Synthesis and NMR Spectra (^{31}P, $^{111/113}$Cd, ^{77}Se) of Adamantane-like Phosphine Complexes with the (μ-ER)$_6$Cd$_4$ Core and the Crystal and Molecular Structure of [(μ-SPr^i)$_6$(CdPPh$_3$)$_2$(CdOClO$_3$)$_2$]·EtOH

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NMR (^{31}P, $^{111/113}$Cd, ^{77}Se) data for the systems Cd(PPh$_3$)$_2$(ClO$_4$)$_2$:Cd(ER)$_2$:PPh$_3$ (ER = SPr^i, S-*c*-C$_6$H$_{11}$, SPh, SePh, SPr^n, S-*n*-C$_5$H$_{11}$) provide evidence for new adamantanoid complexes of the type [(μ-ER)$_6$(CdPPh$_3$)$_n$(Cd)$_{4-n}$]$^{2+}$. Complexes that have been well-characterized in solution are those with n = 2–4 for ER = SPr^i and S-*c*-C$_6$H$_{11}$ and those with n = 3, 4 for the ER = SPh, SePh, SPr^n, and S-*n*-C$_5$H$_{11}$. In all cases there is probably equilibrium coordination of ClO$_4^-$ at the PPh$_3$-free cadmiums. For ER = SPr^i and S-*c*-C$_6$H$_{11}$, the spectra of 1:3:2 mixtures show appreciable dissociation of PPh$_3$ for [(μ-ER)$_6$(CdPPh$_3$)$_4$]$^{2+}$. From 1:3:2 mixtures, the complexes [(μ-ER)$_6$(CdPPh$_3$)$_n$(Cd)$_{4-n}$](ClO$_4$)$_2$ have been isolated with n = 2 for ER = SPr^i and *c*-C$_6$H$_{11}$, n = 4 for ER = SPh and SePh, and n = 3 for ER = SPr^n. NMR spectra of 1:1 mixtures of Cd(PPh$_3$)$_2$(ClO$_4$)$_2$ and Cd(ER)$_2$ show that open complexes [Ph$_3$PCd({μ-ER}CdPPh$_3$)$_3$]$^{5+}$, which are possible precursors to the adamantanoid cage, are formed cleanly for ER = SPh, SePh, SPr^n, and S-*n*-C$_5$H$_{11}$ in CH$_2$Cl$_2$ and for SPr^n and S-*n*-C$_5$H$_{11}$ in CHCl$_3$. Interpretation of the NMR spectra has been aided by metal NMR data for Cd(PPh$_3$)$_n$(ClO$_4$)$_2$ (n = 2–4) and ^{31}P and metal NMR data for [Cd(PPh$_3$)$_n$(OPPh$_3$)$_{4-n}$]$^{2+}$ (n = 2, 3), which are reported for the first time. The structure of [(μ-SPr^i)$_6$(CdPPh$_3$)$_2$(CdOClO$_3$)$_2$]·EtOH was determined by single-crystal X-ray analysis at −40 °C. Crystal data: monoclinic, space group $P2_1/c$, a = 15.006(2) Å, b = 16.250(2) Å, c = 28.227(3) Å, β = 98.79(1)°, d_{obsd} = 1.62(5) g cm^{-3}, Z = 4, V = 6802(2) Å^3. The compound has an adamantane-like skeleton, (μ-S)$_6$Cd$_4$. Four-coordination at two cadmium atoms is completed by terminal PPh$_3$ and at the other two by terminal η^1-ClO$_4^-$. The configurations of the isopropyl groups attached to the bridging S atoms in the four Cd$_3$S$_3$ chairs are [aae, aae, aee, aee] with two 1,3-axial–axial interactions between the isopropyl substituents.

Introduction

A previous paper from these laboratories[1] has described the synthesis and multinuclear magnetic resonance spectra of a wide range of mercury(II) complexes of the type [(μ-ER)$_6$(HgL)$_4$]$^{2+}$ (E = S or Se; L = tertiary phosphine or arsine), all as ClO$_4^-$ salts. A related paper[2] reported the synthesis and multi-NMR spectra of [(μ-TePh)$_6$(HgPR'$_3$)$_{3,4}$(Hg)$_{1,0}$]$^{2+}$. An unresolved question for the unusual tris(phosphine) complexes is whether the unique mercury center is three-coordinate in the solid state and in non-coordinating solvents or four-coordinate with an attached ClO$_4^-$. In DMF, this site has solvent coordinated.

The cadmium analogues of the Hg$_4$ cations have not been scrutinized in depth.[3] We considered investigation of the Cd$_4$ cations to be worthwhile because it has become evident that the behavior of complexes with (μ-ER)$_6$M$_4$ cages need not be parallel for cadmium and mercury; e.g., [(μ-ER)$_6$(CdX)$_4$]$^{2-}$ compounds (ER = SePh, SPh, S-alkyl; X = Cl–I) are quite stable at ambient temperature[5,6] whereas the Hg$_4$ analogues dissociate.[6] We present here a study of several systems Cd(PPh$_3$)$_2$(ClO$_4$)$_2$:Cd(ER)$_2$:PPh$_3$ (ER = SePh, SPh, S-alkyl). This has provided multi-NMR evidence for a variety of cations of the general type [(μ-ER)$_6$(CdPPh$_3$)$_n$(Cd)$_{4-n}$]$^{2+}$ as well as for several *open* tetranuclear complexes [Ph$_3$PCd({μ-ER}CdPPh$_3$)$_3$]$^{5+}$. Several examples of the adamantanoid complexes have been isolated, and a description of an X-ray analysis of [(μ-SPr^i)$_6$(CdPPh$_3$)$_2$(CdOClO$_3$)$_2$]·EtOH is given also.

Experimental Section

Materials and General Procedures. All starting materials were from commercial sources and were used as received except that PPh$_3$ was recrystallized from EtOH. The compounds Cd(ER)$_2$ (E = S, R = *n*-Pr, *i*-Pr, *n*-C$_5$H$_{11}$ (*n*-Pe), *c*-C$_6$H$_{11}$ (Cy), or Ph; E = Se, R = Ph) were synthesized by literature methods.[5b,7] Following ref 8, OPPh$_3$ was prepared by KMnO$_4$ oxidation of PPh$_3$ in Me$_2$CO. In our hands the literature synthesis[9a] of Cd(PPh$_3$)$_2$(ClO$_4$)$_2$ (**1**) gave an initial product heavily contaminated by Cd(PPh$_3$)$_3$(ClO$_4$)$_2$, as indicated by reduced-temperature ^{31}P NMR. [*Caution!* Although no problems were experienced in the current work, perchlorate salts of metal complexes with organic ligands are known to be explosive.[9b] They should be prepared in small amounts and handled with great caution.] Addition of Et$_2$O to a dilute solution of the crude product in CH$_2$Cl$_2$ gave **1** that was pure by ^{31}P NMR. Solvents for use in synthesis and the preparation of NMR samples were stored over 3A molecular sieves and deoxygenated by sparging with Ar.

Cd$_4$(SePh)$_6$(PPh$_3$)$_4$(ClO$_4$)$_2$ (2). A mixture of Cd(PPh$_3$)$_2$(ClO$_4$)$_2$ (0.418 g, 0.5 mmol), Cd(SePh)$_2$ (0.637 g, 1.5 mmol), and PPh$_3$ (0.262 g, 1.0 mmol) in CH$_2$Cl$_2$ (5 mL) was stirred for 20 min. A small amount of gelatinous insoluble material was then removed by filtration. Addition of Et$_2$O (5 mL) to the filtrate gave an oil. After refrigeration to 0 °C overnight, the supernatant liquid was removed. The remaining oil was shaken with a further 5-mL portion of Et$_2$O and refrigerated for several days to give a white solid product. The product was separated by filtration, washed with Et$_2$O, and dried in vacuo, yield 0.70 g (53%). Anal. Calcd for C$_{108}$H$_{90}$Cd$_4$Cl$_2$O$_8$P$_4$Se$_6$ (mol wt 2634.11): C, 49.25; H 3.44. Found: C, 48.83; H, 3.28. ^{1}H NMR (CDCl$_3$): δ_H 6.8–7.5 (phenyl H).

Cd$_4$(SPh)$_6$(PPh$_3$)$_4$(ClO$_4$)$_2$ (3). The procedure was the same as that for **2**, except that the volume of CH$_2$Cl$_2$ was 10 mL and the addition of a single 6-mL portion of Et$_2$O resulted in a white crystalline product after the CH$_2$Cl$_2$:Et$_2$O mixture was refrigerated overnight, yield 51%. Anal. Calcd for C$_{108}$H$_{90}$Cd$_4$Cl$_2$O$_8$P$_4$S$_6$ (mol wt 2352.71): C, 55.14, H, 3.86. Found: C, 54.76; H, 3.76. ^{1}H NMR (CDCl$_3$): δ_H 6.6–7.5 (phenyl H).

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$Cd_4(SPr^n)_6(PPh_3)_3(ClO_4)_2$ (4). This synthesis followed that of **3**, with a 1:3:2 mixture of the appropriate reactants, except that only 2.5 mL of Et_2O was used. The yield of the white tris(phosphine) complex was 74%. Anal. Calcd for $C_{72}H_{87}Cd_4Cl_2O_8P_3S_6$ (mol wt 1886.31): C, 45.85; H, 4.65. Found: C, 45.13; H, 4.66. ^1H NMR ($CDCl_3$): δ_H 0.53 (t, $-CH_3$), 1.26 (m, $-CH_2$), 2.38 (t, $-SCH_2-$), 7.3–7.6 (phenyl H).

$Cd_4(SPr^i)_6(PPh_3)_2(ClO_4)_2$ (5). The same method used for **3** gave this white bis(phosphine) complex in 43% yield. Anal. Calcd for $C_{54}H_{72}Cd_4Cl_2O_8P_2S_6$ (mol wt 1623.96): C, 39.94; H, 4.47. Found: C, 39.66; H, 5.06. ^1H NMR (CD_3CN): 1.28 (d, $-CH_3$), 3.22 (m, $-CH=$); 7.4–7.5 (phenyl H). A reactant ratio of 1:3:0 also gave **5**, as shown by ^1H, ^{31}P, and ^{111}Cd NMR.

