

Electrospray Mass Spectrometry of Thiophenolate-Capped Clusters of CdS, CdSe, and ZnS and of Cadmium and Zinc Thiophenolate Complexes: Observation of Fragmentation and Metal, Chalcogenide, and Ligand Exchange Processes

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Electrospray mass spectrometry provides a rapid, convenient technique for characterizing and studying the chemistry of anionic metal sulfide thiolate clusters. Negative-ion electrospray mass spectra have been recorded for the thiophenolate-capped clusters $[\text{Me}_4\text{N}]_4[\text{E}_4\text{Cd}_{10}(\text{SPh})_{16}]$ (E = S, Se), $[\text{Me}_4\text{N}]_4[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]$, and $[\text{Me}_4\text{N}]_2[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]$ and of the metal thiophenolate complexes $[\text{Me}_4\text{N}]_2[\text{M}(\text{SPh})_4]$, $[\text{Me}_4\text{N}]_2[\text{M}_4(\text{SPh})_{10}]$ (M = Cd, Zn), and $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{X}_4(\text{SPh})_6]$ (X = Cl, Br, I). The exchanges of M, E, and X which occur in various mixtures of these clusters and complexes and the fragmentation processes have been investigated. In the clusters the M–E bonds involving the sulfide or selenide core remain intact during the observed fragmentation at low cone voltages. At high cone voltages, monoions are ultimately formed by loss of charged species and neutral $\text{M}(\text{SPh})_2$, resulting in almost complete removal of the SPh[−] ligands from the cluster core. Fragmentation of the ME core unit itself occurs only at very high voltages. The exchange of X in $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{X}_4(\text{SPh})_6]$ (X = Br, I) gives peaks due to the ions $[\text{Cd}_4\text{I}_n\text{Br}_m(\text{SPh})_{10-(n+m)}]^{2-}$ ($n + m = 0-4$) and fragment ions with mixed ligands. The nature of the detected species suggests that the halides only exist as terminal ligands. The exchange of M in $[\text{Me}_4\text{N}]_2[\text{M}_4(\text{SPh})_{10}]$ and $[\text{Me}_4\text{N}]_4[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]$ results in the mixed-metal complexes $[\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{10}]^{2-}$ ($n = 0-4$) and the mixed-metal clusters $[\text{S}_4\text{Cd}_{10-n}\text{Zn}_n(\text{SPh})_{16}]^{4-}$ ($n = 0-10$). The exchange follows random statistics in $[\text{M}_4(\text{SPh})_{10}]^{2-}$ but is biased toward equilibrium association of the same metal in $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$. The rates of exchange within the different structural elements of $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{M}_{17}(\text{SPh})_{28}]^{2-}$ decrease for the atoms located toward the center of the clusters.

Introduction

Electrospray mass spectrometry (ESMS) is a soft ionization technique¹ that has been successful in the study of large biomolecules such as proteins and oligonucleotides² and is gaining increased application in the characterization of a range of inorganic and organometallic systems.^{3,4} Recently, in a preliminary communication,⁵ we reported the electrospray mass spectra of the thiophenolate complexes $[\text{Cd}(\text{SPh})_4]^{2-}$ and $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and the SPh[−]-capped CdS cluster $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$. Spectra were obtained which showed minimal fragmentation of the ions, indicating the power of ESMS in the characterization of thiometalate complexes and of thiolate-capped metal chalcogenide clusters.⁶ It has been shown that semiconductor nanoclusters (quantum dots), which are a topic of intense research in materials chemistry,⁷ can be formed from such molecular precursors.⁸⁻¹² A number of new potential precursor complexes have been postulated,^{8,13} but experimental verification for the existence of these has not always been easy

to obtain. The ESMS technique should be of value in the identification of such species and in revealing the fundamental chemistry of metal sulfide thiolate clusters. This would provide insight into the mechanisms of formation of larger nanoclusters. Here we present a more detailed study which includes the ES mass spectra of the zinc thiophenolate complexes $[\text{Zn}(\text{SPh})_4]^{2-}$ and $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$, the halide derivatives $[\text{Cd}_4\text{X}_4(\text{SPh})_6]^{2-}$ (X = Cl, Br, I), and the clusters $[\text{Se}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$, $[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$, and $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$. The structures of $[\text{M}_4(\text{SPh})_{10}]^{2-}$ (M = Cd, Zn),¹⁴ $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ (E = S, Se),¹⁵ and $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ ¹⁶ are shown in Figure 1. ESMS is a powerful technique for the investigation of rapidly-exchanging systems and has been compared with low-temperature NMR studies.¹⁷⁻¹⁹ Investigations of the exchange reactions of M, E, and X in $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$, $[\text{S}_4\text{M}_{17}(\text{SPh})_{28}]^{2-}$, $[\text{M}_4(\text{SPh})_{10}]^{2-}$,

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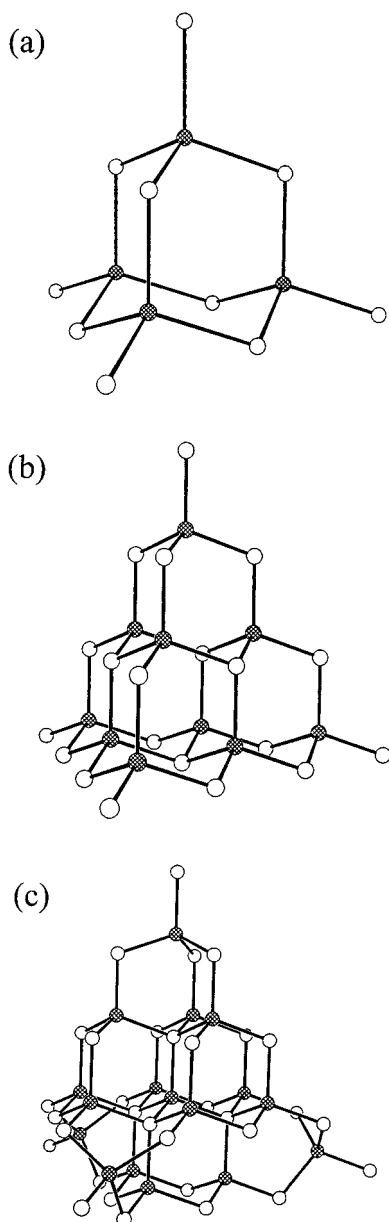


Figure 1. Structures of (a) the M_4S_{10} skeleton of $[M_4(SPh)_{10}]^{2-}$ ($M = Cd, Zn$), (b) the $E_4M_{10}S_{16}$ skeleton of $[E_4M_{10}(SPh)_{16}]^{4-}$ ($M = Cd, Zn$; $E = S, Se$), and (c) the $Cd_{17}S_{32}$ skeleton of $[S_4Cd_{17}(SPh)_{28}]^{2-}$. Shaded atoms are Cd or Zn; unshaded atoms with one or two bonds are the S atoms of terminal or doubly bridging thiolate, respectively; unshaded atoms with three or four bonds are non-thiolate S or Se atoms.

and $[Cd_4X_4(SPh)_6]^{2-}$ have been undertaken. Metal exchange has been shown to occur in $[M_4(SPh)_{10}]^{2-}$ for Fe^{2+}/Co^{2+} , Co^{2+}/Zn^{2+} , Co^{2+}/Cd^{2+} , and Zn^{2+}/Cd^{2+} and in $[S_4M_{10}(SPh)_{16}]^{4-}$ for Zn^{2+}/Cd^{2+} by NMR studies.^{20,21} Applied to clusters, metal ion exchange represents a way of generating new precursors that contain a mixture of metals. Additionally, by exchange of the metal atoms associated with the capping layer, an interface can be created for growth of a second material layered around the primary particle. Examples include core-shell particles of CdS and ZnS,^{22,23} Ag_2S and CdS,²⁴ Ag_2S and AgI,²⁵ and CdS and

HgS^{26} and co-colloids such as CdSe–ZnS²⁷ and CdSe–ZnSe.²⁸ These materials have electronic properties that differ considerably from the sum of those of the separate materials. The study of mixed-ligand systems is of interest, for example, from the viewpoint of replacing the capping ligands of precursors with less tightly-bound ligands, in order to effect controlled aggregation to larger cluster species.¹⁰ Ligand exchange provides a way by which the clusters can be functionalized to aid dispersion of the clusters into a host such as an oxide or polymer etc. Recently, Au particles were coated with a layer of silica using the bifunctional ligand (3-aminopropyl)trimethoxysilane $[NH_2(CH_2)_3Si(OCH_3)_3]$ as a coupler.²⁹

Experimental Section

Materials. The complexes $[Me_4N]_2[M(SPh)_4]$, $[Me_4N]_2[M_4(SPh)_{10}]$, and $[Et_4N]_2[Cd_4X_4(SPh)_6]$ ($X = Cl, Br, I$) and the clusters $[Me_4N]_4[S_4M_{10}(SPh)_{16}]$ ($M = Cd, Zn$) and $[Me_4N]_4[Se_4Cd_{10}(SPh)_{16}]$ were prepared by the previously described methods.^{15,30} Anal. Calcd for $[Et_4N]_2[Cd_4Cl_4(SPh)_6]$: C, 41.45; H, 4.68; N, 1.86. Found: C, 41.99; H, 4.43; N, 1.64. Calcd for $[Et_4N]_2[Cd_4I_4(SPh)_6]$: C, 33.35; H, 3.77; N, 1.50. Found: C, 34.02; H, 3.73; N, 1.38. The cluster $[Me_4N]_2[S_4Cd_{17}(SPh)_{28}]$ was prepared by the following method.^{16,31} To a well-stirred solution of thiophenol (PhSH, 11.4 g) and triethylamine (Et_3N , 10.5 g) in acetonitrile (60 mL) were added alternately $Cd(NO_3)_2 \cdot 4H_2O$ (20.0 g) in acetonitrile (40 mL) and $Na_2S \cdot 9H_2O$ (5.76 g) in methanol (100 mL). At the beginning of the addition of the Cd^{2+} solution, a transient white solid was observed which redissolved to give a clear solution. Approximately 25 mL was added before a permanent white solid was observed. The addition of the Cd^{2+} solution was stopped, and the S^{2-} solution was added. The solid present dissolved, and after addition of approximately 57 mL of the S^{2-} solution, a pale yellow solid precipitated. The addition of S^{2-} was then stopped, and the Cd^{2+} solution was added again, and so on until all the Cd^{2+} and S^{2-} solutions were added. A misty pale yellow solution resulted. $(Me_4N)Cl$ (2.56 g) in methanol (20 mL) was added in one portion, resulting in the precipitation of a pale yellow solid. The mixture was allowed to remain undisturbed for 8 days and then filtered. Recrystallization was from hot acetonitrile. Colorless crystals were obtained and vacuum-dried. Yield: 7.30 g. The recrystallized material contained Cl impurities and consisted of a mixture of $[Me_4N]_2[S_4Cd_{17}(SPh)_{28}]$, $[Me_4N]_2[S_4Cd_{17}Cl(SPh)_{27}]$, and $[Me_4N]_2[S_4Cd_{17}Cl_2(SPh)_{26}]$ in the ratio 100:31:3, as determined from the electrospray mass spectrum. This corresponds to $[Me_4N]_2[S_4Cd_{17}(SPh)_{27.75}Cl_{0.25}]$ for which the calculated analysis (C, 40.31; H, 3.15; N, 0.53) agrees well with the experimental values (C, 40.03; H, 3.24; N, 0.94).

Electrospray Mass Spectrometry (ESMS). Mass spectra were obtained in the negative-ion mode using a VG Platform II mass spectrometer. Acetonitrile was used as the mobile phase because of the high solubility of the clusters in this solvent. The spectrometer employed a quadrupole mass filter with an m/z range 0–3000. The compounds were dissolved in the mobile phase to give a solution

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typically of approximate concentration 0.1 mmol L^{-1} , and spectra were recorded on the freshly prepared solutions. The diluted solution was injected into the spectrometer *via* a Rheodyne injector fitted with a $10 \mu\text{L}$ 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 as both drying and nebulizing gas. Cone voltages were varied from 5 to 190 V in order to investigate the effect of higher voltages on the fragmentation of the intact gas-phase ions, called precursors in the remainder of this paper. Confirmation of species was aided by comparison of the observed and predicted isotope distribution patterns. Theoretical isotope distribution patterns were calculated using the Isotope computer program.³²

Results and Discussion

The $[\text{M}(\text{SPh})_4]^{2-}$ and $[\text{M}_4(\text{SPh})_{10}]^{2-}$ ($\text{M} = \text{Cd}, \text{Zn}$) Complexes. (a) Parent Complexes. The ES mass spectrum of $[\text{Me}_4\text{N}]_2[\text{Cd}(\text{SPh})_4]$ has already been reported.⁵ Here we compare it to that of the zinc complex. The relative intensities of the detected species in each case are given in Table 1. At a cone voltage of 20 V, only monoanion species are observed. These include the species $[\text{M}_2(\text{SPh})_5]^-$ and $[\text{M}_3(\text{SPh})_7]^-$, formed by addition of neutral $\text{M}(\text{SPh})_2$ to $[\text{M}(\text{SPh})_3]^-$, and $[(\text{Me}_4\text{N})\text{-Cd}(\text{SPh})_4]^-$, formed by aggregation of Me_4N^+ with $[\text{Cd}(\text{SPh})_4]^{2-}$. At the low cone voltage of 5 V, a peak due to the intact ion $[\text{Cd}(\text{SPh})_4]^{2-}$ is observed. This is in accord with the expectation that the degree of fragmentation decreases with decreasing cone voltage. The corresponding zinc species $[\text{Zn}(\text{SPh})_4]^{2-}$ and $[(\text{Me}_4\text{N})\text{Zn}(\text{SPh})_4]^-$ are still absent at this voltage, indicating that the zinc complex is less stable than the cadmium complex. The lower stability of the zinc complex is also confirmed by the fact that the strongest peak in the 5 V spectrum is due to $[\text{Zn}_2(\text{SPh})_5]^-$, while for the cadmium complex, $[\text{Cd}(\text{SPh})_3]^-$ is the most abundant species; a more facile loss of SPh^- from $[\text{Zn}(\text{SPh})_4]^{2-}$ than from $[\text{Cd}(\text{SPh})_4]^{2-}$ would produce more $\text{Zn}(\text{SPh})_2$ species to combine with $[\text{Zn}(\text{SPh})_3]^-$ and give $[\text{Zn}_2(\text{SPh})_5]^-$. In both cases, the $[\text{M}(\text{SPh})_3]^-$ ion is particularly stable and remains the most abundant species (apart from one at m/z 292 due to $[(\text{Me}_4\text{N})(\text{SPh})_2]^-$), at cone voltages up to 120 V.

