Electrospray mass spectrometry of some cadmium thiophenolate complexes and of a thiophenolate capped CdS cluster

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Electrospray mass spectra of $[\mathrm{Cd(SPh)_4}]^{2-}$, $[\mathrm{Cd_4(SPh)_{10}}]^{2-}$ and $[\mathrm{S_4Cd_{10}(SPh)_{16}}]^{4-}$ show peaks due to the parent ions and some stable dissociation products; in the sulfide cluster the Cd–S bonds involving the sulfide remain intact during the observed fragmentation.

Molecular clusters with diameters of a few nanometers are under intense investigation as synthetic precursors to bulk and extended solids.[1] In the case of semiconductor materials (quantum dots) special attention is paid to their unique and size-dependent transport and optical properties.[2] Given the strong size dependence of these properties, a key objective of research in this field is to find synthetic routes that give crystallites with well defined sizes. One such method involves the use of ligands that cap the particle surface by direct coordination to surface atoms. This approach has proved very effective for metal chalcogenides [(ME), M = Cd, Zn; E = S, Se] using thiolates[3–6] and in particular thiophenolate $(\mathrm{SPh^-})$[7,8] as the capping ligand. The well defined clusters $[\mathrm{E_1Cd_8(SPh)_{16}}]^{2-}$,[9] $[\mathrm{E_4Cd_{10}(SPh)_{16}}]^{4-}$,[10] $[\mathrm{S_4Cd_{17}(SPh)_{28}}]^{2-}$[11] and $[\mathrm{S_{14}Cd_{32}(SPh)_{36}}]\cdot 4\mathrm{DMF}$[12] have been characterised by single-crystal X-ray crystallography. In general, however, crystallisation of these capped materials is difficult, resulting in less rigorous characterisation by methods such as powder X-ray diffraction and UV absorption spectroscopy. Recently the existence of $[\mathrm{S_1Cd_4(SR)_{12}}]^{6-}$, $[\mathrm{S_1Cd_8(SR)_{16}}]^{2-}$, $[\mathrm{S_4Cd_{10}(SR)_{12}}]$, $[\mathrm{S_4Cd_{17}(SR)_{24}}]^{2+}$ in solution has been suggested on the basis of NMR studies.[4] An independent method of identifying such species would be of great value in extending our understanding of this area of chemistry.

Electrospray mass spectrometry (ESMS) is a relatively new soft ionisation technique which has been successful in the study of large biomolecules such as proteins and oligonucleotides,[13] and is gaining increased application in the characterization of a range of charged inorganic species.[14,15] Recently, electrospray mass spectra of some multiply charged polyoxoanions were reported,[15] showing the molecular ion as the base peak with a minimal degree of fragmentation. To investigate whether ESMS can be used to characterize and study the formation of semiconductor nanoclusters, we have investigated the mass spectra of the SPh-capped CdS cluster $[\mathrm{S_4Cd_{10}(SPh)_{16}}]^{4-}$, and of the cadmium thiolate complexes $[\mathrm{Cd(SPh)_4}]^{2-}$ and $[\mathrm{Cd_4(SPh)_{10}}]^{2-}$.† The structures of $[\mathrm{Cd_4(SPh)_{10}}]^{2-}$ and $[\mathrm{S_4Cd_{10}(SPh)_{16}}]^{4-}$ are shown in Fig. 1.

The predominant anionic species which were detected in the ESMS spectra are listed in Table 1. In the spectrum of $[\mathrm{Me_4N}]_2[\mathrm{Cd(SPh)_4}]$, there is an additional strong peak due to $\mathrm{SPh^-}$ at *m/z* 109, which is *ca.* 20 times as intense as the peak due to the most intense Cd-containing species, and which has been omitted from Table 1 in order to allow a more accurate comparison of the peaks due to the cadmium complexes. The presence of this peak indicates a strong tendency for $[\mathrm{Cd(SPh)_4}]^{2-}$ to dissociate by loss of $\mathrm{SPh^-}$, and this is confirmed by the fact that the most intense peak due to Cd-containing species is that of $[\mathrm{Cd(SPh_3)}]^-$. At a cone voltage of 20 V, only monoanion species are observed. These include the species $[\mathrm{Cd_2(SPh)_5}]^-$, $[\mathrm{Cd_3(SPh)_7}]^-$, formed by addition of neutral $\mathrm{Cd(SPh)_2}$ to $[\mathrm{Cd(SPh)_3}]^-$, and $[(\mathrm{Me_4N})\mathrm{Cd(SPh)_4}]^-$, formed by addition of $[\mathrm{Me_4N}]^+$ to $[\mathrm{Cd(SPh)_4}]^{2-}$. At a cone voltage of 5 V the most abundant Cd-containing species is still $[\mathrm{Cd(SPh)_3}]^-$, but a peak due to the 'parent' ion $[\mathrm{Cd(SPh)_4}]^{2-}$ is now clearly evident. This is in accord with the expectation that the degree of fragmentation decreases with decreasing cone voltage. In this connection, it is interesting that $[\mathrm{Cd(SPh)_3}]^-$ is still evident, and is still the most intense peak {apart from one at *m/z* 292 due to $[(\mathrm{Me_4N})(\mathrm{SPh})_2]^-$}, at a cone voltage of 120 V, implying that this is a very stable species (many species undergo extensive fragmentation at such high voltages). This is consistent with the observation that this species is always present in the spectra of the other Cd–$\mathrm{SPh^-}$ compounds studied in this work (see below).

