oxidative current did not decay to the background level after 1 coulomb equiv needed for the complete oxidation of a one-electron process had been passed. The UV–vis spectral changes during the constant-potential electrolysis experiment are shown in Figure 7. Nice isosbestic points were maintained throughout the electrolysis reaction. The 306-nm band (p_π(Cl) → d_π(Os(III))) gradually disappeared, and a new band at 365 nm developed. This 365-nm species would be immediately reconverted to the starting species *trans*-[Os^{III}(16-TMC)Cl$_2$]$^+$ upon addition of ascorbic acid (over 95% yield), indicating that it does not come from the degradative side reactions. We attributed the 365-nm band to be the p_π(Cl) → d_π(Os(IV)) LMCT transition of *trans*-[Os^{IV}(16-TMC)Cl$_2$]$^{2+}$; similar findings for *trans*-[Os^{IV}(NH$_3$)$_4$Cl$_2$]$^{2+}$ (λ_{max} ~ 357 nm) have previously been reported.[19] The observed blue shift in the p_π(Cl) → d_π(M) transition from Ru(IV) (λ_{max} for *trans*-[Ru^{IV}(16-TMC)Cl$_2$]$^{2+}$ is ~410 nm)[15] to Os(IV) is in parallel with the corresponding decrease in the formal potential of the M(IV)/M(III) couple. The differences in the $E_{1/2}$ values between Ru and Os are 430 and 830 mV for the *trans*-[M(16-TMC)Cl$_2$]$^{2+/+}$ and *trans*-[M(16-TMC)Cl$_2$]$^{+/0}$ couples, respectively. The results suggest that the effect of replacing the metal (Ru with Os) on the reduction potential of the metal complex is more prominent in the trivalent [M(III)] than the tetravalent [M(IV)] state.

The electrochemistry of *trans*-[Os^{III}(16-TMC)Cl$_2$]$^+$ has also been studied in an aqueous medium. In 0.1 M HCl, the Os(IV)/Os(III) couple is fully reversible ($E_{1/2}$ = 0.81 V vs. NHE) with ΔE_p = 60–70 mV and i_{pc}/i_{pa} = 1. At pH 7, the electrochemical oxidation is less reversible but the Os(IV)/Os(III) couple still exists with i_{pc}/i_{pa} = 0.73 at a scan rate of 50 mV s^{-1}. The finding is different from Taube's work[19] where the electrochemical oxidation of *trans*-[Os^{III}(NH$_3$)$_4$Cl$_2$]$^+$ to *trans*-[Os^{IV}(NH$_3$)$_4$Cl$_2$]$^{2+}$ is completely irreversible at pH 7.6. The instability of *trans*-[Os^{IV}(NH$_3$)$_4$Cl$_2$]$^{2+}$ has been attributed to the oxidative deprotonation reaction of Os–NH$_3$ in a high-pH medium. *The usefulness of saturated macrocyclic tertiary amines in the stabilization of highly oxidizing transition-metal complexes is once again illustrated here.* The possibility of developing stable but strongly oxidizing osmium complexes for uses in oxidative reactions is under active investigation in our laboratories.

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a listing of calculated and observed structure factors (5 pages).

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Syntheses of (Me$_4$N)$_2$[(μ-EPh)$_6$(MX)$_4$] (M = Cd, Zn; E = S, Se; X = Cl, Br, I). Crystal and Molecular Structures of (Me$_4$N)$_2$[(μ-EPh)$_6$(CdBr)$_4$] (E = S, Se) and Characterization of [(μ-EPh)$_6$(CdX)$_4$]$^{2-}$ in Solution by ^{113}Cd and ^{77}Se NMR

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The direct, quantitative reaction of the adamantanoid anions [(μ-EPh)$_6$(MEPh)$_4$]$^{2-}$ (M = Cd, Zn; E = S, Se) with X$_2$ (X = Cl, Br, I) in acetone or MeCN or, for X = Cl, PhICl$_2$ in MeCN, provides a simple route to the new complexes [M$_4$(EPh)$_6$X$_4$]$^{2-}$ isolated as Me$_4$N$^+$ salts in high yield. The structurally representative salts (Me$_4$N)$_2$[Cd$_4$(EPh)$_6$Br$_4$] (E = S, Se) have been fully characterized by single-crystal X-ray diffractometry techniques. Both crystallize in the cubic space group $P2_13$ with four formula units in the cell. The dimensions are a = 17.869 (2) Å for (Me$_4$N)$_2$[Cd$_4$(SPh)$_6$Br$_4$] (**1**) and a = 18.062 (2) Å for (Me$_4$N)$_2$[Cd$_4$(SePh)$_6$Br$_4$] (**2**). The structures have been refined by full-matrix least-squares techniques on F to agreement factors R = 0.033 (1343 observations with $F_o > 5\sigma(F_o)$) for **1** and R = 0.033 (989 observations with $F_o > 5\sigma(F_o)$) for **2**. In each salt, both cations and anions lie on a crystallographic threefold axis. In the chiral [(μ-EPh)$_6$(CdBr)$_4$] anions in **1** and **2**, the Cd$_4$E$_6$Br$_4$ core consists of a Cd$_4$ tetrahedron, regular within experimental error, inscribed in a slightly irregular octahedron defined by the bridging E atoms in an adamantanoid cage. Each Cd atom is tetrahedrally coordinated by one terminal Br and three bridging E atoms. The average Cd···Cd distance is 4.166 (3) for **1** and 4.251 (6) Å for **2**, the Cd–Br distances are 2.559 (3) and 2.565 (2) Å for **1** and 2.568 (4) and 2.581 (2) Å for **2**, the Cd–S distances are in the range 2.541 (3)–2.554 (3) Å for **1**, and the Cd–Se distances are in the range 2.627 (2)–2.654 (2) Å for **2**. The anions in **1** and **2** represent the first examples containing the M$_4$(μ-EPh)$_6$ core in which the axial/equatorial dispositions of the EPh groups in the tetracyclic structure are aaa,aee,aee,aee. The absolute structures of **1** and **2** have been determined by measurement of Bijvoet pairs. NMR (^{113}Cd, ^{77}Se) studies of [Cd$_4$(EPh)$_6$X$_4$]$^{2-}$ show the persistence of fully terminally halogen substituted tetranuclear structures in solution. At reduced temperatures, exchange of both chalcogenates and halogens between clusters is slow on the NMR time scale. In addition, a slow-exchange ^{77}Se NMR spectrum has been observed for [(μ-SePh)$_6$(CdSePh)$_4$]$^{2-}$.

Introduction

Recent advances in the chemistry of metalloproteins have stimulated interest in the fundamental coordination chemistry of simple metal thiolate complexes.[1–6] Frequently encountered among such complexes is the adamantane-like cage structure, with a tetrahedrally disposed set of metal atoms and an octahedrally disposed core of bridging sulfur atoms giving overall (idealized) T_d symmetry. This structural type has been established for the thiolate complexes [(μ-SR)$_6$Cu$_4$]$^{2-}$ (R = Me, Ph)[2] and [(μ-SPh)$_6$(MSPh)$_4$]$^{2-}$ (M = Mn(II),[3] Fe(II),[4] Co(II),[5] Cd(II),[6] Zn-

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(II),[7]), as well as for the related selenolate complexes $[(\mu\text{-SePh})_6(\text{MSePh})_4]^{2-}$ (M = Cd(II), Zn(II)).[8] The M_4E_6 (E = S, Se) cage being stable, selective substitution of the terminal thiolate or selenolate ligands appears feasible, giving rise to an interesting class of heteroligated clusters. Earlier, Coucouvanis et al.[9] built up the fully terminally halogen substituted adamantanoid clusters $[(\mu\text{-SPh})_6(\text{FeX})_4]^{2-}$ (X = Cl, Br) from $FeCl_2$, Ph_4PCl, and KSPh in a 2:1:3 ratio, or from $Fe(SPh)_4{}^{2-}$ and FeX_2 (X = Cl, Br) in a 1:2.4 ratio, in acetonitrile. Attempts to prepare the corresponding halogen-substituted zinc and cobalt clusters in a similar manner resulted only in the doubly terminally substituted products.[5,10]