The spectra of $[\text{Me}_4\text{N}]_2[\text{M}_4(\text{SPh})_{10}]$ contain peaks due to $[\text{M}_2(\text{SPh})_5]^-$ and $[\text{M}_3(\text{SPh})_7]^-$, as were observed in the spectrum of $[\text{Me}_4\text{N}]_2[\text{M}(\text{SPh})_4]$, Table 1. This is not surprising, as the facile loss of SPh^- , which was observed in the spectra of the latter complexes, would result in an M/SPh^- composition which would approach that of $[(\text{Me}_4\text{N})_2\text{M}_4(\text{SPh})_{10}]$. Again, $[\text{M}(\text{SPh})_3]^-$ is the dominant species at a cone voltage of 20 V. However, at a cone voltage of 5 V, the m/z 771 peak and the m/z 677 peak (assigned to $[\text{Cd}_2(\text{SPh})_5]^-$ and $[\text{Zn}_2(\text{SPh})_5]^-$, respectively, in the 20 V spectra) become dominant. Comparison of the isotopic mass distribution for the m/z 771 peak in the 20 V spectrum with the calculated distribution for $[\text{Cd}_2(\text{SPh})_5]^-$ confirms that, at 20 V, the signal is due entirely to $[\text{Cd}_2(\text{SPh})_5]^-$. At 5 V, however, additional peaks appear at half-integral mass units. This is characteristic of a dianionic species and thus corresponds to $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$. The m/z 771 peak contains contributions from $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and $[\text{Cd}_2(\text{SPh})_5]^-$ in a 6:1 ratio. Similarly, the m/z 677 peak in the 20 V spectrum of $[\text{Me}_4\text{N}]_2[\text{Zn}(\text{SPh})_4]$ is due entirely to $[\text{Zn}_2(\text{SPh})_5]^-$ but contains contributions from both $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ and $[\text{Zn}_2(\text{SPh})_5]^-$ in a 12:1 ratio in the 5 V spectrum. Again, the decrease in the degree of fragmentation with decreasing cone voltage allows the observation of the intact ions.

(b) Ligand Exchange. In the complexes $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{X}_4(\text{SPh})_6]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) each of the four terminal SPh^- ligands of $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ in Figure 1a has been replaced by a halide.

The predominant species detected in the ES mass spectra are listed in Table 2. Relatively intense peaks due to the X^- , $[\text{CdX}_3]^-$, and $[\text{CdX}_2(\text{SPh})]^-$ ions are observed in all spectra, showing a tendency for $[\text{Cd}_4\text{X}_4(\text{SPh})_6]^{2-}$ to dissociate by loss of these species. This is confirmed in the 5 V spectrum by the fact that one of the more abundant species is the heptakis(thiophenolate) ion $[\text{Cd}_4\text{X}_3(\text{SPh})_7]^{2-}$, formed by loss of X^- and addition of SPh^- . Of the $[\text{Cd}_3\text{X}_{4-n}(\text{SPh})_{3+n}]^-$ ions, the species $[\text{Cd}_3\text{X}(\text{SPh})_6]^-$ and $[\text{Cd}_3\text{X}_2(\text{SPh})_5]^-$, formed by loss of $[\text{CdX}_3]^-$ and $[\text{CdX}_2(\text{SPh})]^-$, respectively, dominate. Some aspects of the fragmentation patterns suggest that $[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]^{2-}$ loses halide more readily than its bromo and iodo counterparts. Thus, in the 5 V spectra, the $[\text{Cd}_4\text{X}_4(\text{SPh})_6]^{2-}$ ions are the most abundant in the case of $\text{X} = \text{Br}, \text{I}$, while $[\text{Cd}_4\text{Cl}_3(\text{SPh})_7]^{2-}$ is the most abundant ion in the spectrum of $[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]^{2-}$. Also, while the m/z 771 peak assigned to both $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and $[\text{Cd}_2(\text{SPh})_5]^-$ is absent in the 5 V spectrum of $[\text{Cd}_4\text{Br}_4(\text{SPh})_6]^{2-}$ and $[\text{Cd}_4\text{I}_4(\text{SPh})_6]^{2-}$, this peak is clearly visible in the spectrum of $[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]^{2-}$. The isotopic mass distribution showed peaks at half-integral mass units, which is characteristic of $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$, and this is further evidence for the tendency of the $[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]^{2-}$ complex to lose Cl^- in favor of binding SPh^- .

It is interesting to note that in the intact ion group the detected species all have at least six SPh^- ligands, the composition of bridging ligands in the original structure, Figure 1a. Additionally, all ions that contain more than two cadmium atoms have at least one SPh^- ligand for every metal ion. For example, the $[\text{Cd}_2\text{X}_3(\text{SPh})_2]^-$ ion is observed, but $[\text{Cd}_2\text{X}_4(\text{SPh})]^-$ is not. These observations suggest that, in the structures containing two or more metal atoms, these are bridged by the SPh^- ligands, and the halide ligands are terminal only. This is consistent with the fact that evidence for the existence of multinuclear complexes with bridging halides, both in the solid state and in solution, is scarce.³³ The complexes $[\text{Cd}_2\text{X}_6]^{2-}$ have been identified in the solid state. The similarity between the solid state and solution vibrational spectra of $[\text{Cd}_2\text{Cl}_6]^{2-}$ suggests that these species are also present in solution.³⁴ The limited observations of such halide-bridged solution species probably arise from the tendency of such species to dissociate to mononuclear ions. This, and the presence of the much stronger bridging thiophenolate ligands, would explain the absence of species containing bridging halides in the spectrum of $[\text{Cd}_4\text{X}_4(\text{SPh})_6]^{2-}$.

A mixed-ligand system of iodide, bromide, and thiophenolate was obtained by dissolving equimolar amounts of $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{-Br}_4(\text{SPh})_6]$ and $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{I}_4(\text{SPh})_6]$ in acetonitrile. Figure 2 shows the spectrum at a cone voltage of 5 V. The predominant species, listed in Table 3, are the hexakis(thiophenolate) ions $[\text{Cd}_4\text{I}_4(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{I}_3\text{Br}(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{I}_2\text{Br}_2(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{-IBr}_3(\text{SPh})_6]^{2-}$, and $[\text{Cd}_4\text{Br}_4(\text{SPh})_6]^{2-}$ and the heptakis(thiophenolate) ions $[\text{Cd}_4\text{IBr}_2(\text{SPh})_7]^{2-}$, $[\text{Cd}_4\text{I}_2\text{Br}(\text{SPh})_7]^{2-}$, $[\text{Cd}_4\text{I}_3(\text{SPh})_7]^{2-}$, and $[\text{Cd}_4\text{Br}_3(\text{SPh})_7]^{2-}$. The integrated intensity ratio of $[\text{Cd}_4\text{I}_4(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{I}_3\text{Br}_2(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{I}_2\text{Br}_2(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{IBr}_3(\text{SPh})_6]^{2-}$, and $[\text{Cd}_4\text{Br}_4(\text{SPh})_6]^{2-}$ is 1:3:5:3:1. This agrees well with the 1:4:6:4:1 ratio predicted for statistical exchange. Comparison of the observed isotope patterns with the calculated patterns confirmed that at this low voltage the peaks contain minimal contribution from the fragment ions $[\text{Cd}_2\text{I}_2(\text{SPh})_3]^-$ (m/z 712), $[\text{Cd}_2\text{IBr}(\text{SPh})_3]^-$ (m/z 759), and $[\text{Cd}_2\text{Br}_2(\text{SPh})_3]^-$ (m/z 806). The species $[\text{Cd}_4\text{IBr}_2(\text{SPh})_7]^{2-}$ and

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(34) Goggin, P. L.; Goodfellow, R. J.; Kessler, K. J. *Chem. Soc., Dalton Trans.* **1977**, 1914.

Table 1. Anionic Species Observed in the ES Mass Spectra of [Me₄N]₂[Cd(SPh)₄], [Me₄N]₂[Zn(SPh)₄], [Me₄N]₂[Cd₄(SPh)₁₀], [Me₄N]₂[Zn₄(SPh)₁₀], [Me₄N]₄[S₄Cd₁₀(SPh)₁₆], [Me₄N]₄[Se₄Cd₁₀(SPh)₁₆], and [Me₄N]₄[S₄Zn₁₀(SPh)₁₆]^a

| compound | ion | <i>m/z</i> | relative peak height (%) | | |
|--|---|--------------------------------------|--------------------------|-----------|-----------|
| | | | cone 5 V | cone 10 V | cone 20 V |
| [Me ₄ N] ₂ [Cd(SPh) ₄] ^b | [Cd(SPh) ₃] ⁻ | 440 | 100 | | 100 |
| | [Cd ₂ (SPh) ₅] ⁻ | 771 | 55 | | 12 |
| | [Cd ₄ (SPh) ₁₀] ²⁻ | 771 | <i>c</i> | | |
| | [Cd ₃ (SPh) ₇] ⁻ | 1101 | | | 7 |
| | [(Me ₄ N)Cd(SPh) ₄] ⁻ | 624 | 7 | | 5 |
| | [Cd(SPh) ₄] ²⁻ | 275 | 37 | | |
| [Me ₄ N] ₂ [Zn(SPh) ₄] ^b | [Zn(SPh) ₃] ⁻ | 393 | 15 | | 100 |
| | [Zn ₂ (SPh) ₅] ⁻ | 677 | 100 | | 46 |
| | [Zn ₄ (SPh) ₁₀] ²⁻ | 677 | <i>d</i> | | |
| | [Zn ₃ (SPh) ₇] ⁻ | 960 | 5 | | 46 |
| | [Zn ₄ (SPh) ₉] ⁻ | 1242 | 7 | | 3 |
| [Me ₄ N] ₂ [Cd ₄ (SPh) ₁₀] | [Cd(SPh) ₃] ⁻ | 441 | 48 | | 100 |
| | [Cd ₂ (SPh) ₅] ⁻ | 771 | <i>c</i> | | 33 |
| | [Cd ₃ (SPh) ₇] ⁻ | 1101 | 3 | | 6 |
| | [Cd ₄ (SPh) ₁₀] ²⁻ | 771 | 100 | | |
| [Me ₄ N] ₂ [Zn ₄ (SPh) ₁₀] | [Zn(SPh) ₃] ⁻ | 393 | 22 | | 100 |
| | [Zn ₂ (SPh) ₅] ⁻ | 677 | <i>d</i> | | 19 |
| | [Zn ₃ (SPh) ₇] ⁻ | 960 | 3 | | 81 |
| | [Zn ₄ (SPh) ₁₀] ²⁻ | 677 | 100 | | |
| | [(Me ₄ N)Zn ₄ (SPh) ₁₀] ⁻ | 1427 | 8 | | 9 |
| | [Zn ₄ (SPh) ₉] ⁻ | 1242 | 1 | | 1 |
| | | | | | |
| [Me ₄ N] ₄ [S ₄ Cd ₁₀ (SPh) ₁₆] | [Cd(SPh) ₃] ⁻ | 441 | 5 | 24 | 100 |
| | [S ₄ Cd ₈ (SPh) ₁₀] ²⁻ | 1060 | | 5 | 85 |
| | [S ₄ Cd ₉ (SPh) ₁₂] ²⁻ | 1226 | | 2 | 21 |
| | [S ₄ Cd ₁₀ (SPh) ₁₅] ³⁻ | 964 | 49 | 18 | 8 |
| | [(Me ₄ N)S ₄ Cd ₁₀ (SPh) ₁₆] ³⁻ | 1025 | 33 | 18 | 6 |
| | [S ₄ Cd ₁₀ (SPh) ₁₆] ⁴⁻ | 750 | 100 | 100 | 45 |
| | [(Me ₄ N)S ₄ Cd ₉ (SPh) ₁₃] ²⁻ | 1317 | 5 | 7 | 11 |
| | [(Me ₄ N)S ₄ Cd ₁₀ (SPh) ₁₅] ²⁻ | 1482 | 13 | 10 | 10 |
| | [(Me ₄ N) ₂ S ₄ Cd ₁₀ (SPh) ₁₆] ²⁻ | 1574 | 7 | 4 | 10 |
| | [(Me ₄ N)S ₄ Cd ₈ (SPh) ₁₀] ⁻ | 2193 | | | 8 |
| | | | | | |
| | | | | | |
| | [Me ₄ N] ₄ [Se ₄ Cd ₁₀ (SPh) ₁₆] | [Cd(SPh) ₃] ⁻ | 440 | 1 | 20 |
| [Se ₄ Cd ₈ (SPh) ₁₀] ²⁻ | | 1153 | | 5 | 25 |
| [Se ₄ Cd ₉ (SPh) ₁₂] ²⁻ | | 1319 | 1 | 20 | 100 |
| [Se ₄ Cd ₁₀ (SPh) ₁₅] ³⁻ | | 1026 | 100 | 100 | 6 |
| [(Me ₄ N)Se ₄ Cd ₁₀ (SPh) ₁₆] ³⁻ | | 1087 | | 13 | |
| [(Me ₄ N)Se ₄ Cd ₁₀ (SPh) ₁₅] ³⁻ | | 1576 | 19 | 22 | 24 |
| [Se ₄ Cd ₁₀ (SPh) ₁₄] ²⁻ | | 1484 | 12 | 14 | 26 |
| [Se ₄ Cd ₁₀ (SPh) ₁₆] ⁴⁻ | | 797 | 33 | 34 | 1 |
| [(Me ₄ N)S ₄ Cd ₈ (SPh) ₁₀] ⁻ | | 2381 | | | 3 |
| | | | | | |
| [Me ₄ N] ₄ [S ₄ Zn ₁₀ (SPh) ₁₆] | [Zn(SPh) ₃] ⁻ | 393 | 54 | 85 | 70 |
| | [S ₄ Zn ₉ (SPh) ₁₂] ²⁻ | 1013 | 26 | 100 | 100 |
| | [S ₄ Zn ₁₀ (SPh) ₁₅] ³⁻ | 806 | 97 | 26 | |
| | [(Me ₄ N)S ₄ Zn ₁₀ (SPh) ₁₆] ³⁻ | 868 | 100 | 74 | 39 |
| | [(Me ₄ N)S ₄ Zn ₁₀ (SPh) ₁₅] ²⁻ | 1247 | 76 | 52 | 30 |
| | [S ₄ Zn ₁₀ (SPh) ₁₄] ²⁻ | 1155 | 29 | 17 | 15 |
| | [S ₄ Zn ₁₀ (SPh) ₁₆] ⁴⁻ | 632 | 70 | 66 | |
| | [(Me ₄ N)S ₄ Zn ₉ (SPh) ₁₂] ⁻ | 2001 | | | 4 |
| | [(Me ₄ N) ₂ S ₄ Zn ₁₀ (SPh) ₁₆] ²⁻ | 1338 | 22 | 16 | 14 |
| | [(Me ₄ N)S ₄ Zn ₈ (SPh) ₁₀] ⁻ | 1817 | | 2 | 11 |
| | [(Me ₄ N) ₂ S ₄ Zn ₉ (SPh) ₁₃] ⁻ | 2284 | | | 1 |
| | [(Me ₄ N)S ₄ Zn ₉ (SPh) ₁₃] ²⁻ | 1105 | 3 | 4 | 5 |

