

Substitution and Redistribution Reactions of the Tetranuclear Clusters [(μ -SePh) $_6$ (ZnSePh) $_4$] $^{2-}$ and [(μ -SePh) $_6$ (ZnX) $_4$] $^{2-}$: A ^{77}Se NMR Study

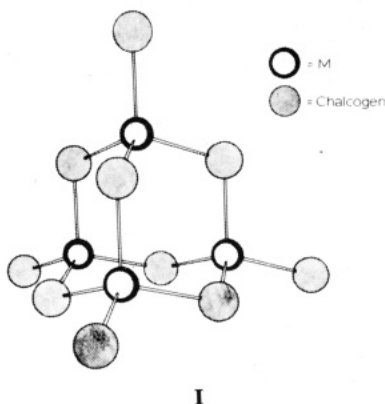
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Selenium-77 NMR has been used to study $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ (**1**) and a wide variety of its substitution and redistribution products. At 296 K, **1** gives a slow-exchange ^{77}Se NMR spectrum consistent with the adamantanoid structure $[(\mu\text{-SePh})_6(\text{ZnSePh})_4]^{2-}$. Oxidative halogen substitution of **1** is shown to proceed through $[(\mu\text{-SePh})_6(\text{ZnSePh})_{4-x}(\text{ZnX})_x]^{2-}$ ($x = 0-4$), which can be characterized individually by ^{77}Se NMR at ambient probe temperature for $\text{X} = \text{Cl}$ or I . Redistribution of $[(\mu\text{-SePh})_6(\text{ZnX})_4]^{2-}$ and $[(\mu\text{-SePh})_6(\text{ZnX}')_4]^{2-}$ ($\text{X} = \text{I}$, $\text{X}' = \text{Cl}$; $\text{X} = \text{I}$, $\text{X}' = \text{Br}$) is shown to occur close to statistically, giving the series $[(\mu\text{-SePh})_6(\text{ZnX})_{4-x}(\text{ZnX}')_x]^{2-}$ in which each member has again been characterized. Mixtures of $[(\mu\text{-SePh})_6(\text{ZnI})_4]^{2-}$ and $[(\mu\text{-SPh})_6(\text{ZnI})_4]^{2-}$ give room-temperature ^{77}Se NMR spectra consistent with the formation of the species $[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(\text{ZnI})_4]^{2-}$ with mixed chalcogenate cores. Similarly the ready oxidative substitution of $[(\mu\text{-SePh})_6(\text{ZnI})_4]^{2-}$ with Me_2Se_2 is shown to give $[(\mu\text{-SePh})_{6-x}(\mu\text{-SeMe})_x(\text{ZnI})_4]^{2-}$ with a mixed-ligand core. Redistribution of **1** and its sulfur analogue gives complex mixtures of species of the type $[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(\text{ZnSePh})_{4-y}(\text{ZnSPh})_y]^{2-}$, in which there is a slight preference of PhSe over PhS for the terminal positions. For comparison, ^{77}Se NMR data have been obtained for $[\text{Zn}(\text{SPh})_4(\text{SPh})_x]^{2-}$ ($x = 0-2$) also. The mixed-metal complexes $[(\mu\text{-SePh})_6(\text{ZnI})_{4-x}(\text{CdI})_x]^{2-}$ form nearly statistically in mixtures of $[(\mu\text{-SePh})_6(\text{ZnI})_4]^{2-}$ and its cadmium analogue; ^{77}Se NMR is a more informative probe of this system than ^{113}Cd NMR.

Introduction

The tetranuclear adamantanoid clusters $[(\mu\text{-SPh})_6(\text{MSPH})_4]^{2-}$ ($\text{M} = \text{Zn}$ or Cd) are of interest, in part, as simple models for the four-metal cysteinyl-bridged cluster that occurs, along with a three-metal cluster, in Zn,Cd-metallothionein.¹ Both $[\text{M}_4(\text{SPh})_{10}]^{2-}$ ions have been characterized in the solid state by X-ray analysis.^{2,3} They have the skeleton I. In addition, $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$



has been investigated in solution by ^1H , ^{13}C , and $^{111/113}\text{Cd}$ NMR spectroscopies.⁴⁻⁶ The solution studies show that the Cd_4 core remains intact on the $^{111/113}\text{Cd}$ NMR time scale while intramolecular exchange of terminal and bridging thiolates is rapid on the ^1H and ^{13}C NMR time scales. Cadmium-113 NMR has proved an informative probe for metal- and ligand-substituted analogues of $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ also. Thus, intermolecular metal exchange between various $[\text{Cd}_x\text{Zn}_{4-x}(\text{SPh})_{10-x}]^{2-}$ is slow,^{4,7,8} while rapid intramolecular terminal-bridging exchange has been found⁷ to simplify the spectra of $[\text{Cd}_4(\text{EPh})_x(\text{E'R})_{10-x}]^{2-}$. In the case of halogen-substituted clusters such as $[(\mu\text{-SPh})_6(\text{CdI})_x(\text{CdSPh})_{4-x}]^{2-}$ and $[(\mu\text{-SPh})_x(\mu\text{-SePh})_{6-x}(\text{CdX})_4]^{2-}$ separate signals

can be observed^{9,10} for the different cadmium kernels that occur, indicating slow ^{113}Cd exchange between sites.

Proton NMR spectroscopy of $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ shows that the lability of the ligands in the zinc complex is significantly less than that in its cadmium analogue: terminal-bridging exchange of PhS^- is slow on the ^1H NMR time scale at ambient probe temperature.^{3,4} This observation suggests that further NMR study of the tetranuclear zinc complexes might be fruitful provided a suitably structure-sensitive probe nucleus can be found. Because of signal broadness, application of the quadrupolar ^{67}Zn nuclide¹¹ is problematical.¹³ However, as we show here, substitution of the recently prepared^{9b} $[\text{Zn}_4(\text{SePh})_{10}]^{2-}$ for $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ allows the use of ^{77}Se NMR¹¹ to follow substitution and redistribution in the Zn_4 cluster system.

Experimental Section

Materials and General Procedures. Literature syntheses were used for PhCl_2 ,¹⁴ $(\text{Me}_4\text{N})_2[\text{Zn}_4(\text{SPh})_{10}]$,⁴ and $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SePh})_{10}]$,⁷ and the synthesis of $(\text{Me}_4\text{N})_2[\text{Zn}_4(\text{SePh})_{10}]$ will be given elsewhere.^{9b} The syntheses of $(\text{Et}_4\text{N})_2[\text{Zn}_4(\text{SPh})_{10}]$ and $(\text{Et}_4\text{N})_2[\text{Zn}_4(\text{SePh})_{10}]$ paralleled those of the Me_4N^+ salts, and their authenticity was checked by comparison of their ^{13}C and ^{77}Se NMR spectra, respectively, with those of the Me_4N^+ analogues (ref 9b and see below). Dimethyl diselenide (Strem Chemicals, Inc.) showed no significant impurity by ^{77}Se NMR and was used as received, as were all other chemicals, which were of reagent grade from commercial sources.

Solvents were purified by distillation and stored over 3A molecular sieves. Solvents used in synthesis or preparation of NMR samples were thoroughly deoxygenated with Ar before use.

NMR Spectra. All NMR samples were prepared under Ar in 10-mm-o.d. NMR tubes.