In this paper we report the direct syntheses of $[M_4(EPh)_6X_4]^{2-}$ (M = Cd(II), Zn(II); X = Cl, Br, I), starting from $[M_4(EPh)_{10}]^{2-}$. The crystal and molecular structures of the representative compounds $(Me_4N)_2[(\mu\text{-EPh})_6(CdBr)_4]$ (E = S, Se) have been determined. In addition, details of the ^{113}Cd and (where appropriate) ^{77}Se NMR spectra of the Cd_4 clusters in solution are given; these extend our earlier communication.[11]

Experimental Section

Materials and General Procedures. All the chemicals were of reagent grade and were used without further purification. Cadmium metal enriched in ^{113}Cd (~90%) was from Technabsexport, Moscow, U.S.S.R., and was converted into $^{113}Cd(NO_3)_2\cdot 4H_2O$ for subsequent use. $PhICl_2$ was prepared by the literature method,[12] and freshly prepared samples were used for all chlorination reactions. Literature syntheses were used for $(Me_4N)_2[M_4(SPh)_{10}]$ (M = Zn and natural Cd)[13] and $(Me_4N)_2[Cd_4(SePh)_{10}]$,[14] together with the corresponding ^{113}Cd-enriched compounds.[13,14] All the syntheses were carried out by using solvents that had been dried over 3A molecular sieves and thoroughly deoxygenated with argon. NMR samples were also prepared by using deoxygenated solvents under argon. The syntheses and halogenation reactions were performed under an inert atmosphere. However, the air sensitivity of the compounds described here does not seem to be high. Carbon, hydrogen, and nitrogen microanalyses were performed by Guelph Chemical Laboratories Ltd.

Synthesis of $(Me_4N)_2[Zn_4(SePh)_{10}]$. A 1.45-g portion (9.2 mmol) of benzeneselenol was added to 0.22 g (9.6 mmol) of sodium metal dissolved in 100 mL of methanol. The resultant solution of NaSePh was added to a stirred solution of 1.06 g (3.4 mmol) of $Zn(NO_3)_2\cdot 6H_2O$ in 10 mL of water, producing a yellow solution containing some light yellow precipitate. After the mixture was stirred for about 10 min, a solution of 0.38 g (3.5 mmol) of Me_4NCl in 10 mL of methanol was added. The mixture was warmed to 60 °C, and acetonitrile was added until a clear solution was obtained, which was filtered while hot and left at 5 °C overnight for crystallization to occur. Pale yellow transparent crystals formed; these were separated by decantation of the mother liquor, washed with 10 mL of methanol and, in succession, 20-mL portions of water, methanol, and diethyl ether, and then dried under vacuum. A second crop of crystals was obtained by concentrating the mother liquor; total yield 1.6 g (90%). Anal. Calcd for $C_{68}H_{74}N_2Se_{10}Zn_4$: C, 41.45; H, 3.79; N, 1.42. Found: C, 41.38; H, 3.40; 1.50. ^{13}C NMR (CD_3CN): δ_C 56.0 (Me_4N^+), 125.7 (C_4), 128.6 ($C_{3,5}$), 136.4 ($C_{2,6}$), 130.2 (C_1, bridging), 132.1 (C_1, terminal).

Chlorination Reactions. A typical chlorination reaction is described here for the preparation of $(Me_4N)_2[Cd_4(SPh)_6Cl_4]$. The procedure is similar for the selenium analogue and the two tetrachloro derivatives of zinc with appropriate changes in starting materials. The Cd compounds are less soluble in MeCN than their Zn analogues. Also, the solubility is lower in acetone than in MeCN for both Zn and Cd clusters. In general the solubility of the tetrahalo anions as their Me_4N^+ salts is in the order Cl ≪ Br < I in both MeCN and acetone.

Synthesis of $(Me_4N)_2[Cd_4(SPh)_6Cl_4]$. Freshly prepared solid $PhICl_2$ (0.165 g, 0.60 mmol) was added with stirring to a solution of $(Me_4N)_2[Cd_4(SPh)_{10}]$ (0.507 g, 0.30 mmol) in 15 mL of MeCN. Rapid reaction occurred with the formation of a precipitate. After 10 min the solvent was removed under vacuum. The residue was extracted three times with 20-mL portions of diethyl ether to remove PhSSPh and PhI. The crude residue was purified by recrystallization from a mixture of acetonitrile and diethyl ether; isolated yield 0.28 g (67%). The compound is soluble in MeCN but sparingly soluble in acetone. Anal. Calcd for $C_{44}H_{54}Cl_4Cd_4N_2S_6$: C, 37.89; H, 3.90; N, 2.01. Found: C, 38.45, and 38.34; H 4.14, 3.97; N, 2.05, 2.06. ^{13}C NMR (CD_3CN): δ_C 56.1 (Me_4N^+), 125.6 (C_4), 129.1 ($C_{3,5}$), 133.9 ($C_{2,6}$), 136.0 (C_1).

Synthesis of $(Me_4N)_2[Cd_4(SePh)_6Cl_4]$: isolated yield 76%. Anal. Calcd for $C_{44}H_{54}Cl_4Cd_4N_2Se_6$: C, 31.53; H, 3.25; N, 1.67. Found: C, 31.14, 31.06; H, 3.15, 3.06; N, 1.23, 1.38. ^{13}C NMR (CD_3CN): δ_C 56.1 (Me_4N^+), 126.1 (C_4), 129.3 ($C_{3,5}$), 135.9 ($C_{2,6}$), 136.6 (C_1).

Synthesis of $(Me_4N)_2[Zn_4(SPh)_6Cl_4]$: isolated yield 89%. Anal. Calcd for $C_{44}H_{54}Cl_4N_2S_6Zn_4$: C, 43.80; H, 4.51; N, 2.32. Found: C, 43.68; H, 4.71; N, 2.24. ^{13}C NMR (CD_3CN): δ_C 56.1 (Me_4N^+), 126.1 (C_4), 128.9 ($C_{3,5}$), 134.5 ($C_{2,6}$), 134.7 (C_1).

Synthesis of $(Me_4N)_2[Zn_4(SePh)_6Cl_4]$: isolated yield 85%. Anal. Calcd for $C_{44}H_{54}Cl_4N_2Se_6Zn_4$: C, 35.52; H, 3.66; N, 1.88. Found: C, 35.65; H, 3.91; N, 1.78. ^{13}C NMR (CD_3CN): δ_C 56.1 (Me_4N^+), 126.5 (C_4), 129.2 ($C_{3,5}$), 135.9 ($C_{2,6}$), 136.1 (C_1).

The chlorination reactions were tried with Cl_2 gas also. Chloro complexes were formed as evidenced by chemical analysis and ^{113}Cd NMR (Cd complexes) and ^{77}Se NMR (Zn complexes), at reduced and ambient probe temperatures, respectively.

Bromination Reactions. A typical bromination reaction is described for the preparation of $(Me_4N)_2[Cd_4(SPh)_6Br_4]$. The same procedure was used to synthesize other bromo derivatives with appropriate changes in starting materials.

Synthesis of $(Me_4N)_2[Cd_4(SPh)_6Br_4]$. Br_2 (0.184 g, 1.15 mmol) in 5 mL of CCl_4 was added to a stirred solution containing $(Me_4N)_2[Cd_4(SPh)_{10}]$ (0.972 g, 0.575 mmol) in 15 mL of acetone. Decolorization occurred quickly, leaving a clear solution with a small amount of white solid. After 10 min, the solvents were removed under vacuum. The residue was extracted with three 40-mL portions of diethyl ether to remove PhSSPh. The residue was purified by recrystallization from a mixture of acetone and cyclohexane; isolated yield 0.81 g (90%). Anal. Calcd for $C_{44}H_{54}Br_4Cd_4N_2S_6$: C, 33.61; N, 3.46; N, 1.78. Found: C, 33.36; H, 3.48; N, 1.77. ^{13}C NMR ($(CD_3)_2CO$): δ_C 55.9 (Me_4N^+), 125.3 (C_4), 128.8 ($C_{3,5}$), 135.3 ($C_{2,6}$), 134.3 (C_1).