^a The observed *m/z* values are those of the most intense peaks 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⁻ at *m/z* 109 is also observed in this case (see text). ^c The isotopic mass distribution pattern shows that the *m/z* 771 peak in the spectra of [Me₄N]₂[Cd(SPh)₄] and [Me₄N]₂[Cd₄(SPh)₁₀] contains contributions from [Cd₄(SPh)₁₀]²⁻ and [Cd₂(SPh)₅]⁻. In the the 5 V spectrum of [Me₄N]₂[Cd₄(SPh)₁₀], the intensity ratio of [Cd₄(SPh)₁₀]²⁻ and [Cd₂(SPh)₅]⁻ is 6:1. ^d The *m/z* 677 peak in the spectrum of [Me₄N]₂[Zn₄(SPh)₁₀] at 5 V contains contributions from [Zn₄(SPh)₁₀]²⁻ and [Zn₂(SPh)₅]⁻ in the ratio 12:1.

[Cd₄I₂Br(SPh)₇]²⁻ with opposite I:Br ratios give peaks of similar intensities. This is also the case for the [Cd₄I₃(SPh)₇]²⁻ and [Cd₄Br₃(SPh)₇]²⁻ and indicates that the tendency to fragment is not affected by the I:Br ratio. This observation is confirmed by the fact that the [CdX_{3-n}(SPh)_n]⁻ ions (the main fragment species) which have opposite I:Br ratios give peaks of similar intensities. On the basis that the tendency to fragment is unaffected by the I:Br composition, one can assume that the

peak ratio 1:3:5:3:1 represents the equilibrium distribution of species. The observation that the heptakis(thiophenolate) species [Cd₄I₂Br(SPh)₇]²⁻ and [Cd₄I₃Br₂(SPh)₇]²⁻ are dominant species is in accord with the presence of strong peaks due to analogous species observed in the spectra of the pure compounds. As in the case of the pure compounds, no exchange species are observed which have more than four halides. Again, this confirms the poorly bridging nature of the halide ligands

Table 2. Anionic Species Observed in the ES Mass Spectra of $[\text{Me}_4\text{N}]_2[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]$, $[\text{Me}_4\text{N}]_2[\text{Cd}_4\text{Br}_4(\text{SPh})_6]$, and $[\text{Me}_4\text{N}]_2[\text{Cd}_4\text{I}_4(\text{SPh})_6]^a$

| compound | ion | m/z | relative peak height (%) | | |
|---|---|-------|--------------------------|-----------|-----------|
| | | | cone 5 V | cone 10 V | cone 20 V |
| $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]$ | $[\text{CdCl}_3]^-$ | 219 | 7 | 15 | 21 |
| | $[\text{CdCl}_2(\text{SPh})]^-$ | 292 | 13 | 56 | 59 |
| | $[\text{CdCl}(\text{SPh})_2]^-$ | 366 | 8 | 54 | 58 |
| | $[\text{Cd}(\text{SPh})_3]^-$ | 440 | 1 | 9 | 12 |
| | $[\text{Cd}_2\text{Cl}_3(\text{SPh})_2]^-$ | 550 | 1 | 9 | 13 |
| | $[\text{Cd}_2\text{Cl}_2(\text{SPh})_3]^-$ | 623 | <i>b</i> | <i>b</i> | 38 |
| | $[\text{Cd}_2\text{Cl}(\text{SPh})_4]^-$ | 697 | <i>b</i> | <i>b</i> | 33 |
| | $[\text{Cd}_2(\text{SPh})_5]^-$ | 771 | <i>b</i> | 5 | 6 |
| | $[\text{Cd}_3\text{Cl}_4(\text{SPh})_3]^-$ | 807 | 1 | 4 | 5 |
| | $[\text{Cd}_3\text{Cl}_3(\text{SPh})_4]^-$ | 880 | 4 | 45 | 52 |
| | $[\text{Cd}_3\text{Cl}_2(\text{SPh})_5]^-$ | 954 | 9 | 98 | 100 |
| | $[\text{Cd}_3\text{Cl}(\text{SPh})_6]^-$ | 1028 | 5 | 40 | 44 |
| | $[\text{Cd}_3(\text{SPh})_7]^-$ | 1101 | 1 | 3 | 3 |
| | $[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]^{2-}$ | 623 | 95 | 100 | |
| | $[\text{Cd}_4\text{Cl}_3(\text{SPh})_7]^{2-}$ | 660 | 100 | 71 | |
| | $[\text{Cd}_4\text{Cl}_2(\text{SPh})_8]^{2-}$ | 697 | 36 | 48 | |
| | $[\text{Cd}_4\text{Cl}(\text{SPh})_9]^{2-}$ | 734 | 7 | 5 | |
| | $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ | 771 | 5 | | |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{Cl}_4(\text{SPh})_6]^-$ | 1377 | 7 | 25 | 21 |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{Cl}_3(\text{SPh})_7]^-$ | 1450 | 7 | 19 | 13 |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{Cl}_2(\text{SPh})_8]^-$ | 1524 | 1 | 2 | |
| $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{Br}_4(\text{SPh})_6]$ | $[\text{CdBr}_3]^-$ | 352 | 43 | 84 | 93 |
| | $[\text{CdBr}_2(\text{SPh})]^-$ | 382 | 22 | 100 | 100 |
| | $[\text{CdBr}(\text{SPh})_2]^-$ | 411 | 5 | 49 | 49 |
| | $[\text{Cd}(\text{SPh})_3]^-$ | 440 | | 6 | 5 |
| | $[\text{Cd}_2\text{Br}_3(\text{SPh})_2]^-$ | 683 | 3 | 2 | 12 |
| | $[\text{Cd}_2\text{Br}_2(\text{SPh})_3]^-$ | 712 | <i>b</i> | <i>b</i> | 40 |
| | $[\text{Cd}_2\text{Br}(\text{SPh})_4]^-$ | 741 | <i>b</i> | <i>b</i> | 32 |
| | $[\text{Cd}_2(\text{SPh})_5]^-$ | 771 | | 9 | 5 |
| | $[\text{Cd}_3\text{Br}_3(\text{SPh})_4]^-$ | 1014 | 2 | 5 | 21 |
| | $[\text{Cd}_3\text{Br}_2(\text{SPh})_5]^-$ | 1043 | 6 | 22 | 97 |
| | $[\text{Cd}_3\text{Br}(\text{SPh})_6]^-$ | 1072 | 3 | 22 | 51 |
| | $[\text{Cd}_3(\text{SPh})_7]^-$ | 1101 | | 5 | 7 |
| | $[\text{Cd}_4\text{Br}_4(\text{SPh})_6]^{2-}$ | 712 | 100 | 45 | |
| | $[\text{Cd}_4\text{Br}_3(\text{SPh})_7]^{2-}$ | 727 | 63 | 85 | |
| | $[\text{Cd}_4\text{Br}_2(\text{SPh})_8]^{2-}$ | 741 | 16 | 81 | |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{Br}_2(\text{SPh})_8]^-$ | 1613 | 1 | 5 | 2 |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{Br}_3(\text{SPh})_7]^-$ | 1584 | 5 | 7 | 12 |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{Br}_4(\text{SPh})_6]^-$ | 1555 | 8 | 3 | 18 |
| $[(\text{Et}_4\text{N})\text{Cd}_4(\text{SPh})_{10}]^-$ | 1615 | 1 | | | |
| $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{I}_4(\text{SPh})_6]$ | $[\text{CdI}_3]^-$ | 493 | 32 | 100 | 91 |
| | $[\text{CdI}_2(\text{SPh})]^-$ | 475 | 16 | 53 | 100 |
| | $[\text{CdI}(\text{SPh})_2]^-$ | 458 | 3 | 11 | 30 |
| | $[\text{Cd}_2\text{I}(\text{SPh})_4]^-$ | 788 | <i>a</i> | 9 | 20 |
| | $[\text{Cd}_2\text{I}_2(\text{SPh})_3]^-$ | 806 | <i>a</i> | <i>a</i> | 44 |
| | $[\text{Cd}_2\text{I}_3(\text{SPh})_2]^-$ | 824 | 1 | 5 | 1 |
| | $[\text{Cd}_3(\text{SPh})_7]^-$ | 1101 | | 1 | 3 |
| | $[\text{Cd}_3\text{I}(\text{SPh})_6]^-$ | 1119 | 4 | 16 | 44 |
| | $[\text{Cd}_3\text{I}_2(\text{SPh})_5]^-$ | 1137 | 8 | 32 | 98 |
| | $[\text{Cd}_3\text{I}_3(\text{SPh})_4]^-$ | 1155 | 1 | 7 | 26 |
| | $[\text{Cd}_4\text{I}_2(\text{SPh})_8]^{2-}$ | 788 | 5 | | |
| | $[\text{Cd}_4\text{I}_3(\text{SPh})_7]^{2-}$ | 797 | 32 | 18 | |
| | $[\text{Cd}_4\text{I}_4(\text{SPh})_6]^{2-}$ | 806 | 100 | 50 | |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{I}_3(\text{SPh})_7]^-$ | 1725 | 3 | 5 | 5 |
| | $[(\text{Et}_4\text{N})\text{Cd}_4\text{I}_4(\text{SPh})_6]^-$ | 1743 | 9 | 18 | 18 |

^a A strong peak due to X^- in each spectrum has been omitted to allow a more accurate comparison of Cd-containing species. ^b Peak contains a contribution from the corresponding doubly charged intact ion with twice the mass, but with the same m/z value. For example, the m/z 623 peak in the 10 V spectrum of $[\text{Me}_4\text{N}]_2[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]$ contains contributions from both the intact ion $[\text{Cd}_4\text{Cl}_4(\text{SPh})_6]^{2-}$ and the monoion $[\text{Cd}_2\text{Cl}_2(\text{SPh})_3]^-$. In the 20 V spectra, the isotope pattern of these peaks showed that the intensity was entirely due to the monoion species.