The spectrum of $[\mathrm{Me_4N}]_2[\mathrm{Cd_4(SPh)_{10}}]$ contains peaks due to $[\mathrm{Cd(SPh)_3}]^-$, $[\mathrm{Cd_2(SPh)_5}]^-$ and $[\mathrm{Cd_3(SPh)_7}]^-$, as were observed in the spectrum of $[\mathrm{Me_4N}]_2[\mathrm{Cd(SPh)_4}]$. This is not surprising, as the facile loss of $\mathrm{SPh^-}$ which is observed in the spectra of the latter complex would result in a Cd/$\mathrm{SPh^-}$ composition which would approach that of $[\mathrm{Me_4N}]_2[\mathrm{Cd_4(SPh)_{10}}]$. Again, $[\mathrm{Cd(SPh)_3}]^-$ is the dominant species at a cone voltage of 20 V. However, at a cone voltage of 5 V, the *m/z* 771 peak {assigned to $[\mathrm{Cd_2(SPh)_5}]^-$ in the 20 V spectrum} becomes dominant. The isotopic mass distribution for the peak in the 20 V spectrum is shown in Fig. 2(*a*). Comparison with the calculated distribution for $[\mathrm{Cd_2(SPh)_5}]^-$ confirms that at 20 V the signal is due entirely to $[\mathrm{Cd_2(SPh)_5}]^-$. At 5 V, however, additional peaks appear in the pattern at half-integral mass units, Fig. 2(*b*). This is characteristic of a dianionic species, and thus corresponds to $[\mathrm{Cd_4(SPh)_{10}}]^{2-}$, presumably with a structure the same as that determined for this species in the solid state [Fig. 1(*a*)]. Again, it is observed that the decrease in the degree of fragmentation with decreasing cone voltage allows the observation of the 'parent' species.

The full spectrum of $[\mathrm{Me_4N}]_4[\mathrm{S_4Cd_{10}(SPh)_{16}}]$ is shown in Fig. 3. As in the spectra of the compounds discussed above, this shows a strong peak due to $[\mathrm{Cd(SPh)_3}]^-$, and this is the

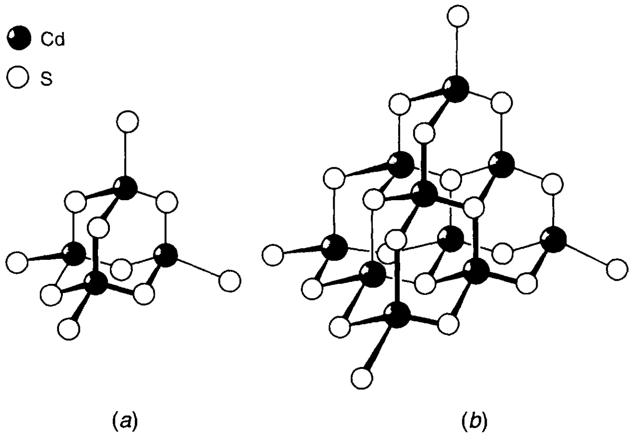

Fig. 1 The structure of (*a*) the $\mathrm{Cd_4S_{10}}$ skeleton of $[\mathrm{Cd_4(SPh)_{10}}]^{2-}$ and (*b*) the $\mathrm{Cd_{10}S_{20}}$ skeleton of $[\mathrm{S_4Cd_{10}(SPh)_{16}}]^{4-}$

Table 1 Anionic species observed in the ESMS spectra[a]

