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

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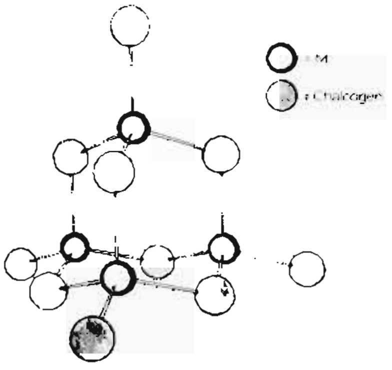
Selenium-77 NMR has been used to study $[\text{Zn}_4(\text{SePh})_{10}]^{2-}$ (1) and a wide variety of its substitution and redistribution products. At 296 K, **1** gives a slow-exchange ^{77}Se NMR spectrum consistent with the adamantanoid structure $[(\mu\text{-SePh})_6(\text{ZnSePh})_4]^{2-}$. Oxidative 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 X = Cl or I. Redistribution of $[(\mu\text{-SePh})_6(\text{ZnX})_4]^{2-}$ and $[(\mu\text{-SePh})_6(\text{ZnX}')_4]^{2-}$ (X = I, X′ = Cl; X = I, X′ = 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 $[\text{Zn}(\text{SePh})_{4-x}(\text{SPh})_x]^{2-}$ (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 $[(\mu\text{-SPh})_6(\text{MSPh})_4]^{2-}$ (M = 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 ^{1}H, ^{13}C, and $^{111/113}$Cd NMR spectroscopies.[4-6] The solution studies show that the Cd_4 core remains intact on the $^{111/113}$Cd NMR time scale while intramolecular exchange of terminal and bridging thiolates is rapid on the ^{1}H 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 found[7] to simplify the spectra of $[\text{Cd}_4(\text{EPh})_x(\text{E}'\text{R})_{10-x}]^{2-}$. 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.



I

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 ^{1}H 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 nuclide[11] 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 NMR[11] to follow substitution and redistribution in the Zn_4 cluster system.

Experimental Section

Materials and General Procedures. Literature syntheses were used for PhICl_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 $\text{Cd}(\text{ClO}_4)_2$(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, $D^c = 0.670$; ^{77}Se, spin $I = {}^1/_2$, 7.58% natural abundance, $D^c = 3.01$.[12]

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Table I. Selenium-77 NMR Spectral Parameters[a] of $[Zn_4(SePh)_{10}]^{2-}$ and $[Zn_4(SePh)_6X_4]^{2-}$

salt	solvent	concn, M	T, K	δ_{Se}[b] ($\Delta\nu_{1/2}$(approx), Hz) PhSe$_t$	δ_{Se}[b] ($\Delta\nu_{1/2}$(approx), Hz) PhSe$_{br}$
$(Me_4N)_2[Zn_4(SePh)_{10}]$	acetone	satd	296	46.3 (70)	−6.7 (50)
	MeCN	0.05	296	38.0 (75)	−8.8 (55)
$(Et_4N)_2[Zn_4(SePh)_{10}]$	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)
$(Et_4N)_2[Zn_4(SePh)_6Cl_4]$[e]	MeCN	0.05	297		−19.8 (17)
	acetone	satd	295		−18.0 (7)
$(Et_4N)_2[Zn_4(SePh)_6Br_4]$[f]	MeCN	0.05	296		−11.7 (10)
	acetone	satd	297		−10.4 (14)
$(Me_4N)_2[Zn_4(SePh)_6I_4]$[g]	MeCN	0.05	298		1.9 (10)
	acetone	0.05	296		2.4 (13)
$(Et_4N)_2[Zn_4(SePh)_6I_4]$[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 Me_2Se. [c] Measured at 57.20 MHz. [d] Estimated error ±0.3 ppm. [e] Prepared in situ from $[Zn_4(SePh)_{10}]^{2-}$ and $PhICl_2$. [f] Prepared in situ from $[Zn_4(SePh)_{10}]^{2-}$ and Br_2. [g] Prepared in situ from $[Zn_4(SePh)_{10}]^{2-}$ and I_2.