Synthesis of $(Me_4N)_2[Cd_4(SePh)_6Br_4]$: isolated yield 87%. Anal. Calcd for $C_{44}H_{54}Br_4Cd_4N_2Se_6$: C, 28.51; H, 2.94; N, 1.51. Found: C, 28.36; H, 2.66; N, 1.82. ^{13}C NMR ($(CD_3)_2CO$): δ_C 56.1 (Me_4N^+), 125.4 (C_4), 129.3 ($C_{3,5}$), 135.9 ($C_{2,6}$), 136.0 (C_1).

Synthesis of $(Me_4N)_2[Zn_4(SPh)_6Br_4]$: isolated yield 89%. Anal. Calcd for $C_{44}H_{54}Br_4N_2S_6Zn_4$: C, 38.17; H, 3.93; N, 2.02. Found: C, 37.89; H, 4.00; N, 2.20. ^{13}C NMR (CD_3CN): δ_C 56.0 (Me_4N^+), 126.1 (C_4), 128.7 ($C_{3,5}$), 134.7 ($C_{2,6}$), 134.5 (C_1).

Synthesis of $(Me_4N)_2[Zn_4(SePh)_6Br_4]$: isolated yield 65%. Anal. Calcd for $C_{44}H_{54}Br_4N_2Se_6Zn_4$: C, 31.73; H, 3.27; N, 1.68. Found: C, 31.77; H, 3.57; N, 1.61. ^{13}C NMR (CD_3CN): δ_C 56.1 (Me_4N^+), 125.0 (C_4), 129.0 ($C_{3,5}$), 135.9 ($C_{2,6}$), 136.1 (C_1).

Iodination Reactions. A typical iodination reaction is described for the preparation of $(Me_4N)_2[Cd_4(SPh)_6I_4]$. The procedure is essentially identical for the other iodo derivatives described here with appropriate changes in starting materials.

Synthesis of $(Me_4N)_2[Cd_4(SPh)_6I_4]$. Solid iodine (0.31 g, 1.2 mmol) was added to a stirred solution of $(Me_4N)_2[Cd_4(SPh)_{10}]$ (1.0 g, 0.6 mmol) in 15 mL of acetone. Immediate decolorization occurred, leaving a clear solution. Acetone was removed under vacuum. The residue was extracted with three 25-mL portions of diethyl ether to remove PhSSPh. The remaining white solid was purified by recrystallization from acetone–cyclohexane; isolated yield 0.95 g (90%). Anal. Calcd for $C_{44}H_{54}Cd_4N_2I_4S_6$: C, 30.02; H, 3.09; N, 1.59. Found: C, 30.06; H, 3.14; N, 1.53. ^{13}C NMR ($((CD_3)_2)_2CO$): δ_C 55.9 (Me_4N^+), 125.3 (C_4), 128.7 ($C_{3,5}$), 134.8 ($C_{2,6}$), 135.7 (C_1).

Synthesis of $(Me_4N)_2[Cd_4(SePh)_6I_4]$: isolated yield 90%. Anal. Calcd for $C_{44}H_{54}Cd_4N_2I_4Se_6$: C, 25.88; H, 2.66; N, 1.37. Found: C, 26.13; H, 2.82; N, 1.40. ^{13}C NMR ($(CD_3)_2CO$): δ_C 55.9 (Me_4N^+), 126.0 (C_4), 129.0 ($C_{3,5}$), 136.3 ($C_{2,6}$), 137.1 (C_1).

Synthesis of $(Me_4N)_2[Zn_4(SPh)_6I_4]\cdot(CH_3)_2CO$: isolated yield 76%. Anal. Calcd for $C_{47}H_{60}N_2I_4OS_6Zn_4$: C, 34.59; H, 3.70; N, 1.72. Found: C, 34.97, 34.99; H, 3.88, 3.93; N, 1.71, 1.79. ^{13}C NMR (CD_3CN): δ_C 30.2 ($(\mathit{C}H_3)_2CO$), 55.9 (Me_4N^+), 126.2 (C_4), 128.6 ($C_{3,5}$), 135.3 ($C_{2,6}$), 134.3 (C_1), 207.0 ($Me_2\mathit{C}O$).

Synthesis of $(Me_4N)_2[Zn_4(SePh)_6I_4]$ (from MeCN–Et_2O): isolated yield 80%. Anal. Calcd for $C_{44}H_{54}N_2I_4Se_6Zn_4$: C, 28.51; H, 2.94; N, 1.51. Found: C, 28.89; H, 3.18; N, 1.40. ^{13}C NMR (CD_3CN): δ_C 55.9 (Me_4N^+), 126.0 (C_4), 128.0 ($C_{3,5}$), 135.0 ($C_{2,6}$), 136.0 (C_1).

Preparation of Samples for NMR. All samples for ^{113}Cd and ^{77}Se NMR were prepared in either acetone or acetonitrile solution in 10 mm o.d. NMR tubes. The concentrations used were in the approximate range 35–50 mM. Enrichment with ^{113}Cd was used in some experiments. In addition to the obvious advantage of shortening the time to acquire the

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Table I. Summary of X-ray Structure Determinations

	1	2
Crystal Data		
compd, fw	$C_{44}H_{54}Br_4Cd_4N_2S_6$, 1572.5	$C_{44}H_{54}Br_4Cd_4N_2Se_6$, 1853.9
cryst syst, space group	cubic, $P2_13$ (No. 198)	
systematic absences	*h*00, *h* odd; 0*k*0, *k* odd; 00*l*, *l* odd	
cell dimens, Å; temp, °C	17.869 (2); 23	18.062 (2); 23
cell vol, Å^3; *Z*	5706 (2); 4	5893 (2); 4
obsd and calcd density, g cm^{-3}	1.86 (2), 1.83	2.11 (2), 2.09
Experimental Details		
diffractometer, monochromator	Enraf-Nonius CAD4F, graphite	
radiation; wavelength, Å	Mo; $\lambda(K\alpha) = 0.71073$ (mean)	
cryst–detector dist, mm; takeoff angle, deg	205; 2.5	
aperture, mm, vert and horiz	4.0, 6.0 + 0.35 tan θ	
ctring reflecn; θ range, deg	19; $30.0 < 2\theta < 35.0$	
Data Collection		
approx cryst dimens, mm	0.40 × 0.40 × 0.36	0.28 × 0.14 × 0.12
cryst vol, mm^3; no. of faces	2.14×10^{-3}; 14	3.81×10^{-4}; 10
face indices	{011} with 101 replaced by 103, $\bar{1}\bar{1}\bar{1}$, and $11\bar{1}$	101, $\bar{1}0\bar{1}$, $10\bar{1}$, $\bar{1}01$, $1\bar{1}0$, $\bar{1}\bar{1}0$, $01\bar{1}$, $0\bar{1}1$, $0\bar{1}\bar{1}$, 132
ω-scan widths before and after collecn	0.11, 0.11	0.10, 0.11
scan mode; width, deg	ω–2θ; 0.7 + 0.35 tan θ	
index ranges; θ range, deg	$0 \le h \le 21$, $-21 \le k \le 0$, $0 \le l \le 21$; $0 \le \theta \le 25$	
scan speed, deg min^{-1}	2.8–0.9	3.3–1.0
max time/datum, s; total time, h	75; 148	
std reflecns	200, $0\bar{2}0$, 002, $1\bar{1}1$	200, $0\bar{2}0$, 002, $1\bar{1}4$
monitor frequency, min; variation, %	180; 0.0	180; 0.5
no. of data and stds collected	5529, 204	5700, 204
Data Processing		
cor	Lorentz, polarizn, and monochromator polarizn	
decay, abs cor	none, Gaussian	
abs coeff, cm^{-1}; grid size	44.83; 14 × 14 × 10	78.08; 14 × 10 × 12
max, min transmission	0.474, 0.258	0.548, 0.275
R(*F*) for av before and after collecn	0.044, 0.024	0.052, 0.035
no. of unique data signif	1851 > 0	1908 > 0
Structure Refinement		
no. of observns, variables	1343, 98	989, 94
final model R_1 and R_2	0.0326, 0.0349	0.0328, 0.0326
extinction param	0.00012 (3)	0.00007 (1)
top resid, e Å^{-3} (coord)	0.52 (0.437, 0.167, 0.311)	0.53 (0.478, 0.227, −0.447)
largest shift, param	0.1, *x* of C(16)I	0.04, *y* of C(16)T
inverted model R_1 and R_2	0.0477, 0.0517	0.0448, 0.0489