Cadmium-113 spectra and most of the ^{77}Se NMR spectra were measured by using a Varian XL-200 NMR spectrometer system operating at 44.37 and 38.15 MHz, respectively, without field/frequency lock, as outlined previously.⁷ A 2-W broad-band proton decoupling was applied for the ^{77}Se NMR spectra by using the WALTZ-16 sequence.¹⁵ No proton decoupling was applied for the ^{113}Cd NMR spectra. A few of the ^{77}Se NMR spectra were obtained in an analogous manner by using a Varian XL-300 spectrometer system running at 57.20 MHz, with 2.5-W broad-band decoupling via WALTZ-16. The spectra were referenced to external 0.1 M $\text{Cd}(\text{ClO}_4)_2(\text{aq})$ and neat Me_2Se , for ^{113}Cd and ^{77}Se NMR, respectively, by sample interchange. No corrections for diamagnetic susceptibility difference were applied. Selenium-77 chemical

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- (10) Reduction in temperature is needed in some cases.
- (11) ^{67}Zn , spin $I = 5/2$, 4.11% natural abundance, receptivity relative to ^{13}C , $D^6 = 0.670$; ^{77}Se , spin $I = 1/2$, 7.58% natural abundance, $D^6 = 3.01$.¹²
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Table I. Selenium-77 NMR Spectral Parameters^a of [Zn₄(SePh)₁₀]²⁻ and [Zn₄(SePh)₆X₄]²⁻

| salt | solvent | concn, M | T, K | δ_{Se}^b ($\Delta\nu_{1/2}$ (approx), Hz) | |
|--|----------------------|----------|------|--|--------------------|
| | | | | PhSe _t | PhSe _{br} |
| (Me ₄ N) ₂ [Zn ₄ (SePh) ₁₀] | acetone | satd | 296 | 46.3 (70) | -6.7 (50) |
| | MeCN | 0.05 | 296 | 38.0 (75) | -8.8 (55) |
| (Et ₄ N) ₂ [Zn ₄ (SePh) ₁₀] | acetone | 0.05 | 297 | 46.0 (60) | -7.4 (40) |
| | acetone ^c | 0.05 | 298 | 47.0 (90) | -6.8 (80) |
| | MeCN | 0.05 | 295 | 38.8 (80) | -8.6 (75) |
| | MeCN ^c | 0.05 | 298 | 39.2 (90) | -8.3 (80) |
| | acetone | satd | 261 | 38.3 ^d (95) | -23.0 (65) |
| (Et ₄ N) ₂ [Zn ₄ (SePh) ₆ Cl ₄] ^e | MeCN | 0.05 | 297 | | -19.8 (17) |
| | acetone | satd | 295 | | -18.0 (7) |
| (Et ₄ N) ₂ [Zn ₄ (SePh) ₆ Br ₄] ^f | MeCN | 0.05 | 296 | | -11.7 (10) |
| | acetone | satd | 297 | | -10.4 (14) |
| (Me ₄ N) ₂ [Zn ₄ (SePh) ₆ I ₄] ^g | MeCN | 0.05 | 298 | | 1.9 (10) |
| | acetone | 0.05 | 296 | | 2.4 (13) |
| (Et ₄ N) ₂ [Zn ₄ (SePh) ₆ I ₄] ^g | MeCN | 0.05 | 298 | | 2.0 (10) |
| | acetone | 0.05 | 297 | | 2.4 (13) |

^a Measured at 38.15 MHz unless noted otherwise. ^b Relative to external neat Me₂Se. ^c Measured at 57.20 MHz. ^d Estimated error ± 0.3 ppm. ^e Prepared in situ from [Zn₄(SePh)₁₀]²⁻ and PhICl₂. ^f Prepared in situ from [Zn₄(SePh)₁₀]²⁻ and Br₂. ^g Prepared in situ from [Zn₄(SePh)₁₀]²⁻ and I₂.

shifts could generally be measured to at least ± 0.2 ppm. This error is assumed in Tables I–V except where noted otherwise. However, reproducibility between samples was less than this, the chemical shifts being sensitive, apparently, to changes in solution composition and minor changes in temperature. Tables I–V contain typical chemical shifts. Incremental shifts, given in some of the tables, were more reproducible.

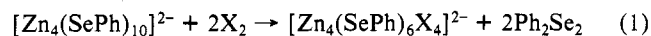
Temperatures were measured on the calibrated digital thermometers of the spectrometers and corrected for the heating effect of ¹H decoupling by use of a thermocouple probe in a stationary dummy sample of the appropriate solvent.

Results and Discussion

[Zn₄(SePh)₁₀]²⁻ (1). The ⁷⁷Se NMR spectrum of **1** in acetone or MeCN solution at ambient probe temperature consists of two signals with relative intensities 2 and 3, the smaller signal being less shielded. Table I includes the values of δ_{Se} and line widths observed under various conditions. These spectra are readily interpreted in terms of a [(μ -SePh)₆(ZnSePh)₄]²⁻ ion having skeleton I, as found³ for [Zn₄(SPh)₁₀]²⁻. The more shielded signal can be assigned to the bridging PhSe groups (PhSe_{br}) and the less shielded to the terminal PhSe groups (PhSe_t). The observation of two signals shows that t \rightleftharpoons br interchange is slow on the ⁷⁷Se NMR time scale. The values of δ_{Se} measured for [Zn₄(SePh)₁₀]²⁻ may be compared with δ 15.7 obtained for a saturated methanolic solution of [Zn(SePh)₄]²⁻ at 217 K (see below) and δ 21.2 (PhSe_t) and -59.6 (PhSe_{br}) found^{9b} for (Me₄N)₂[Cd₄(SePh)₁₀] as a 0.05M solution in MeCN at 234 K. (As reported earlier⁷ the ⁷⁷Se NMR spectrum of [Cd₄(SePh)₁₀]²⁻ consists of a single broad line at ambient probe temperature.)

X-ray structural analyses of (Me₄N)₂[Zn₄(SePh)₁₀] and (Me₄N)₂[Cd₄(SePh)₁₀] are currently in progress.¹⁶

[Zn₄(SePh)₆X₄]²⁻ (X = Cl, **2a; X = Br, **2b**; X = I, **2c**).** Reaction of [Zn₄(SePh)₁₀]²⁻ with 2 mol of halogen (or, for **2a**, PhICl₂) yields the [Zn₄(SePh)₆X₄]²⁻ ions quantitatively by oxidative substitution^{9b,17} (eq 1). The ⁷⁷Se NMR spectra of **2b** and **2c** consist of

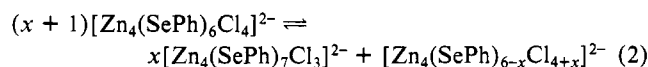


a single line (Table I) shielded relative to Me₂Se. The spectrum of **2a** also consists of a single line, similarly shielded. However the spectra of samples of **2a** invariably show the presence of small amounts of [(μ -SePh)₆(ZnSePh)(ZnCl)₃]²⁻ (see below) and it is clear that **2a** is in equilibrium in solution with its redistribution products (eq 2).¹⁷ By comparison of their ⁷⁷Se NMR chemical

Table II. Incremental ⁷⁷Se NMR Chemical Shifts, $\Delta\delta_{\text{Se}}$,^a of [Zn₄(SePh)₆I_{4-x}X_x]²⁻ in MeCN

| complex | adjacent terminal halogens ^b | nonadjacent terminal halogens ^c | $\Delta\delta_{\text{Se}}^a$ | |
|--|---|--|------------------------------|---------------------|
| | | | X = Br ^d | X = Cl ^e |
| [Zn ₄ (SePh) ₆ I ₄] ²⁻ | I, I | I, I | 0.00 | 0.00 |
| [Zn ₄ (SePh) ₆ I ₃ X] ²⁻ | I, I | I, X | -0.55 | -0.52 |
| | I, X | I, I | -6.20 | -10.35 |
| [Zn ₄ (SePh) ₆ I ₂ X ₂] ²⁻ | I, I | X, X | -0.92 ^f | -0.89 |
| | I, X | I, X | -6.87 | -11.20 |
| | X, X | I, I | -11.85 ^f | -19.51 |
| [Zn ₄ (SePh) ₆ IX ₃] ²⁻ | I, X | X, X | -7.52 | -11.96 |
| | X, X | I, X | -12.86 | -20.74 |
| [Zn ₄ (SePh) ₆ X ₄] ²⁻ | X, X | X, X | -13.66 | -21.87 |