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 ^{1}H decoupling by use of a thermocouple probe in a stationary dummy sample of the appropriate solvent.

Results and Discussion

$[Zn_4(SePh)_{10}]^{2-}$ (1). The ^{77}Se 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 $[(\mu\text{-}SePh)_6(ZnSePh)_4]^{2-}$ ion having skeleton I, as found[3] for $[Zn_4(SPh)_{10}]^{2-}$. 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 ⇄ br interchange is slow on the ^{77}Se NMR time scale. The values of δ_{Se} measured for $[Zn_4(SePh)_{10}]^{2-}$ 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 $(Me_4N)_2[Cd_4(SePh)_{10}]$ as a 0.05M solution in MeCN at 234 K. (As reported earlier[7] the ^{77}Se NMR spectrum of $[Cd_4(SePh)_{10}]^{2-}$ consists of a single broad line at ambient probe temperature.)

X-ray structural analyses of $(Me_4N)_2[Zn_4(SePh)_{10}]$ and $(Me_4N)_2[Cd_4(SePh)_{10}]$ are currently in progress.[16]

$[Zn_4(SePh)_6X_4]^{2-}$ (X = Cl, 2a; X = Br, 2b; X = I, 2c). Reaction of $[Zn_4(SePh)_{10}]^{2-}$ with 2 mol of halogen (or, for **2a**, $PhICl_2$) yields the $[Zn_4(SePh)_6X_4]^{2-}$ ions quantitatively by oxidative substitution[9b,17] (eq 1). The ^{77}Se NMR spectra of **2b** and **2c** consist of

$$[Zn_4(SePh)_{10}]^{2-} + 2X_2 \rightarrow [Zn_4(SePh)_6X_4]^{2-} + 2Ph_2Se_2 \qquad (1)$$

a single line (Table I) shielded relative to Me_2Se. 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 $[(\mu\text{-}SePh)_6(ZnSePh)(ZnCl)_3]^{2-}$ (see below) and it is clear that **2a** is in equilibrium in solution with its redistribution products (eq 2).[17] By comparison of their ^{77}Se NMR chemical shifts with those of $[(\mu\text{-}SePh)_6(ZnSePh)_4]^{2-}$ (see above), the anions may be formulated $(\mu\text{-}SePh)_6(ZnX)_4]^{2-}$, containing only bridging PhSe, as was found for the cadmium analogous also.[9] The data in Table I show that δ_{Se}(PhSe$_{br}$) varies with the terminal substituents in the order I > PhSe > Br > Cl.

Table II. Incremental ^{77}Se NMR Chemical Shifts, $\Delta\delta_{Se}$,[a] of $[Zn_4(SePh)_6I_{4-x}X_x]^{2-}$ in MeCN

complex	adjacent terminal halogens[b]	nonadjacent terminal halogens[c]	$\Delta\delta_{Se}$[a] X = Br[d]	$\Delta\delta_{Se}$[a] X = Cl[e]
$[Zn_4(SePh)_6I_4]^{2-}$	I, I	I, I	0.00	0.00
$[Zn_4(SePh)_6I_3X]^{2-}$	I, I	I, X	−0.55	−0.52
	I, X	I, I	−6.20	−10.35
$[Zn_4(SePh)_6I_2X_2]^{2-}$	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
$[Zn_4(SePh)_6IX_3]^{2-}$	I, X	X, X	−7.52	−11.96
	X, X	I, X	−12.86	−20.74
$[Zn_4(SePh)_6X_4]^{2-}$	X, X	X, X	−13.66	−21.87

[a] $\Delta\delta_{Se} = \delta_{Se}(\text{obsd}) - \delta_{Se}([Zn_4(SePh)_6I_4]^{2-})$; 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 Br_4 and I_4 parents as Et_4N^+ salts; some Br-rich solutions were saturated. [e] At 298 K in equilibrium mixtures prepared from 0.035 M solutions of the I_4 and Cl_4 parents as Me_4N^+ and Et_4N^+ salts, respectively. [f] Estimated error ±0.15 ppm.