when compared to thiophenolate. Halide-rich exchange species of the type $[\text{Cd}_4\text{X}_5(\text{SPh})_5]^{2-}$ probably fragment to $[\text{CdX}_3]^-$ and $[\text{Cd}_3\text{X}_2(\text{SPh})_5]^-$ ions, which are abundant species in the spectra at 5 and 20 V. The results are consistent with the fact that only the four terminal SPh⁻ ligands of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ can be replaced by a halide.^{6,10}

(c) Metal Exchange. The spectrum of an equimolar mixture of $[\text{Me}_4\text{N}]_2[\text{Cd}_4(\text{SPh})_{10}]$ and $[\text{Me}_4\text{N}]_2[\text{Zn}_4(\text{SPh})_{10}]$ at a cone voltage of 5 V is shown in Figure 3. The large number of peaks in this spectrum is due to mixed-metal species. The detected species are listed in Table 4 and include the intact ions $[\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{10}]^{2-}$ ($n = 0-4$), the Me_4N^+ aggregates

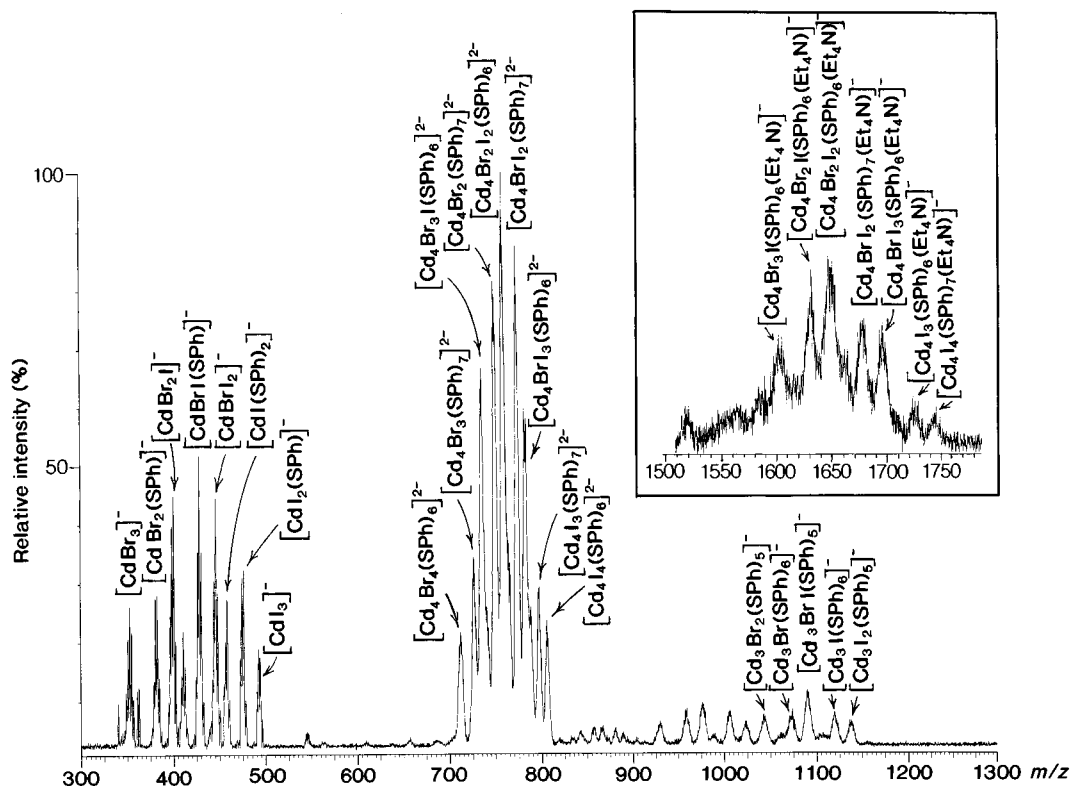
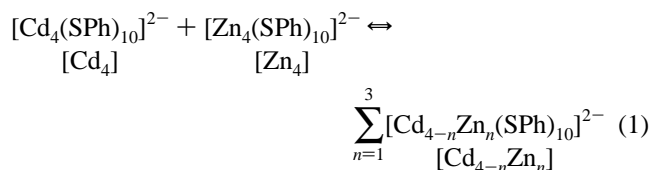


Figure 2. ES mass spectrum at a cone voltage of 5 V for an equimolar mixture of $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{Br}_4(\text{SPh})_6]$ and $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{I}_4(\text{SPh})_6]$. The inset shows an expanded plot of a series of weak peaks observed at high m/z values. The ratio of the integrated peak intensities of $[\text{Cd}_4\text{I}_4(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{I}_3\text{Br}(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{I}_2\text{Br}_2(\text{SPh})_6]^{2-}$, $[\text{Cd}_4\text{IBr}_3(\text{SPh})_6]^{2-}$, and $[\text{Cd}_4\text{Br}_4(\text{SPh})_6]^{2-}$ is 1:3:5:3:1, compared to 1:4:6:4:1 for the statistical distribution of these species.

$(\text{Me}_4\text{N})\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{10}]^-$ ($n = 0-4$), and the fragment species $[\text{Cd}_{3-n}\text{Zn}_n(\text{SPh})_7]^-$ ($n = 0-3$) and $[\text{Cd}_{2-n}\text{Zn}_n(\text{SPh})_5]^-$ ($n = 0-2$). The intact dianions $[\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{10}]^{2-}$ dominate, as was also the case for the pure compounds at this voltage. The exchange of metal ions may be represented by the process



The relative intensities of the peaks did not change with aging of the mixture for several weeks. The spectrum is therefore assumed to be characteristic of an equilibrium exchange state. The contribution to the intensities of the peaks of $[\text{Cd}_4]$, $[\text{Cd}_2\text{Zn}_2]$, and $[\text{Zn}_4]$ from the fragment species $[\text{Cd}_{2-n}\text{Zn}_n(\text{SPh})_5]^-$ ($n = 0-2$) was less than 10%. The distribution of the five intact ions $[\text{Cd}_4]$, $[\text{Cd}_3\text{Zn}]$, $[\text{Cd}_2\text{Zn}_2]$, $[\text{CdZn}_3]$, and $[\text{Zn}_4]$ was estimated to 2.6:3.6:4.9:2.0:1.0 by peak integration. The relative abundances would be 1:4:6:4:1 in the case of statistical exchange. The two Cd-rich species $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and $[\text{Cd}_3\text{Zn}(\text{SPh})_{10}]^{2-}$ are both more abundant than the corresponding Zn-rich species $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ and $[\text{CdZn}_3(\text{SPh})_{10}]^{2-}$. This is in accord with the finding that the Zn complex has a higher tendency to fragment. In the spectrum, this is confirmed by the intensity of the peak due to $[\text{Zn}(\text{SPh})_3]^-$, which is ca. twice as intense as the peak due to $[\text{Cd}(\text{SPh})_3]^-$. Hagen et al.²⁰ studied a series of $[\text{M}_4(\text{SPh})_{10}]^{2-}$ complexes by NMR and found that the equilibrium constants for the mixed-metal systems, $\text{Fe}^{2+}/\text{Co}^{2+}$, $\text{Co}^{2+}/\text{Zn}^{2+}$, and $\text{Co}^{2+}/\text{Cd}^{2+}$ were all similar and near the statistical values. Dance²¹ also observed ^{113}Cd NMR signals for the $\text{Cd}^{2+}/\text{Zn}^{2+}$ case with relative intensities that were consistent with those calculated from random distribution of

the metals. However, a resonance for the $[\text{Cd}_2\text{Zn}_2(\text{SPh})_{10}]^{2-}$ ion was absent, and the two possible explanations were given: (i) that the resonance of $[\text{Cd}_2\text{Zn}_2(\text{SPh})_{10}]^{2-}$ overlaps that of $[\text{Cd}_3\text{Zn}(\text{SPh})_{10}]^{2-}$; (ii) that the substitution is biased against $[\text{Cd}_2\text{Zn}_2(\text{SPh})_{10}]^{2-}$ for size reasons. Electrospray mass spectrometry, however, clearly shows that the latter is not the case.

The $[\text{E}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ ($\text{E} = \text{S}, \text{Se}$) Clusters. (a) Parent Complexes. The ES mass spectra of the clusters $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$, $[\text{Se}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$, and $[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ at a cone voltage of 20 V are shown in Figure 4. Similar fragmentation patterns are observed for all three clusters, and the major species are listed in Table 1. As in the case of the compounds discussed above, these spectra also show a strong peak due to $[\text{M}(\text{SPh})_3]^-$. The $[\text{M}(\text{SPh})_3]^-$ ions dominate the spectra at a cone voltage of 20 V. The other dominant species at this voltage all contain an E_4M_x unit ($x = 8-10$), including the intact ions $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$. The intact ions become abundant in the spectra at a cone voltage of 5 V. The isotopic mass distribution for the $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ peak has been shown to have peaks at quarter-integral mass units consistent with the 4- charge on this species.⁵ The Me_4N^+ "adducts" of the $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ species, $[(\text{Me}_4\text{N})\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{3-}$, are also observed, and these give strong peaks for cone voltages up to 20 V. The formation of such aggregates with Me_4N^+ is a means by which the more highly charged $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ clusters can lose negative charge and remain intact under the electric field of the applied cone voltage. The other peaks in the spectra correspond to fragmentation originating from the precursor ions: $[\text{E}_4\text{M}_{10}(\text{SPh})_{15}]^{3-}$ (loss of SPh^-); $[\text{S}_4\text{M}_9(\text{SPh})_{12}]^{2-}$ (loss of $[\text{M}(\text{SPh})_4]^{2-}$); $[\text{E}_4\text{M}_8(\text{SPh})_{10}]^{2-}$ (loss of two $[\text{M}(\text{SPh})_3]^-$). In each case, the species that are lost are ones which give rise to the more intense peaks in the spectra of $[\text{Me}_4\text{N}]_2[\text{M}(\text{SPh})_4]$ and $[\text{Me}_4\text{N}]_2[\text{M}_4(\text{SPh})_{10}]$. Comparison of peak intensities shows that the $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ cluster is the most stable among the three

Table 3. Anionic Species Observed in the ES Mass Spectrum of a Mixture of $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{Br}_4(\text{SPh})_6]$ and $[\text{Et}_4\text{N}]_2[\text{Cd}_4\text{I}_4(\text{SPh})_6]$ in Equimolar Fractions

| ion | m/z | relative peak height (%) | |
|---|-------|--------------------------|-----------|
| | | cone 5 V | cone 20 V |
| $[\text{CdBr}_3]^-$ | 352 | 25 | 50 |
| $[\text{CdBr}_2(\text{SPh})]^-$ | 381 | 26 | 86 |
| $[\text{CdBr}_2\text{I}]^-$ | 399 | 44 | 49 |
| $[\text{CdBr}(\text{SPh})_2]^-$ | 411 | 21 | 72 |
| $[\text{CdIBr}(\text{SPh})]^-$ | 428 | 51 | 100 |
| $[\text{Cd}(\text{SPh})_3]^-$ | 440 | 4 | 18 |
| $[\text{CdI}_2\text{Br}]^-$ | 446 | 43 | 37 |
| $[\text{CdI}(\text{SPh})_2]^-$ | 458 | 26 | 61 |
| $[\text{CdI}_2(\text{SPh})]^-$ | 475 | 31 | 50 |
| $[\text{CdI}_3]^-$ | 493 | 17 | 26 |
| $[\text{Cd}_2\text{Br}_3(\text{SPh})_2]^-$ | 683 | 1 | 2 |
| $[\text{Cd}_2\text{Br}_2(\text{SPh})_3]^-$ | 712 | <i>a</i> | 13 |
| $[\text{Cd}_2\text{IBr}_2(\text{SPh})_2]^-$ | 730 | <i>b</i> | 3 |
| $[\text{Cd}_2\text{Br}(\text{SPh})_4]^-$ | 741 | <i>a</i> | 29 |
| $[\text{Cd}_2\text{IBr}(\text{SPh})_3]^-$ | 759 | <i>a</i> | 23 |
| $[\text{Cd}_2(\text{SPh})_5]^-$ | 771 | <i>a</i> | 17 |
| $[\text{Cd}_2\text{BrI}_2(\text{SPh})_2]^-$ | 777 | <i>b</i> | 2 |
| $[\text{Cd}_2\text{I}(\text{SPh})_4]^-$ | 788 | <i>a</i> | 28 |
| $[\text{Cd}_2\text{I}_2(\text{SPh})_3]^-$ | 806 | <i>a</i> | 10 |
| $[\text{Cd}_2\text{I}_3(\text{SPh})_2]^-$ | 824 | | 1 |
| $[\text{Cd}_3\text{Br}_3(\text{SPh})_4]^-$ | 1014 | | 5 |
| $[\text{Cd}_3\text{Br}_2(\text{SPh})_5]^-$ | 1043 | 5 | 29 |
| $[\text{Cd}_3\text{IBr}_2(\text{SPh})_4]^-$ | 1061 | 1 | 9 |
| $[\text{Cd}_3\text{Br}(\text{SPh})_6]^-$ | 1072 | 7 | 51 |
| $[\text{Cd}_3\text{IBr}(\text{SPh})_5]^-$ | 1090 | 10 | 44 |
| $[\text{Cd}_3(\text{SPh})_7]^-$ | 1101 | | 24 |
| $[\text{Cd}_3\text{I}_2\text{Br}(\text{SPh})_4]^-$ | 1107 | | <i>a</i> |
| $[\text{Cd}_3\text{I}(\text{SPh})_6]^-$ | 1119 | 6 | 40 |
| $[\text{Cd}_3\text{I}_2(\text{SPh})_5]^-$ | 1137 | 5 | 17 |
| $[\text{Cd}_3\text{I}_3(\text{SPh})_4]^-$ | 1155 | | 2 |
| $[\text{Cd}_4\text{Br}_4(\text{SPh})_6]^{2-}$ | 712 | 20 | |
| $[\text{Cd}_4\text{Br}_3(\text{SPh})_7]^{2-}$ | 727 | 32 | |
| $[\text{Cd}_4\text{IBr}_3(\text{SPh})_6]^{2-}$ | 736 | 66 | |
| $[\text{Cd}_4\text{Br}_2(\text{SPh})_8]^{2-}$ | 741 | 24 | |
| $[\text{Cd}_4\text{IBr}_2(\text{SPh})_7]^{2-}$ | 750 | 81 | |
| $[\text{Cd}_4\text{I}_2\text{Br}_2(\text{SPh})_6]^{2-}$ | 759 | 100 | |
| $[\text{Cd}_4\text{IBr}(\text{SPh})_8]^{2-}$ | 765 | <i>a</i> | |
| $[\text{Cd}_4\text{I}_2\text{Br}(\text{SPh})_7]^{2-}$ | 774 | 87 | |
| $[\text{Cd}_4\text{I}_3\text{Br}(\text{SPh})_6]^{2-}$ | 783 | 59 | |
| $[\text{Cd}_4\text{I}_2(\text{SPh})_8]^{2-}$ | 788 | 24 | |
| $[\text{Cd}_4\text{I}_3(\text{SPh})_7]^{2-}$ | 797 | 27 | |
| $[\text{Cd}_4\text{I}_4(\text{SPh})_6]^{2-}$ | 806 | 22 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{Br}_3(\text{SPh})_7]^-$ | 1583 | 1 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{IBr}_3(\text{SPh})_6]^-$ | 1602 | 4 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{IBr}_2(\text{SPh})_6]^-$ | 1631 | 6 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{I}_2\text{Br}_2(\text{SPh})_6]^-$ | 1649 | 7 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{I}_2\text{Br}(\text{SPh})_7]^-$ | 1679 | 5 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{I}_3\text{Br}(\text{SPh})_6]^-$ | 1696 | 5 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{I}_3(\text{SPh})_7]^-$ | 1725 | 1 | |
| $[(\text{Et}_4\text{N})\text{Cd}_4\text{I}_4(\text{SPh})_6]^-$ | 1743 | 1 | |