^a $\Delta\delta_{\text{Se}} = \delta_{\text{Se}}(\text{obsd}) - \delta_{\text{Se}}([\text{Zn}_4(\text{SePh})_6\text{I}_4]^{2-})$; estimated error ± 0.05 ppm, except where noted otherwise. ^b A, B in diagram II. ^c C, D in diagram II. ^d At 296 K in equilibrium mixtures prepared from 0.05 M solutions of the Br₄ and I₄ parents as Et₄N⁺ salts; some Br-rich solutions were saturated. ^e At 298 K in equilibrium mixtures prepared from 0.035 M solutions of the I₄ and Cl₄ parents as Me₄N⁺ and Et₄N⁺ salts, respectively. ^f Estimated error ± 0.15 ppm.



shifts with those of [(μ -SePh)₆(ZnSePh)₄]²⁻ (see above), the anions may be formulated (μ -SePh)₆(ZnX)₄]²⁻, containing only bridging PhSe, as was found for the cadmium analogous also.⁹ The data in Table I show that $\delta_{\text{Se}}(\text{PhSe}_{\text{br}})$ varies with the terminal substituents in the order I > PhSe > Br > Cl.

Noteworthy in Table I are the large differences in linewidth between the resonances of **1** and those of the [Zn₄(SePh)₆X₄]²⁻ ions. Presumably t \rightleftharpoons br interchange of PhSe moieties is still occurring slowly in **1**; i.e., the ⁷⁷Se NMR spectrum of **1** is a slow-exchange spectrum but not a limiting spectrum. However, reduction in temperature does not sharpen the spectrum of **1**, probably because of the large temperature sensitivity of the chemical shifts coupled with the leeway allowed by the spectrometer temperature controller.^{5,18}

The mechanism proposed⁴ for t \rightleftharpoons br exchange in [M₄(SPh)₁₀]²⁻ can occur in **1** also. A similar mechanism involving a short-lived halogen-bridged isomeric species could produce br \rightleftharpoons br exchange in [Zn₄(SePh)₆X₄]²⁻. Such a process would not produce detectable broadening of the ⁷⁷Se NMR signals of the halo complexes, consistent with the relative sharpness observed. Therefore its existence cannot be ruled out in general. However, for the iodo complexes at least, br \rightleftharpoons br interchange is not facile. As shown below, the complexes [(μ -SePh)_{6-x}(μ -ER)_x(ZnI)₄]²⁻ (ER = SPh or SeMe) have chalcogenate cores that are static on the ⁷⁷Se NMR time scale at ambient probe temperature.

For all further experiments except redistribution of [Zn₄(SPh)₆I₄]²⁻ and [Zn₄(SePh)₆I₄]²⁻, the [Zn₄(SePh)₆X₄]²⁻ ions were prepared and used in situ. Test experiments showed that Ph₂Se₂, the other product of reaction 1, produced no complications.

[(μ -SePh)₆(ZnX)_{4-x}(ZnX')_x]²⁻ (X = I, X' = Br; X = I, X' = Cl). Clear evidence for the formation of species with mixed terminal halogens is found when solutions of [(μ -SePh)₆(ZnX)₄]²⁻ and [(μ -SePh)₆(ZnX')₄]²⁻ are mixed. The representative series of chloro-iodo and bromo-iodo complexes were examined in detail.

When **2b** is added stepwise to **2c** the first new species to be formed gives rise to two equally intense new resonances, one close to that of **2c** and one in a region between the signals of **2b** and **2c** (see Table II and Figure 1). This spectrum can be assigned to [(μ -SePh)₆(ZnI)₃(ZnBr)]²⁻. With time-averaged symmetry of C₃ or higher, there are two equally probable environments for a bridging ⁷⁷Se in this ion: in diagram II these correspond to A = B = C = I, D = Br and A = C = D = I, B = Br. The two

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(17) At present we have been unable to completely characterize species more halogen-rich than [(μ -SePh)₆(ZnX)₄]²⁻.

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Table III. Selenium-77 NMR Chemical Shifts^a of $(\text{Et}_4\text{N})_2[(\mu\text{-SePh})_6(\text{ZnSePh})_{4-x}(\text{ZnX})_x]$

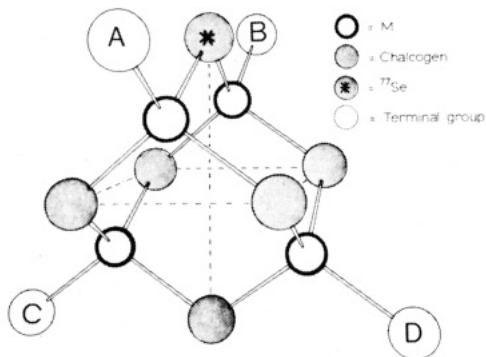
| <i>x</i> | adjacent terminal groups ^b | nonadjacent terminal groups ^c | $\delta_{\text{Se}}(\text{PhSe}_{\text{br}})$ | | | $\delta_{\text{Se}}(\text{PhSe}_{\text{t}})$ | | |
|----------|---------------------------------------|--|---|-----------------------|------------------------|--|-----------------------|------------------------|
| | | | X = Cl ^d | X = Br ^{e-g} | X = I ^{e,h,i} | X = Cl ^d | X = Br ^{e-g} | X = I ^{e,h,i} |
| 0 | PhSe, PhSe | PhSe, PhSe | -9.1 | -6.8 | -7.4 | 38.3 | 47.1 | 46.0 |
| 1 | PhSe, PhSe | X, PhSe | -10.6 | ~-6.2 ^j | ~-8.4 | 36.2 | 44.8 | 44.5 |
| 2 | X, PhSe | PhSe, PhSe | -11.5 | ~-8.0 ^j | -0.9 | 34.1 | 42.4 | 42.4 |
| | PhSe, PhSe | X, X | ~-11.8 | ~-5.5 ^j | ~-9.5 | | | |
| | X, PhSe | X, PhSe | -13.7 | ~-7.8 | -2.0 | | | |
| | X, X | PhSe, PhSe | ~-15.4 | ~-10.2 ^j | 5.0 | | | |
| 3 | X, PhSe | X, X | -15.9 | ~-7.8 ^j | -3.3 | 31.5 | 40.2 | 40.7 |
| 4 | X, X | X, PhSe | -17.4 | ~-10.2 ^j | 3.7 | | | |
| | X, X | X, X | -20.0 | -10.4 | 2.3 | | | |

^a Relative to external neat Me_2Se . ^b A, B in diagram II. ^c C, D in diagram II. ^d At 298 K, in equilibrium mixtures in MeCN, prepared in situ by stepwise addition of PhICl_2 to a 0.035 M solution of $[\text{Zn}_4(\text{SePh})_{10}]^{2-}$. ^e In equilibrium mixtures in acetone. ^f Prepared in situ by stepwise addition of Br_2 in CCl_4 to a 0.05 M solution of $[\text{Zn}_4(\text{SePh})_{10}]^{2-}$ followed by solvent removal in a flow of Ar and redissolution in acetone. See text for a discussion of these spectra. ^g At 298 K. ^h Prepared in situ by stepwise addition of I_2 to a 0.05 M solution of $[\text{Zn}_4(\text{SePh})_{10}]^{2-}$. ⁱ At 297 K. ^j The assignment for this pair of lines in this complex may be reversed (see text).