Compound	Ion	m/z	Relative peak height (%) Cone 20 V	Relative peak height (%) Cone 5 V
$[Me_4N]_2[Cd(SPh)_4]$[b]	$[Cd(SPh)_3]^-$	441	100	100
	$[Cd_2(SPh)_5]^-$	771	12	55
	$[Cd_3(SPh)_7]^-$	1101	7	—
	$[(Me_4N)Cd(SPh)_4]^-$	624	5	7
	$[Cd(SPh)_4]^{2-}$	275	—	37
	$[Cd_4(SPh)_{10}]^{2-}$	771	—	—[c]
$[Me_4N]_2[Cd_4(SPh)_{10}]$	$[Cd(SPh)_3]^-$	441	100	48
	$[Cd_2(SPh)_5]^-$	771	33	100
	$[Cd_3(SPh)_7]^-$	1101	6	3
	$[Cd_4(SPh)_{10}]^{2-}$	771	—	—[c]
				Cone 10 V
$[Me_4N]_4[S_4Cd_{10}(SPh)_{16}]$	$[Cd(SPh)_3]^-$	441	100	24
	$[S_4Cd_8(SPh)_{10}]^{2-}$	1060	85	5
	$[S_4Cd_9(SPh)_{12}]^{2-}$	1226	21	2
	$[S_4Cd_{10}(SPh)_{15}]^{3-}$	964	8	18
	$[(Me_4N)S_4Cd_{10}(SPh)_{16}]^{3-}$	1025	6	18
	$[S_4Cd_{10}(SPh)_{16}]^{4-}$	750	45	100

[a] The observed m/z values are those of the most intense peak within the isotopic mass distribution for the species concerned. In all cases the observed isotopic mass distribution agreed well with the calculated pattern, and the observed m/z agreed with that calculated for the most abundant species. [b] A strong peak due to SPh^- m/z 109 is also observed in this case (see text). [c] The isotope distribution pattern shows that the m/z 771 peak contains contributions from $[Cd_4(SPh)_{10}]^{2-}$ and $[Cd_2(SPh)_5]^-$ in the ratio 6 : 1 [see text, and Fig. 2(*b*)].

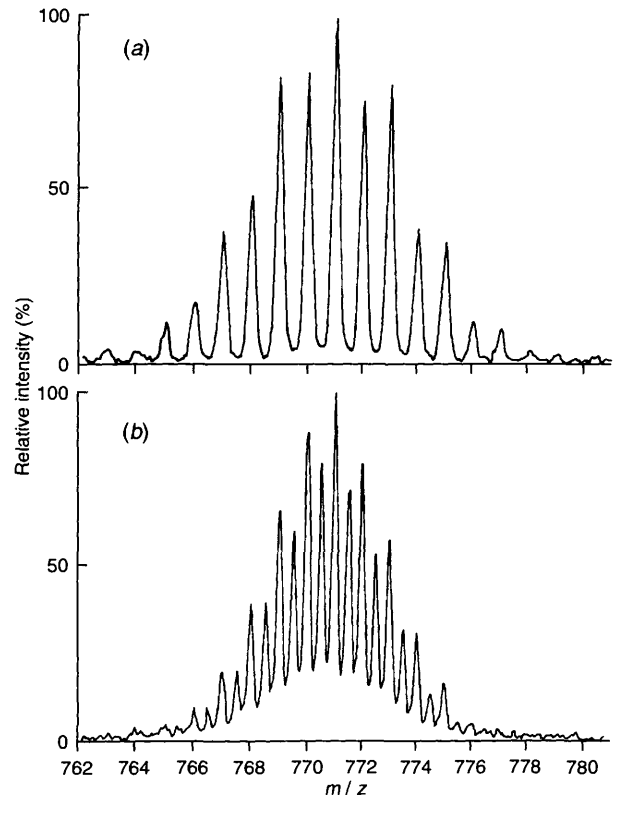

Fig. 2 Expansion of the peak due to $[Cd_2(SPh)_5]^-$ and $[Cd_4(SPh)_{10}]^{2-}$ in the spectrum of $[Me_4N]_2[Cd_4(SPh)_{10}]$ at a cone voltage of (*a*) 20 and (*b*) 5 V. The ratios of the intensities $[Cd_4(SPh)_{10}]^{2-}$: $[Cd_2(SPh)_5]^-$ at the two voltages are (*a*) 0.08, (*b*) 6.