$$(x + 1)[Zn_4(SePh)_6Cl_4]^{2-} \rightleftharpoons x[Zn_4(SePh)_7Cl_3]^{2-} + [Zn_4(SePh)_{6-x}Cl_{4+x}]^{2-} \qquad (2)$$

Noteworthy in Table I are the large differences in linewidth between the resonances of **1** and those of the $[Zn_4(SePh)_6X_4]^{2-}$ ions. Presumably t ⇄ br interchange of PhSe moieties is still occurring slowly in **1**; i.e., the ^{77}Se 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 proposed[4] for t ⇄ br exchange in $[M_4(SPh)_{10}]^{2-}$ can occur in **1** also. A similar mechanism involving a short-lived halogen-bridged isomeric species could produce br ⇄ br exchange in $[Zn_4(SePh)_6X_4]^{2-}$. Such a process would not produce detectable broadening of the ^{77}Se 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 ⇄ br interchange is not facile. As shown below, the complexes $[(\mu\text{-}SePh)_{6-x}(\mu\text{-}ER)_x(ZnI)_4]^{2-}$ (ER = SPh or SeMe) have chalcogenate cores that are static on the ^{77}Se NMR time scale at ambient probe temperature.

For all further experiments except redistribution of $[Zn_4(SPh)_6I_4]^{2-}$ and $[Zn_4(SePh)_6I_4]^{2-}$, the $[Zn_4(SePh)_6X_4]^{2-}$ ions were prepared and used in situ. Test experiments showed that Ph_2Se_2, the other product of reaction 1, produced no complications.

$[(\mu\text{-}SePh)_6(ZnX)_{4-x}(ZnX')_x]^{2-}$ (X = I, X′ = Br; X = I, X′ = Cl). Clear evidence for the formation of species with mixed terminal halogens is found when solutions of $[(\mu\text{-}SePh)_6(ZnX)_4]^{2-}$ and $[(\mu\text{-}SePh)_6(ZnX'_4)]^{2-}$ 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 $[(\mu\text{-}SePh)_6(ZnI)_3(ZnBr)]^{2-}$. With time-averaged symmetry of C_3 or higher, there are two equally probable environments for a bridging ^{77}Se 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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[16] Dean, P. A. W.; Payne, N. C.; Vittal, J. J., to be submitted for publication.

[17] At present we have been unable to completely characterize species more halogen-rich than $[(\mu\text{-}SePh)_6(ZnX)_4]^{2-}$.

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Table III. Selenium-77 NMR Chemical Shifts[a] of $(Et_4N)_2[(\mu\text{-}SePh)_6(ZnSePh)_{4-x}(ZnX)_x]$

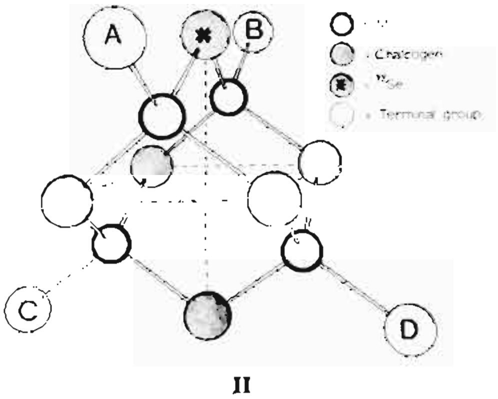
	adjacent terminal	nonadjacent terminal	$\delta_{Se}(PhSe_{br})$			$\delta_{Se}(PhSe_t)$		
x	groups[b]	groups[c]	X = Cl[d]	X = Br[e-g]	X = I[e,h,i]	X = Cl[d]	X = Br[e-g]	X = I[e,h,i]
0	PhSe, PhSe	PhSe, PhSe	−9.1	−6.8	−7.4	38.3	47.1	46.0
1	PhSe, PhSe	X, PhSe	−10.6	∼−6.2[j]	∼−8.4			
						36.2	44.8	44.5
	X, PhSe	PhSe, PhSe	−11.5	∼−8.0[j]	−0.9			
2	PhSe, PhSe	X, X	∼−11.8	∼−5.5[j]	∼−9.5			
	X, PhSe	X, PhSe	−13.7	∼−7.8	−2.0	34.1	42.4	42.4
	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
	X, X	X, PhSe	−17.4	∼−10.2[j]	3.7			
4	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 $[Zn_4(SePh)_{10}]^{2-}$. [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 $[Zn_4(SePh)_{10}]^{2-}$ 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 $[Zn_4(SePh)_{10}]^{2-}$. [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, $\Delta\delta_{Se}$,[a] of $(Me_4N)_2[(\mu\text{-}SePh)_{6-x}(\mu\text{-}SPh)_x(ZnI)_4]$ in MeCN at 297 K[b]