Table IV. Incremental ^{77}Se NMR Chemical Shifts, $\Delta\delta_{\text{Se}}$,^a of $(\text{Me}_4\text{N})_2[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(\text{ZnI})_4]$ in MeCN at 297 K^b

| chalcogenate core | $\Delta\delta_{\text{Se}}$ ^a | chalcogenate core | $\Delta\delta_{\text{Se}}$ ^a |
|---|---|--|---|
| $(\text{SePh})_6$ | 0.0 | $abc\text{-}(\text{SePh})_3(\text{SPh})_3$ | -3.9 |
| $abcde\text{-}(\text{SePh})_5(\text{SPh})$ | -0.1 (<i>a</i> -Se) | $af\text{-}(\text{SePh})_2(\text{SPh})_4$ | -9.1 |
| | -2.0 (<i>bcd</i> -Se) | $ab\text{-}(\text{SePh})_2(\text{SPh})_4$ | -6.1 |
| $abdf\text{-}(\text{SePh})_4(\text{SPh})_2$ | -4.3 | $(\text{SePh})(\text{SPh})_5$ | -8.5 |
| $abcd\text{-}(\text{SePh})_4(\text{SPh})_2$ | <i>c</i> | | |
| $abf\text{-}(\text{SePh})_3(\text{SPh})_3$ | -3.9 (<i>b</i> -Se) | | |
| | -6.7 (<i>af</i> -Se) | | |

^a $\Delta\delta_{\text{Se}} = \delta_{\text{Se}}(\text{obsd}) - \delta_{\text{Se}}([\text{Zn}_4(\text{SePh})_6\text{I}_4]^{2-})$; estimated error ± 0.2 ppm or less. ^b Samples were prepared by mixing 0.05 M solutions of the S_6 and Se_6 parents; some were saturated. ^c This complex appears to be present in small amount, if at all. For *bd*-Se and *ac*-Se = -4.4 and -2.0, respectively, from eq 4.

**II**

signals can be assigned unambiguously on the basis of the ^{77}Se NMR spectrum of $[(\mu\text{-SePh})_6(\text{ZnI})_2(\text{ZnBr})_2]^{2-}$, which is the major species present in the equilibrium mixture formed from equimolar amounts of the two parent ions. The I_2Br_2 ion gives three ^{77}Se resonances with intensities 1:4:1. This is the pattern expected for this ion when the time-averaged symmetry is C_{2v} . In this case the environments that can occur for $^{77}\text{SePh}$ are as follows: A = B = I, C = D = Br; A = C = I, B = D = Br; A = B = Br, C = D = I (see diagram II). These occur with probabilities 1, 4, and 1, respectively. Thus the most intense line, which occurs in a region between the signals of the parent complexes, is attributable to PhSe_{br} with the local environment I-Zn-Se(Ph)-Zn-Br. By comparison, the signal of the I_3Br ion occurring in the same region must be similarly assigned. Then the second ^{77}Se NMR resonance of the I_3Br ion must be due to the local environment I-Zn-Se(Ph)-Zn-I, and the nearby signal of the I_2Br_2 ion can be assigned likewise. This leaves the third most shielded resonance of the I_2Br_2 ion to be assigned to the local environment Br-Zn-Se(Ph)-Zn-Br, consistent with its closeness to the signal of **2b**.

Table V. Selenium-77 NMR Chemical Shifts^a of the Octahedral Core of $[(\mu\text{-SePh})_x(\mu\text{-SeMe})_{6-x}(\text{ZnI})_4]^{2-}$ in Acetone at 296 K^c

| no. of dissimilar cis substituents ^c | $\delta_{\text{SePh}} (\Delta\delta_{\text{SePh}}^d)$ | δ_{SeMe}^e |
|---|---|--------------------------|
| 0 | 3.3 ^f (1.2), 2.1 (0.0) | -274.3 |
| 1 | -0.9 ^f (-3.0), -2.0 (-4.1) | -279.2 |
| 2 | ~-5.6 ^g (-7.7) | -265.6 |
| 3 | -9.6 ^f (-11.7), -11.3 (-13.4) | -262.5 |
| 4 | -14.8 ^f (-16.9) | -260.4 |

^a Relative to external Me_2Se at 296 K. ^b 0.05 M (total) as Et_4N^+ salts; produced in situ by equilibration of $[\text{Zn}_4(\text{SePh})_6\text{I}_4]^{2-}$ (itself produced in situ from $[\text{Zn}_4(\text{SePh})_{10}]^{2-}$ and I_2) with Me_2Se_2 . ^c For discussion of these spectra, see text. ^d $\Delta\delta_{\text{SePh}} = \delta_{\text{SePh}}(\text{obsd}) - \delta_{\text{Se}}([\text{Zn}_4(\text{SePh})_6\text{I}_4]^{2-})$. ^e No fine structure was observed in this region. ^f Trans MeSe present (see text). ^g Broad.

In more bromine-rich mixtures a third new species, $[(\mu\text{-SePh})_6(\text{ZnI})(\text{ZnBr})_3]^{2-}$, is formed. This ion is characterized by two equally intense ^{77}Se NMR signals, one close to the resonance of **2b** and one in the intermediate region. By analogy with the results just described, the lines may be assigned to PhSe_{br} in the environments A = B = C = Br and D = I and A = C = D = Br and B = I, respectively (see diagram II).

From the details of the ^{77}Se NMR spectra of $[(\mu\text{-SePh})_6(\text{ZnI})_{4-x}(\text{ZnBr})_x]^{2-}$ in Table II, it can be seen that bromine substitution of an iodine in the A or B sites (see diagram II) shields the ^{77}Se NMR signal of PhSe_{br} by 5.7–6.6 ppm; bromine substitution of an iodine in the C or D sites causes a shielding of 0.4–1.0 ppm. Also, the spectrum in Figure 1 shows that redistribution of the I and Br occurs nearby randomly; from statistical considerations¹⁹ an intensity pattern 1:2:1:2:4:2:1:2:1 is expected for an equimolar mixture of the I_4 and Br_4 ions. This is close to the observed intensity distribution. At present we can offer no good explanation for the comparative broadness evident in the third and seventh lines in Figure 1.

The system **2a:2c** behaves in a manner very similar to that described for **2b:2c** mixtures, and the ^{77}Se NMR spectra can be interpreted and assigned in the same way. Spectral details are included in Table II. In this case chlorine substitution of an iodine in the A or B sites (see diagram II) causes a shielding of 9.2–11.1 ppm in the ^{77}Se NMR signal of PhSe_{br} , while chlorine substitution into the C or D sites causes a shielding of 0.4–1.2 ppm.

$[(\mu\text{-SePh})_6(\text{ZnSePh})_{4-x}(\text{ZnX})_x]^{2-}$ (X = Cl, Br, I). As noted above, oxidative halogen substitution of **1** gives the fully terminally halogen substituted clusters $[(\mu\text{-SePh})_6(\text{ZnX})_4]^{2-}$ when $\text{X}_2/\mathbf{1} = 2$. At lower $\text{X}_2/\mathbf{1}$ ratios (or in $1\text{-}[\text{Zn}_4(\text{SePh})_6\text{X}_4]^{2-}$ mixtures), the ^{77}Se NMR spectra of individual partially halogen-substituted ions $[(\mu\text{-SePh})_6(\text{ZnSePh})_{4-x}(\text{ZnX})_x]^{2-}$ can be observed for X = Cl or I. Good ^{77}Se NMR spectral evidence for the occurrence of the Br-containing analogues was obtained also.