^{113}Cd NMR spectra, a high concentration of ^{113}Cd has the secondary advantages of simplifying the spectra by removal of ^{111}Cd–^{113}Cd coupling,[13] making ^{113}Cd–^{77}Se coupling easier to observe in ^{77}Se NMR spectra, and reducing line broadening of ^{113}Cd resonances caused by slight variation in probe temperature during spectral accumulation coupled with the appreciable temperature dependence of δ_{Cd} in many of these compounds.[13]

NMR Spectra. All of the ^{113}Cd and ^{77}Se NMR spectra were obtained as outlined previously,[13,15] with a Varian XL-200 NMR spectrometer system operating at 44.37 and 38.15 MHz for ^{113}Cd and ^{77}Se, respectively, without field/frequency lock (field drift ≪1 Hz/day). The spectra were referenced by sample interchange with 0.1 M $Cd(ClO_4)_2$(aq) and neat Me_2Se as primary references. No corrections for diamagnetic susceptibility were applied. To minimize thermal broadening, usually no proton decoupling was used in collecting ^{113}Cd NMR data while ^{77}Se NMR data were collected with 2-W continuous decoupling via the WALTZ-16 sequence. Carbon-13 NMR spectra were obtained at 75.43 MHz and ambient probe temperature with a Varian XL-300 spectrometer system.

X-ray Structure Determinations

Data Collection and Reduction. Colorless, air-stable crystals with equant habit of $(Me_4N)_2[Cd_4(SPh)_6Br_4]$ (**1**) and $(Me_4N)_2[Cd_4(SePh)_6Br_4]$ (**2**) were grown by diffusion of cyclohexane into acetone solutions at room temperature. A preliminary photographic examination showed Laue symmetry $m\bar{3}$, and a careful examination of the films showed that **1** and **2** were isomorphous and isostructural. The systematic absences observed uniquely determine the space group as $P2_13$.[16] Crystal densities were determined by neutral buoyancy in mixtures of 1,2-$C_2H_4Br_2$ and CCl_4, and with four formula units per cell, site symmetry 3 is imposed upon both cations and anions. Crystal data for **1** and **2** are given in Table I.

The structure determination of **1** was undertaken first. Cell constants and an orientation matrix were refined by using the angular settings for carefully centered, high-angle reflections.[17] ω scans of intense, low-angle reflections indicated a satisfactory crystal quality.[18] Intensity data were recorded at variable scan speeds so chosen as to optimize counting statistics within a maximum time per datum of 75 s. Background estimates were made by extending the scan by 25% on each side. Standard reflections were monitored regularly, and the final scan was made for all observations.[17] The data were processed by using the Enraf-Nonius Structure Determination Package, Version 3.0,[19] running on a PDP 11/23+ computer. Standard deviations were assigned on the basis of counting statistics, a starting value of 0.04 was chosen for *p*,[20] and an absorption correction was applied.[21] Since three equivalent forms had been collected, these were averaged. Agreement factors for averaging showed a marked improvement after the correction. The same procedure was followed for the selenolate structure **2**. A value of 0.04 was chosen for *p*. Full details for both studies are presented in Table I.

Solution and Refinement of the Structures. The structures were solved by Patterson and Fourier techniques and refined by full-matrix least-squares techniques on *F*.[19] With all non-hydrogen atoms included, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where F_o and F_c are the observed and calculated structure amplitudes and the weight *w* is defined

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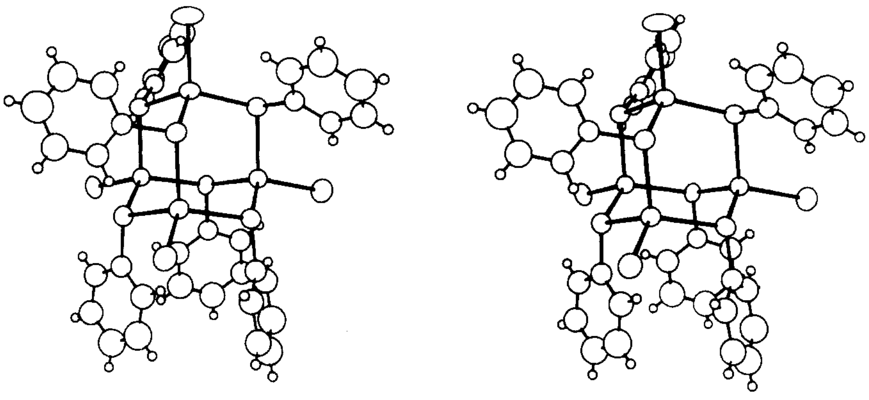

Figure 1. Stereoview of the $[(\mu\text{-SPh})_6(CdBr)_4]^{2-}$ cluster anion. Atoms are drawn as 50% probability thermal ellipsoids.

as $4F_o^2/\sigma^2(F_o^2)$; refinement of **1** converged at agreement factors $R_1 = \sum(||F_o| - |F_c||)/\sum(|F_o|) = 0.046$ and R_2 $(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.056$ and that of **2** with values of 0.041 and 0.049, respectively. Scattering factors for neutral, non-hydrogen atoms were taken from ref 16b, and real and imaginary dispersion corrections were included for all atoms.[16b] Difference Fourier syntheses showed clear evidence for all 10 H atoms on phenyl carbon atoms at peak heights ranging from 0.7 (1) to 0.4 (1) e Å^{-3} in **1** and 0.5 (1) to 0.3 (1) e Å^{-3} in **2**. All were included in idealized positions (C–H = 0.90 Å, sp^2 hybridization) with fixed isotropic thermal parameters. The scattering factor values were taken from Stewart et al.[22] With all non-hydrogen atoms assigned anisotropic thermal parameters, and hydrogen atom positions recalculated to maintain ideal geometries, refinement of 114 variables converged at $R_1 = 0.042$ and $R_2 = 0.053$, with a p factor of 0.05 and 1214 observations with $F_o > 3\sigma(F_o)$ for **1**, and $R_1 = 0.046$ and $R_2 = 0.048$, with a p factor of 0.05 and 1049 observations with $F_o > 2\sigma(F_o)$ for **2**.

Since $P2_13$ is a chiral space group, with polar axis [111], an η refinement[23] was performed to determine the absolute structure[24] of the crystals examined. The results were inconclusive, so the models were inverted and refined to agreement factors of $R_2 = 0.035$ and 0.033 for **1** and **2**, respectively. The inverted models were also free from polar dispersion error[25,26] and were therefore retained.

Large and physically unreasonable thermal parameters for the atoms in one cation in both structures provided evidence for disorder. After many trials, refinement was completed by using the SHELX-76 package,[27] imposing tetrahedral symmetry at the N atoms of the cations, and refining the N–C bond length as a free variable. For structure **1**, the final model consisted of a major component, (C(16), 60%), a second, related to the first by a twist of some 60° about [111] (C(16)T, 30%), and a third minor component, related to the first by an inversion at the N atom, (C(15)I and C(16)I, 10%). A simpler model sufficed for structure **2**, with no inverted component (major, C(16), 75%; minor, C(16)T, 25%). The 12 hydrogen atoms in each cation could not be found. By employment of data with $F_o > 5\sigma(F_o)$, refinement of an extinction parameter, imposition of rigid-group D_{6h} symmetry (C–C = 1.392 Å) upon the two phenyl rings, and inclusion of the 10 phenyl hydrogen atoms in idealized positions (C–H = 0.90 Å), refinement converged for both **1** and **2**. Details are given in Table I.