chalcogenate core	$\Delta\delta_{Se}$[a]	chalcogenate core	$\Delta\delta_{Se}$[a]
$(SePh)_6$	0.0	*abc*-$(SePh)_3(SPh)_3$	−3.9
abcde-$(SePh)_5(SPh)$	−0.1 (*a*-Se) −2.0 (*bcde*-Se)	*af*-$(SePh)_2(SPh)_4$	−9.1
		ab-$(SePh)_2(SPh)_4$	−6.1
abdf-$(SePh)_4(SPh)_2$	−4.3	$(SePh)(SPh)_5$	−8.5
abcd-$(SePh)_4(SPh)_2$	*c*		
abf-$(SePh)_3(SPh)_3$	−3.9 (*b*-Se) −6.7 (*af*-Se)		

[a] $\Delta\delta_{Se} = \delta_{Se}(\text{obsd}) - \delta_{Se}([Zn_4(SePh)_6I_4]^{2-})$; 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 $[(\mu\text{-}SePh)_6(ZnI)_2(ZnBr)_2]^{2-}$, 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 $^{77}SePh$ 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 $[(\mu\text{-}SePh)_x(\mu\text{-}SeMe)_{6-x}(ZnI)_4]^{2-}$ [b] in Acetone at 296 K[c]

no. of dissimilar cis substituents[c]	δ_{SePh} ($\Delta\delta_{SePh}$[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 $[Zn_4(SePh)_6I_4]^{2-}$ (itself produced in situ from $[Zn_4(SePh)_{10}]^{2-}$ and I_2) with Me_2Se_2. [c] For discussion of these spectra, see text. [d] $\Delta\delta_{SePh} = \delta_{SePh}(\text{obsd}) - \delta_{Se}([Zn_4(SePh)_6I_4]^{2-})$. [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, $[(\mu\text{-}SePh)_6(ZnI)(ZnBr)_3]^{2-}$, 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 $[(\mu\text{-}SePh)_6(ZnI)_{4-x}(ZnBr)_x]^{2-}$ 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 considerations[19] 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.

$[(\mu\text{-}SePh)_6(ZnSePh)_{4-x}(ZnX)_x]^{2-}$ (X = Cl, Br, I). As noted above, oxidative halogen substitution of **1** gives the fully terminally halogen substituted clusters $[(\mu\text{-}SePh)_6(ZnX)_4]^{2-}$ when $X_2/\mathbf{1}$ = 2. At lower $X_2/\mathbf{1}$ ratios (or in **1**–$[Zn_4(SePh)_6X_4]^{2-}$ mixtures), the ^{77}Se NMR spectra of individual partially halogen-substituted ions $[(\mu\text{-}SePh)_6(ZnSePh)_{4-x}(ZnX)_x]^{2-}$ 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.

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(19) Calingaert, G.; Beatty, H. A. *J. Am. Chem. Soc.* **1939**, *61*, 2748.

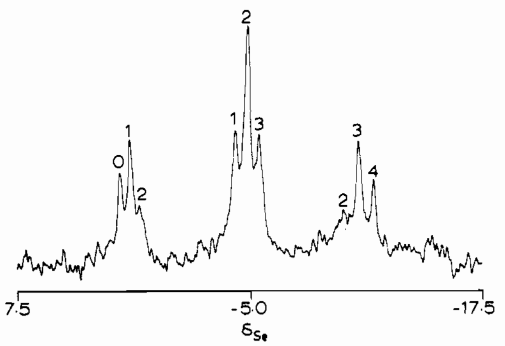

Figure 1. Proton-decoupled ^{77}Se NMR spectrum, at 295 K and 38.15 MHz, of a 1:1 mixture in MeCN of $[(\mu\text{-SePh})_6(ZnBr)_4]^{2-}$ and $[(\mu\text{-SePh})_6(ZnI)_4]^{2-}$ (both prepared in situ as Et_4N^+ salts, with $[Zn_4]_{total}$ = 0.05 M), showing the formation of $[(\mu\text{-SePh})_6(ZnI)_{4-x}(ZnBr)_x]^{2-}$. 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.