^a Peak contains contribution from the corresponding doubly charged intact ion with twice the mass, but with the same m/z value. ^b Peak obscured by adjacent and more intense peak.

clusters. The intact ion $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ gives the strongest peak in the spectrum at voltages of 5 and 10 V. The strongest peak at these voltages for the $[\text{Se}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ cluster is due to $[\text{Se}_4\text{Cd}_{10}(\text{SPh})_{15}]^{3-}$ at m/z 1026, formed from the precursor ion $[\text{Se}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ by loss of SPh^- . By comparison, the $[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ cluster loses both SPh^- and $[\text{Zn}(\text{SPh})_3]^-$ or $[\text{Zn}(\text{SPh})_4]^{2-}$ at a cone voltage of 10 V to give $[\text{S}_4\text{Zn}_9(\text{SPh})_{12}]^{2-}$ as the most abundant ion. Furthermore, the intact ions $[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{Se}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ disappear completely from the spectrum at 20 V while $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ still remains an abundant ion.

It is noteworthy that no fragmentation is evident in the 20 V spectra which involve breaking of the metal–sulfide or metal–

selenide bonds; i.e., the fragments all contain an E_4M_x unit with $x \geq 8$. For example, the four sulfide sulfur atoms of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and the cadmium atoms which are directly bonded to them constitute a S_4Cd_6 unit, but the smallest unit observed in the fragments at a cone voltage of 20 V is S_4Cd_8 in $[\text{S}_4\text{Cd}_8(\text{SPh})_{10}]^{2-}$, which derives from the precursor ion by loss of two $[\text{Cd}(\text{SPh})_3]^-$. Removal of a third $[\text{Cd}(\text{SPh})_3]^-$ would yield $[\text{S}_4\text{Cd}_7(\text{SPh})_7]^-$, which would have an m/z value of 1679. 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 voltages of 30 and 60 V, Table 5. At the very high cone voltage of 120 V, the S_4Cd_6 core of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ is observed to fragment completely. The dominant species in this spectrum are $[\text{S}_4\text{Cd}_7(\text{SPh})_7]^-$, $[\text{S}_4\text{Cd}_6(\text{SPh})_5]^-$, $[\text{S}_4\text{Cd}_5(\text{SPh})_3]^-$, and $[\text{S}_4\text{Cd}_4(\text{SPh})]^-$, all formed from $[\text{S}_4\text{Cd}_7(\text{SPh})_7]^-$ by loss of one or more neutral $\text{Cd}(\text{SPh})_2$ species, and the core fragments $[\text{S}_3\text{Cd}_3(\text{SPh})]^-$, $[\text{S}_2\text{Cd}_2(\text{SPh})]^-$, and $[\text{SCd}(\text{SPh})]^-$. A second series of weaker peaks appear at positions 183 m/z units higher than the dominant peaks. This shift corresponds to the mass of $[\text{SPh}(\text{Me}_4\text{N})]$. Thus, these species are ion combination products of the more dominant species and $\text{SPh}(\text{Me}_4\text{N})$. Electrospray mass spectra of salts typically give such aggregates at high cone voltages.

(b) Metal Exchange. The ES spectrum at a cone voltage of 5 V of an equimolar mixture of $[\text{Me}_4\text{N}]_4[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]$ and $[\text{Me}_4\text{N}]_4[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]$ equilibrated for 7 days is shown in Figure 5. The predominant species observed are listed in Table 6. Peaks due to intact ions of all the possible metal compositions $[\text{S}_4\text{Cd}_{10-n}\text{Zn}_n(\text{SPh})_{16}]^{4-}$ ($n = 0-10$) are observed. The fragmentation pathways for these ions are the same as those for the pure materials, resulting in dissociation products with different metal compositions. The peak pattern due to the intact ions $[\text{S}_4\text{Cd}_{10-n}\text{Zn}_n(\text{SPh})_{16}]^{4-}$ is compared with the statistical distribution of species in Figure 6 b,c. The statistical ratio for the 11 different species $[\text{Cd}_{10-n}\text{Zn}_n]$ ($n = 0-10$) is 1:10:45:120:210:252:210:120:45:10:1. The integrated peak ratio 1.0:5.8:13.4:21.2:29.4:26.3:20.1:12.3:6.2:2.8:0.7 shows that the species with a high proportion of either metal type are preferred. This observation agrees with the ^{113}Cd NMR results of Dance.²¹ The integrated intensities of the resonances of the outer Cd^0 and Zn^0 atoms on $[\text{S}_4\text{Cd}_i^i]$ and $[\text{S}_4\text{Zn}_i^i]$ cores showed a marked preference for M^0 atoms to be associated with M^i of the same metal. That is, the equilibrium state involves incomplete exchange.

We note that the m/z 690 peak due to $[\text{S}_4\text{Cd}_5\text{Zn}_5(\text{SPh})_{16}]^{4-}$, which is the most abundant species in the statistical distribution, is slightly weaker than the m/z 702 peak due to $[\text{S}_4\text{Cd}_6\text{Zn}_4(\text{SPh})_{16}]^{4-}$, the most intense peak. In fact, all the peaks due to the Zn-rich species are less abundant than those of the corresponding Cd-rich species. Again, the peak due to $[\text{Zn}(\text{SPh})_3]^-$ is more than twice as intense as the peak due to $[\text{Cd}(\text{SPh})_3]^-$, and this suggests that the asymmetric peak pattern is caused by the higher tendency for the Zn-rich species to fragment. In the spectrum of a freshly prepared solution of $[\text{S}_4\text{Cd}_{10-n}\text{Zn}_n(\text{SPh})_{16}]^{4-}$, peaks appear as two “bands”, Figure 6a; one band is due to species with Zn as the dominant metal, and the other band is due to species with Cd as the dominant metal. The strongest peaks are due to $[\text{S}_4\text{Zn}_8\text{Cd}_2(\text{SPh})_{16}]^{4-}$ at m/z 654 and $[\text{S}_4\text{Cd}_8\text{Zn}_2(\text{SPh})_{16}]^{4-}$ at m/z 727. The weakest peak (apart from those due to the pure clusters $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$) is the m/z 690 peak due to $[\text{S}_4\text{Cd}_5\text{Zn}_5(\text{SPh})_{16}]^{4-}$. The difference in the distribution of species in a fresh solution, and after aging for 7 days, shows that the outer M^0 metal ions, which bond only to SPh^- , undergo fast exchange, while exchange is much slower for the metal ions belonging to

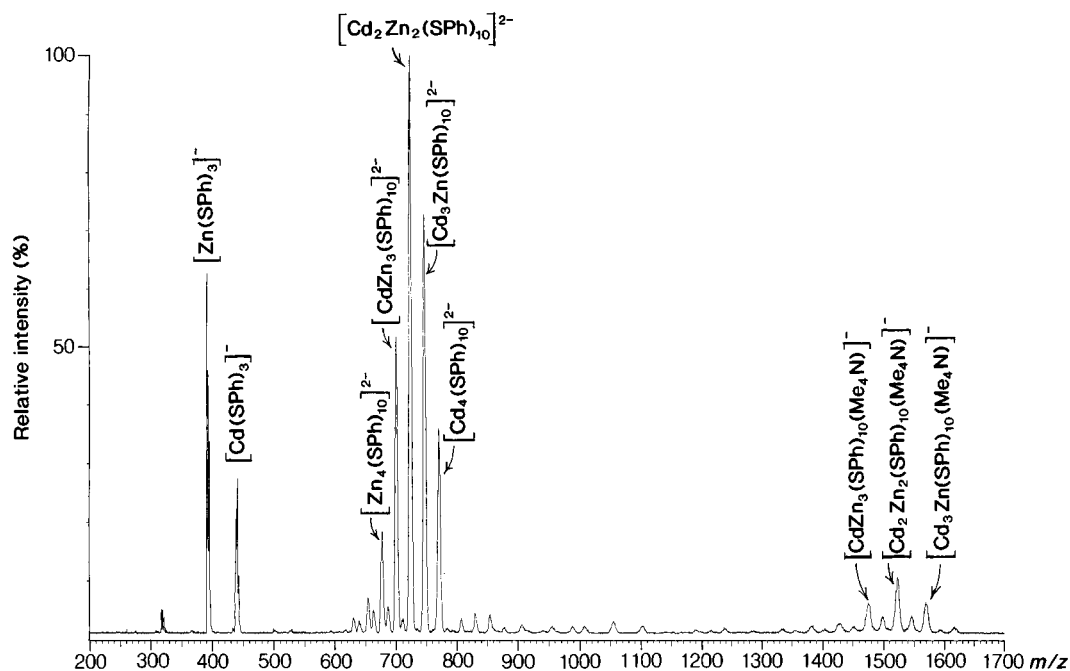


Figure 3. ES mass spectrum at a cone voltage of 5 V for an equimolar mixture of $[(\text{Me}_4\text{N})_2\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and $[(\text{Me}_4\text{N})_2\text{Zn}_4(\text{SPh})_{10}]^{2-}$. The integrated peak ratio for the metal-exchanged ions $[\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{10}]^{2-}$ is 1.0:2.0:4.9:3.6:2.6, compared to the 1:4:6:4:1 ratio for the statistical distribution of these species. The greater tendency for Zn-rich complexes to fragment, seen from the strong $[\text{Zn}(\text{SPh})_3]^-$ peak, accounts for the lower intensity of the two Zn-rich species $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ and $[\text{CdZn}_3(\text{SPh})_{10}]^{2-}$ compared with the corresponding Cd-rich species $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and $[\text{Cd}_3\text{Zn}(\text{SPh})_{10}]^{2-}$.