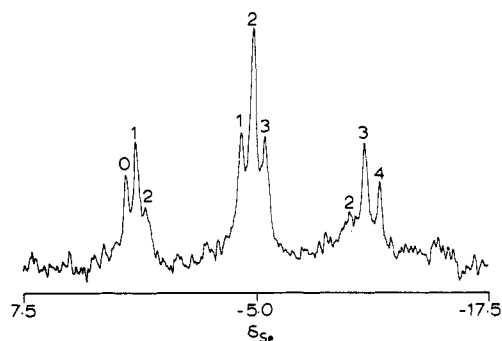


Figure 1. Proton-decoupled ⁷⁷Se NMR spectrum, at 295 K and 38.15 MHz, of a 1:1 mixture in MeCN of [(μ-SePh)₆(ZnBr)₄]²⁻ and [(μ-SePh)₆(ZnI)₄]²⁻ (both prepared in situ as Et₄N⁺ salts, with [Zn₄]_{total} = 0.05 M), showing the formation of [(μ-SePh)₆(ZnI)_{4-x}(ZnBr)_x]²⁻. The correlation of the individual lines with x is shown; for further discussion of these assignments see text. This spectrum results from 53 514 28° (5-μs) pulses with an acquisition and recycle time of 1.5 s. In the recording 3.5-Hz line broadening has been applied.

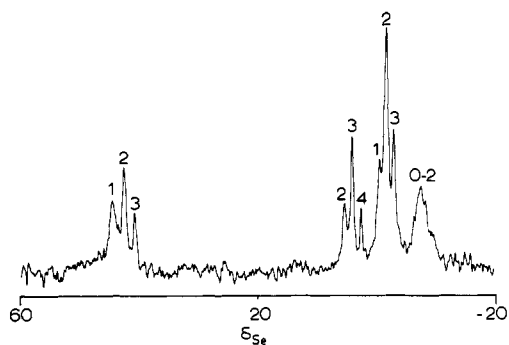


Figure 2. Proton-decoupled ⁷⁷Se NMR spectrum, at 297 K and 38.15 MHz, of the equilibrium mixture produced from a 1:1 mixture of (Et₄N)₂[(μ-SePh)₆(ZnSePh)₄]²⁻ (0.05 M) and I₂ in acetone, showing the formation of [(μ-SePh)₆(ZnSePh)_{4-x}(ZnI)_x]²⁻. The correlation of individual lines with x is shown; for further discussion of these assignments see text. This spectrum results from 21 347 28° (5-μs) pulses with an acquisition and recycle time of 1.5 s. In the recording 7.5-Hz line broadening has been applied.

Stepwise addition of I₂ (or 2c) to 1 causes sequential production of the complexes with one, two, and three terminal iodines. Each of these species gives rise to a new ⁷⁷Se NMR signal in the PhSe_t region of the spectrum, which becomes increasingly shielded with increasing halogen substitution (see Figure 2 and Table III). As expected from the results for [(μ-SePh)₆(ZnX)_{4-x}(ZnX')_x]²⁻ (see above), the patterns observed in the PhSe_{br} region are of two equally intense lines for the complexes with one and three iodines and a 1:4:1 three-line pattern for the diiodo species. The PhSe_{br} resonances of [(μ-SePh)₆(ZnSePh)_{4-x}(ZnI)_x]²⁻ again fall into three distinct groups, as can be seen in Figure 2. In order of increasing shielding these groups can be associated with A/B in diagram II being I/I, I/SePh, and SePh/SePh. The assignment of the individual lines are given in Table III; these follow from the treatment given above. It is notable that the most shielded group of lines, which is due to PhSe_{br} in the environment PhSe_t-Zn-Se(Ph)-Zn-SePh_t, is broad with ill-resolved individual components. (Resolution is not significantly improved in the 57.20 MHz spectrum, or by reduction in temperature.) We attribute the observed broadness at ambient probe temperature to the slow intramolecular PhSe_t ⇌ PhSe_{br} exchange that appears to occur in this environment (see above).

The data in Table III show that the ⁷⁷Se NMR signal of a PhSe_{br} group is deshielded by 5.7–6.5 ppm on iodine substitution of PhSe_t in the A or B sites (see II) and deshielded by ~1.0–1.4 ppm on a similar iodine substitution into the C or D sites. From the 1:2:1:2:4:2:1:2:1 pattern observed in the PhSe_{br} region of the spectrum of a sample of composition [Zn₄(SePh)₈I₂]²⁻ (Figure 2) it is evident that the terminal SePh and I groups in the series

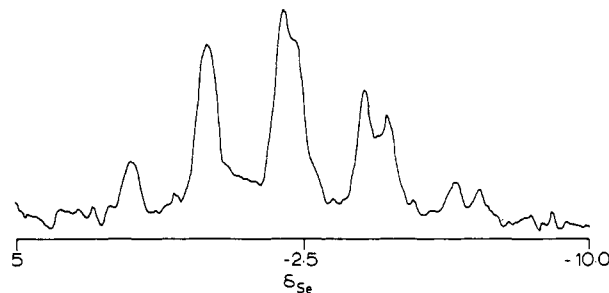


Figure 3. Proton-decoupled ⁷⁷Se NMR spectrum, at 296 K and 38.15 MHz, of a 1:1 mixture in MeCN of [(μ-SePh)₆(ZnI)₄]²⁻ and [(μ-SPh)₆(ZnI)₄]²⁻ (both as Ph₂E₂-free Et₄N⁺ salts, with [Zn₄]_{total} = 0.05 M), showing the formation of [(μ-SePh)_{6-x}(μ-SPh)_x(ZnI)₄]²⁻. See text for a discussion of this spectrum which results from 12 500 28° (5-μs) pulses with an acquisition and recycle time of 1.5 s and has been recorded with 5.0-Hz line broadening applied.

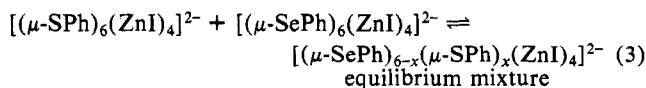
[(μ-SePh)₆(ZnSePh)_{4-x}(ZnI)_x]²⁻ are distributed close to randomly.¹⁹

The system PhICl₂-1 (or 2a-1) produces complexes with chlorine in the terminal positions. These behave chemically and ⁷⁷Se NMR spectroscopically like their iodine-containing analogues, except that the spread of the spectra in the PhSe_{br} region is smaller, so that clearer NMR results are obtained at 57.20 MHz than at 38.15 MHz. The ⁷⁷Se NMR spectra are readily interpreted in terms of complexes with different numbers of terminal chlorine atoms. The assignments are included in Table III. In this system it is found that chlorine substitution of PhSe_t in the A or B sites of II causes the ⁷⁷Se NMR signal of an adjacent PhSe_{br} group to be shielded by 2.4–4.1 ppm; substitution of PhSe_t in the C or D sites causes PhSe_{br} to be shielded by 1.2–2.6 ppm.