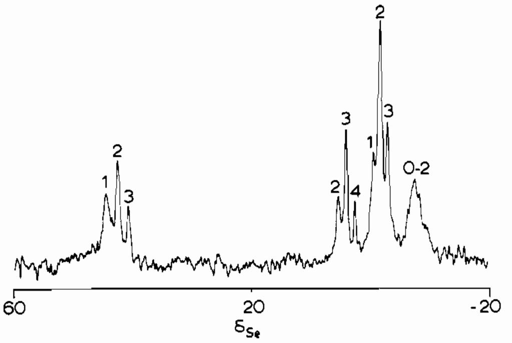

Figure 2. Proton-decoupled ^{77}Se NMR spectrum, at 297 K and 38.15 MHz, of the equilibrium mixture produced from a 1:1 mixture of $(Et_4N)_2[(\mu\text{-SePh})_6(ZnSePh)_4]^{2-}$ (0.05 M) and I_2 in acetone, showing the formation of $[(\mu\text{-SePh})_6(ZnSePh)_{4-x}(ZnI)_x]^{2-}$. The correlation of 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 I_2 (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 ^{77}Se 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 $[(\mu\text{-SePh})_6(ZnX)_{4-x}(ZnX')_x]^{2-}$ (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 $[(\mu\text{-SePh})_6(ZnSePh)_{4-x}(ZnI)_x]^{2-}$ 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 $PhSe_t \rightleftarrows PhSe_{br}$ exchange that appears to occur in this environment (see above).

The data in Table III show that the ^{77}Se 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 $[Zn_4(SePh)_8I_2]^{2-}$ (Figure 2) it is evident that the terminal SePh and I groups in the series $[(\mu\text{-SePh})_6(ZnSePh)_{4-x}(ZnI)_x]^{2-}$ are distributed close to randomly.[19]

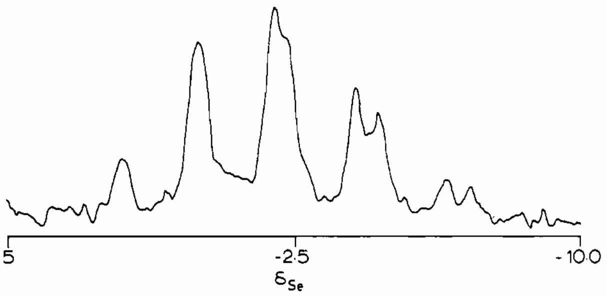

Figure 3. Proton-decoupled ^{77}Se NMR spectrum, at 296 K and 38.15 MHz, of a 1:1 mixture in MeCN of $[(\mu\text{-SePh})_6(ZnI)_4]^{2-}$ and $[(\mu\text{-SPh})_6(ZnI)_4]^{2-}$ (both as Ph_2E_2-free Et_4N^+ salts, with $[Zn_4]_{total}$ = 0.05 M), showing the formation of $[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(ZnI)_4]^{2-}$. 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.

The system $PhICl_2$–**1** (or **2a**–**1**) produces complexes with chlorine in the terminal positions. These behave chemically and ^{77}Se 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 ^{77}Se 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 ^{77}Se 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 Br_2–**1** (or **2b**–**1**) provides evidence for complexes containing terminal bromine atoms. However, the ^{77}Se 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 $[(\mu\text{-SePh})_6(ZnSePh)_{4-x}(ZnBr)_x]^{2-}$ (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 $Br_2/\mathbf{1}$ 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 $\delta_{Se}(PhSe_{br})$, 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.