$Cd_4(SCy)_6(PPh_3)_2(ClO_4)_2$ (6). A mixture of $Cd(PPh_3)_2(ClO_4)_2$ (0.42 g, 0.50 mmol) and $Cd(SCy)_2$ (0.51 g, 1.5 mmol) dissolved completely in CH_2Cl_2 (5 mL) when stirred for 1 h. Addition of Et_2O (3 mL) and refrigeration of the $CH_2Cl_2{:}Et_2O$ mixture overnight gave 0.75 g (80%) of **6** in white microcrystalline form. Anal. Calcd for $C_{72}H_{96}Cd_4Cl_2O_8P_2S_6$ (mol wt 1864.41): C, 46.38, H, 5.19. Found: C, 46.24; H, 5.37. ^1H NMR (CD_3CN): δ_H 0.9–2.8 ($-C_6H_{11}$), 7.4–7.6 (phenyl H).

If the ratio of reactants was changed to 1:3:2, the same product was obtained (by ^1H, ^{31}P, and ^{111}Cd NMR).

NMR Spectra. Proton NMR spectra were obtained at ambient probe temperature using a Varian Gemini-200 spectrometer system with solutions in standard 5 mm o.d. NMR tubes. The ^2D resonance of the solvent was used as a field/frequency lock and signals from the solvent were used as internal references ($\delta_H(CHCl_3$ in $CDCl_3) = 7.24$; $\delta_H(CD_2HCN$ in $CD_3CN = 1.93$).

All other NMR spectra (^{31}P, ^{77}Se, $^{111/113}Cd$) were measured using a Varian XL-200 spectrometer system operating without a ^2D field/frequency lock (drift < 0.03 ppm/day), with the samples in 10 mm o.d. NMR tubes, as described in previous papers from these laboratories.[1,2,5b] Samples were prepared using mass of solute/volume of solvent at ambient temperature as the concentration unit. For cadmium, spectra for the system 1:3 $Cd(SPr^i)_2{:}PPh_3$ were measured using the ^{113}Cd nuclide.[10] Since these initial spectra contained a number of artifacts in the region of interest, the ^{111}Cd nuclide[10] was studied subsequently. No primary isotope effect is expected, i.e. chemical shifts should be the same for both ^{111}Cd and ^{113}Cd. The external references were 85% H_3PO_4, 0.1 M $Cd(ClO_4)_2$ (aq), and pure Me_2Se (all at ambient probe temperature), for ^{31}P, ^{77}Se, and ^{111}Cd, respectively. Reproducibility of δ_P, δ_{Cd} and δ_{Se} between sessions was ±0.1, ±1, and ±0.1 ppm or better. In a single session, reproducibility of δ_{Cd} is thought to be ±0.1 ppm or better. Probe temperatures were measured using a thermocouple probe in a stationary sample of the appropriate solvent.

NMR spectra were simulated as described previously.[1]

X-ray Structure Determination. During attempts to obtain single crystals of a quality suitable for diffraction studies, three different habits of compound **5** were grown. Crystals **5a** were grown at ca. 0 °C by diffusion of Et_2O into a solution of **5** in $CHCl_3$. Single crystals **5b** were obtained by layering Et_2O over a solution of **5** in $CHCl_3$ at room temperature, and crystals **5c** were produced by addition of Et_2O to a solution of **5** in CH_2Cl_2 at room temperature. The crystals **5a–c** all belong to the monoclinic crystal system, and their cell dimensions and space groups are summarized as follows:

	cryst **5a**	cryst **5b**	cryst **5c**
cryst system	monoclinic	monoclinic	monoclinic
proposed space group	$P2_1/c$	$C2/c$	Cc or $C2/c$
temp (°C)	23	23	23
cell dimens			
a (Å)	15.170(2)	37.377(9)	27.581(4)
b (Å)	16.456(1)	14.569(5)	14.448(3)
c (Å)	28.469(3)	27.886(9)	19.978(3)
β (deg)	99.20(1)	105.43(2)	115.36(2)
V (Å^3)	7015(1)	14634(8)	7194(2)
Z	4	8	4

The first data set was collected at room temperature from a crystal of **5a** sealed inside a capillary tube. The standard reflections decayed more than 30% during data collection, and the crystal did not diffract above a θ value of 18°. However, a data collection was completed successfully at reduced temperature (see below). Crystals of **5b** gave ω-scans that were very broad and split; crystals of this habit were not considered further. We were unable to solve the structure using data collected from a crystal of type **5c**.

The density of crystal **5a** was determined by the neutral bouyancy method using a mixture of CCl_4 and $1,2\text{-}C_2H_4Br_2$. With this crystal, preliminary investigations and the data collection were made on an Enraf-Nonius CAD4F diffractometer using graphite-monochromated Mo Kα radiation[12] at −40(2) °C. Photo and automatic indexing routines, followed by least-squares fits of 21 accurately centered reflections ($22.0 \leq 2\theta \leq 23.2°$), gave cell constants and an orientation matrix. The Niggli matrix suggested the monoclinic system with symmetry $2/m$, and this was confirmed from an inspection of equivalent reflections. Intensity data were recorded in shells in ω–2θ mode, at variable scan speeds (0.92–4.12 deg·min^{-1}) and a scan width of $0.75 + 0.35 \tan \theta$, with a maximum time per datum of 60 s. Static background measurements were made at the end points of the width $0.85 + 0.35 \tan \theta$. Three standard reflections were monitored every 180 min of X-ray exposure time. There were 7487 reflections in the 2θ range 0–42° ($-15 \leq h \leq 15$, $-16 \leq k \leq 0$, $0 \leq l \leq 28$), and 50 repetitions of the standards were recorded. The data collection was stopped at a 2θ maximum of 42° as little intensity was observed above this value.

Corrections were made for Lorentz, monochromator and crystal polarization, background radiation effects, and decay using the NRCVAX crystal structure programs[13] running on a SUN 3/80 workstation. The faces were indexed (five faces with face indices (012), (102), $(10\bar{2})$, $(01\bar{2})$ and $(\bar{4}\bar{3}1)$), and the interfacial distances were measured using a microscope equipped with a filar eyepiece. The data were corrected for absorption by the Gaussian method, giving an absorption profile with maximum and minimum transmission values of 0.745 and 0.687, respectively. There were 4885 ($I \geq 2.5\sigma$) unique data. The systematic absences[14] indicated that the space group was $P2_1/c$. The positions of the Cd, S, and P atoms were determined using SHELXS-86, and the remaining atoms in the molecule were located by difference Fourier techniques. Structure refinement was by full-matrix least-squares techniques on F. Anisotropic thermal parameters were refined for the Cd, S, P, and Cl atoms. The phenyl ring C atoms were constrained as regular hexagons with d(C–C) = 1.392 Å, and individual isotropic thermal parameters were refined. The H atoms in phenyl rings were placed in ideal calculated positions with d(C–H) = 0.95 Å, and a common thermal parameter was assigned ($U = 0.1200$). Four out of the six isopropyl groups attached to the S atoms were found to be disordered. Two different orientations were seen for the methyl C atoms (occupancies 0.8/0.2) of the groups attached to S(12) and S(24), whereas rotational disorders (by 120°) were observed for the methyl C atoms of the isopropyl groups attached to S(14) (occupancies of 0.666 each) and S(34) (occupancies of 0.5, 0.5, 1.00). All the isopropyl C atoms were restrained to ideal geometry with d(C–C) = 1.542 Å and the C–C–C angle = 109.5°. The O atoms attached to Cl(1) were disordered in a way that can be best described as a rotation about the Cl(1)–O(4) bond axis, resulting in two Cd–O (Cd(1)–O(1) and Cd(1)–O(1a)) bonds with occupancy 0.5/0.5. The atom Cl(2) was found to be disordered also, and the two disordered Cl(2) atoms (occupancy 0.5/0.5) are related by a mirror with three oxygen atoms (including one bonded to Cd(4)) sitting on the mirror. Both the ClO_4^- ions were treated as regular tetrahedra with d(Cl–O) = 1.400 Å. For the disordered methyl groups a common isotropic thermal parameter was assigned and refined in the least-squares cycles. Common isotropic thermal parameters were refined for the oxygen atoms in each ClO_4 group. There was some leftover electron density which was recognized as an ethanol molecule with the support of ^1H NMR data. The ethanol must have come from the 0.75% of this substance that is present as a stabilizer in $CHCl_3$. The solvent molecule was found to be severely disordered also. This disorder was resolved into three components and their isotropic thermal parameters were refined in the least-squares cycles. One bad reflection (026) was omitted in the least-squares refinements. Using 4756 ($I \geq 3\sigma(I)$) observations with weighting scheme of the form $3.3626/(\sigma^2(F) + 0.001231F^2)$, refinement of 394 parameters gave convergence at R_f = 0.0778 and R_w = 0.0884. In a final difference Fourier synthesis, the electron density ranges from 1.37 to −0.92 e·Å^{-3}. The top four peaks have electron density greater than 1.00 e·Å^{-3} and are associated with

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(10) Cadmium-111 and -113 are both spin-$^1/_2$ nuclei. They have similar receptivities; e.g., the receptivities relative to ^{13}C, D^c, are 6.97 and 7.67, respectively.[11]

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Table I. Crystal Data and Experimental Details

compd, fw	$C_{54}H_{72}Cd_4Cl_2O_8P_2S_6 \cdot C_2H_5OH$, 1664.07
cryst system, space group	monoclinic, $P2_1/c$ (No. 14)
cell dimens (Å, deg)	$a = 15.006(2)$, $b = 16.250(2)$, $c = 28.227(3)$, $\beta = 98.79(1)$
temp (°C)	–40(2)
cell volume (Å^3), Z	6802(2), 4
density, g·cm^{-3} (calcd)	1.62(5), 1.625
$F(000)$ (electrons)	3352
diffractometer, monochromator	Enraf-Nonius CAD4F, graphite
radiation, wavelength (Å)	Mo Kα, 0.710 73
abs coeff (cm^{-1})	15.8
no. of observns, variables	4756 ($I \geq 3\sigma(I)$), 394
final model R and R_w	0.0778, 0.0884

Cd(1), O(2a), O(8), and Cl(2a) at distances of 0.89, 0.17, 0.70, and 0.54 Å, respectively. The largest Δ/σ was 0.19. Although the quality of these results is poorer than that of our earlier studies, they serve to fully characterize complex **5a**.