Total difference Fourier syntheses for both structures showed no peaks with any chemical significance. An analysis of variance showed no unusual trends. Inversion of the models and refinement to convergence confirmed that the choice of absolute structures was correct. This result was substantiated by recording Friedel pairs for selected reflections (Table SIII, supplementary material). There were no hemihedral facets to enable us to relate the absolute configurations determined for the anions to the crystal habit.[28,29]

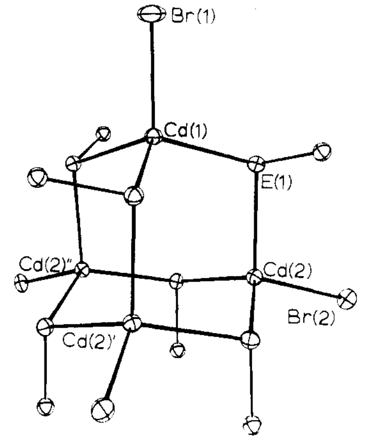

Figure 2. The $Cd_4E_6Br_4$ cage skeleton and the atom-numbering scheme.

Positional and U_{eq} thermal parameters are given for the refined atoms of both structures in Table II. Tables of hydrogen atom parameters, anisotropic thermal parameters, and structure amplitudes have been deposited.[30]

Results and Discussion

Syntheses of $(Me_4N)_2[(\mu\text{-EPh})_6(MX)_4]$ Clusters (M = Cd, Zn; E = S, Se; X = Cl, Br, I). The tetrahalo anions $[(\mu\text{-EPh})_6(CdX)_4]^{2-}$ are simply prepared as their Me_4N^+ salts by the quantitative oxidative substitution reactions of $Cd_4(EPh)_{10}]^{2-}$ with Cl_2 (or $PhICl_2$), Br_2, and I_2 in acetone or acetonitrile (eq 1a).

$$[M_4(EPh)_{10}]^{2-} + 2X_2 \rightarrow [M_4(EPh)_6X_4]^{2-} + 2Ph_2E_2 \quad (1)$$

(a) M = Cd; (b) M = Zn

Iodine was added conveniently as a solid to an acetone solution of $[Cd_4(EPh)_{10}]^{2-}$, whereas bromine in CCl_4 was added and shaken with an acetone solution of the anion. Controlled addition of Cl_2 was found to be difficult. Therefore, the easily weighed out chlorine carrier (dichloroiodo)benzene, $PhICl_2$, was used in preference to the element to add chlorine in stoichiometric quantity.[31]

The formation of the tetrahalo derivatives is quantitative as monitored by ^{113}Cd NMR of the reaction mixture (see later discussion). The isolated and purified yield, however, varies from 65 to 90%.

To explore the generality of the oxidative halogen substitution method, it has been extended here to the syntheses of the corresponding zinc clusters $[Zn_4(EPh)_6X_4]^{2-}$ as Me_4N^+ salts (eq 1b).

Structure of $(Me_4N)_2[(\mu\text{-EPh})_6(CdBr)_4]$ (E = S, 1; E = Se, 2). Compounds **1** and **2** are isomorphous and isostructural. The crystal structure of each compound consists of discrete $[(\mu\text{-EPh})_6(CdBr)_4]^{2-}$ anions and Me_4N^+ cations, well-separated from each other. The closest distances of approach are 2.54 Å for

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Table II. Atomic Positional (×10^4) and Thermal (×10^3) Parameters for **1** and **2**

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
		Compound **1**		
Cd(1)	5728.4 (5)	5728.4	5728.4	46.7 (4)
Cd(2)	4780.7 (5)	3613.9 (5)	5500.4 (5)	42.4 (5)
Br(1)	6555.3 (8)	6555.3	6555.3	90.8 (10)
Br(2)	4690.6 (8)	2323.1 (7)	6122.1 (8)	56.5 (8)
S(1)	5598 (2)	4445 (2)	6328 (2)	46 (2)
S(2)	3517 (2)	4266 (2)	5479 (2)	44 (2)
C(1)	5063 (5)	4574 (4)	7174 (4)	46 (3)
C(2)	4636 (5)	3991 (4)	7466 (4)	52 (3)
C(3)	4276 (5)	4078 (4)	8151 (4)	71 (4)
C(4)	4343 (5)	4747 (4)	8545 (4)	102 (6)
C(5)	4771 (5)	5329 (4)	8253 (4)	90 (5)
C(6)	5130 (5)	5243 (4)	7567 (4)	77 (4)
C(7)	2880 (4)	3685 (5)	4970 (5)	53 (3)
C(8)	3078 (4)	2971 (5)	4730 (5)	69 (4)
C(9)	2548 (4)	2513 (5)	4389 (5)	93 (6)
C(10)	1820 (4)	2770 (5)	4288 (5)	91 (5)
C(11)	1621 (4)	3484 (5)	4528 (5)	73 (4)
C(12)	2151 (4)	3941 (5)	4870 (5)	65 (4)
N(1)	1818 (5)	1818	1818	69 (6)
C(13)	1347 (6)	1347	1347	110 (11)
C(14)	2240 (9)	1356 (9)	2333 (8)	102 (14)
N(2)	7847 (4)	7847	7847	44 (4)
C(15)	8315 (5)	8315	8315	63 (4)
C(15)I	7376 (7)	7376	7376	63 (4)
C(16)	7747 (12)	8176 (11)	7114 (8)	63 (4)
C(16)I	7735 (59)	7642 (54)	8627 (9)	63 (4)
C(16)T	8269 (15)	7586 (23)	7203 (16)	63 (4)
		Compound **2**		
Cd(1)	5734.6 (7)	5734.6	5734.6	45.3 (6)
Cd(2)	4782.2 (7)	3599.6 (7)	5503.9 (7)	43.7 (8)
Br(1)	6555.5 (11)	6555.5	6555.5	88.5 (14)
Br(2)	4673.3 (11)	2313.9 (10)	6117.5 (11)	58.1 (13)
Se(1)	5682.9 (10)	4405.7 (10)	6339.6 (10)	44.6 (11)
Se(2)	3488.8 (10)	4263.3 (10)	5539.9 (10)	46.5 (11)
C(1)	5093 (7)	4557 (5)	7221 (6)	44 (5)
C(2)	4656 (7)	3990 (5)	7505 (6)	58 (6)
C(3)	4274 (7)	4092 (5)	8166 (6)	65 (6)
C(4)	4328 (7)	4763 (5)	8543 (6)	86 (7)
C(5)	4764 (7)	5330 (5)	8258 (6)	85 (7)
C(6)	5147 (7)	5228 (5)	7597 (6)	69 (6)
C(7)	2844 (7)	3640 (5)	4957 (6)	49 (5)
C(8)	3046 (7)	2933 (5)	4725 (6)	62 (6)
C(9)	2528 (7)	2478 (5)	4380 (6)	93 (8)
C(10)	1808 (7)	2731 (5)	4266 (6)	85 (7)
C(11)	1607 (7)	3438 (5)	4498 (6)	69 (6)
C(12)	2125 (7)	3892 (5)	4843 (6)	70 (6)
N(1)	1841 (8)	1841	1841	89 (10)
C(13)	1361 (7)	1361	1361	88 (13)
C(14)	2287 (12)	1359 (10)	2350 (12)	103 (19)
N(2)	7826 (6)	7826	7826	52 (7)
C(15)	8303 (6)	8303	8303	73 (7)
C(16)	7592 (16)	8244 (11)	7149 (11)	73 (7)
C(16)T	8270 (20)	7541 (43)	7184 (30)	73 (7)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i{\cdot}a_j$.

C(15)I to Br(1) in **1** and 2.79 Å for C(16)T to H(3) in **2**. Figure 1 gives a perspective stereoview of the anion. Figure 2 shows the $Cd_4E_6Br_4$ cage skeleton and the atom-numbering scheme. Selected intraionic dimensions for **1** and **2** are compiled in Table III.