Table 4. Anionic Species Observed in the ES Mass Spectra of a Mixture of $[\text{Me}_4\text{N}]_2[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and $[\text{Me}_4\text{N}]_2[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ in Equimolar Fractions

| ion | m/z | peak height (%) | | | |
|--|-------|-----------------|-----------|-----------|-----------|
| | | cone 5 V | cone 10 V | cone 20 V | cone 40 V |
| $[\text{Zn}(\text{SPh})_3]^-$ | 393 | 62 | 93 | 100 | 100 |
| $[\text{Cd}(\text{SPh})_3]^-$ | 440 | 26 | 34 | 44 | 51 |
| $[\text{Zn}_2(\text{SPh})_5]^-$ | 677 | <i>a</i> | <i>a</i> | 7 | 9 |
| $[\text{ZnCd}(\text{SPh})_5]^-$ | 724 | <i>a</i> | <i>a</i> | 33 | 27 |
| $[\text{Cd}_2(\text{SPh})_5]^-$ | 771 | <i>a</i> | <i>a</i> | 28 | 26 |
| $[\text{Zn}_3(\text{SPh})_7]^-$ | 960 | | 2 | 7 | 3 |
| $[\text{Zn}_2\text{Cd}(\text{SPh})_7]^-$ | 1007 | 1 | 10 | 26 | 10 |
| $[\text{ZnCd}_2(\text{SPh})_7]^-$ | 1054 | 2 | 15 | 40 | 19 |
| $[\text{Cd}_3(\text{SPh})_7]^-$ | 1101 | 1 | 9 | 25 | 13 |
| $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ | 677 | 18 | 19 | | |
| $[\text{Zn}_3\text{Cd}(\text{SPh})_{10}]^{2-}$ | 700 | 52 | 45 | 1 | |
| $[\text{Zn}_2\text{Cd}_2(\text{SPh})_{10}]^{2-}$ | 724 | 100 | 100 | | |
| $[\text{ZnCd}_3(\text{SPh})_{10}]^{2-}$ | 747 | 73 | 60 | 1 | |
| $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ | 771 | 36 | 42 | | |
| $[(\text{Me}_4\text{N})\text{Zn}_4(\text{SPh})_{10}]^-$ | 1427 | 1 | 1 | 1 | 1 |
| $[(\text{Me}_4\text{N})\text{Zn}_3\text{Cd}(\text{SPh})_{10}]^-$ | 1474 | 5 | 5 | 3 | 3 |
| $[(\text{Me}_4\text{N})\text{Zn}_2\text{Cd}_2(\text{SPh})_{10}]^-$ | 1521 | 9 | 9 | 5 | 3 |
| $[(\text{Me}_4\text{N})\text{ZnCd}_3(\text{SPh})_{10}]^-$ | 1568 | 5 | 5 | 3 | 3 |
| $[(\text{Me}_4\text{N})\text{Cd}_4(\text{SPh})_{10}]^-$ | 1615 | 1 | 1 | 1 | 1 |

^a Peak contains a contribution from the corresponding dianionic intact ion of twice the mass, but with same m/z value. The contribution from the monoion species was found to be less than 10% at a cone voltage of 5 V; thus, at this voltage, the relative peak heights indicate the distribution of the $[\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{10}]^{2-}$ intact ion species. Note that the fragment ion $[\text{Zn}(\text{SPh})_3]^-$ is ca. twice as intense as $[\text{Cd}(\text{SPh})_3]^-$ which results in a lower intensity of the Zn-rich intact ions.

the S_4M_6 core unit. This observation was also made by Dance, on the basis of NMR measurements.²¹ Facile metal exchange involving the M^0 atoms of $[\text{S}_4\text{M}_6\text{M}^0_4(\text{SPh})_{16}]^{4-}$ is consistent with the fact that these metals and the four SPh^- ligands bound to them (three bridging and one terminal) constitute $(\mu\text{-SPh})_3\text{M}^0(\text{SPh})$ adamantane-like cages similar to those that constitute $[\text{M}_4(\text{SPh})_{10}]^{2-}$. The ratios of the intensities of the ions in the

“Zn-band” and the “Cd-band” in the spectrum of the freshly prepared mixture closely match the 1.0:2.0:4.9:3.6:2.6 ratio observed for $[\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{10}]^{2-}$. Hence, in a fresh mixture of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$, the outer M^0 metals rapidly reach an equilibrium exchange state while most of the S_4M_6 cores are unchanged. The much less facile exchange of the metals involving the S_4M_6 core unit is consistent with the stability of this unit in the ESMS spectra. As seen in the structure of $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ (Figure 1b), the exchange of M^0 atoms involves the breaking and re-forming of four metal–thiophenolate ($\text{M}-\text{SPh}$) bonds. The exchange of M^I atoms in the S_4M_6 unit involves the breaking of two metal–sulfide (M^I-S) bonds and two metal–thiophenolate (M^I-SPh) bonds. The breaking of the (M^I-S) bonds requires the entire core structure to unfold. It is not surprising that this is associated with a higher activation energy, resulting in a much slower exchange process.

(c) Sulfide/Selenide Exchange. An equimolar mixture of $[\text{Me}_4\text{N}]_4[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{Me}_4\text{N}]_4[\text{S}_4\text{SeCd}_{10}(\text{SPh})_{16}]^{4-}$ was prepared to investigate the exchange of the sulfide and selenide ions of the cluster cores. For a freshly prepared solution, we observed no peaks in the electrospray mass spectrum attributable to mixed sulfide–selenide species. After equilibration of the mixture for 24 days at room temperature, peaks due to the mixed sulfide–selenide ions $[\text{S}_3\text{SeCd}_{10}(\text{SPh})_{16}]^{4-}$, $[\text{S}_2\text{Se}_2\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$, and $[\text{SSe}_3\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ were observed, Table 6. The relative intensities of the intact ions show that the original clusters $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{SeCd}_{10}(\text{SPh})_{16}]^{4-}$ are dominant in the aged mixture. The exchange processes do not lead to random substitution of sulfide and selenide. It is probable that the preferred association of the same chalcogenide is a size effect. At a cone voltage of 120 V, the species $[\text{S}_3\text{SeCd}_6(\text{SPh})_5]^-$, $[\text{SSe}_3\text{Cd}_6(\text{SPh})_5]^-$, $[\text{S}_3\text{SeCd}_5(\text{SPh})_3]^-$, $[\text{SSe}_3\text{Cd}_5(\text{SPh})_3]^-$, $[\text{S}_2\text{Se}_2\text{Cd}_5(\text{SPh})_3]^-$, $[\text{S}_2\text{SeCd}_3(\text{SPh})]^-$, $[\text{SSe}_2\text{Cd}_3(\text{SPh})]^-$, and $[\text{SSeCd}_2(\text{SPh})]^-$ were observed. These dissociation products are all in accord with the fragmentation pattern observed for the pure compounds. Species containing SePh^- ligands were not observed, showing that the S–C bond in SPh^- is too strong for substitution of S by Se to occur.

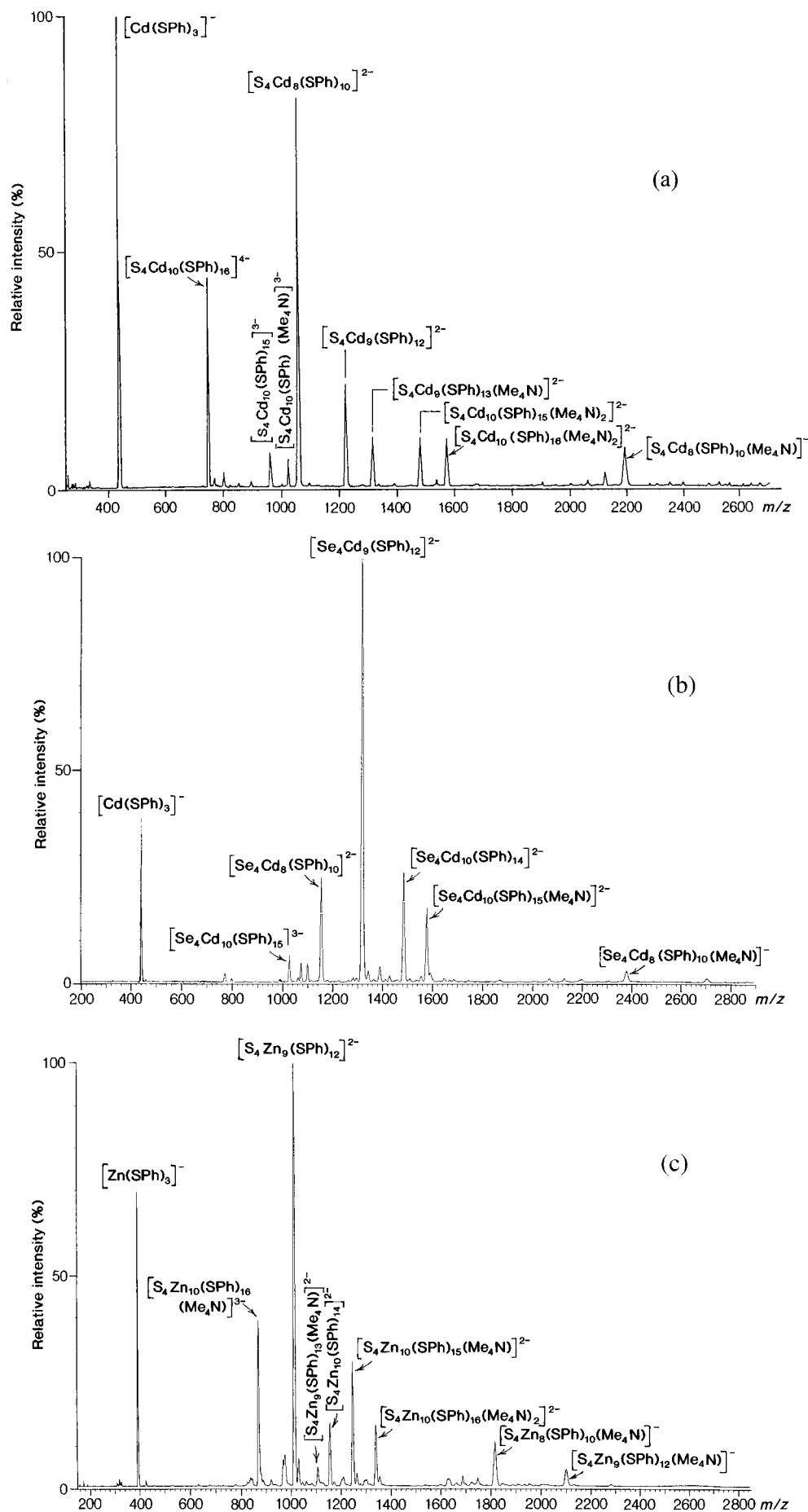


Figure 4. ES mass spectra of (a) $[Me_4N]_4[S_4Cd_{10}(SPh)_{16}]$, (b) $[Me_4N]_4[Se_4Cd_{10}(SPh)_{16}]$, and (c) $[Me_4N]_4[S_4Zn_{10}(SPh)_{16}]$ at a cone voltage of 20 V.

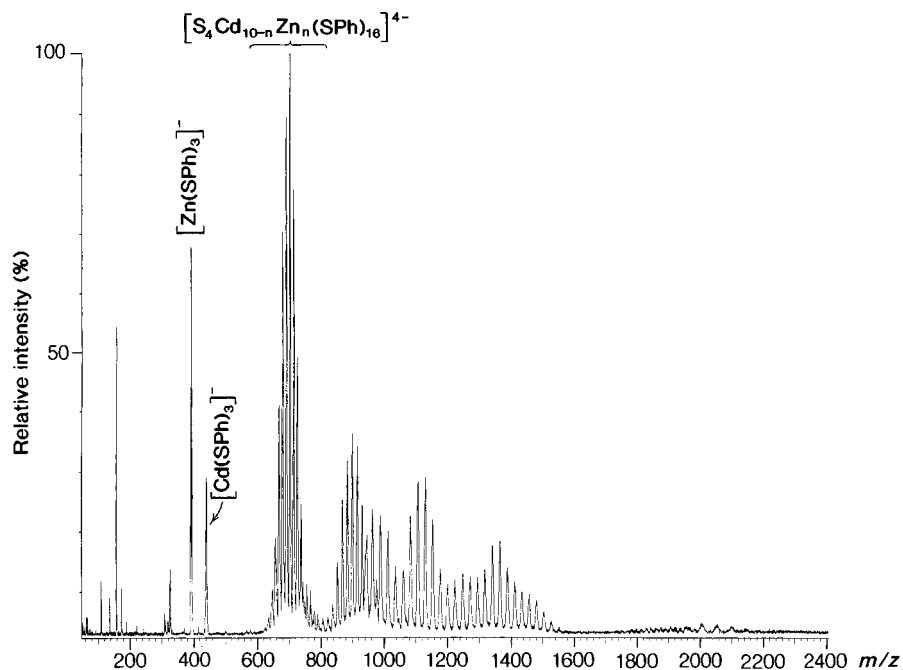


Figure 5. ES mass spectrum at a cone voltage of 10 V for an equimolar mixture of $[(\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[(\text{Me}_4\text{N})_4\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ equilibrated for 7 days.