The experimental details and crystal data are given in Table I, and positional and thermal parameters, in Table II. Tables of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, weighted least-squares planes and dihedral angles, and selected torsional angles have been included in the supplementary material.[15]

Elemental Microanalyses. All C and H microanalyses were performed by Guelph Chemical laboratories Ltd.

Results and Discussion

Synthesis. From 1:3:2 mixtures of **1**, Cd(ER)$_2$, and PPh$_3$ in CH$_2$Cl$_2$, compounds of general formula $Cd_4(ER)_6(PPh_3)_n(ClO_4)_2$ can be isolated. When ER = SPh or SePh, $n = 4$, but when ER = SPr^n, $n = 3$, and when ER = SPr^i or SCy, $n = 2$. The compound $Cd_4(SPe^n)_6(PPh_3)_4(ClO_4)_2$ exists in a 1:3:2 mixture (see below), but high solubility precluded the isolation of this or any other compound of the type $Cd_4(S\text{-alk})_6(PPh_3)_4(ClO_4)_2$. The bis(phosphine) compounds with ER = SPr^i or SCy, $n = 2$, were isolated from 1:3:0 mixtures also. NMR data and an X-ray analysis of the ethanol solvate of **5** (see below) show the occurrence of the $Cd_4(\mu\text{-}ER)_6$ core in these complexes, and the structure of **5** shows that each cadmium is four-coordinate in this compound. Further, ^{111}Cd NMR data suggest that coordination of ClO$_4^-$ is general if $n < 4$. Therefore all the products are probably best formulated as $[(\mu\text{-}ER)_6(CdPPh_3)_n(CdOClO_3)_{4-n}](ClO_4)_{n-2}$. To date mercury(II) analogues are known only for the complexes with $n = 4$.[1] The salts $[(\mu\text{-}EPh)_6(HgPPh_3)_4](ClO_4)_2$ (E = S, Se) have been isolated. (In addition, there is evidence for $[(\mu\text{-}SR)_6(HgPPh_3)_4]^{2+}$ (R = Pr^n and Cy, but not Pr^i) in solution.[1] This result was confirmed during the current work.)

NMR Spectra. (i) Complexes $[Cd(PPh_3)_n]^{2+}$ (n = 2–4) and $[Cd(PPh_3)_n(OPPh_3)_{4-n}]^{2+}$ (n = 2, 3). The mononuclear complexes $[Cd(PPh_3)_n]^{2+}$ are formed in some of the mixtures discussed below. However their $^{111/113}$Cd NMR spectra have not been described, although ^{31}P NMR data are available.[9a] Our ^{31}P NMR results are in agreement with the earlier study:[9a] $Cd(PPh_3)_2(ClO_4)_2$ is converted completely into $[Cd(PPh_3)_3]^{2+}$ by addition of 1 mol equiv of PPh$_3$, though results for the synthesis of $Cd(PPh_3)_2(ClO_4)_2$ (see Experimental Section) show that $[Cd(PPh_3)_3]^{2+}$ must dissociate in solution. An excess of PPh$_3$ is required to convert the majority of $[Cd(PPh_3)_3]^{2+}$ into $[Cd(PPh_3)_4]^{2+}$. As expected, the slow-exchange ^{111}Cd NMR spectra of $[Cd(PPh_3)_n]^{2+}$ that are observed at reduced temperature consist of a triplet, quartet, and pentet for n = 2, 3, and 4, respectively, as a result of one-bond coupling to ^{31}P. NMR data for the PPh$_3$ complexes are given in Table III. For these 1:n complexes, $\delta_{Cd}(1{:}2) < \delta_{Cd}(1{:}3) < \delta_{Cd}(1{:}4)$. A series of the type $[Cd(PR_3)_n]^{2+}$ (n = 2–4) does not seem to have been studied previously by $^{111/113}$Cd NMR,[16] but the same pattern has been observed for $[Cd(SP\{2\text{-}C_6H_4\text{-}Me\}_3)_n]^{2+}$.[17]

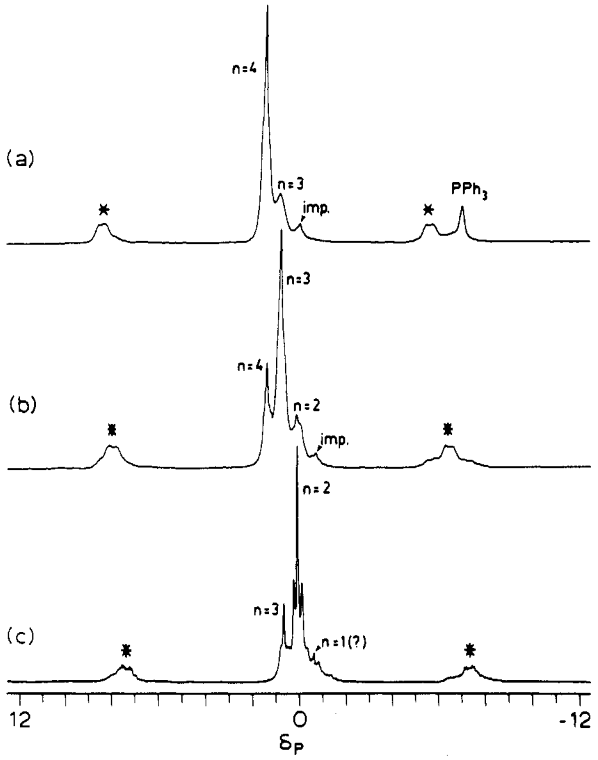

Figure 1. 80.98-MHz ^{31}P NMR spectra of **1**:Cd(SPri)$_2$:PPh$_3$ mixtures in CH$_2$Cl$_2$ at 213 K, showing the formation of $[(\mu\text{-}SPr^i)_6(CdPPh_3)_n(Cd)_{4-n}]^{2+}$. **1**:Cd(SPr$i$)$_2$:PPh$_3$ = (a) 1:3:2, (b) 1:3:1, and (c) 1:3:0. Starred signals are $^{111/113}$Cd satellites.

In some of the mixtures described below, trace amounts of ternary Cd(II):PPh$_3$:OPPh$_3$ complexes appear to be formed, presumably as a result of adventitious O$_2$.[18] The identity of these species was confirmed by the ^{31}P and ^{111}Cd NMR of a 1:2 mixture of **1** and OPPh$_3$ in CH$_2$Cl$_2$. The major ternary complexes present in the mixture are $[Cd(PPh_3)_3(OPPh_3)]^{2+}$ and $[Cd(PPh_3)_2(OPPh_3)_2]^{2+}$ (in the approximate ratio 8:7), both readily identified by their first-order NMR spectra, Table III. The mixture contains no other PPh$_3$, free or coordinated, but the formation of binary Cd^{2+}:OPPh$_3$ is indicated by resonances in the region 32–39 ppm, deshielded relative to the signal of free OPPh$_3$ ($\delta_P(OPPh_3)$ = 28.5), as expected from earlier work.[19]

In comparing NMR data for $[Cd(PPh_3)_n]^{2+}$ and $[Cd(PPh_3)_n(OPPh_3)_{4-n}]^{2+}$ it is particularly interesting to note that for the series of $[Cd(PPh_3)_4]^{2+}$, $[Cd(PPh_3)_3(OPPh_3)]^{2+}$, and $[Cd(PPh_3)_2(OPPh_3)_2]^{2+}$, the value of $^1J(^{31}P\text{–}^{111}Cd)$ decreases as the ratio of PPh$_3$:OPPh$_3$ in the complexes increases. Thus ^1J may be used as an indication of the ratio of soft:hard donors in the complexes. In addition, it can be seen that ^1J is similar for $[Cd(PPh_3)_2]^{2+}$ and $[Cd(PPh_3)_2(OPPh_3)_2]^{2+}$ and for $[Cd(PPh_3)_3]^{2+}$ and $[Cd(PPh_3)_3(OPPh_3)]^{2+}$. A plausible explanation for this observation is that the PPh$_3$ complexes should be formulated $[Cd(PPh_3)_2(OClO_3)_2]$ and $[Cd(PPh_3)_3(OClO_3)]^+$.

(ii) Systems 1:Cd(SR)$_2$:PPh$_3$ (R = Pr^i, Cy). The behavior of these two systems is identical in its most important details and is typified by that of the Pr^{i}S$^-$ complexes. Figures 1 and 2 show ^{31}P and ^{113}Cd NMR spectra for 1:3:x mixtures in CH$_2$Cl$_2$ at 213 K. These spectra are broader and more poorly resolved at ambient probe temperature. When x = 2, the ^{31}P NMR spectrum of the major species consists of a central resonance with shoulders and a $^{111/113}$Cd satellite splitting, $^1J(^{31}P\text{–}^{111/113}Cd)_{av} \approx 1143$ Hz (Figure

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(15) Supplementary material.

(16) ^{113}Cd NMR data are available for $[Cd(PBu_3)_n]^{2+}$ (n = 1–3): Dakternieks, D.; Rolls, C. L. *Inorg. Chim. Acta* **1985**, *105*, 213.

(17) Dean, P. A. W. *Can. J. Chem.* **1981**, *59*, 3221.

(18) Mixed complexes of the formula CdX$_2$(PCy$_3$)(OPCy$_3$) (X = Cl–I) have been described earlier: Goel, R. G.; Henry, W. P.; Jha, N. K. *Inorg. Chem.* **1982**, *21*, 2551.

(19) Dean, P. A. W.; Carson, G. K. *Can. J. Chem.* **1982**, *61*, 1800 and references therein.