$[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(ZnI)_4]^{2-}$. The idealized geometry of the chalcogenate core in **2** and the analogous sulfur complex is octahedral (see diagram II). We have used the ^{77}Se NMR spectra of the $PhSe_{br}$ groups as probes for substitution of PhS_{br} and (below) $MeSe_{br}$ into the octahedral Se_6 core of the representative complex **2c**, which was chosen for its high solubility.

On stepwise addition of Ph_2S_2-free[20] $[Zn_4(SPh)_6I_4]^{2-}$ to Ph_2Se_2-free[20] **2c** in MeCN, redistribution occurs quickly (eq 3),

$$[(\mu\text{-SPh})_6(ZnI)_4]^{2-} + [(\mu\text{-SePh})_6(ZnI)_4]^{2-} \rightleftharpoons \underset{\text{equilibrium mixture}}{[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(ZnI)_4]^{2-}} \quad (3)$$

and a new series of ^{77}Se 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

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[20] Ph_2E_2 was removed to prevent stoichiometry complications caused by direct redox reaction of Ph_2E_2 and $[Zn_4(E'Ph)_6I_4]^{2-}$ (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 $\delta_{Se}(PhSe_{br})$ 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 $\Delta\delta_{Se}$ cannot be accommodated on the basis of simple first order additivity of cis- and trans-substituent effects.[21] However, introduction of a second-order term[22] allows a good fit of $\Delta\delta_{Se}$. Multiple regression analysis gives eq 4. In

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

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*-$[(\mu\text{-SePh})_5(\mu\text{-SPh})(ZnI)_4]^{2-}$ and *abf*-$[(\mu\text{-SePh})_3(\mu\text{-SPh})_3(ZnI)_4]^{2-}$ (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.

$[(\mu\text{-SePh})_{6-x}(\mu\text{-SeMe})_x(ZnI)_4]^{2-}$. Substitution of MeSe groups into the chalcogenate core of **2c** occurs rapidly according to eq 5. Reactions of $[Cd_4(SPh)_{10}]^{2-}$ with R_2S_2 (R = alkyl) are slow

$$[(\mu\text{-SePh})_6(ZnI)_4]^{2-} + Me_2Se_2 \xrightleftharpoons[\text{room temp}]{\text{acetone}} [(\mu\text{-SePh})_{6-x}(\mu\text{-SeMe})_x(ZnI)_4]^{2-} + \underset{\text{equilibrium mixture}}{Ph_2Se_2/PhSeSeMe} \qquad (5)$$

(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 Me_2Se_2/**2c** 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 $[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(ZnI)_4]^{2-}$ (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 Me_2Se_2/**2c**. 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*-SePh and *bcde*-$(SePh)_4$ in an *abcde*-$(PhSe)_5(MeSe)$ core. Comparison of δ_{Se}(*a*-SePh) and δ_{Se}(**2c**) 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 Me_2Se_2/**2c** is consistent with this interpretation. Thus the signal with δ_{Se} −0.9 can be attributed to a PhSe with one cis and one trans MeSe group, i.e. to *ac*-$(PhSe)_2$ of the *abcd*-$(PhSe)_4(MeSe)_2$ core. Similarly, the signal at δ_{Se} −9.6 is from PhSe with three cis MeSe groups and one trans, i.e. from *ab*-$(PhSe)_2$ in *ab*-$(PhSe)_2(MeSe)_4$. Also the signal at δ_{Se} −11.3 is from PhSe with three cis MeSe groups, i.e. from *af*-$(PhSe)_2$ in *abf*-$(PhSe)_3(MeSe)_3$. The unique signal at δ_{Se} −14.8 is not tied in intensity to the −9.6 ppm signal of the *ab*-$(PhSe)_2(MeSe)_4$ core and hence is due to the $(PhSe)(MeSe)_5$ core, rather than the *af*-$(PhSe)_2(MeSe)_4$ core. The rather broad and ill-resolved signal at δ_{Se} ∼−5.6 must contain the resonances of *bd*-$(PhSe)_2$ in the *abcd*-$(PhSe)_4(MeSe)_2$ core and *b*-PhSe of the *abf*-$(PhSe)_3(MeSe)_3$ core. The broadness of this signal suggests the presence of other components also. These could include the lines of the *abdf*-$(PhSe)_4(MeSe)_2$ and *abc*-$(PhSe)_3(MeSe)_3$ cores, both of which contain PhSe with two cis MeSe groups. The only species that appears to occur in undetectable concentration in the Me_2Se_2–**2c** mixtures is that with the *af*-$(PhSe)_2(MeSe)_4$ core.

