-$, and accounts also here for the lesser reactivities of these ions with phosphines, although the relatively rapid reaction of $[Cu_5S_4]^-$ with PTA provides an interesting exception.

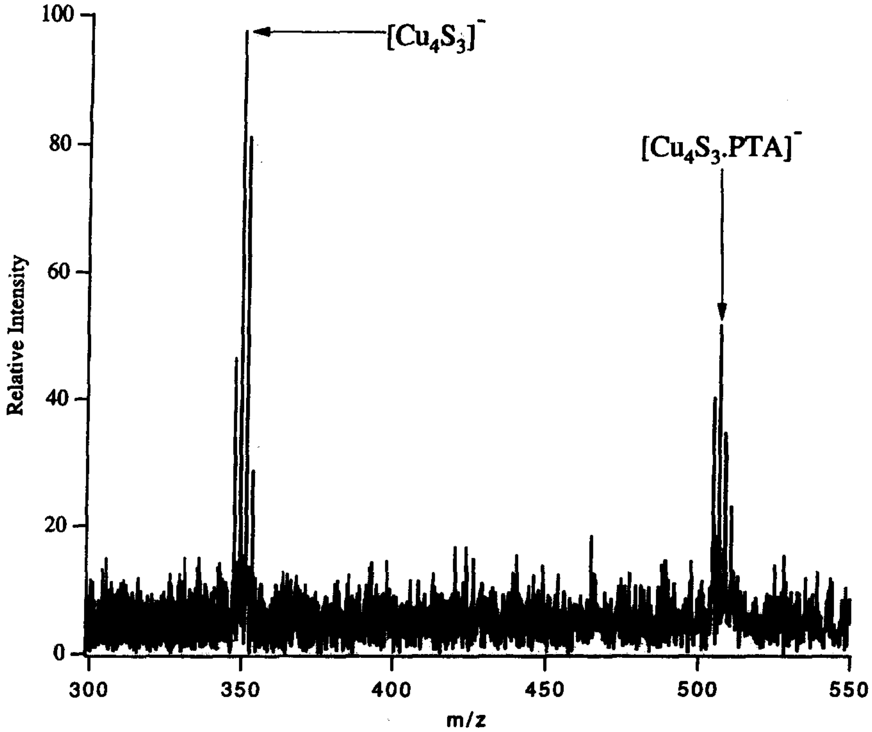

Fig. 3. Negative ion mass spectra of the mixture $[Cu_4S_3]^-$ plus PTA after reaction for 2 s.

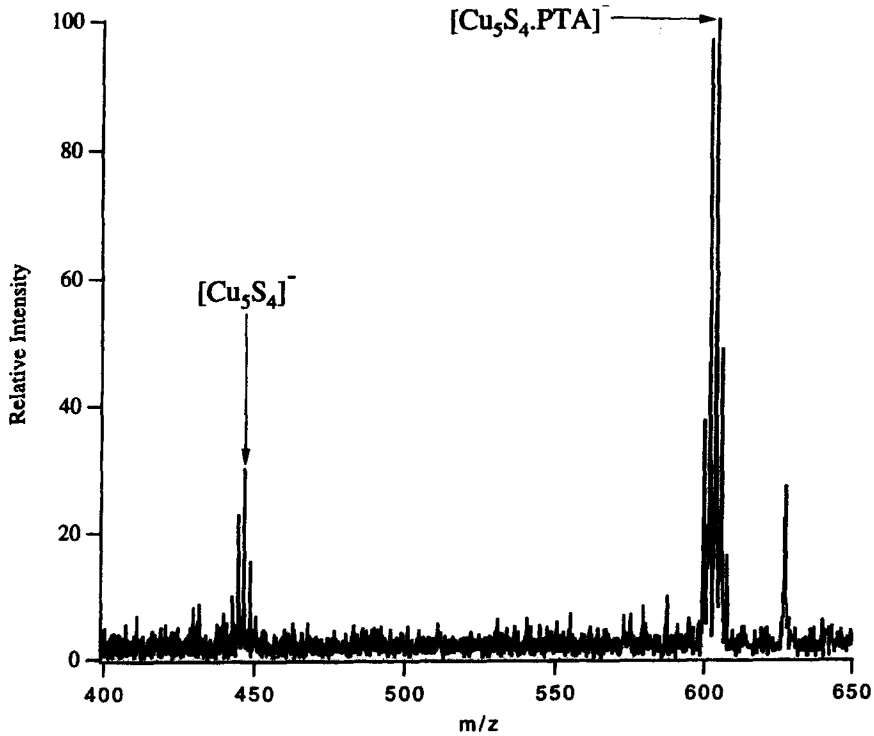

Fig. 4. Negative ion mass spectra of the mixture $[Cu_5S_4]^-$ plus PTA after reaction for 10 s.

The structures of the more reactive ions, $[Cu_2S_2]^-$ and $[Cu_4S_3]^-$, as determined by *ab initio* density functional calculations [23], are shown in Fig. 5 in comparison with the structure of the unreactive $[Cu_3S_3]^-$. $[Cu_4S_3]^-$ contains two pseudo-linear Cu atoms (as in $[Cu_3S_3]^-$) and two Cu atoms which have the same local environ-

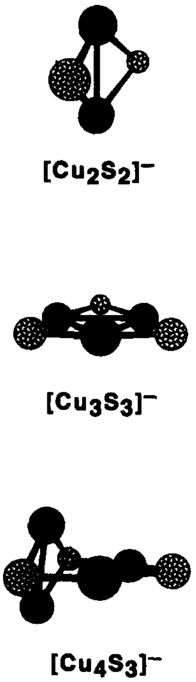

Fig. 5. Structures for $[Cu_2S_2]^-$, $[Cu_3S_3]^-$ and $[Cu_4S_3]^-$ as determined by density functional methods.

ment as those in $[Cu_2S_2]^-$. It is postulated that the phosphine addition reactions occur at the more exposed Cu atoms, completing approximately trigonal coordination for them. While these interpretations provide a consistent picture of the reactions of $[Cu_xS_y]^-$ ions with phosphines, it is not yet clear why only one phosphine molecule adds to $[Cu_2S_2]^-$ and $[Cu_4S_3]^-$ and we are investigating this further by experiments at high pressures of phosphine and by density functional calculations.

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