Table II. Atomic Positional and Thermal Parameters (Å^2) for $[(\mu\text{-SPr}^i)_6(\text{CdPPh}_3)_2(\text{CdOClO}_3)_2]\cdot\text{EtOH}$

atom[a]	*x*	*y*	*z*	B_{iso}	atom[a]	*x*	*y*	*z*	B_{iso}
Cd(1)	0.67008(9)	0.27714(9)	0.11209(6)	5.76(8)	O(7)	0.7847(17)	0.3259(16)	−0.1410(8)	25.1(8)
Cd(2)	0.93831(8)	0.19682(9)	0.13390(5)	4.73(6)	O(8)	0.8253(22)	0.1910(18)	−0.1366(12)	25.1(8)
Cd(3)	0.74476(10)	0.04912(8)	0.08442(5)	5.30(7)	O(8a)	0.7251(26)	0.3618(20)	−0.0747(15)	25.1(8)
Cd(4)	0.79199(10)	0.22699(11)	0.00472(6)	6.56(8)	C(111)	0.4428(9)	0.3629(7)	0.1101(5)	4.3(4)
P(1)	0.5496(3)	0.3662(3)	0.1483(2)	4.9(2)	C(112)	0.4147(9)	0.2873(7)	0.0899(5)	6.5(5)
P(2)	1.0864(3)	0.2135(3)	0.1978(2)	4.3(2)	C(113)	0.3361(9)	0.2823(7)	0.0566(5)	8.8(6)
S(12)	0.8212(3)	0.2860(3)	0.1652(2)	6.1(3)	C(114)	0.2857(9)	0.3530(7)	0.0435(5)	9.9(7)
S(13)	0.6178(3)	0.1293(3)	0.1106(2)	6.1(3)	C(115)	0.3138(9)	0.4287(7)	0.0637(5)	9.7(7)
S(14)	0.6901(4)	0.3310(4)	0.0300(2)	7.5(3)	C(116)	0.3924(9)	0.4336(7)	0.0970(5)	7.5(6)
S(23)	0.8857(3)	0.0518(3)	0.1448(2)	5.7(2)	C(121)	0.5833(8)	0.4730(7)	0.1530(4)	4.7(4)
S(24)	0.9489(3)	0.2511(3)	0.0514(2)	5.7(2)	C(122)	0.6218(8)	0.5076(7)	0.1158(4)	5.1(4)
S(34)	0.7668(4)	0.0748(4)	−0.0002(2)	6.5(3)	C(123)	0.6449(8)	0.5908(7)	0.1172(4)	5.9(4)
C(12)	0.8464(14)	0.3933(16)	0.1653(7)	12.4(20)	C(124)	0.6294(8)	0.6393(7)	0.1558(4)	8.1(6)
C(13)	0.5995(13)	0.1082(10)	0.1725(8)	9.5(16)	C(125)	0.5909(8)	0.6047(7)	0.1929(4)	9.0(7)
C(14)	0.5810(11)	0.3248(12)	−0.0102(6)	11.9(19)	C(126)	0.5678(8)	0.5215(7)	0.1916(4)	8.4(6)
C(23)	0.9706(19)	−0.0131(9)	0.1273(6)	10.4(16)	C(131)	0.5294(8)	0.3380(8)	0.2068(5)	5.8(4)
C(24)	1.0220(11)	0.1860(14)	0.0191(6)	7.7(13)	C(132)	0.4442(8)	0.3379(8)	0.2207(5)	5.9(5)
C(34)	0.6569(10)	0.0511(10)	−0.0375(5)	7.8(13)	C(133)	0.4355(8)	0.3242(8)	0.2684(5)	8.5(6)
C(12a)	0.8730(23)	0.4236(14)	0.1184(8)	10.6(3)	C(134)	0.5120(8)	0.3105(8)	0.3023(5)	9.5(7)
C(12b)	0.9141(21)	0.4200(13)	0.2083(8)	10.6(3)	C(135)	0.5972(8)	0.3106(8)	0.2883(5)	10.7(8)
C(12c)	0.9403(38)	0.4101(19)	0.1522(40)	10.6(3)	C(136)	0.6059(8)	0.3244(8)	0.2406(5)	8.1(6)
C(12d)	0.8378(76)	0.4340(22)	0.2134(20)	10.6(3)	C(211)	1.1285(10)	0.3171(10)	0.1979(4)	4.8(4)
C(13a)	0.6869(14)	0.1235(14)	0.2069(4)	9.0(7)	C(212)	1.1601(10)	0.3589(10)	0.2402(4)	8.8(6)
C(13b)	0.5689(16)	0.0187(11)	0.1760(6)	9.9(7)	C(213)	1.1934(10)	0.4387(10)	0.2385(4)	11.7(9)
C(14a)	0.5275(13)	0.4042(15)	−0.0052(10)	10.6(3)	C(214)	1.1952(10)	0.4768(10)	0.1945(4)	8.2(6)
C(14b)	0.5280(13)	0.2503(16)	0.0037(11)	10.6(3)	C(215)	1.1636(10)	0.4351(10)	0.1522(4)	7.6(6)
C(14c)	0.5986(16)	0.3158(22)	−0.0621(4)	10.6(3)	C(216)	1.1302(10)	0.3552(10)	0.1539(4)	6.8(5)
C(23a)	0.9734(15)	−0.0972(9)	0.1526(8)	9.4(7)	C(221)	1.0664(6)	0.1921(8)	0.2576(5)	4.5(4)
C(23b)	0.9604(17)	−0.0243(14)	0.0729(6)	10.9(8)	C(222)	1.1366(6)	0.1821(8)	0.2956(5)	6.4(5)
C(24a)	1.1074(13)	0.1640(19)	0.0543(8)	10.6(3)	C(223)	1.1174(6)	0.1680(8)	0.3416(5)	7.2(5)
C(24b)	1.0484(17)	0.2381(17)	−0.0224(7)	10.6(3)	C(224)	1.0281(6)	0.1638(8)	0.3496(5)	7.7(6)
C(24c)	1.1149(25)	0.1789(59)	0.0508(22)	10.6(3)	C(225)	0.9580(6)	0.1738(8)	0.3116(5)	7.6(6)
C(24d)	0.9787(43)	0.1000(25)	0.0123(39)	10.6(3)	C(226)	0.9771(6)	0.1879(8)	0.2656(5)	6.5(5)
C(34a)	0.6497(13)	−0.0428(10)	−0.0440(9)	10.6(3)	C(231)	1.1805(8)	0.1475(8)	0.1911(5)	4.5(4)
C(34b)	0.5810(8)	0.0823(19)	−0.0117(11)	10.6(3)	C(232)	1.1702(8)	0.0640(8)	0.2002(5)	7.0(5)
C(34c)	0.6533(19)	0.0936(18)	−0.0860(7)	10.6(3)	C(233)	1.2388(8)	0.0088(8)	0.1943(5)	8.0(6)
Cl(1)	0.6890(4)	−0.1521(3)	0.0953(2)	7.4(3)	C(234)	1.3176(8)	0.0370(8)	0.1794(5)	7.6(6)
O(1)	0.6652(15)	−0.0729(7)	0.0792(6)	8.0(6)	C(235)	1.3279(8)	0.1205(8)	0.1703(5)	6.9(5)
O(2)	0.6103(11)	−0.2014(13)	0.0885(7)	11.1(4)	C(236)	1.2594(8)	0.1758(8)	0.1762(5)	6.7(5)
O(3)	0.7516(12)	−0.1860(15)	0.0691(6)	11.1(4)	O(9)	0.9058(23)	0.0615(22)	0.4621(15)	8.1(11)
O(4)	0.7233(9)	−0.1515(9)	0.1439(3)	11.1(4)	C(1)	0.9524(26)	0.0039(21)	0.4557(20)	4.7(15)
O(1a)	0.7370(18)	−0.0951(16)	0.0713(7)	8.8(10)	C(2)	1.0508(23)	0.0337(35)	0.4589(23)	7.9(15)
O(2a)	0.6973(23)	−0.2301(9)	0.0761(7)	11.1(4)	O(9a)	1.0665(58)	0.0642(39)	0.4908(30)	11.2(30)
O(3a)	0.5979(9)	−0.1288(22)	0.0889(8)	11.1(4)	C(1a)	0.8991(21)	−0.0004(25)	0.4955(10)	8.6(11)
Cl(2)	0.7879(7)	0.2552(10)	−0.1132(4)	14.6(15)	C(2a)	0.9440(25)	0.0337(30)	0.4544(13)	3.3(8)
Cl(2a)	0.7635(11)	0.2977(11)	−0.0982(7)	26.6(32)	O(9b)	1.1268(23)	0.0274(23)	0.4695(11)	5.2(9)
O(5)	0.8386(11)	0.2670(19)	−0.0677(3)	25.1(8)	C(2b)	0.9965(27)	0.0308(42)	0.5090(24)	8.0(20)
O(6)	0.7001(10)	0.2331(17)	−0.1064(9)	25.1(8)					

[a] C atoms in phenyl rings bonded to P(1) are numbered C(111)–C(116), C(121)–C(126), and C(131)–C(136); C atoms in the isopropyl group bonded to S(14) are numbered C(14), C(14a), C(14b), C(14c), and so forth.

Table III. ^{31}P and ^{111}Cd NMR Data for Mononuclear Complexes of Cadmium in CH_2Cl_2[a]

complex	$\delta_P(PPh_3)$[b]	$\delta_P(OPPh_3)$[b]	δ_{Cd}[c]	$^1J(^{31}P–^{111}Cd)$[d] (Hz)	$^2J(P^{31}–Cd)$[e] (Hz)	$^3J(^{31}P–^{31}P)$[f] (Hz)
$[Cd(PPh_3)_2]^{2+}$ [g]	10.7		249	2195		
$[Cd(PPh_3)_3]^{2+}$ [g]	10.1		431	1503		
$[Cd(PPh_3)_4]^{2+}$ [g]	10.3		467[h]	1106		
$[Cd(PPh_3)_2(OPPh_3)_2]^{2+}$ [i]	8.8	43.5	375	2013	23[j]	5[j]
$[Cd(PPh_3)_3(OPPh_3)]^{2+}$ [i]	8.4	44.2	465	1470	50	5

[a] At 213 K for solutions with a cadmium concentration of 0.05 mol/L of solvent at ambient temperature, except as noted. [b] Relative to external 85% H_3PO_4; reproducibility better than ±0.1 ppm. [c] Relative to external 0.1 M $Cd(ClO_4)_2$ (aq); reproducibility better than ±1 ppm. [d] Estimated error ±5 Hz. [e] Average coupling; separate couplings to ^{111}Cd and ^{113}Cd were not resolved. Estimated error ±2 Hz. [f] Estimated error ±1 Hz. [g] ^{31}P NMR data for $[Cd(PPh_3)_n]^{2+}$ ($n = 2–4$) have been reported earlier.[9a] [h] In a solution where **1**:PPh_3 = 1:6. [i] In a mixture where **1**:$OPPh_3$ = 1:2 and the cadmium concentration is 0.10 mol/L of solvent at ambient probe temperature. Cd^{2+}:$OPPh_3$ complexes are formed also. [j] At 183 K; this coupling is not observed at 213 K.