Table 5. Anionic Species Observed in the ES Mass Spectrum of $[(\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ at Cone Voltages of 60, 90, 120, and 190 V^a

| ion | <i>m/z</i> | relative peak height (%) | | | |
|---|------------|--------------------------|------|-------|-------|
| | | 60 V | 90 V | 120 V | 190 V |
| $[\text{Cd}(\text{SPh})_3]^-$ | 441 | 100 | 100 | 100 | 100 |
| $[\text{Cd}_2(\text{SPh})_5]^-$ | 771 | 4 | 7 | 15 | 10 |
| $[\text{Cd}_3(\text{SPh})_7]^-$ | 1101 | | | 1 | 1 |
| $[\text{SCd}(\text{SPh})]^-$ | 254 | | 1 | 7 | 16 |
| $[\text{S}_2\text{Cd}_2(\text{SPh})]^-$ | 398 | | | 1 | 10 |
| $[\text{S}_3\text{Cd}_3(\text{SPh})]^-$ | 543 | | 6 | 20 | 60 |
| $[\text{S}_4\text{Cd}_4(\text{SPh})]^-$ | 687 | | 44 | 100 | 79 |
| $[\text{S}_4\text{Cd}_5(\text{SPh})_3]^-$ | 1018 | 3 | 58 | 35 | 13 |
| $[\text{S}_4\text{Cd}_6(\text{SPh})_5]^-$ | 1349 | 8 | 30 | 33 | 4 |
| $[\text{S}_4\text{Cd}_7(\text{SPh})_7]^-$ | 1679 | 10 | 17 | 20 | 3 |
| $[\text{S}_4\text{Cd}_8(\text{SPh})_9]^-$ | 2010 | 2 | 6 | 1 | 1 |
| $[(\text{Me}_4\text{N})\text{S}_2\text{Cd}_2(\text{SPh})_2]^-$ | 581 | | 9 | 8 | 9 |
| $[(\text{Me}_4\text{N})\text{S}_3\text{Cd}_3(\text{SPh})_2]^-$ | 726 | | 4 | 2 | 5 |
| $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_4(\text{SPh})_2]^-$ | 870 | | 14 | 23 | 16 |
| $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_5(\text{SPh})_4]^-$ | 1201 | | 11 | 14 | 1 |
| $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_6(\text{SPh})_6]^-$ | 1532 | | 7 | 8 | |
| $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_7(\text{SPh})_8]^-$ | 1863 | 2 | 24 | 10 | |
| $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_8(\text{SPh})_{10}]^-$ | 2193 | 3 | 19 | 2 | |
| $[(\text{Me}_4\text{N})_2\text{S}_4\text{Cd}_8(\text{SPh})_{11}]^-$ | 2374 | | 4 | | |
| $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_9(\text{SPh})_{12}]^-$ | 2523 | | 5 | | |
| $[(\text{Me}_4\text{N})_2\text{S}_4\text{Cd}_9(\text{SPh})_{13}]^-$ | 2706 | | 4 | | |

^a A strong peak at *m/z* 109 due to SPh^- has been omitted to allow a more accurate comparison of the peaks due to Cd-containing species.

The $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ Cluster. (a) Parent Complex. The driving force of all the fragmentations observed for the precursor clusters $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ is probably the tendency for them to lose negative charge. The suggestion that a high charge density results in a high tendency to fragment is supported by the high-cone-voltage (60–190 V) spectra of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ (refer to Table 5), which only show species with one negative charge. In this connection, it is interesting to compare the spectrum of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ with that of $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$. The latter is a larger cluster, and because it is only doubly charged, the charge density is less than half that of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$. The main structural difference between this cluster and $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ is the core structure, which in $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ consists of

Table 6. Parent Ion Species Observed in the ESMS Spectra for a 1:1 Mole Ratio Mixture of $[(\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[(\text{Me}_4\text{N})_4\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ (a) as a Freshly Prepared Solution and (b) after 7 days and for a 1:1 Mixture of $[(\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[(\text{Me}_4\text{N})_4\text{S}_4\text{Se}_{10}(\text{SPh})_{16}]^{4-}$ Left To Stand for 24 Days^a

| $[(\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}/[(\text{Me}_4\text{N})_4\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ Mixture | | | |
|---|------------|---------------------------------------|-----|
| ion | <i>m/z</i> | relative peak height (%) at cone 10 V | |
| | | (a) | (b) |
| $[\text{Zn}(\text{SPh})_3]^-$ | 393 | 32 | 67 |
| $[\text{Cd}(\text{SPh})_3]^-$ | 440 | 13 | 27 |
| $[\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ | 632 | 15 | 2 |
| $[\text{S}_4\text{Zn}_9\text{Cd}(\text{SPh})_{16}]^{4-}$ | 644 | 37 | 8 |
| $[\text{S}_4\text{Zn}_8\text{Cd}_2(\text{SPh})_{16}]^{4-}$ | 656 | 45 | 16 |
| $[\text{S}_4\text{Zn}_7\text{Cd}_3(\text{SPh})_{16}]^{4-}$ | 667 | 39 | 39 |
| $[\text{S}_4\text{Zn}_6\text{Cd}_4(\text{SPh})_{16}]^{4-}$ | 679 | 28 | 70 |
| $[\text{S}_4\text{Cd}_5\text{Zn}_5(\text{SPh})_{16}]^{4-}$ | 691 | 19 | 86 |
| $[\text{S}_4\text{Cd}_6\text{Zn}_4(\text{SPh})_{16}]^{4-}$ | 703 | 25 | 100 |
| $[\text{S}_4\text{Cd}_7\text{Zn}_3(\text{SPh})_{16}]^{4-}$ | 714 | 55 | 73 |
| $[\text{S}_4\text{Cd}_8\text{Zn}_2(\text{SPh})_{16}]^{4-}$ | 726 | 100 | 47 |
| $[\text{S}_4\text{Cd}_9\text{Zn}(\text{SPh})_{16}]^{4-}$ | 738 | 89 | 21 |
| $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ | 750 | 27 | 4 |
| $[(\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}/[(\text{Me}_4\text{N})_4\text{S}_4\text{Se}_{10}(\text{SPh})_{16}]^{4-}$ Mixture | | | |
| ion | <i>m/z</i> | relative peak height (%) at cone 5 V | |
| $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ | 749 | | 100 |
| $[\text{S}_3\text{SeCd}_{10}(\text{SPh})_{16}]^{4-}$ | 762 | | 33 |
| $[\text{S}_2\text{Se}_2\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ | 773 | | 9 |
| $[\text{SSe}_3\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ | 785 | | 32 |
| $[\text{Se}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ | 797 | | 91 |

^a The main dissociation products $[\text{Zn}(\text{SPh})_3]^-$ and $[\text{Cd}(\text{SPh})_3]^-$ in the mixture of $[(\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[(\text{Me}_4\text{N})_4\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]^{4-}$ are included to show the difference in fragmentation levels.

tetracoordinated sulfides instead of triply bridging sulfides; see Figure 1b,c. The core and the capping cages of $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ are similar to the hexagonal (wurtzite) lattice of metal chalcogenides.¹⁶ The 10 V spectrum shows only three major species, Table 7. The strongest peak is due to the intact ion $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ at *m/z* 2548. A less intense peak occurs at *m/z* 2510. A 2- charge on this species was confirmed by the isotope peaks that occurred at half-integral mass units. The 90

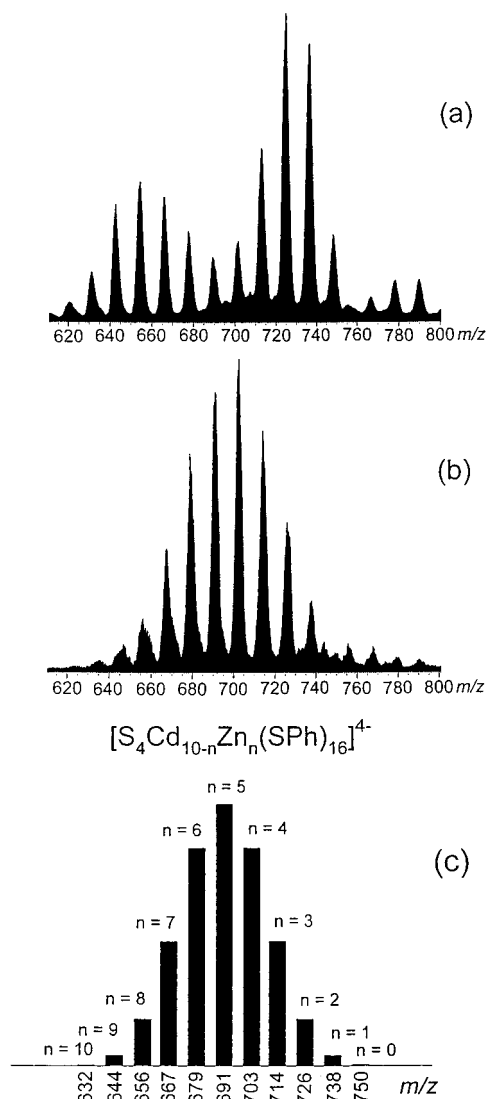


Figure 6. The $[\text{S}_4\text{Cd}_{4-n}\text{Zn}_n(\text{SPh})_{16}]^{4-}$ peaks in the 10 V spectra of an equimolar mixture of $[(\text{Me}_4\text{N})_4][\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]$ and $[(\text{Me}_4\text{N})_4][\text{S}_4\text{Zn}_{10}(\text{SPh})_{16}]$: (a) spectrum of a freshly prepared mixture; (b) spectrum of the mixture after standing for 7 days; (c) calculated distribution of species in the case of statistical exchange of Zn and Cd atoms.

V spectrum shown in Figure 7 reveals that the m/z 2510 peak is due to $[\text{S}_4\text{Cd}_{17}\text{Cl}(\text{SPh})_{27}]^{2-}$, where one SPh^- ligand has been replaced by Cl^- . At this high voltage the fragment species $[\text{Cd}(\text{SPh})_3]^-$, $[\text{Cd}_2(\text{SPh})_5]^-$, and $[\text{Cd}_3(\text{SPh})_7]^-$, which were also observed in the spectrum of $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$, are observed. An additional set of weaker peaks occurs 74 m/z units lower than each of the main fragment ion peaks. This m/z separation corresponds to the difference in molecular mass between SPh and Cl . The peaks can therefore be assigned to $[\text{CdCl}(\text{SPh})_2]^-$, $[\text{Cd}_2\text{Cl}(\text{SPh})_4]^-$, and $[\text{Cd}_3\text{Cl}(\text{SPh})_6]^-$. The Cl^- ions originate from $(\text{Me}_4\text{N})\text{Cl}$ added to the reaction mixture as the source of the Me_4N^+ counterions. We note that the intensities of the peaks due to the chloride-containing species maintain a constant ratio correlating with that of $[\text{Cd}(\text{SPh})_3]^-$, $[\text{Cd}_2(\text{SPh})_5]^-$, and $[\text{Cd}_3(\text{SPh})_7]^-$, and this is consistent with $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ and $[\text{S}_4\text{Cd}_{17}\text{Cl}(\text{SPh})_{27}]^{2-}$ undergoing similar fragmentations. The third, weak peak at m/z 2474 in the 10 V spectrum can be assigned to $[\text{S}_4\text{Cd}_{17}\text{Cl}_2(\text{SPh})_{26}]^{2-}$. Another species with an m/z value of 2474 is $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_{16}(\text{SPh})_{27}]^{2-}$, which would originate from the precursor $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ by loss of $\text{Cd}(\text{SPh})^+$ and addition of Me_4N^+ . None of the species detected in the spectrum of $[(\text{Me}_4\text{N})_4][\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]$ can be attributed to

Table 7. Anionic Species Observed in the ES Mass Spectra of $[(\text{Me}_4\text{N})_2][\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]$ and of a Mixture of $[(\text{Me}_4\text{N})_2][\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]$ and $[(\text{Me}_4\text{N})_2][\text{Zn}_4(\text{SPh})_{10}]$ with a $[\text{Cd}]:[\text{Zn}]$ Ratio of 1:1^a

| | | relative peak height (%) | | |
|---|-------|---------------------------------------|-----------|-----------|
| | | cone 5 V | cone 30 V | cone 90 V |
| [$(\text{Me}_4\text{N})_2[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]$] | | | | |
| ion | m/z | | | |
| $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ | 2548 | 100 | 100 | 16 |
| $[\text{S}_4\text{Cd}_{17}\text{Cl}(\text{SPh})_{27}]^{2-}$ | 2511 | 31 | 48 | 6 |
| $[\text{S}_4\text{Cd}_{17}\text{Cl}_2(\text{SPh})_{26}]^{2-}$ | 2474 | 3 | 10 | 1 |
| $[\text{Cd}_3(\text{SPh})_7]^-$ | 1102 | | | 6 |
| $[\text{Cd}_3\text{Cl}(\text{SPh})_6]^-$ | 1027 | | | 2 |
| $[\text{Cd}_2(\text{SPh})_5]^-$ | 771 | | | 33 |
| $[\text{Cd}_2\text{Cl}(\text{SPh})_4]^-$ | 699 | | | 7 |
| $[\text{Cd}(\text{SPh})_3]^-$ | 440 | | | 100 |
| $[\text{CdCl}(\text{SPh})_2]^-$ | 367 | | | 13 |
| [$(\text{Me}_4\text{N})_2[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]/[(\text{Me}_4\text{N})_2[\text{Zn}_4(\text{SPh})_{10}]$] Mixture | | | | |
| ion | m/z | relative peak height (%) at cone 10 V | | |
| $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ | 2548 | | | 5 |
| $[\text{S}_4\text{Cd}_{16}\text{Zn}(\text{SPh})_{28}]^{2-}$ | 2524 | | | 13 |
| $[\text{S}_4\text{Cd}_{15}\text{Zn}_2(\text{SPh})_{28}]^{2-}$ | 2501 | | | 32 |
| $[\text{S}_4\text{Cd}_{14}\text{Zn}_3(\text{SPh})_{28}]^{2-}$ | 2477 | | | 62 |
| $[\text{S}_4\text{Cd}_{13}\text{Zn}_4(\text{SPh})_{28}]^{2-}$ | 2454 | | | 100 |
| $[\text{S}_4\text{Cd}_{12}\text{Zn}_5(\text{SPh})_{28}]^{2-}$ | 2430 | | | 100 |
| $[\text{S}_4\text{Cd}_{11}\text{Zn}_6(\text{SPh})_{28}]^{2-}$ | 2407 | | | 63 |
| $[\text{S}_4\text{Cd}_{10}\text{Zn}_7(\text{SPh})_{28}]^{2-}$ | 2383 | | | 34 |
| $[\text{S}_4\text{Cd}_9\text{Zn}_8(\text{SPh})_{28}]^{2-}$ | 2360 | | | 17 |
| $[\text{S}_4\text{Cd}_8\text{Zn}_9(\text{SPh})_{28}]^{2-}$ | 2336 | | | 8 |