The $[(\mu\text{-}SPh)_6(CdBr)_4]^{2-}$ cluster in **1** contains four Cd atoms located at the vertices of a tetrahedron that is regular within experimental error. Each Cd atom is tetrahedrally coordinated by three S atoms and a Br atom. Cd(1) and Br(1) lie on the crystallographic threefold axis, while the three basal Cd(2)–Br(2) groups occupy the corners of an equilateral triangle as a result of the threefold symmetry. Within experimental error the Cd···Cd distances are equal at 4.166 (3) Å, and the Cd–Cd–Cd angles are equal at 60.0 (4)°. The six thiolate ligands bridge the edges of the tetrahedron. At Cd(1) the Br–Cd–S angle is 109.31 (7) and the S′–Cd–S angle is 109.63 (7)°, while at Cd(2) the angles range from 104.5 (1) to 117.1 (2)°. All the Cd–S bond distances are normal and comparable to other Cd–S_{br} distances reported in the literature.[6] However, the mean S–Cd–S′ bond angle of 109.2° observed here is lower than the mean value of 112.3° found[6] for the corresponding angles in the $[Cd_4(SPh)_{10}]^{2-}$ anion. The two Cd–Br bond distances of 2.559 (3) and 2.565 (2) Å are not significantly different. Very few Cd–Br bond distances are available for comparison,[32] though the values observed here are higher than that of 2.53 Å reported for $[Cu_3(Budtc)_6][Cd_2Br_6]$.[32b]

The structure of the $[(\mu\text{-}SePh)_6(CdBr)_4]^{2-}$ anion in **2** is similar to that of the sulfur analogue. The average Cd···Cd distance of 4.251 (6) Å is greater than that in **1**, presumably owing to the bridging by the larger Se atom. The Cd–Br distances of 2.568 (4) and 2.581 (2) Å are comparable to those observed in **1** and slightly higher than the value for referred to above.[32b] The mean Cd–Se bond distance of 2.64 (12) Å compares well with the mean value of 2.66 (3) Å found[8] for Cd–Se_{br} in $[(\mu\text{-}SePh)_6(CdSePh)_4]^{2-}$, although the mean Se–Cd–Se angle of 110.1° is higher than the mean Se_{br}–Cd–Se_{br} angle of 107.6° observed in the $[(\mu\text{-}SePh)_6(CdSePh)_4]^{2-}$ ion.

Isomerism. For adamantanoid cages, $M_4(\mu\text{-}EPh)_6$, with four fused six-membered rings, isomerism can occur through inversion at the pyramidal E atoms of the six bridging chalcogenates.[1a] The phenyl substituents adopt either axial (a) or equatorial (e) dispositions relative to the best planes of the rings. Prior to this study, only three isomers had been recognized.[1a,2b] Isomer I (aaa,aae,aee,eee; point symmetry C_1) occurs in $[(\mu\text{-}SPh)_6(FeSPh)_4]^{2-}$, $[(\mu\text{-}SEt)_6(FeSEt)_4]^{2-}$, and $[(\mu\text{-}SPh)_6(FeCl)_4]^{2-}$ and contains four 1,3-axial–axial substituent pairs. Isomer II (aae,aae,aae,eee; point symmetry C_3) has three pairs of axial–axial substituent pairs and has been described for the $[Cu_4(o\text{-}(SCH_2)_2C_6H_4)_3]^{2-}$ anion.[2d] All other reported examples correspond to isomer III (aae,aae,aee,aee; point symmetry C_1) with only two 1,3-axial–axial ligand pairs. Structures **1** and **2** are the first examples of a new isomer, IV (aaa,aee,aee,aee; point symmetry C_3), which, like isomer II, has three 1,3-axial–axial pairs (see Figure 1). It is not clear, at present, why isomer II (aae,aae,aae,eee), which also has three pairs of axial–axial substituents, and the same symmetry, is not observed for **1** or **2**. The new isomer is chiral and can exist in two enantiomeric forms. The crystals of **1** and **2** chosen for analysis were both of the same hand, and it is apparent that a spontaneous resolution has occurred. The asymmetry arises from two sources: the dispositions of the phenyl groups on the bridging chalcogenates E(1) and E(2). Inversion at E(1) can occur by breaking Cd–E bonds, and the NMR data (vide infra) show that this process happens readily on the preparative time scale and perhaps residually on the NMR time scale. By contrast, the torsional isomerism resulting from the disposition of the phenyl substituents on E(2) can be changed merely by a rotation about the E(2)–C(7) bond. Such asymmetry has been observed when the $[CoCl_2(py)_4]^+$ cation is crystallized with chiral anions and has been termed atropisomerism[33] but has not, to the best of our knowledge, been seen before when the counterion is achiral. It is manifest that torsional isomerism is most readily observed in the solid state, and further studies are under way in our laboratories.

These are the first examples of a tetranuclear chalcogenate-bridged cluster of the adamantanoid type possessing such a high crystallographic and ionic symmetry. The analogous iron cluster $[(\mu\text{-}SPh)_6(FeCl)_4]^{2-}$, which was crystallized as the Ph_4P^+ salt, has C_1 symmetry, probably because the cation also has this symmetry.[9] It is interesting to note that the anion in $(Me_4N)_2[Co(SPh)_4]$[5] has a higher crystallographically imposed symmetry (C_2) than that in $(PPh_4)_2[Co(SPh)_4]$ (C_1),[34] perhaps due to the presence of the more symmetrical Me_4N^+ cation.

The E_6 polyhedra are slightly distorted from a regular octahedron in a manner that increases E···E distances between pairs

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Table III. Selected Interatomic Distances (Å) and Angles (deg) for $(Me_4N)_2[(\mu\text{-}EPh)_6(CdBr)_4]$

	1	**2**		**1**	**2**
Cd(1)–Br(1)	2.559 (3)	2.568 (4)	Cd(1)···Cd(2)	4.161 (1)	4.243 (2)
Cd(2)–Br(2)	2.565 (2)	2.581 (2)	Cd(2)···Cd(2)	4.167 (1)	4.254 (2)
Cd(1)–E(1)	2.543 (3)	2.639 (2)	Cd(2)–E(1)	2.554 (3)	2.654 (2)
Cd(2)–E(2)	2.541 (3)	2.627 (2)	Cd(2)–E(2)′	2.541 (3)	2.633 (2)
Br(1)···Br(2)	8.300 (2)	8.419 (3)	Br(2)···Br(2)′	8.398 (2)	8.494 (3)
E(1)···E(1)′	4.157 (4)	4.351 (3)	E(1)···E(2)	4.046 (4)	4.108 (3)
E(1)···E(2)′	4.028 (4)	4.226 (3)	E(2)···E(2)′	4.334 (4)	4.582 (3)
E(1)–C(1)	1.802 (9)	1.935 (11)	E(2)–C(2)	1.790 (9)	1.933 (12)
N–C[a]	1.454 (11)	1.499 (12)			
Br(1)–Cd(1)–E(1)	109.31 (7)	107.85 (6)	Cd(2)···Cd(1)···Cd(2)′	60.10 (2)	60.16 (3)
Br(2)–Cd(2)–E(1)	107.91 (8)	107.22 (7)	Cd(1)···Cd(2)···Cd(2)′	59.95 (2)	59.92 (3)
Br(2)–Cd(2)–E(2)	111.28 (8)	109.41 (8)	Br(2)–Cd(2)–E(2)′	110.23 (8)	109.68 (8)
E(1)–Cd(1)–E(1)′	109.63 (7)	111.04 (7)	Cd(1)–E(1)–C(1)	106.7 (3)	103.4 (3)
E(1)–Cd(2)–E(2)	104.48 (10)	106.30 (7)	Cd(2)–E(1)–C(1)	104.9 (3)	102.0 (3)
E(1)–Cd(2)–E(2)′	105.16 (15)	101.96 (10)	Cd(2)–E(2)–C(7)	107.9 (3)	104.9 (3)
E(2)–Cd(2)–E(2)′	117.07 (17)	121.20 (14)	Cd(2)′–E(2)–C(7)	107.3 (4)	104.9 (4)
Cd(1)–E(1)–Cd(2)	109.44 (11)	106.57 (8)	Cd(2)–E(2)–Cd(2)	110.2 (2)	107.9 (1)

[a] The SHELX76 dfix option was employed to constrain all C–N bonds, ordered and disordered, to one free variable in each analysis. The refined value of that free variable is the C–N distance reported.

of parallel axial EPh substituents without significant variation in M–E distances. Thus in **1**, the S(2)–Cd(2)–S(2)′ (i.e., S_{ax}–Cd–S_{ax}) angle is 117.07 (17)° while S(1)–Cd(2)–S(2) (i.e., S_{eq}–Cd–S_{ax}) angles are 104.48 (10) and 105.16 (15)°. Similar angular distortions occur in **2** also. As a result of this distortion, the averages of the E(1)···E(1) and E(1)···E(2) distances in **1** and **2**, 4.08 and 4.23 Å, respectively, are less than the E(2)···E(2) distances of 4.33 and 4.58 Å. This is consistent with the lower value of the Br(1)···Br(2) distance when compared to that of Br(2)···Br(2) (Table III). Thus the Br_4 tetrahedron and the E_6 octahedron appear to be compressed slightly in the direction of the C_3 (Br(1)–Cd(1)) axis.