1a). The corresponding feature in the ^{113}Cd NMR spectrum is a doublet with $^1J(^{31}P–^{113}Cd) = 1164 \pm 5$ Hz (Figure 2a). Evidently each Cd has one attached PPh_3. Further, δ_{Cd} is similar to that of the CdS_3Cl kernel in $[(\mu\text{-SPr}^i)_6(CdCl)_4]^{2-}$ (602 ppm at 217 K in CH_2Cl_2[5b]) indicating a kernel CdS_3P in the phosphine complex. Consistent with four-coordinate cadmium, the magnitude of ^1J is similar to that for $[Cd(PPh_3)_4]^{2+}$ (Table III). These results can be interpreted in terms of the formation of $[(\mu\text{-SPr}^i)_6(CdPPh_3)_4]^{2+}$ ($\mathbf{I}_{SPr^i}$) with the adamantanoid skeleton I (E = S) (Chart I). The complete analysis of the spectrum is analogous to that given earlier[1] for $[(\mu\text{-ER})_6(HgPR'_3)_4]^{2+}$. (The couplings $^3J(^{31}P–^{111/113}Cd)$ and $^4J(^{31}P–^{31}P)$ are better resolved when $CHCl_3$ is used as solvent, but use of this solvent changes the results for $Cd(PPh_3)_2(ClO_4)_2$:$Cd(SR)_2$ mixtures (see below).)

The 1:3:2 mixture contains free PPh_3 (Figure 1a), making it clear that $\mathbf{I}_{SPr^i}$ is appreciably dissociated, consistent with the isolation of a bis(phosphine) complex from such a solution (see Experimental Section). Adjacent to the centerband resonance

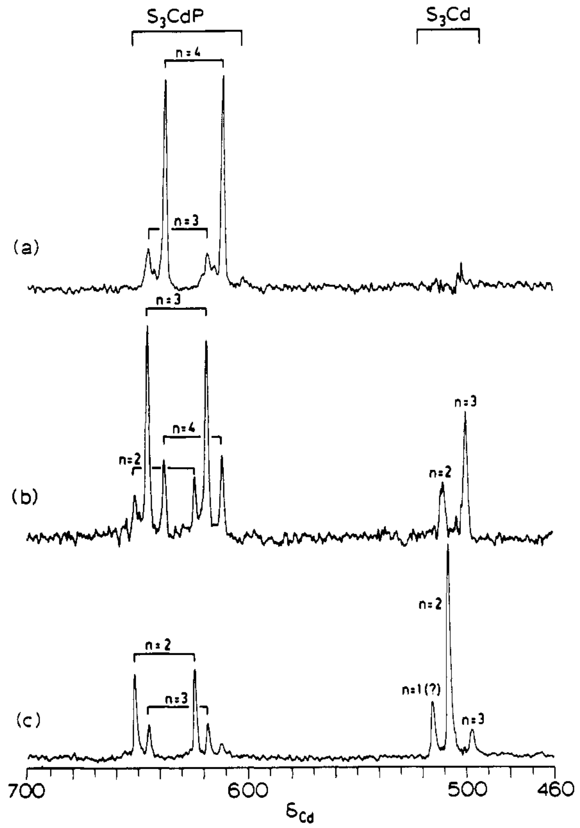
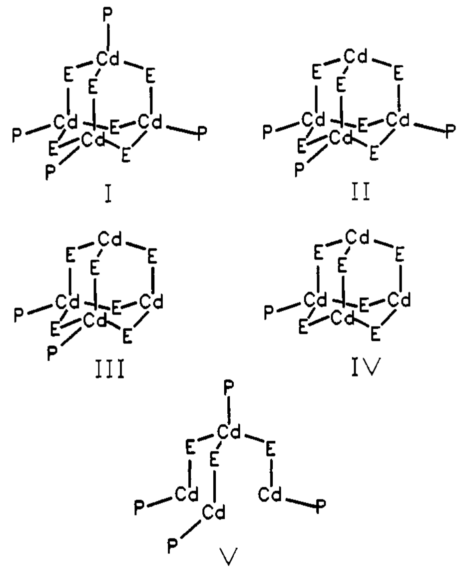


Figure 2. 44.37-MHz ^{113}Cd NMR spectra of 1:Cd(SPr*i*)$_2$:PPh$_3$ mixtures in CH$_2$Cl$_2$ at 213 K, showing the formation of $[(\mu\text{-SPr}^i)_6(\text{CdPPh}_3)_n(\text{Cd})_{4-n}]^{2+}$. 1:Cd(SPr*i*)$_2$:PPh$_3$ = (a) 1:3:2, (b) 1:3:1, and (c) 1:3:0.

Chart I



of I$_{\text{SPr}^i}$ in the ^{31}P NMR spectrum is a second resonance, which becomes major when $x = 1$ (Figure 1b). Again this resonance has shoulders and $^{111/113}$Cd satellites. The ^{113}Cd NMR spectrum of the new species consists of a doublet, in the same region as that of I$_{\text{SPr}^i}$, and a singlet that is more shielded. We interpret this spectrum in terms of $[(\mu\text{-SPr}^i)_6(\text{CdPPh}_3)_3(\text{Cd})]^{2+}$ (**II**$_{\text{SPr}^i}$), with the skeleton **II**. The singlet in the ^{113}Cd NMR spectrum can be assigned to the PPh$_3$-free site. For this cadmium, δ_{Cd} is smaller than values found for planar three-coordinate Cd in Cd(SR)$_3^-$ (δ_{Cd} = 577–568[20]). It is possible that the cadmium is three-coordinate but *pyramidal* in order to fit into the adamantanoid skeleton, but another possibility is that ClO$_4^-$ is coordinated at this site. Support for equilibrium coordination of ClO$_4^-$ (eq 1)

$$\text{S}_3\text{Cd} + \text{ClO}_4^- \rightleftarrows \text{S}_3\text{CdOClO}_3^- \qquad (1)$$

comes from the relatively large composition dependence of δ_{Cd} for the PPh$_3$-free site (several ppm) compared with that for the site with bound PPh$_3$ (≤1 ppm), as well as from the structure of $[(\mu\text{-SPr}^i)_6(\text{CdPPh}_3)_2(\text{CdOClO}_3)_2]$ given below. In the discussion of solution studies further, coordination of ClO$_4^-$ at sites of this type will be assumed but not included specifically.

Table IV. ^{31}P and $^{111/113}$Cd NMR Data for $[(\mu\text{-ER})_6(\text{Cd}_A\text{PPh}_3)_n(\text{Cd}_B)_{4-n}]^{2+}$.[a]

ER	n	δ_P[b]	δ_{Cd_A}[c]	δ_{Cd_B}[c,d]	^1J-(^{31}P–^{111}Cd)[e] (Hz)	^3J-(^{31}P–Cd)[f] (Hz)	^4J-(^{31}P–^{31}P)[g] (Hz)
SPr^i	1?[h]	–0.7	*i*	514	*i*	≈30[h,j]	*i*
	2	0.0	636	507	1164	29[j]	*i*
	3	0.7	631	499	1141	21,[j,k] 23[k,l]	6[k]
	4	0.9	623		1117	20[k,l]	6[k]
SCy	2	–2.0	637	510	1134	28[j]	*i*
	3	–1.0	630	504	1115	*i*	*i*
	4	–0.7	621		1094	20[l]	6
SPh	1?[h]	9.7	*i*	*i*	*i*	27[j]	*i*
	2?[h]	8.8	*i*	*i*	*i*	27[j]	*i*
	3	8.0	604	450	1503	≈23,[j] 15[l]	5
	4	7.4	597		1514	16[l]	5
SePh	2?[h]	7.0	*i*	*i*	*i*	*i*	*i*
	3	5.6	577	508	1236	23,[j] 23[l]	*i*
	4[m]	4.3	568		1260	19[l]	7
SPr^n	2?[h]	*i*	662	522	≈1200	*o*	*i*
	3	–1.8	657	517	1168	16[l,n,p]	7[k]
	4	–1.7	651		1154	18[l,n]	7[n]
SPe^n [q]	3	–2.4	658	516	1157	*i*	*i*
	4	–2.0	652		1136	18[l]	6

[a] In CH$_2$Cl$_2$ at 213 K except as noted. Constituents were mixed to give a Cd$_4$ concentration of 0.05 mol/L of solvent at ambient temperature. [b] Reproducibility ±0.1 ppm or better. [c] From ^{113}Cd NMR spectrum for E = SPr^i, ^{111}Cd NMR spectra in all other cases (see Experimental Section); reproducibility ±1 ppm or better. [d] These resonances show significant composition dependence. Typical values are shown. [e] Estimated error ±5 Hz. [f] Average coupling; separate couplings to ^{113}Cd and ^{111}Cd were not resolved. Estimated error ±2 Hz. [g] Estimated error ±1 Hz. [h] Tentative assignment. [i] Not observed. [j] $^3J(^{31}\text{P–Cd}_B)$. [k] In CHCl$_3$ at 213 K. [l] $^3J(^{31}\text{P–Cd}_A)$. [m] $\delta_{Se} = -96.8 \pm 0.2$; $^1J(^{77}\text{Se–Cd})_{av} = 142 \pm 2$ Hz; $^2J(^{31}\text{P–}^{77}\text{Se}) = 27 \pm 1$ Hz. [n] At 193 K. [o] Could not be measured with certainty. [p] From the ^{111}Cd NMR spectrum. $^3J(^{31}\text{P–Cd}_B)$ could not be measured with certainty. [q] Pe^n = n-C$_5$H$_{11}$.