^a For this mixture the peaks due to $[(\text{Me}_4\text{N})_2[\text{Zn}_4(\text{SPh})_{10}]]$ are omitted. The observation of $[\text{S}_4\text{Cd}_{17}\text{Cl}(\text{SPh})_{27}]^{2-}$ and $[\text{S}_4\text{Cd}_{17}\text{Cl}_2(\text{SPh})_{26}]^{2-}$ shows that Cl^- ions (added as $[(\text{Me}_4\text{N})\text{Cl}]$ to the reaction mixture) occur as ligand species in the cluster.

loss of $\text{Cd}(\text{SPh})^+$ species from $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$. Loss of cadmium from this cluster occurred by removal of $\text{Cd}(\text{SPh})_2$. On this basis, we believe the contribution from $[(\text{Me}_4\text{N})\text{S}_4\text{Cd}_{16}(\text{SPh})_{27}]^{2-}$ to the m/z 2474 peak to be insignificant. Hence, only intact-ion species are observed in the 10 V spectrum. Some loss of Cl^- and SPh^- may be expected to occur on the basis of the facile loss of these species observed in the spectra of $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ and $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$. The resulting singly charged species would be invisible with the 3000 m/z range of the instrument. The relative peak intensity ratio of $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$, $[\text{S}_4\text{Cd}_{17}\text{Cl}(\text{SPh})_{27}]^{2-}$, and $[\text{S}_4\text{Cd}_{17}\text{Cl}_2(\text{SPh})_{26}]^{2-}$ is 100:31:3 in the 10 V spectrum. Since minimal fragmentation occurs at this voltage, this ratio can be taken as a rough estimate of the relative concentrations of these clusters in the material. Hence, it is shown here that the ESMS technique provides a tool for analysis of the purity of these cluster compounds. No additional species are observed for cone voltages up to ca. 60 V, and this clearly confirms the higher stability of these clusters against fragmentation. At 60 V, a very weak peak at m/z 440 due to $[\text{Cd}(\text{SPh})_3]^-$ appears and signals the onset of fragmentation. We note that in the spectrum of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ complete fragmentation of the S_4Cd_6 core unit was observed at this voltage.

In the 120 V spectrum, the intact ion $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ gave a weak peak and several new peaks occurred. These were due to species of the general formula $[\text{S}_4\text{Cd}_{17-n}(\text{SPh})_{27-2n}]^{2-}$ ($n = 0-13$) and included peaks due to $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{13}]^-$ at m/z 2667, $[\text{S}_4\text{Cd}_9(\text{SPh})_{11}]^-$ at m/z 2341, $[\text{S}_4\text{Cd}_8(\text{SPh})_9]^-$ at m/z 2010, $[\text{S}_4\text{Cd}_7(\text{SPh})_7]^-$ at m/z 1679, $[\text{S}_4\text{Cd}_6(\text{SPh})_5]^-$ at m/z 1348, $[\text{S}_4\text{Cd}_5(\text{SPh})_3]^-$ at m/z 1018, and $[\text{S}_4\text{Cd}_4(\text{SPh})]^-$ at m/z 687. All these species originate from $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ by loss of a multiple of neutral $[\text{Cd}(\text{SPh})_2]$. The $[\text{S}_4\text{Cd}_{11}(\text{SPh})_{15}]^-$ ion at m/z 3002 and the heavier members of this series, which presumably also were present, have m/z values which lie outside

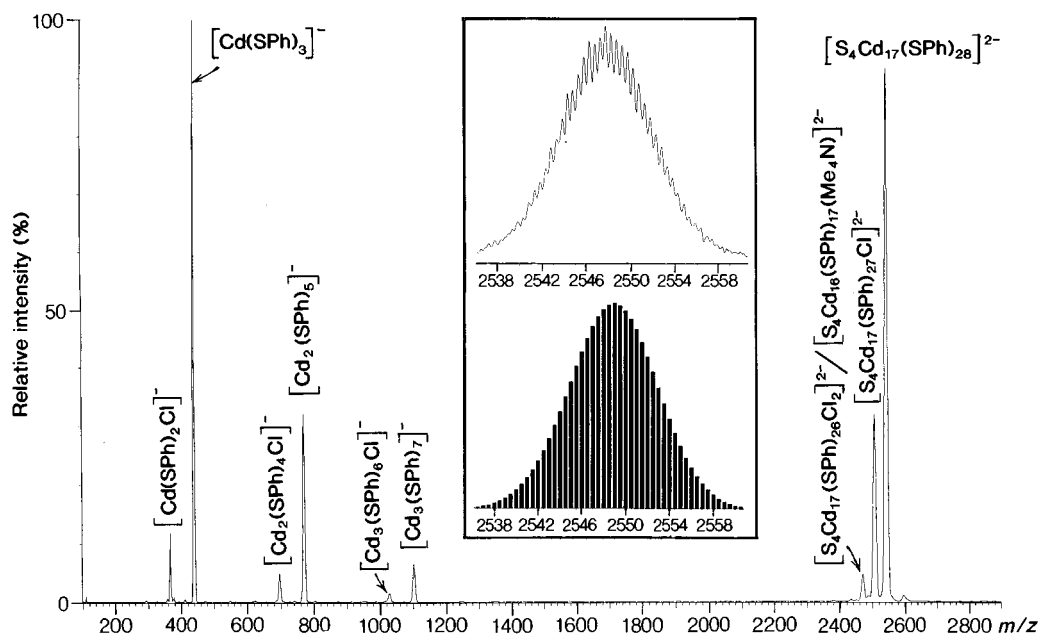


Figure 7. ES mass spectrum of $[\text{Me}_4\text{N}]_2[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ at a cone voltage of 90 V. The observation of $[\text{S}_4\text{Cd}_{17}\text{Cl}(\text{SPh})_{27}]^{2-}$ and $[\text{S}_4\text{Cd}_{17}\text{Cl}_2(\text{SPh})_{26}]^{2-}$ shows that Cl^- added as $(\text{Me}_4\text{N})\text{Cl}$ to the reaction mixture during synthesis occurs as a ligand species in the cluster. The inset shows an expansion of the $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ peak (top) and the calculated isotopic distribution of the ion (bottom). The peak separations are 0.5 m/z unit, characteristic of a doubly charged ion. Note the low level of fragmentation in this spectrum due to the low charge density on the clusters.

the 3000 m/z range of the instrument and were not observed. Again it was observed that only 1- species are present in the spectrum at high cone voltages. The main difference in the electrospray spectra of $[\text{S}_4\text{Cd}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ is a significantly higher stability of the latter. The fragmentation processes are similar. Once the initial fragmentation process has removed excess negative charge from the cluster to produce monoions, subsequent fragment ions are formed by loss of neutral $[\text{Cd}(\text{SPh})_2]$ species. Fragmentation of the CdS core unit in both cluster types occurs only at very high voltages. The study of cluster fragmentation processes by ESMS is relevant to the deposition of chalcogenide semiconductor materials via pyrolysis processes, for example IR laser-powered homogeneous pyrolysis (IR LPHP).^{35,36} The mechanisms of pyrolysis processes and the species they generate are often closely related to the dissociation mechanisms and the dominant species observed in mass spectra. Suitable precursors for this process are generally compounds that give minimal carbon contamination. The fragmentation processes of $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ lead to nearly complete removal of the SPh⁻ ligands from the cluster cores and suggest that these clusters could be suitable precursors.

(b) Metal Exchange. Metal exchange in $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ was investigated by adding $[(\text{Me}_4\text{N})_2\text{Zn}_4(\text{SPh})_{10}]$ to a solution of $[(\text{Me}_4\text{N})_2\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]$ to give a $[\text{Zn}]:[\text{Cd}]$ ratio of 1:1. The mixture was allowed to stand for 7 days before the spectrum was recorded. The dominant cluster species detected were the mixed-metal ions $[\text{S}_4\text{Cd}_{17-n}\text{Zn}_n(\text{SPh})_{28}]^{2-}$ ($n = 0-9$). The two most abundant ions were $[\text{S}_4\text{Cd}_{13}\text{Zn}_4(\text{SPh})_{28}]^{2-}$ and $[\text{S}_4\text{Cd}_{12}\text{Zn}_5(\text{SPh})_{28}]^{2-}$. The least abundant ion was $[\text{S}_4\text{Cd}_8\text{Zn}_9(\text{SPh})_{28}]^{2-}$ at m/z 2336, which has the highest proportion of Zn atoms. The dominant ion of the $[\text{Zn}_{4-n}\text{Cd}_n(\text{SPh})_{10}]^{2-}$ species generated from $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ by the exchange with $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ is $[\text{Zn}_3\text{Cd}(\text{SPh})_{10}]^{2-}$. The fact that the Zn-rich species $[\text{Zn}_3\text{Cd}(\text{SPh})_{10}]^{2-}$ is the more abundant ion is consistent with the observation that the cluster species are dominated by Cd-rich species. The exchange of the metals is expected to be

slower in $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ than in $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$. Of the 17 Cd atoms, four are associated with the $(\mu\text{-SPh})_3\text{Cd}^0(\text{SPh})$ caps at the cluster corners, and these are expected to exchange rapidly, as in $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$. At the cluster faces are 12 cadmium atoms which are externally bridged as $(\mu\text{-SPh})$ and internally bridged to one sulfide, forming a $(\mu\text{-S}^{2-})\text{Cd}(\mu\text{-SPh})_3$ unit. At the center is one cadmium tetraordinated as $\text{Cd}(\text{S}^{2-})_4$. The observation of $[\text{S}_4\text{Cd}_8\text{Zn}_9(\text{SPh})_{28}]^{2-}$ after 1 week shows the exchange of only five of the 12 inner cadmium atoms externally bridged as $(\mu\text{-SPh})$ and internally bridged to one sulfide. In $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$, these metals exchange during the same time period. The incomplete exchange in $[\text{S}_4\text{M}_{17}(\text{SPh})_{28}]^{2-}$ may therefore be due to preferred associations of the same metal (Cd) atoms in the core, which is likely to be more influential in larger clusters.

Summary and Conclusions

This work demonstrates the application of ESMS to the study of metal thiolate complexes and metal chalcogenide thiolate clusters. The method is particularly attractive because of the fundamental cluster chemistry that it reveals. The results of such studies may inspire and direct new preparative chemistry. The main principles can be summarized as follows. The ionic nature and the stability of the complexes $[\text{M}(\text{SPh})_4]^{2-}$ and $[\text{M}_4(\text{SPh})_{10}]^{2-}$ and the clusters $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ result in high-quality ES mass spectra, which show minimal fragmentation of the ions. The dissociation of the ions at high cone voltages is characteristic of loss of SPh⁻ and $[\text{M}(\text{SPh})_3]^-$. The measurements yield relative stability data: The ions containing zinc as the metal showed a lower resistance to fragmentation compared with the cadmium analogues. The behavior of ligand-substituted species is revealed. Substitution of thiophenolate ions with halide ligands enhances the tendency for loss of $[\text{M}(\text{SPh})_{3-n}\text{X}_n]^-$ due to the halides acting as terminal ligands only in these systems. Similarly, the fragmentation mechanisms of the clusters yield information about their chemistry. The clusters $[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ dissociate in the first step by loss of $[\text{M}(\text{SPh})_3]^-$. At higher cone voltages, smaller monoions form by loss of neutral

(35) Russell, D. K. *Chem. Soc. Rev.* **1990**, *19*, 407.

(36) Russell, D. K. *Coord. Chem. Rev.* **1992**, *112*, 131.

$M(\text{SPh})_2$ species, resulting in almost complete removal of the SPh^- ligands from the cluster core. Fragmentation of the $(\text{EM})_n$ core units occurs only at very high voltages.

ESMS confirms earlier NMR data showing that the exchange of M ($M = \text{Cd}, \text{Zn}$) follows random statistics in $[\text{M}_4(\text{SPh})_{10}]^{2-}$ but is biased toward equilibrium association of the same metal in $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$. The rates of metal ion exchange within the different structural elements of $[\text{S}_4\text{M}_{10}(\text{SPh})_{16}]^{4-}$ and $[\text{S}_4\text{Cd}_{17}(\text{SPh})_{28}]^{2-}$ decrease for atoms located toward the center of the clusters. Advantage can be taken of the different rates of exchange observed by ESMS to control the composition and properties of clusters and semiconductor heterostructures prepared from these precursors. The use of ESMS for monitoring

the reactions of clusters with various ligand types is attractive. It should facilitate the development of the chemistry of functionalized clusters, which are important precursors in nanostructured materials processing.

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