The mean Cd–E–Cd, Br–Cd–E, and E–Cd–E angles of 109.8, 109.7, and 109.1° for **1** and 107.3, 108.5, and 110.1° for **2** show that on average there is no severe distortion from the ideal angle of 109.5°. Further, the ratio of the mean Cd···Cd to mean E···E distances is 1.005 for **1** and 0.9835 for **2**. This indicates that along the threefold and pseudothreefold axes there is only a slight outward displacement of Cd atoms in **1** and an inward displacement in **2**. In all the reported examples of the adamantanoid type the metal atoms are displaced slightly outward along the pseudothreefold axes.[1a]

Table IV. ^{113}Cd and ^{77}Se NMR Data[a] for $[(\mu\text{-}EPh)_6(CdX)_4]^{2-}$ Anions

E	X	concn, M	δ_{Cd}[b] (approx $\Delta\nu_{1/2}$, Hz)	δ_{Se}[c] (approx $\Delta\nu_{1/2}$, Hz)
S	SPh	0.050	575[d] (8)	
Se	SePh	0.020	519[e,f] (65)	−12[f] (250)
		0.050[g]	524 (75)	−20 (265)
		satd[g,h]	537 (130)	18 (195),[i] −62 (225)[j]
S	Cl	satd	551 (100)	
		satd[g,k]	564 (70)	
S	Br	0.025	535[f] (90)	
S	I	0.025	501[f] (50)	
Se	Cl	satd	520 (100)	−69 (290)
		satd[g,k]	529 (110)	−80 (85)
Se	Br	0.025	492[f] (75)	−67[f,l] (105)
Se	I	0.025	441[f,m] (85)	−57[m] (40)

[a] For acetone solutions at 295 K unless otherwise mentioned. [b] Relative to 0.1 M $Cd(ClO_4)_2(aq)$ at 295 K. [c] Relative to neat Me_2Se at 295 K. [d] Data from ref 13. [e] Data from ref 14. [f] In a ^{113}Cd-enriched sample. [g] In MeCN. [h] At 234 K. [i] Terminal PhSe. [j] Bridging PhSe. [k] At 260 K. [l] In a 0.05 M solution at 273 K; $^1J(^{113}Cd-^{77}Se) \approx 120$ Hz. [m] For a 0.05 M solution of $[^{nat}Cd_4(SePh)_6I_4]^{2-}$, $^1J(^{113}Cd-^{77}Se) = 120 \pm 10$ Hz at 273 and 213 K; $^2J(^{111}Cd-^{113}Cd)$ is not observed at ambient probe temperature but can be seen at reduced temperature, e.g. 52 ± 2 Hz at 231 K.

NMR Spectral Studies. Halogenation Reactions. In our earlier communication[11] we described ^{113}Cd NMR data showing that oxidative iodine substitution of $[(\mu\text{-}EPh)_6(CdEPh)_4]^{2-}$ (E = S, Se) occurs via the intermediate species $[Cd_4(EPh)_{10-x}I_x]^{2-}$ (x = 1–3). At ambient probe temperature the intermediate complexes are characterized by two ^{113}Cd NMR signals. For E = S, $\delta_{Cd} \approx 575$ and 500 (in acetone), corresponding to the local environments CdS_4 and CdS_3I (expected for the $[(\mu\text{-}SPh)_6(CdSPh)_{4-x}(CdI)_x]^{2-}$ ions). For E = Se, $\delta_{Cd} \approx 519$ and 440 (in acetone), corresponding to the local environments $CdSe_4$ and $CdSe_3I$ in the analogous selenolate complexes. In the last case, ^{77}Se NMR confirms the formation of Ph_2Se_2 ($\delta_{Se} = 453$). Addition of 2 mol equiv of I_2 to $[(\mu\text{-}EPh)_6(CdEPh)_4]^{2-}$ produces the tetraiodo derivative quantitatively. Similarly, solutions in which $0 < Br_2/[(\mu\text{-}SePh)_6(^{113}CdSePh)_4]^{2-} < 2$ give ^{113}Cd NMR spectra showing signals in two regions. At 296 K the two signals are partly coalesced. However, at 260 K relatively sharp signals are observed ($\Delta\nu_{1/2} < 150$ Hz). In acetone, $\delta_{Cd} \approx 581$ and 541 for E = S and 528 and 496 for E = Se. In each case the two regions can be assigned to the sites $^{113}CdE_4$ and $^{113}CdE_3Br$ in the clusters $[(\mu\text{-}EPh)_6(^{113}CdEPh)_{4-x}(^{113}CdBr)_x]^{2-}$. When $Br_2/[Cd_4(EPh)_{10}]^{2-} = 2$, only the relatively sharp singlet of $[(\mu\text{-}EPh)_6(^{113}CdBr)_4]^{2-}$ is observed. Somewhat differently, when 1 mol equiv of $PhICl_2$ is added to $[(\mu\text{-}SPh)_6(^{113}CdSPh)_4]^{2-}$ in MeCN, the 295 K ^{113}Cd NMR spectrum shows only one ^{113}Cd NMR signal, at $\delta_{Cd} = 551$ with $\Delta\nu_{1/2} \approx 100$ Hz. However, the 260 K ^{113}Cd NMR spectrum of the same sample shows two regions of resonance with δ_{Cd} = 564 and 584, attributable to the CdS_4 and CdS_3Cl kernels in $[(\mu\text{-}SPh)_6(CdSPh)_{4-x}(CdCl)_x]^{2-}$. At $PhICl_2/[Cd_4(SPh)_{10}]^{2-} = 2$, the spectrum becomes the singlet of $[(\mu\text{-}SPh)_6(CdCl)_4]^{2-}$. A similar result is obtained for the system $[(\mu\text{-}SePh)_6(CdSePh)_4]^{2-}$ and $PhICl_2$.

In qualitative terms, our results show that the rate of exchange of ^{113}Cd between $^{113}CdE_4$ and $^{113}CdE_3X$ kernels in the intermediate complexes $[(\mu\text{-}EPh)_6(CdEPh)_{4-x}(CdX)_x]^{2-}$ is in the order Cl > Br > I.

$[(\mu\text{-}EPh)_6(CdX)_4]^{2-}$ Anions. Table IV gives ^{113}Cd and ^{77}Se NMR data for the clusters $[(\mu\text{-}EPh)_6(CdX)_4]^{2-}$, together with data for the precursor complexes $[(\mu\text{-}EPh)_6(CdEPh)_4]^{2-}$ for comparison. The halogen derivatives are characterized by a single ^{113}Cd NMR resonance. The chemical shifts, δ_{Cd}, are in the order Cl > Br > I, which is the same order found in CdX_4^{2-} (see, for example, ref 35). The full widths at half-height, $\Delta\nu_{1/2}$, are also in the order Cl > Br > I. These values of $\Delta\nu_{1/2}$ suggest residual exchange, perhaps via disproportionation to undetectably small concentrations of $[Cd_4(EPh)_7X_3]^{2-}$ and a more fully halogen substituted complex for the complexes of the lighter halogens (cf. ref 36). With natural Cd, spin-spin coupling between ^{113}Cd and ^{111}Cd is clear in the ^{113}Cd NMR spectrum of $[(\mu\text{-}SePh)_6(CdI)_4]^{2-}$ at reduced temperature; e.g., $^2J = 52 \pm 2$ Hz at 213 K. Only shoulders attributable to this coupling appear in the reduced-temperature ^{113}Cd NMR spectra of $[(\mu\text{-}SPh)_6(CdI)_4]^{2-}$ and

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$[(\mu\text{-EPh})_6(\text{CdBr})_4]^{2-}$ (E = S, Se). The coupling measured for $[(\mu\text{-SePh})_6(\text{CdI})_4]^{2-}$ is comparable to the 45-Hz coupling observed[13] for $^2J(^{113}\text{Cd–S–}^{111}\text{Cd})$ in $[(\mu\text{-SPh})_6(\text{CdSPh})_4]^{2-}$.