Figures 1b and 2b show that **II**$_{\text{SPr}^i}$ is in equilibrium with **I**$_{\text{SPr}^i}$ and a third species. The latter becomes major at 1:3:0 (Figures 1c and 2c). Its ^{31}P NMR spectrum (Figure 1c) shows the same general pattern as for **I**$_{\text{SPr}^i}$ and **II**$_{\text{SPr}^i}$, and like **II**$_{\text{SPr}^i}$ its ^{113}Cd NMR spectrum (Figure 2c) shows signals in two regions, but this time the more shielded signal is relatively more intense. Pure **5** gives identical spectra. The spectra are assigned to $[(\mu\text{-SPr}^i)_6(\text{CdPPh}_3)_2(\text{Cd})_2]^{2+}$ (**III**$_{\text{SPr}^i}$), with skeleton **III**.

Spectrum 1c shows that **III**$_{\text{SPr}^i}$ is in equilibrium with **II**$_{\text{SPr}^i}$. As indicated in the figure, an additional weak resonance is also seen. This is most probably due to $[(\mu\text{-SPr}^i)_6(\text{CdPPh}_3)(\text{Cd})_3]^{2+}$ (**IV**$_{\text{SPr}^i}$) of structure **IV**, but it is not the major component of any solution and its complete ^{113}Cd NMR spectrum could not be observed, so this assignment is tentative.

Details of the NMR spectra of $[(\mu\text{-SPr}^i)_6(\text{CdPPh}_3)_n(\text{Cd})_{4-n}]^{2+}$ are included in Table IV. In these tetranuclear species, two-bond Cd–Cd nuclear spin–spin coupling is possible (see, for example ref 4 and references therein), but it has not been observed by either ^{31}P or ^{111}Cd NMR. The ^2J(Cd–Cd) coupling is expected[4] to be 1 order of magnitude smaller than $^2J(^{199}\text{Hg–}^{199}\text{Hg})$, which was measured[1] for $[(\mu\text{-SR})_6(\text{HgPR}'_3)_4]^{2+}$.

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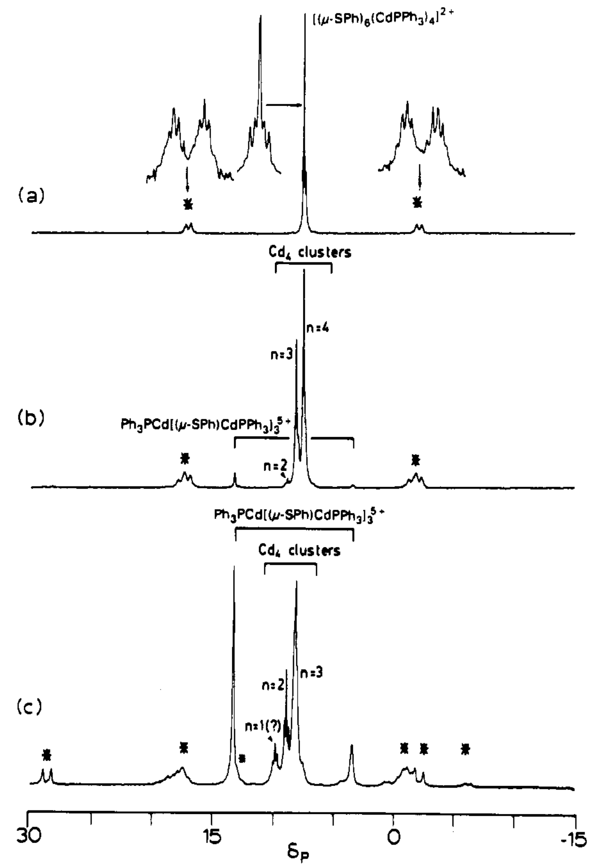

Figure 3. 80.98-MHz ^{31}P NMR spectra of the supernatant liquid from **1**:$Cd(SPh)_2$:PPh_3 mixtures in CH_2Cl_2 at 213 K, showing the formation of $[(\mu\text{-}SPh)_6(CdPPh_3)_n(Cd)_{4-n}]^{2+}$ and $[PPh_3Cd(\{\mu\text{-}SPh\}CdPPh_3)_3]^{5+}$. **1**:$Cd(SPh)_2$:$PPh_3$ = (a) 1:3:2 (isolated solid), (b) 1:3:1, and (c) 1:3:0. Starred signals are $^{111/113}Cd$ satellites.

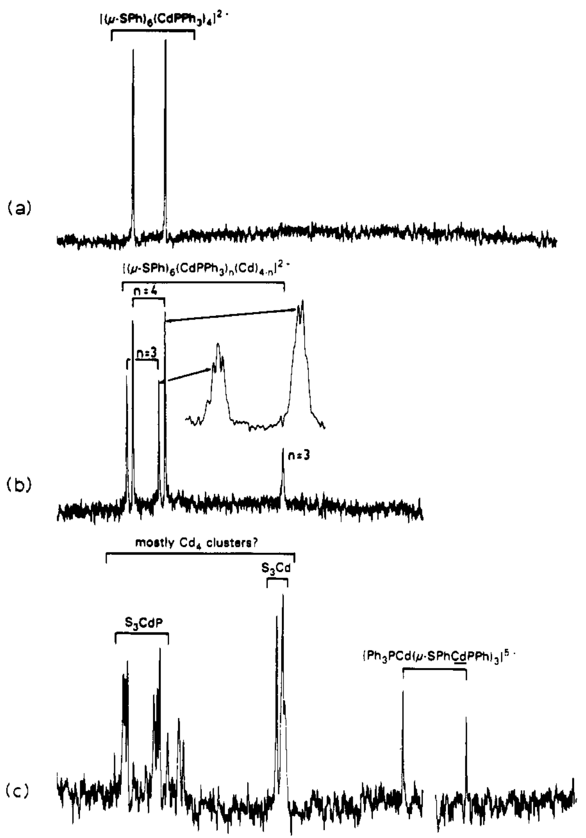

Figure 4. 42.41-MHz ^{111}Cd NMR spectra of the supernatant liquid from **1**:$Cd(SPh)_2$:PPh_3 mixtures in CH_2Cl_2 at 213 K, showing the formation of $[(\mu\text{-}SPh)_6(CdPPh_3)_n(Cd)_{4-n}]^{2+}$ and $[Ph_3PCd(\{\mu\text{-}SPh\}\text{-}CdPPh_3)_3]^{5+}$. **1**:$Cd(SPh)_2$:$PPh_3$ = (a) 1:3:2 (isolated solid), (b) 1:3:1, and (c) 1:3:0.

When the **1**:$Cd(SPr^i)_2$ = 1:<3 in CH_2Cl_2, complicated ^{31}P and ^{111}Cd NMR spectra are observed.[15] At a 1:1 ratio, the complexes present in the equilibrium mixture include $[(\mu\text{-}SPr^i)_6(CdPPh_3)_n(Cd)_{4-n}]^{2+}$ (n = 2 and possibly 1), $Cd(PPh_3)_2^{2+}$, $Cd(PPh_3)_3^{2+}$, and two additional species. Of these latter two, that giving the weaker ^{31}P resonance has $\delta_P = 9.0$ (singlet) and $^1J(^{31}P\text{-}^{111}Cd) = 2162 \pm 5$ Hz. Comparison with the ^1J coupling in $[Cd(PPh_3)_2]^{2+}$ and $[Cd(PPh_3)_2(OPPh_3)_2]^{2+}$ (Table III) shows that it must have two soft donor atoms attached to Cd and hence may be $[Pr^iSCdPPh_3]^+$. Unfortunately, no metal resonance could be observed. The second species has $\delta_P = 5.8$(singlet), $^1J(^{31}P\text{-}^{111}Cd) = 1728 \pm 5$ Hz, and $\delta_{Cd} = 461$ (doublet). Comparison of ^1J with values in Table I puts it closest to those of $[Cd(PPh_3)_3]^{2+}$ and $[(Cd(PPh_3)_3(OPPh_3)]^{2+}$, suggesting that the species has three soft donor atoms. Accordingly, it is tentatively characterized as $[(\mu\text{-}SPr^i)CdPPh_3]_m^{m+}$. For $m = 3$, this type of complex is a possible precursor to the adamantanoid complexes. It is interesting that 1:1 mixtures of **1** and $Cd(SPr^i)_2$ in $CHCl_3$ do not contain appreciable amounts of $[Pr^iSCdPPh_3]^+$ or $[(\mu\text{-}SPr^i)\text{-}CdPPh_3]_m^{m+}$ but instead contain mainly Cd_4 clusters and $Cd(PPh_3)_3^{2+}$.[15]

NMR spectroscopic data for $[(\mu\text{-}SCy)_6(CdPPh_3)_n(Cd)_{4-n}]^{2+}$ are given in Table IV. In this system we could observe no analogue of the proposed $[Pr^iSCdPPh_3]^+$. However, for the proposed $[CySCdPPh_3]_m^{m+}$, $\delta_P = 5.3$ (singlet), $^1J(^{31}P\text{-}^{113}) = 1720 \pm 5$ Hz, and $\delta_{Cd} = 471$ (doublet).

(iii) Systems 1:Cd(EPh)₂:PPh₃ (E = S, Se). Both ^{31}P and ^{111}Cd NMR spectra of **1**:$Cd(SPh)_2$:PPh_3 in the range 1:3:x ($0 \leq x \leq 2$) in CH_2Cl_2 (Figures 3 and 4) show that the only adamantanoid species that occur in significant amounts are $[(\mu\text{-}SPh)_6(CdPPh_3)_{3,4}(Cd)_{1,0}]^{2+}$ ($\mathbf{I}_{SPh}$ and $\mathbf{II}_{SPh}$, with skeletons **I** and **II**). Both ^{31}P and ^{111}Cd NMR spectra of these two complexes are particularly well-resolved. The spectra are assigned, interpreted, and analyzed in the same way as their SPr^{i-} and SCy^- analogues. The spectra of $[(\mu\text{-}SPh)_6(CdPPh_3)_4]^{2+}$ are the same for both isolated **3** and 1:3:2 mixtures.

Even at the ratio 1:3:0, ^{31}P and ^{111}Cd NMR spectra show that the major adamantanoid species is $[(\mu\text{-}SPh)_6(CdPPh_3)_3(Cd)]^{2+}$ (Figures 3c and 4c). The complex $[(\mu\text{-}SPh)_6(CdPPh_3)_2(Cd)_2]^{2+}$ is present in minor amount, while only tentative identification of $[(\mu\text{-}SPh)_6(CdPPh_3)_1(Cd)_3]^{2+}$ is possible. Details of the NMR spectra of $[(\mu\text{-}SPh)_6(CdPPh_3)_n(Cd)_{4-n}]^{2+}$ are given in Table IV.