The system Br₂-1 (or 2b-1) provides evidence for complexes containing terminal bromine atoms. However, the ⁷⁷Se NMR spectroscopic results for this system are simpler than those found for the analogous iodine- or chlorine-containing systems. In the PhSe_t region a total of four signals are observed, showing that all the complexes [(μ-SePh)₆(ZnSePh)_{4-x}(ZnBr)_x]²⁻ (x = 0–3) exist. However, in the PhSe_{br} region, three signals are observed in all. These are approximately equally spaced between that of 1 and that of 2b, with positions that appear to change slightly as the Br₂/1 ratio is changed. They have intensities showing them to be linked to the expected populations of the terminal pairs SePh/SePh, SePh/Br, and Br/Br (from high to low frequency.) Evidently either adjacent (A or B) or nonadjacent (C or D) bromine substitution produces a near-zero effect on δ_{Se}(PhSe_{br}), which is consistent with the opposing effects produced by iodine and chlorine substitution (see above). The assignments included in Table III have been made on the assumption that the effect of nonadjacent (C or D) substitution is near-zero, which is our prejudice. However, the alternative assignments cannot be excluded.

[(μ-SePh)_{6-x}(μ-SPh)_x(ZnI)₄]²⁻. The idealized geometry of the chalcogenate core in 2 and the analogous sulfur complex is octahedral (see diagram II). We have used the ⁷⁷Se NMR spectra of the PhSe_{br} groups as probes for substitution of PhSe_t and (below) MeSe_{br} into the octahedral Se₆ core of the representative complex 2c, which was chosen for its high solubility.

On stepwise addition of Ph₂S₂-free²⁰ [Zn₄(SPh)₆I₄]²⁻ to Ph₂S₂-free²⁰ 2c in MeCN, redistribution occurs quickly (eq 3),



and a new series of ⁷⁷Se signals is observed, as shown in Figure 3. All of the new lines are shielded relative to the signal of 2c, the line of highest frequency in Figure 3. Details of the spectra are given in Table IV. From Figure 3 it can be seen that in gross terms the signals fall into five regions. These can be attributed

(20) Ph₂E₂ was removed to prevent stoichiometry complications caused by direct redox reaction of Ph₂E₂ and [Zn₄(E'Ph)₆I₄]²⁻ (see ref 7).

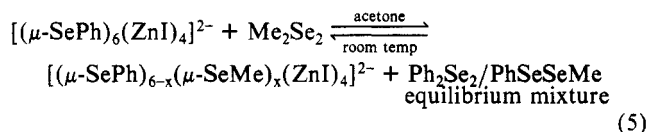
to PhSe_{br} groups having different numbers of cis PhS_{br} substituents, from zero-four (in order of increasing shielding) in the octahedral core. Each cis substituent is geminal to the probe PhSe_{br} group, i.e. occupies an equatorial position in diagram II. The three more shielded regions each contain two lines, indicating that $\delta_{\text{Se}}(\text{PhSe}_{\text{br}})$ is influenced by the nature of the trans substituent also. Detailed assignments can be made on this basis together with the variation in signal intensities with variation in S_6/Se_6 ratio. From the results (Table IV) it is clear that $\Delta\delta_{\text{Se}}$ cannot be accommodated on the basis of simple first order additivity of cis- and trans-substituent effects.²¹ However, introduction of a second-order term²² allows a good fit of $\Delta\delta_{\text{Se}}$. Multiple regression analysis gives eq 4. In

$$\Delta\delta_{\text{Se}} = -2.28F + 0.18T + 0.13 \quad (4)$$

this equation, F is the number of PhS groups cis to the PhSe probe and T is the number of cis PhS to trans PhS interactions. The equation accounts for the observed shifts with a multiple correlation coefficient of 0.999, lending strong support to the assignments given in Table IV.

Two ^{77}Se NMR signals occur for both $abcde-[(\mu-\text{SePh})_5(\mu-\text{SPh})(\text{ZnI})_4]^{2-}$ and $abf-[(\mu-\text{SePh})_3(\mu-\text{SPh})_3(\text{ZnI})_4]^{2-}$ (see Table IV). As each of these ions contains PhSe_{br} groups in two different environments, it is clear that chemical exchange of PhSe_{br} groups within the chalcogen core is slow on the ^{77}Se NMR time scale in these species.

$[(\mu-\text{SePh})_{6-x}(\mu-\text{SeMe})_x(\text{ZnI})_4]^{2-}$. Substitution of MeSe groups into the chalcogenate core of **2c** occurs rapidly according to eq 5. Reactions of $[\text{Cd}_4(\text{SPh})_{10}]^{2-}$ with R_2S_2 ($\text{R} = \text{alkyl}$) are slow



(hours) at room temperature and favor coordination of the PhS group heavily.⁷ However, reaction 5 is complete in the ca. 0.25 h needed to measure the sharp ^{77}Se NMR spectra of the MeSe (in diselenide) region (see below) and favors coordination of MeSe and PhSe groups approximately equally.

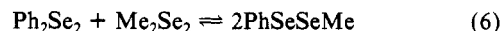
With variation in the $\text{Me}_2\text{Se}_2/2\text{c}$ ratio a total of five roughly equally spaced signals are observed in the region found for MeSe on Zn (Table V). By analogy with the results for $[(\mu-\text{SePh})_{6-x}(\mu-\text{SPh})_x(\text{ZnI})_4]^{2-}$ (see above), these signals must result from differing numbers of cis PhSe_{br} groups, from 0–4, in the octahedral chalcogenate core. (See diagram II also.) Specific assignments were made from the way in which the signal intensities vary with variation in $\text{Me}_2\text{Se}_2/2\text{c}$. It was found that shielding of ^{77}Se decreases as the number of cis PhSe_{br} groups increases. There is no obvious influence of the nature of the trans RSe group. As a result it was not possible to make assignments to specific complexes.

In the PhSe -on- Zn region of the ^{77}Se NMR spectrum a total of five regions of resonance are again observed (Table V). However, three of these regions exhibit two signals. Here the five major regions are readily attributed to the presence of from zero to four (from low to high shielding) cis MeSe groups. The multiplicity within regions must reflect a sensitivity to the nature of the trans chalcogenate.

When Me_2Se_2 is initially added to **2c**, the first new species produced is characterized by two ^{77}Se NMR signals with relative intensities 1 and 4, deshielded by 1.2 ppm and shielded by 4.1 ppm, respectively, from the resonance of **2c** (Table V). The signals can be assigned straightforwardly to $a\text{-SePh}$ and $bcd\text{-}(\text{SePh})_4$ in an $abcde\text{-}(\text{PhSe})_5(\text{MeSe})$ core. Comparison of $\delta_{\text{Se}}(a\text{-SePh})$ and $\delta_{\text{Se}}(2\text{c})$ shows that the presence of a trans MeSe group causes deshielding. On this basis the less shielded resonance in each of the regions showing multiplicity is assigned to a PhSe group located trans to MeSe . Variation in signal intensity with variation of $\text{Me}_2\text{Se}_2/2\text{c}$ is consistent with this interpretation. Thus the signal

with $\delta_{\text{Se}} -0.9$ can be attributed to a PhSe with one cis and one trans MeSe group, i.e. to $ac\text{-}(\text{PhSe})_2$ of the $abcd\text{-}(\text{PhSe})_4(\text{MeSe})_2$ core. Similarly, the signal at $\delta_{\text{Se}} -9.6$ is from PhSe with three cis MeSe groups and one trans, i.e. from $ab\text{-}(\text{PhSe})_2$ in $ab\text{-}(\text{PhSe})_2(\text{MeSe})_4$. Also the signal at $\delta_{\text{Se}} -11.3$ is from PhSe with three cis MeSe groups, i.e. from $af\text{-}(\text{PhSe})_2$ in $abf\text{-}(\text{PhSe})_3\text{-}(\text{MeSe})_3$. The unique signal at $\delta_{\text{Se}} -14.8$ is not tied in intensity to the -9.6 ppm signal of the $ab\text{-}(\text{PhSe})_2(\text{MeSe})_4$ core and hence is due to the $(\text{PhSe})(\text{MeSe})_5$ core, rather than the $af\text{-}(\text{PhSe})_2\text{-}(\text{MeSe})_4$ core. The rather broad and ill-resolved signal at $\delta_{\text{Se}} \sim -5.6$ must contain the resonances of $bd\text{-}(\text{PhSe})_2$ in the $abcd\text{-}(\text{PhSe})_4(\text{MeSe})_2$ core and $b\text{-PhSe}$ of the $abf\text{-}(\text{PhSe})_3(\text{MeSe})_3$ core. The broadness of this signal suggests the presence of other components also. These could include the lines of the $abdf\text{-}(\text{PhSe})_4(\text{MeSe})_2$ and $abc\text{-}(\text{PhSe})_3(\text{MeSe})_3$ cores, both of which contain PhSe with two cis MeSe groups. The only species that appears to occur in undetectable concentration in the $\text{Me}_2\text{Se}_2\text{-}2\text{c}$ mixtures is that with the $af\text{-}(\text{PhSe})_2(\text{MeSe})_4$ core.