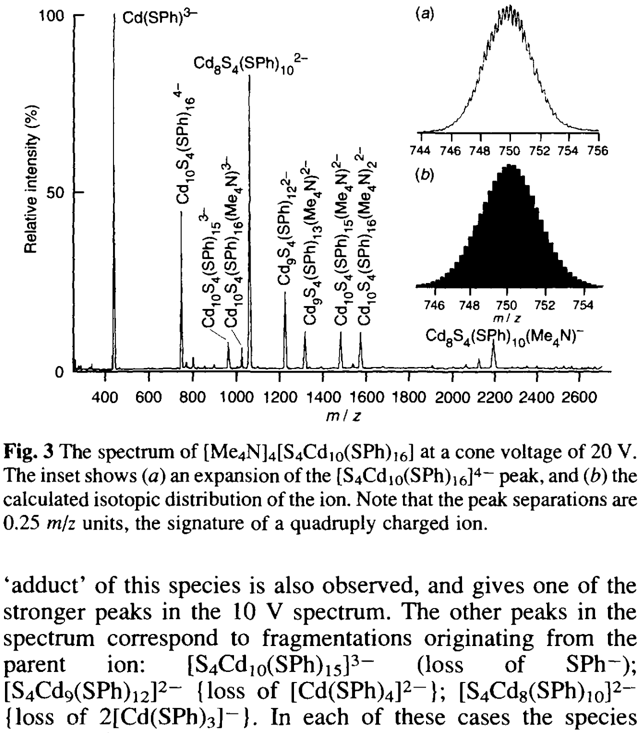

Fig. 3 The spectrum of $[Me_4N]_4[S_4Cd_{10}(SPh)_{16}]$ at a cone voltage of 20 V. The inset shows (*a*) an expansion of the $[S_4Cd_{10}(SPh)_{16}]^{4-}$ peak, and (*b*) the calculated isotopic distribution of the ion. Note that the peak separations are 0.25 m/z units, the signature of a quadruply charged ion.

dominant peak in the 20 V spectrum. The other dominant species in the spectrum at this voltage all contain an S_4Cd_x unit (x = 8–10), including the 'parent' ion $[S_4Cd_{10}(SPh)_{16}]^{4-}$. The isotopic mass distribution for this species, which becomes the dominant species at a cone voltage of 10 V, is shown in Fig. 3 (inset). The appearance of peaks at quarter-integral mass units is a clear indication of the 4− charge on the species. The $[Me_4N]^+$ 'adduct' of this species is also observed, and gives one of the stronger peaks in the 10 V spectrum. The other peaks in the spectrum correspond to fragmentations originating from the parent ion: $[S_4Cd_{10}(SPh)_{15}]^{3-}$ (loss of SPh^-); $[S_4Cd_9(SPh)_{12}]^{2-}$ {loss of $[Cd(SPh)_4]^{2-}$}; $[S_4Cd_8(SPh)_{10}]^{2-}$ {loss of 2$[Cd(SPh)_3]^-$}. In each of these cases the species which are lost are ones which give rise to the more intense peaks in the spectra of $[Me_4N]_2[Cd(SPh)_4]$ or $[Me_4N]_2[Cd_4(SPh)_{10}]$. The driving force for these fragmentations is probably the tendency of the parent $[S_4Cd_{10}(SPh)_{16}]^{4-}$ cluster to lose negative charge. It is noteworthy that no fragmentation is evident which involves breaking of the cadmium–sulfide bonds, *i.e.* the fragments all contain S_4Cd_x units with $x \geqslant 8$. The four sulfide sulfur atoms and the cadmium atoms which are directly bonded to them constitute an S_4Cd_6 unit, but the smallest unit observed in the fragments is S_4Cd_8, in $[S_4Cd_8(SPh)_{10}]^{2-}$, which derives from the parent ion by loss of two $[Cd(SPh)_3]^-$. Removal of a third $[Cd(SPh)_3]^-$ would yield $[S_4Cd_7(SPh)_7]^-$ with m/z 1678. There is only a very weak peak in the 20 V spectrum at this position, although the relative intensity of this peak increases significantly at the higher cone voltage of 30 V.

The facile loss of $[Cd(SPh)_4]^{2-}$, $[Cd(SPh)_3]^-$ *etc.* which is observed in the ESMS spectrum is of interest in relation to the formation of the large $[S_{14}Cd_{32}(SPh)_{36}]$ cluster from $[S_4Cd_{10}(SPh)_{16}]^{4-}$. The exact mechanism of this process is not known,[12] but it involves removal of negative charge, Cd atoms, and SPh groups, and this is obviously closely related to the fragmentation processes observed in the ESMS spectra.

The present study thus demonstrates the power of ESMS in the characterization of thiolatometallate complexes and thiolate-capped metal chalcogenide clusters, and this technique should prove to be of value in the identification of other species of this type which have been postulated in the past,[4] and in providing a better understanding of the mechanism of formation of larger metal chalcogenide clusters.[7,8,12]

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Footnote

† Electrospray mass spectra were obtained in the negative-ion mode using a VG Platform II mass spectrometer using an acetonitrile–water ($v/v = 1:1$) mobile phase. The compounds were dissolved in the mobile phase to give a solution typically of approximate concentration 0.1 mmol dm^{-3} and spectra were recorded on the freshly prepared solutions. The diluted solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 10 μl sample loop. A Thermo Separation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60 °C) at a flow rate of 0.01 ml min^{-1}, and nitrogen was employed both as drying and nebulising gas. Cone voltages were varied from 5 to 60 V in order to investigate the effect of higher voltages on the fragmentation of parent ions. Confirmation of the species detected is aided by comparison of the observed and predicted isotope distribution patterns. Theoretical isotope distribution patterns were calculated using the *Isotope* computer program.[16]

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