At the 1:3:0 ratio both ^{31}P and ^{111}Cd NMR spectra show the presence of a new complex that is evidently not adamantane-like. A study of **1**:$Cd(SPh)_2$ mixtures shows that this new species is the only one observable by ^{31}P and ^{111}Cd NMR at **1**:$Cd(SPh)_2$ = 1:1. At this ratio the ^{31}P spectrum consists of two resonances, a doublet and a quartet, with a common coupling $J(^{31}P\text{-}^{31}P) = 4 \pm 1$ Hz. The doublet:quartet intensity ratio is 3:1, and both centerbands have satellite spectra from both long- and short-range coupling to $^{111/113}Cd$ (Figure 5a). Let the doublet and quartet be assigned to P_A and P_B, respectively. The ^{111}Cd NMR spectrum of the 1:1 mixture consists of two doublets (Figure 5b), the more shielded being the more intense.[21] The splitting patterns show that the two different types of cadmium each have only one PPh_3 attached. From the values of ^1J, the more shielded doublet may be assigned to the Cd, Cd_A, associated with the doublet in the ^{31}P NMR spectrum and the less shielded to that, Cd_B, associated with the quartet.

When compared with the data in Table III, the combination of $^1J(^{31}P\text{-}^{111}Cd_A)$, 2443 ± 5 Hz, and $\delta_{Cd}(Cd_A)$, 290 ppm, shows

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[21] Presumably RF saturation prevents this ratio from having the expected value of 3.

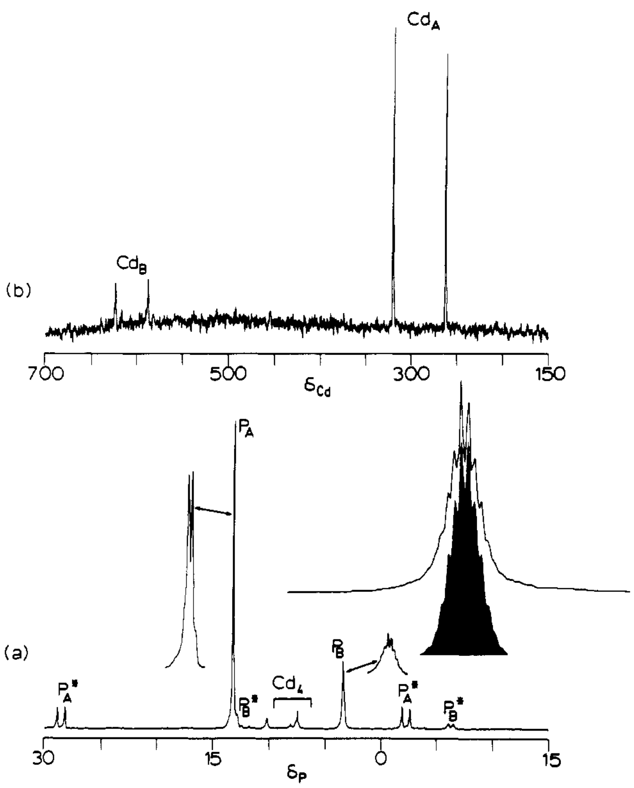

Figure 5. NMR spectra of a mixture containing **1**:Cd(SPh)$_2$ = 1:1 in CH$_2$Cl$_2$ at 213 K, showing the formation of [Ph$_3$P$_B$Cd$_B$({μ-SPh}-Cd$_A$P$_A$Ph$_3$)$_3$]$^{5+}$: (a) 80.98-MHz ^{31}P NMR spectrum with simulation inset (starred signals $^{111/113}$Cd satellites), (b) 42.41-MHz ^{111}Cd NMR spectrum.

that Cd$_A$ must have two soft donors attached. Since one is PPh$_3$, the other must be SPh$^-$. On the other hand, $^1J(^{31}$P–^{111}Cd$_B$) and δ_{Cd}(Cd$_B$), 1531 ± 1 Hz and 604 ppm, are remarkably similar to values for the four-coordinate cadmiums in [(μ-SPh)$_6$(CdPPh$_3$)$_n$(Cd)]$_{4-n}$]$^{2+}$ (Table IV), indicating a Cd$_B$S$_3$P$_B$ core. Data for other [(μ-ER)$_6$(CdPPh$_3$)$_n$(Cd)]$_{4-n}$]$^{2+}$ compounds (Table IV) lend weight to this assignment.

The ^{31}P and ^{111}Cd NMR data for the new complex are consistent with the skeleton V (E = S) and the full formulation [Ph$_3$P$_B$-Cd$_B$({μ-SPh}Cd$_A$P$_A$Ph$_3$)$_3$]$^{5+}$ (V$_{SPh}$). NMR data for V$_{SPh}$ and related species are given in Table V. The simulated ^{31}P centerband resonance of P$_B$ is inset in Figure 5a; the form of this resonance is particularly sensitive to the stoichiometry of the species and the value of $^3J(^{31}$P$_B$–$^{111/113}$Cd$_A$). Species like V$_{SPh}$ do not seem to have been described previously. It is tempting to speculate that such open species are another type of precursor to the adamantane-like cage system.

The complex V$_{SPh}$ is not formed when CHCl$_3$ (containing ca. 0.75% EtOH as stabilizer) is used as the solvent. NMR spectra of mixtures with **1**:Cd(SPh)$_2$ = 1:1 in CHCl$_3$ show the presence of [Cd(PPh$_3$)$_3$]$^{2+}$ and I$_{SPh}$ as the major recognizable species.[15]

The behavior of the system **1**:Cd(SePh)$_2$:PPh$_3$ parallels that of the sulfur analogue in all respects. For the selenolates, further characterization is available via ^{77}Se NMR. NMR data for [(μ-SePh)$_6$(CdPPh$_3$)$_n$(Cd)$_{4-n}$]$^{2+}$ are included in Table IV, and those for [Ph$_3$PCd({μ-SePh}CdPPh$_3$)$_3$]$^{5+}$, in Table V.

(iv) Systems 1:Cd(SR)$_2$:PPh$_3$ (R = Pr^n, Pe^n). These systems behave very like their PhE$^-$ analogues. NMR data for [(μ-SR)$_6$(CdPPh$_3$)$_n$(Cd)$_{4-n}$]$^{2+}$ are included in Table IV, and those for [Ph$_3$PCd({μ-SR}CdPPh$_3$)$_3$]$^{2+}$, in Table V. A notable difference between the systems containing the primary alkanethiolates and those containing the phenylchalcogenates is that for the former the open tetranuclear complexes persist in CHCl$_3$.

Enhanced Solubility of Cd(ER)$_2$ (Cd(ER)$_2$/Cd(PPh$_3$)$_2$$^{2+}$ > 3). The compounds Cd(SR)$_2$ and Cd(SePh)$_2$ are poorly soluble in CH$_2$Cl$_2$ but partially or completely solubilized in the presence of **1**, as noted above. It is interesting that in some cases solutions containing **1** dissolve significantly more Cd(ER)$_2$ than the 3 mol equiv needed to form [(μ-ER)$_6$(CdPPh$_3$)$_2$(Cd)$_2$]$^{2+}$. When the concentration of **1** is 0.05 mol/L of solvent, the Cd(ER)$_2$/**1** ratios that can be reached at room temperature are approximately 3, 4, 6, 4, 4, and >12 for ER = SPh, SePh, SPr^n, SPr^i, SPe^n, and SCy, respectively. To date we have been unable to isolate or otherwise characterize the Cd(ER)$_2$-rich species occurring in these solutions. For higher Cd(ER)$_2$/**1** ratios, at least, they may be related to the recently-characterized[22] 6Hg(SCy)$_2$·HgBr$_2$.

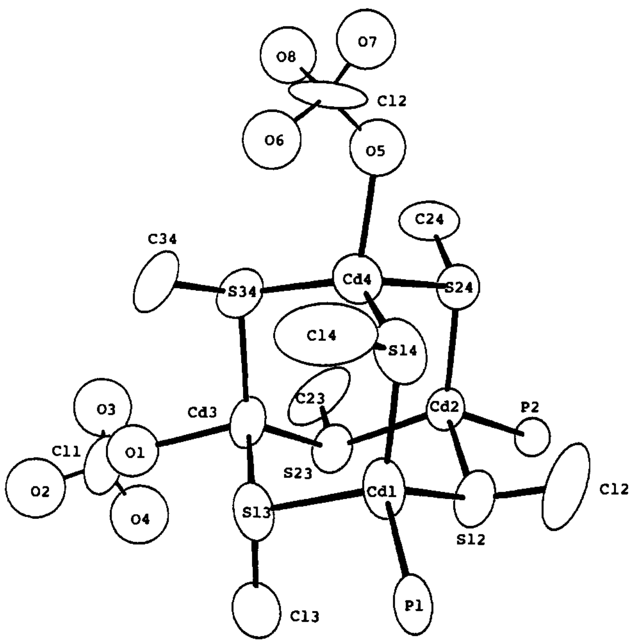

Figure 6. View of the adamantane-like skeleton in [(μ-SPr^i)$_6$(CdPPh$_3$)$_2$(CdOClO$_3$)$_2$].