Equilibrated mixtures of Me_2Se_2 and **2c** in acetone show ^{77}Se NMR signals from the two parent diselenides ($\delta_{\text{Se}}(\text{Me}_2\text{Se}_2) = 261$; $\delta_{\text{Se}}(\text{Ph}_2\text{Se}_2) = 459$) as well as the unsymmetrical diselenide ($\delta_{\text{Se}}(\text{MeSeSePh}) = 289$; $\delta_{\text{Se}}(\text{MeSeSePh}) = 432$). These chemical shifts are consistent with those found in earlier work.²³ From the signal intensities measured here, we find the equilibrium constant for (6) to be ca. 5 at 298 K, close to the statistical value¹⁹ of 4.



$[(\mu-\text{SePh})_{6-x}(\mu-\text{SPh})_x(\text{ZnSePh})_{4-y}(\text{ZnSPh})_y]^{2-}$. At ambient probe temperature, mixtures of **1** and its sulfur analogue give ^{77}Se NMR spectra composed of two ill-resolved broad resonances. For instance for an acetone solution in which $1/[\text{Zn}_4(\text{SPh})_{10}]^{2-} = 3/2$ and $[\text{Zn}_4]_{\text{total}} = 0.05$ M, these resonances are centered at $\delta_{\text{Se}} \approx 36$ ($\Delta\nu_{1/2} \approx 500$ Hz (possibly a poorly resolved quartet)) and ≈ -11 ($\Delta\nu_{1/2} \approx 280$ Hz). By comparison with the spectrum of **1** (see earlier) the less shielded region is assignable to PhSe_t and the more shielded to PhSe_{br} . The intensity ratio $\text{PhSe}_{\text{br}}/\text{PhSe}_t \approx 1.2$, when compared with the statistical value of 1.5, suggests a slight preference of PhSe over PhS for the terminal positions. This same preference occurs at different $1/[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ ratios, e.g. $\text{PhSe}_{\text{br}}/\text{PhSe}_t \approx 1.1$ with the parents in a $2/3$ ratio. The observed preference is not so marked as to preclude any of the possible mixed-ligand species, however. Therefore extremely complicated equilibrium mixtures can be anticipated, comprised not only of species with different values of x in $[\text{Zn}_4(\text{SePh})_{10-x}(\text{SPh})_x]^{2-}$ but also of mixtures of isomers for a given value of x . (When $x = 5$, the most complicated case, 19 isomers are possible!) Nevertheless, some information can be obtained from reduced-temperature ^{77}Se NMR spectra.

At 261 K, the ^{77}Se NMR spectrum of the $3/2$ mixture shows a featureless resonance with $\delta_{\text{Se}} \approx -19.4$ in the region due to PhSe_{br} . However, in the PhSe_t region four major resonances are found, approximately evenly spaced with $\delta_{\text{Se}} \approx 38.7, 32.3, 25.8$, and 19.0 and relative intensities roughly 1,3,3 and 1 (Figure 4a). From the overall intensities of the PhSe_t and PhSe_{br} regions (see above) it can be shown that the population ratio $\text{PhSe}_{\text{br}}/\text{PhSe}_t \approx 1.2$. Most likely $\delta_{\text{Se}}(\text{PhSe}_t)$ is affected mainly by the nature of the three chalcogens in geminal bridging positions (see I). As expected then, the four resonances observed in the PhSe_t region do have intensities correlated very approximately with the statistical¹⁹ populations of the combinations $(\text{PhSe}_{\text{br}})_3$, $(\text{PhSe}_{\text{br}})_2\text{-}(\text{PhS}_{\text{br}})$, $(\text{PhSe}_{\text{br}})(\text{PhS}_{\text{br}})_2$, and $(\text{PhS}_{\text{br}})_3$. The least shielded signal, with $\delta_{\text{Se}} \approx 38.7$, has a chemical shift close to that of **1** in which the geminal groups are $(\text{PhSe}_{\text{br}})_3$. Thus increase in the number of geminal PhS_{br} groups causes an increase in $\delta_{\text{Se}}(\text{PhSe}_t)$.

A second, less probable explanation for the spectrum observed in the PhSe_t region, is that the nature of either the *nongeminal* bridging groups or the other terminal groups in the cluster (see

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(22) Vladimiroff, T.; Malinowski, E. R. *J. Chem. Phys.* **1967**, *46*, 1830 and references therein.

(23) McFarlane, W.; Wood, R. J. *J. Chem. Soc. Dalton Trans.* **1972**, 1397 and references therein. Anderson, J. A.; Odom, J. D.; Zozulin, A. J. *Organometallics*, **1984**, *3*, 1458 and references therein.

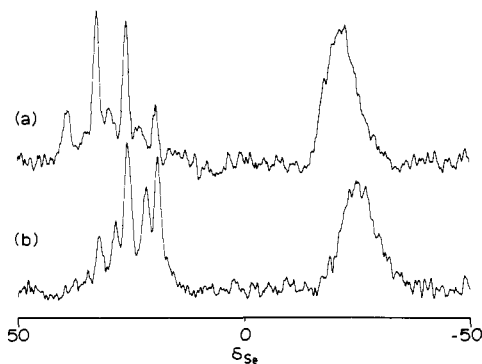
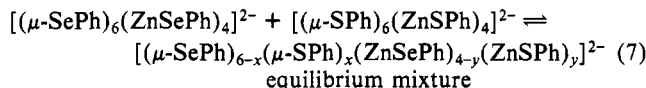


Figure 4. Proton-decoupled ^{77}Se NMR spectrum, at 261 K and 38.15 MHz of acetone solutions containing $(\text{Et}_4\text{N})_2[\text{Zn}_4(\text{SePh})_{10}]$ and $(\text{Et}_4\text{N})_2[\text{Zn}_4(\text{SPh})_{10}]$ with $[\text{Zn}_4]_{\text{total}} = 0.05$ M, showing the formation of $[\text{Zn}_4(\text{SePh})_{10-x}(\text{SPh})_x]^{2-}$. The ratio $[\text{Zn}_4(\text{SePh})_{10}]^{2-}/[\text{Zn}_4(\text{SPh})_{10}]^{2-} = 3/2$ for spectrum a and $2/3$ for spectrum b. Spectrum a results from 17 500 42° (7.5- μs) pulses with an acquisition and recycle time of 1.5 s and has been recorded with 15.0 Hz line broadening applied. Spectrum b was obtained similarly by using 25 000 pulses and has been recorded in the same way.