Equilibrated mixtures of Me_2Se_2 and **2c** in acetone show ^{77}Se NMR signals from the two parent diselenides ($\delta_{Se}(Me_2Se_2) = 261$; $\delta_{Se}(Ph_2Se_2) = 459$) as well as the unsymmetrical diselenide (δ_{Se}(Me*Se*SePh) = 289; δ_{Se}(MeSe*Se*Ph) = 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 value[19] of 4.

$$Ph_2Se_2 + Me_2Se_2 \rightleftharpoons 2PhSeSeMe \qquad (6)$$

$[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(ZnSePh)_{4-y}(ZnSPh)_y]^{2-}$. 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**/$[Zn_4(SPh)_{10}]^{2-}$ = $^3/_2$ and $[Zn_4]_{total}$ = 0.05 M, these resonances are centered at $\delta_{Se} \approx$ 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 $PhSe_{br}/PhSe_t$ $\approx$ 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**/$[Zn_4(SPh)_{10}]^{2-}$ ratios, e.g. $PhSe_{br}/PhSe_t \approx 1.1$ 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 $[Zn_4(SePh)_{10-x}(SPh)_x]^{2-}$ 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 $\delta_{Se} \approx -19.4$ in the region due to $PhSe_{br}$. However, in the $PhSe_t$ region four major resonances are found, approximately evenly spaced with $\delta_{Se} \approx$ 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 $PhSe_{br}/PhS_{br}$ $\approx$ 1.2. Most likely $\delta_{Se}(PhSe_t)$ 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 statistical[19] populations of the combinations $(PhSe_{br})_3$, $(PhSe_{br})_2(PhS_{br})$, $(PhSe_{br})(PhS_{br})_2$, and $(PhS_{br})_3$. The least shielded signal, with $\delta_{Se} \approx 38.7$, has a chemical shift close to that of **1** in which the geminal groups are $(PhSe_{br})_3$. Thus increase in the number of geminal PhS_{br} groups causes an increase in $\delta_{Se}(PhSe_t)$.

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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[21] Dean, P. A. W.; Evans, D. F. *J. Chem. Soc. A* **1968**, 1154.

[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.

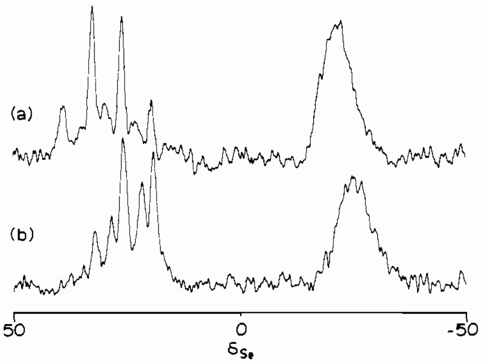

Figure 4. Proton-decoupled ^{77}Se NMR spectrum, at 261 K and 38.15 MHz of acetone solutions containing $(Et_4N)_2[Zn_4(SePh)_{10}]$ and $(Et_4N)_2[Zn_4(SPh)_{10}]$ with $[Zn_4]_{total}$ = 0.05 M, showing the formation of $[Zn_4(SePh)_{10-x}(SPh)_x]^{2-}$. The ratio $[Zn_4(SePh)_{10}]^{2-}/[Zn_4(SPh)_{10}]^{2-}$ = $^3/_2$ 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 $\delta_{Se}(PhSe_t)$. 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 $[Zn(SePh)_{4-x}(SPh)_x]^{2-}$ (see below). Nevertheless, in some cases it does seem that the nature and/or position of the nongeminal chalcogen atoms affects $\delta_{Se}(PhSe_t)$. In the spectrum of the $^3/_2$ mixture, and more noticeably the $^2/_3$ mixture, there are other minor resonances in the $PhSe_t$ region: at $\delta_{Se} \approx$ 28.4 (apparently linked in intensity with the signal having $\delta_{Se} \approx$ 25.8) and $\delta_{Se} \approx$ 21.6 (apparently linked in intensity with the resonance having $\delta_{Se} \approx$ 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).