Structure of [(μ-SPr^i)$_6$(CdPPh$_3$)$_2$(CdOClO$_3$)$_2$]·EtOH. The structure consists of discrete, well-separated molecules of [(μ-SPr^i)$_6$(CdPPh$_3$)$_2$(CdOClO$_3$)$_2$] and EtOH. The solvent molecules are disordered and will not be discussed further. Between the Cd$_4$ clusters, the shortest intermolecular distance is 2.21 Å between H(225)···O7) (x, $^1/_2 - y$, $^1/_2 + z$). Particularly noteworthy features of the discrete thiolate-bridged adamantanoid clusters are the lack of charge, the presence of alkanethiolates, and the presence of mixed terminal ligands. Only one discrete uncharged species of this general type, [(μ-SPh)$_6$(CoCl)$_2$(CoPPh$_3$)(CoOPPh$_3$)], has been characterized structurally hitherto.[23] Similarly, only one other (μ-S-alk)$_6$M$_4$ cage has been characterized structurally for Zn–Hg, that also a cadmium complex, [(μ-SPr^i)$_6$(CdBr)$_4$]$^{2-}$.[5b] Finally, structural data[24] are available for only two other discrete thiolate-bridged adamantanoid clusters with mixed terminal ligands, the Co$_4$ cluster already mentioned and [(μ-SPh)$_6$(ZnSPh)$_2$(ZnCl)$_2$]$^{2-}$.[25]

Disorder of some of the Pr^i groups, the ClO$_4^-$ ions, and the EtOH molecule limits the overall precision of the structure, but the adamantane-like skeleton of [(μ-SPr^i)$_6$(CdPPh$_3$)$_2$(CdOClO$_3$)$_2$] is determined with good precision and is shown in Figure 6. Selected bond distances and angles are listed in Table VI. In the (μ-SPr^i)$_6$Cd$_4$ cage, each Cd atom is attached to three bridging S atoms and each bridging S atom to two Cd atoms, such that the Cd atoms are at the corners of a distorted tetrahedron (Cd···Cd

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Table V. ^{31}P and ^{111}Cd NMR Data for $[\mathrm{PPh_3Cd_B(\{\mu\text{-}ER\}Cd_APPh_3)_3}]^{5+}$ in CH_2Cl_2 at 213 K

ER	δ_{P_A}[a]	δ_{P_B}[a]	δ_{Cd_A}[b]	δ_{Cd_B}[b]	$^1J(^{31}P\text{–}^{111}Cd_A)$[c] (Hz)	$^1J(^{31}P\text{–}^{111}Cd_B)$[c] (Hz)	$^3J(^{31}P\text{–}Cd_A)$[d,e] (Hz)	$^3J(^{31}P\text{–}Cd_B)$[d,e] (Hz)	$^4J(^{31}P\text{–}^{31}P)$[d] (Hz)
SPh	13.1	3.3	290	604	2443	1531	16	9	4
SePh[f]	11.8	1.1	281	580	2300	1278	19	10	5
SPr^n	11.1	–0.3	326	650	2273	1116	19	9	4
SPe^n[g]	10.4	–0.4	323	651	2260	1109	20	9	4

[a] Reproducibility ±0.1 pm or better. [b] Reproducibility ±1 pm or better. [c] Estimated error ±5 Hz. [d] Estimated error ±1 Hz. [e] Average coupling; separate couplings to ^{111}Cd and ^{113}Cd were not resolved. [f] $\delta_{Se} = -71.2 \pm 0.2$; $(^2J(^{31}P_A - {}^{77}Se) + {}^2J(^{31}P_B - {}^{77}Se)) = 52 \pm 2$ Hz. $^1J(^{77}Se - {}^{111}Cd_{A/B})$ could not be measured with certainty. [g] $\mathrm{Pe}^n = n\text{-}C_5H_{11}$.

Table VI. Bond Distances (Å) and Angles (deg) for $[(\mu\text{-}\mathrm{SPr}^i)_6(\mathrm{CdPPh_3})_2(\mathrm{CdOClO_3})_2]\cdot\mathrm{EtOH}$

	Bond Distances		
Cd(1)–P(1)	2.643(5)	Cd(2)–P(2)	2.656(4)
Cd(1)–S(12)	2.525(5)	Cd(2)–S(12)	2.542(5)
Cd(2)–S(13)	2.527(5)	Cd(3)–S(13)	2.513(6)
Cd(1)–S(14)	2.544(7)	Cd(4)–S(14)	2.459(6)
Cd(2)–S(23)	2.520(5)	Cd(3)–S(23)	2.508(5)
Cd(2)–S(24)	2.523(5)	Cd(4)–S(24)	2.549(5)
Cd(3)–S(34)	2.502(6)	Cd(4)–S(34)	2.504(6)
Cd(3)–O(1)	2.309(17)	Cd(3)–O(1a)	2.375(18)
Cd(4)–O(5)	2.356(9)	P–C(mean)	1.799(8)
	Bond Angles		
	S–Cd–P		
S(12)–Cd(1)–P(1)	110.1(2)	S(13)–Cd(1)–P(1)	107.4(2)
S(14)–Cd(1)–P(1)	110.4(2)	S(12)–Cd(2)–P(2)	104.8(2)
S(23)–Cd(2)–P(2)	104.9(2)	S(24)–Cd(2)–P(2)	115.4(2)
	S–Cd–S		
S(13)–Cd(1)–S(12)	108.2(2)	S(14)–Cd(1)–S(12)	107.6(2)
S(14)–Cd(1)–S(13)	113.1(2)	S(23)–Cd(2)–S(12)	104.1(2)
S(24)–Cd(2)–S(12)	105.6(2)	S(24)–Cd(2)–S(23)	120.4(2)
S(23)–Cd(3)–S(13)	112.9(2)	S(34)–Cd(3)–S(13)	114.4(2)
S(34)–Cd(3)–S(23)	115.3(2)	S(24)–Cd(4)–S(14)	108.1(2)
S(34)–Cd(4)–S(14)	126.9(2)	S(34)–Cd(4)–S(24)	107.5(2)
	O–Cd–S		
O(1)–Cd(3)–S(13)	93.2(5)	O(1)–Cd(3)–S(23)	115.6(4)
O(1)–Cd(3)–S(34)	103.0(5)	O(1a)–Cd(3)–S(13)	122.5(5)
O(1a)–Cd(3)–S(23)	98.1(5)	O(1a)–Cd(3)–S(34)	91.5(6)
O(5)–Cd(4)–S(14)	110.2(7)	O(5)–Cd(4)–S(24)	91.9(4)
O(5)–Cd(4)–S(34)	106.7(7)		
	Cd–S–Cd		
Cd(2)–S(12)–Cd(1)	111.5(2)	Cd(3)–S(13)–Cd(1)	104.5(2)
Cd(4)–S(14)–Cd(1)	101.3(2)	Cd(3)–S(23)–Cd(2)	100.4(2)
Cd(4)–S(34)–Cd(3)	98.8(2)	Cd(4)–S(24)–Cd(2)	104.0(2)
	Cl–O–Cd		
Cl(1)–O(1)–Cd(3)	132.0(12)	Cl(1)–O(1a)–Cd(3)	126.1(13)
Cl(2)–O(5)–Cd(4)	124.6(9)	Cl(2a)–O(5)–Cd(4)	108.4(12)

distances, 3.801(3)–4.188(3) Å; Cd–Cd–Cd angles, 56.3(1)–64.4(1)°) and the S atoms at the corners of a distorted octahedron (geminal S···S distances, 3.992(3)–4.439(3) Å). Two Cd atoms are bonded to terminal PPh_3 and two to monodentate ClO_4^- ligands, completing tetrahedral coordination geometry about the metal atoms. The structure confirms the coordination of ClO_4^- that was postulated from the metal NMR data described above.

The Cd–P distances are 2.643(5) and 2.656(5) Å. These are larger than Cd–P distances of 2.524(2) Å in $[(\mu\text{-}CF_3CO_2)_4(CdPPh_3)_2]$[26] and 2.612(1) Å in $[\mathrm{Cd(S_2COPr}^i)_2\mathrm{PPh_3}]$.[27] It appears that the Cd–P bond distance is sensitive to either the nature of the other ligands attached to Cd or steric effects or both. The Cd–O distances observed in the cage complex are 2.31(2), 2.38(2), and 2.36(1) Å. So far as we are aware, only one other $Cd\text{–}OClO_3$ linkage has been characterized by X-ray analysis. In $[\mathrm{CdL(OH_2)(ClO_4)}][\mathrm{ClO_4}]\cdot\mathrm{MeOH}$ (L = macrocyclic nitrogen analogue of [18]annulene), the $Cd\text{–}OClO_3$ distance is 2.33(3) Å.[28] The Cd–S distances in the Pr^i-bridged cage are in the range 2.459(6)–2.544(7) Å. Such values are similar to the mean distance found[5b] for $[(\mu\text{-}\mathrm{SPr}^i)_6(\mathrm{CdBr})_4]^{2-}$ (2.53(1) Å), but the range of values in the phosphine complex is approximately twice the range of 2.512(7)–2.555(7) Å observed for the bromo complex. This does not seem to be a reflection of the disparate terminal groups (PPh_3 vs ClO_4^-) in the phosphine complex. The Cd–S distances for S atoms geminal to P are in the range 2.520(5)–2.544(7) Å (mean: 2.53(1) Å), while Cd–S distances for S atoms geminal to O are in the overlapping range of 2.459(6)–2.549(5) Å.

The disposition of the R groups in a $(\mu\text{-ER})_6M_4$ cage (axial (a) or equatorial (e) with respect to a particular M_3E_3 chair of the cage) leads to isomerism.[29] For $[(\mu\text{-}\mathrm{SPr}^i)_6(\mathrm{CdPPh_3})_2(\mathrm{CdOClO_3})_2]$ the conformation of the Pr^i groups at S in the four Cd_3S_3 chairs is [aae, aae, aee, aee]. This particular configuration (called Isomer III) has two 1,3-axial–axial interactions between substituents, the minimum number possible. Such interactions in $(\mu\text{-ER})_6M_4$ cages lead to distortions of M_4 from ideal tetrahedral geometry and of E_6 from ideal octahedral geometry, as is observed here for Cd_4 and S_6. In agreement with earlier results,[28] the S–Cd–S angles and geminal S···S distances in $[(\mu\text{-}\mathrm{SPr}^i)_6(\mathrm{CdPPh_3})_2(\mathrm{CdOClO_3})_2]$ fall into three groups depending in the nature of the 1,3-interaction in the particular CdS_2 fragment, in the order aa > ae > ee. For example, the largest S–Cd–S angles (S(34)–Cd(4)–S(14) = 126.9(2), S(24)–Cd(2)–S(23) = 120.4(2)°) and largest geminal S···S distances (S(34)···S(14) = 4.439(3), S(24)···S(23) = 4.377(3) Å) are associated with 1,3-axial–axial interactions.

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Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen positional parameters, and selected torsion angles and figures of the ^{31}P and ^{111}Cd NMR spectra of mixtures containing 1:1 $\mathrm{Cd(PPh_3)_2(ClO_4)_2}$:$\mathrm{Cd(SPr}^i)_2$ in CH_2Cl_2 and $CHCl_3$ (6 pages). Ordering information is given on any current masthead.

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