I) has the major influence on $\delta_{\text{Se}}(\text{PhSe})$. Each of these possibilities could produce the same overall intensity pattern. We judge these two possibilities unlikely on the basis of the spectra of the mononuclear complexes $[\text{Zn}(\text{SePh})_{4-x}(\text{SPh})_x]^{2-}$ (see below). Nevertheless, in some cases it does seem that the nature and/or position of the nongeminal chalcogen atoms affects $\delta_{\text{Se}}(\text{PhSe})$. In the spectrum of the $3/2$ mixture, and more noticeably the $2/3$ mixture, there are other minor resonances in the PhSe region: at $\delta_{\text{Se}} \approx 28.4$ (apparently linked in intensity with the signal having $\delta_{\text{Se}} \approx 25.8$) and $\delta_{\text{Se}} \approx 21.6$ (apparently linked in intensity with the resonance having $\delta_{\text{Se}} \approx 19.0$) (see Figure 4). Unfortunately, no further assignment seems possible, but in any event our results demonstrate unambiguously the formation of clusters with mixed terminal and bridging ligands (eq 7).

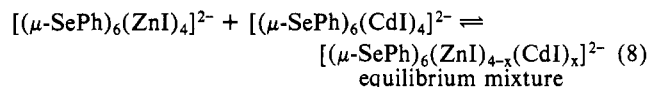


$[\text{Zn}(\text{SePh})_{4-x}(\text{SPh})_x]^{2-}$. For comparison with the results obtained for $1-[\text{Zn}_4(\text{SPh})_{10}]^{2-}$ mixtures, we have measured the ^{77}Se NMR spectra of the mononuclear analogues $[\text{Zn}(\text{SePh})_{4-x}(\text{SPh})_x]^{2-}$. These are formed in mixtures of the metal nitrate with excess $\text{PhSe}^-/\text{PhS}^-$ in MeOH, like their Cd(II) analogues.²⁴

A methanolic solution in which $[\text{Zn}^{2+}]_{\text{total}} = 0.10$ M and $[\text{PhSe}^-]_{\text{total}} = 1.2$ M gives a single broad ^{77}Se NMR line at ambient probe temperature. On cooling, separate signals from $[\text{Zn}(\text{SePh})_4]^{2-}$ and excess PhSe^- are resolved. For these species δ_{Se} ($\Delta\nu_{1/2}$) are 15.7 (70) and ~ 51.8 (320) at 217 K. Essentially the same spectrum is obtained from a saturated mixture with $\text{Zn}^{2+}/\text{PhSe}^-/\text{PhS}^- = 1/10/2$ and $[\text{Zn}^{2+}]_{\text{total}} = 0.05$ M, showing that the metal ion binds PhSe^- preferentially over PhS^- , as was observed for Cd^{2+} also.²⁴ A similar saturated mixture having $\text{Zn}^{2+}/\text{PhSe}^-/\text{PhS}^- = 1/2/10$ shows the resonance of $[\text{Zn}(\text{SePh})_4]^{2-}$ and two new signals shielded from this by 5.0 ± 0.5 and 8.3 ± 0.5 ppm, which can be assigned to $[\text{Zn}(\text{SePh})_3(\text{SPh})]^{2-}$ and $[\text{Zn}(\text{SePh})_2(\text{SPh})_2]^{2-}$, respectively. The solubility of $[\text{Zn}(\text{SePh})(\text{SPh})_3]^{2-}$ seems to be too low at 217 K under our conditions

to allow its detection. Of particular interest here, the change in δ_{Se} on substitution of a geminal SePh by SPh in the mononuclear complexes is of comparable magnitude to the effect on $\delta_{\text{Se}}(\text{PhSe})$ of the proposed geminal substitution of PhS_{br} for PhSe_{br} in $[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(\text{ZnSePh})_{4-y}(\text{ZnSPh})_y]^{2-}$ (see above). This supports our contention that changes in geminal groups dominate $\delta_{\text{Se}}(\text{PhSe})$ in the Zn_4 clusters. However, the changes in δ_{Se} are not additive in $[\text{Zn}(\text{SePh})_{4-x}(\text{SPh})_x]^{2-}$ as they appear to be for the clusters.

$[(\mu\text{-SePh})_6(\text{ZnI})_{4-x}(\text{CdI})_x]^{2-}$. The ^{77}Se NMR spectra of mixtures of **2c** and its cadmium analogue were measured by using MeCN solutions in which $[\text{M}_4]_{\text{total}} = 0.05$ M. Overall, three regions of resonance occur as the Cd/Zn ratio is varied. At 297 K the observed spectral line widths of these regions increase with decrease in chemical shift and with increase in Cd/Zn. As Cd/Zn is increased, the least shielded region shows first the signal of **2c** with $\delta_{\text{Se}} 2.2$, then a second signal grows having $\delta_{\text{Se}} 3.1$ before increase in line width precludes further resolution. We attribute the lines in this region to the grouping I–Zn–Se(Ph)–Zn–I. The resonance at 3.1 ppm is probably due to this grouping in the species $[(\mu\text{-SePh})_6(\text{ZnI})_3(\text{CdI})]^{2-}$. The most shielded region, at $\delta_{\text{Se}} \sim -50.6$ (with $\Delta\nu_{1/2} \approx 170$ when Cd/Zn = 3) is close to that found⁹ for $[(\mu\text{-SePh})_6(\text{CdI})_4]^{2-}$ and can evidently be assigned to the grouping I–Cd–Se(Ph)–Cd–I. It follows then that the region of intermediate chemical shift (e.g. $\delta_{\text{Se}} \sim -22.3$, $\Delta\nu_{1/2} \approx 120$ when Cd/Zn = 1) arises from the grouping I–Zn–Se(Ph)–Cd–I. Clearly, mixed-metal species are being formed, according to eq 8. From the intensities of the three regions, e.g. ca 1:2:1 in the



mixture with Cd/Zn = 1, it is clear that scrambling of the two metals in **2c**– $[\text{Cd}_4(\text{SePh})_6\text{I}_4]^{2-}$ mixtures is close to random.¹⁹

The Zn–Se(Ph)–Zn linkage is nonlabile on the ^{77}Se NMR time scale at 297 K (see above), so the broadness of the lines at ambient probe temperature must be triggered by intermolecular exchange of cadmium. Reduction in the temperature of the samples leads to sharpening of, particularly, the lower frequency regions of the ^{77}Se NMR spectra. For example, at 261 K the signal from I–Cd–Se(Ph)–Cd–I is at $\delta_{\text{Se}} -60.7$ with $\Delta\nu_{1/2} \approx 80$ when Cd/Zn = 3). Beyond signal sharpening, however, no new features are revealed on cooling. Indeed the fine structure seen for the least shielded region at 297 K is lost at 261 K, probably due to either viscosity broadening or slight variations in temperature within the sample,^{5,18} or both.

It is interesting that the ^{113}Cd NMR spectra of $1-[(\mu\text{-SePh})_6(\text{CdI})_4]^{2-}$ mixtures provide little evidence for the formation of mixed-metal complexes. For example, at 261 K, the ^{113}Cd NMR spectrum of a mixture with Cd/Zn = 3 consists of a single broad line ($\delta_{\text{Cd}} = 461$, $\Delta\nu_{1/2} \approx 110$ Hz). In $[(\mu\text{-SPh})_6(\text{ZnSPh})_{4-x}(\text{CdSPh})_x]^{2-}$ the change in δ_{Cd} on Zn substitution is only 0.45 ppm/Zn,^{4,7,8} and changes of this magnitude could easily be hidden by the larger line width observed in the present case. The linewidth must also obscure any one-bond ^{77}Se – ^{113}Cd coupling. Such couplings fall in the range 40–130 Hz.^{9b,24}

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