A 0.05 M solution of $[(\mu\text{-SePh})_6(\text{CdSePh})_4]^{2-}$ in MeCN at 295 K has a ^{77}Se NMR spectrum consisting of a single broad line (Table IV), consistent with an earlier result[14] for an acetone solution. At 234 K, a saturated MeCN solution of $[(\mu\text{-SePh})_6(\text{CdSePh})_4]^{2-}$ gives two signals at 18 and −62 ppm with relative intensities approximately 2 and 3. The signals are readily assigned to the terminal and bridging SePh groups of a static (or near-static) $[(\mu\text{-SePh})_6(\text{CdSePh})_4]^{2-}$ ion, confirming that in solution this ion retains the adamantanoid structure found recently in the solid state using X-ray analysis.[8] By comparison with the reduced-temperature ^{77}Se NMR spectrum of $[(\mu\text{-SePh})_6(\text{CdSePh})_4]^{2-}$, the ^{77}Se NMR chemical shifts of the $[(\mu\text{-SePh})_6(\text{CdX})_4]^{2-}$ ions (Table IV) confirm that these contain only bridging PhSe groups.

As in $[(\mu\text{-SePh})_6(\text{CdSePh})_4]^{2-}$, exchange of PhSe groups is slow in $[(\mu\text{-SePh})_6(\text{CdI})_4]^{2-}$ at reduced temperature. An acetone solution at 273 K gives a ^{77}Se NMR signal with $\delta_{\text{Se}} = -57$, flanked symmetrically by one pair of satellites due to ^{113}Cd–^{77}Se spin–spin coupling with $^1J(^{113}\text{Cd–}^{77}\text{Se}) \approx 120 \pm 10$ Hz. Similarly, an incompletely resolved ^{113}Cd–^{77}Se coupling of ~120 Hz is observed in the ^{77}Se resonance found at −67 ppm for a solution of $[(\mu\text{-SePh})_6(^{113}\text{CdBr})_4]^{2-}$ in acetone at 273 K. The corresponding $[(\mu\text{-SePh})_6(\text{CdCl})_4]^{2-}$ ion in MeCN at 260 K has a ^{77}Se NMR signal with $\delta_{\text{Se}} = -80$ and $\Delta\nu_{1/2} \approx 75$ Hz; there is no observable ^{113}Cd–^{77}Se coupling in this spectrum. The 120-Hz value found for $^1J(^{113}\text{Cd–}^{77}\text{Se})$ in the tetrabromo and -iodo clusters can be compared with values of 46–126 Hz reported[37] for the series $[\text{Cd(SPh)}_n(\text{SePh})_{4-n}]^{2-}$.

$[(\mu\text{-SPh})_n(\mu\text{-SePh})_{6-n}(\text{CdX})_4]^{2-}$ Anions. In the ^{113}Cd NMR spectra of mixtures of $[(\mu\text{-SPh})_6(^{113}\text{CdI})_4]^{2-}$ and $[(\mu\text{-SePh})_6(^{113}\text{CdI})_4]^{2-}$ in acetone at 295 K, four broad resonances are found with chemical shifts ~500, ~480, ~462, and ~440 ppm. These spectra are better resolved at reduced temperature, as shown, for example, in Figure 1 of ref 11. Similarly, the ^{113}Cd NMR spectra of mixtures of $[(\mu\text{-SPh})_6(^{113}\text{CdBr})_4]^{2-}$ and $[(\mu\text{-SePh})_6(^{113}\text{CdBr})_4]^{2-}$ in acetone at 273 K show a total of four broad resonances with chemical shifts ~539, ~526, ~513, and ~499 ppm, while mixtures of $[(\mu\text{-SPh})_6(\text{CdCl})_4]^{2-}$ and $[(\mu\text{-SePh})_6(\text{CdCl})_4]^{2-}$ in MeCN at 260 K behave analogously, showing ^{113}Cd NMR signals at ~563, ~553, ~542, and ~530 ppm. In each system the least shielded resonance is approximately that of $[(\mu\text{-SPh})_6(\text{CdX})_4]^{2-}$, in which the local environment is CdS_3X, and the most shielded approximately that of $[(\mu\text{-SePh})_6(\text{CdX})_4]^{2-}$, in which the local environment is CdSe_3X. It thus seems reasonable to assign the other two resonances, in order of increasing shielding, to the CdS_2SeX and CdSSe_2X kernels, which can occur in the anions $[(\mu\text{-SPh})_n(\mu\text{-SePh})_{6-n}(\text{CdX})_4]^{2-}$ with mixed bridging chalcogenate groups. These results again make it clear that the species existing in solution have terminally halogen substituted tetrameric adamantanoid structures analogous to those found for **1** and **2** in the solid state (see above). In addition, it is evident that at reduced temperature interconversion between the four different Cd kernels occurring in $[(\mu\text{-SPh})_n(\mu\text{-SePh})_{6-n}(\text{CdX})_4]^{2-}$ is slow on the ^{113}Cd NMR time scale.

The signal intensities found for $[(\mu\text{-SPh})_6(\text{CdX})_4]^{2-}$–$[(\mu\text{-SePh})_6(\text{CdX})_4]^{2-}$ mixtures (see, for example, Figure 1 of ref 11) are close to those expected[38] for a statistical distrbution of the two different PhE groups. Also, the results for the clusters with mixed chalcogenates show that δ_{Cd} in these clusters is affected mainly by the atoms in the first coordination sphere. Seitz and Brown[39] have described an analogous "local environment" effect for the ^{7}Li spectra of $\text{Li}_4\text{R}_{4-n}\text{X}_n$. The approximately equal spacing of the four ^{113}Cd NMR signals for each mixed-chalcogenate system is consistent with the nearly linear dependence of δ_{Cd} on n found[37] for the mononuclear species $[\text{Cd(SPh)}_n(\text{SePh})_{4-n}]^{2-}$.

$[(\mu\text{-SePh})_6(\text{CdBr})_x(\text{CdI})_{4-x}]^{2-}$ Anions. The ^{113}Cd NMR spectrum obtained from a 50:50 mixture of $[(\mu\text{-SePh})_6(\text{CdBr})_4]^{2-}$ and $[(\mu\text{-SePh})_6(\text{CdI})_4]^{2-}$ in acetone at 260 K has signals in two regions, ~492 ppm ($\Delta\nu_{1/2} \approx 75$ Hz) and ~441 ppm ($\Delta\nu_{1/2} \approx 85$ Hz). The two signals can be attributed to the CdSe_3I and CdSe_3Br kernels, respectively. This result shows that net exchange of halogens is slow under these conditions, though it does not show unambiguously that redistribution to $[(\mu\text{-SePh})_6(\text{CdBr})_x(\text{CdI})_{4-x}]^{2-}$ occurs. That redistribution occurs is confirmed by the ^{77}Se NMR spectrum, at 273 K, of the same mixture. This shows three broad signals at −56, −62, and −67 ppm with relative intensities approximately 1, 2, and 1. By comparison with the ^{77}Se NMR data for the parent tetrahalo complexes (see Table IV), the ^{77}Se NMR spectrum is readily assigned to Se with the three different possible next-nearest-neighbor environments for selenium, namely I–Cd–Se(Ph)–Cd–I, I–Cd–Se(Ph)–Cd–Br, and Br–Cd–Se(Ph)–Cd–Br, in order of increasing ^{77}Se shielding. Evidently the mixed-halogen species $[(\mu\text{-SePh})_6(\text{CdBr})_x(\text{CdI})_{4-x}]^{2-}$ are formed; the ^{77}Se NMR signal intensities show that their distribution is approximately that expected[38] from statistical considerations.

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, and selected Friedel pairs (3 pages); listings of structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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