$$[(\mu\text{-SePh})_6(ZnSePh)_4]^{2-} + [(\mu\text{-SPh})_6(ZnSPh)_4]^{2-} \rightleftharpoons [(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(ZnSePh)_{4-y}(ZnSPh)_y]^{2-} \quad (7)$$

equilibrium mixture

$[Zn(SePh)_{4-x}(SPh)_x]^{2-}$. For comparison with the results obtained for **1**–$[Zn_4(SPh)_{10}]^{2-}$ mixtures, we have measured the ^{77}Se NMR spectra of the mononuclear analogues $[Zn(SePh)_{4-x}(SPh)_x]^{2-}$. These are formed in mixtures of the metal nitrate with excess $PhSe^-/PhS^-$ in MeOH, like their Cd(II) analogues.[24]

A methanolic solution in which $[Zn^{2+}]_{total}$ = 0.10 M and $[PhSe^-]_{total}$ = 1.2 M gives a single broad ^{77}Se NMR line at ambient probe temperature. On cooling, separate signals from $[Zn(SePh)_4]^{2-}$ 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 $Zn^{2+}/PhSe^-/PhS^-$ = 1/10/2 and $[Zn^{2+}]_{total}$ = 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 $Zn^{2+}/PhSe^-/PhS^-$ = 1/2/10 shows the resonance of $[Zn(SePh)_4]^{2-}$ and two new signals shielded from this by 5.0 ± 0.5 and 8.3 ± 0.5 ppm, which can be assigned to $[Zn(SePh)_3(SPh)]^{2-}$ and $[Zn(SePh)_2(SPh)_2]^{2-}$, respectively. The solubility of $[Zn(SePh)(SPh)_3]^{2-}$ 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 $\delta_{Se}(PhSe_t)$ of the proposed geminal substitution of PhS_{br} for $PhSe_{br}$ in $[(\mu\text{-SePh})_{6-x}(\mu\text{-SPh})_x(ZnSePh)_{4-y}(ZnSPh)_y]^{2-}$ (see above). This supports our contention that changes in geminal groups dominate $\delta_{Se}(PhSe_t)$ in the Zn_4 clusters. However, the changes in δ_{Se} are not additive in $[Zn(SePh)_{4-x}(SPh)_x]^{2-}$ as they appear to be for the clusters.

$[(\mu\text{-SePh})_6(ZnI)_{4-x}(CdI)_x]^{2-}$. The ^{77}Se NMR spectra of mixtures of **2c** and its cadmium analogue were measured by using MeCN solutions in which $[M_4]_{total}$ = 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 δ_{Se} 2.2, then a second signal grows having δ_{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 $[(\mu\text{-SePh})_6(ZnI)_3(CdI)]^{2-}$. The most shielded region, at δ_{Se} ~ –50.6 (with $\Delta\nu_{1/2} \approx$ 170 when Cd/Zn = 3) is close to that found[9] for $[(\mu\text{-SePh})_6(CdI)_4]^{2-}$ 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. δ_{Se} ~ –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**–$[Cd_4(SePh)_6I_4]^{2-}$ mixtures is close to random.[19]

$$[(\mu\text{-SePh})_6(ZnI)_4]^{2-} + [(\mu\text{-SePh})_6(CdI)_4]^{2-} \rightleftharpoons [(\mu\text{-SePh})_6(ZnI)_{4-x}(CdI)_x]^{2-} \quad (8)$$

equilibrium mixture

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 δ_{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**–$[(\mu\text{-SePh})_6(CdI)_4]^{2-}$ 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 (δ_{Cd} = 461, $\Delta\nu_{1/2} \approx$ 110 Hz). In $[(\mu\text{-SPh})_6(ZnSPh)_{4-x}(CdSPh)_x]^{2-}$ 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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[24] Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 37.