strong interactions between the butatriene chain and the $Fe_2(CO)_6$ fragment[3b] are certainly responsible for this lack of reactivity.

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Registry No. **1**, 67400-66-2; **2**, 99748-42-2; Fe, 7439-89-6; Ru, 7440-18-8.

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Cadmium-113 Nuclear Magnetic Resonance Spectroscopic Study of Mixed-Ligand Tetranuclear Clusters of the Type $[Cd_4(EPh)_x(E'R)_{10-x}]^{2-}$ and of the Mixed-Metal Clusters $[Cd_xZn_{4-x}(SPh)_{10}]^{2-}$

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The synthesis of $(Me_4N)_2[Cd_4(SePh)_{10}]$ (**1**) is described. The ^{113}Cd-enriched compound (**1***) undergoes ligand redistribution with the sulfur analogue (**2***) to give the series $[^{113}Cd_4(SPh)_x(SePh)_{10-x}]^{2-}$ (x = 0–10), in which each member is characterized by a single line in the 44.4-MHz ^{113}Cd NMR spectrum at ambient probe temperature. The same complexes can be made in solution by redox reaction of **1*** with Ph_2S_2 or **2*** with Ph_2Se_2. Similarly, at ambient probe temperature, resolvable single ^{113}Cd NMR lines characterize the species $[Cd_4(SPh)_x(SR)_{10-x}]^{2-}$ (R = Me, x = 8–10; R = Bu, x = 4–10; R = $PhCH_2$, x = 7–10; R = 2-C_6H_4Me, x = 0–10), produced from **2** or **2*** and R_2S_2, $[Cd_4(SePh)_x(SBu)_{10-x}]$ (x = 5–10), produced from **1** and Bu_2S_2, $[^{113}Cd_4(SPh)_x(TePh)_{10-x}]^{2-}$ (x = 8–10), produced from **2*** and Ph_2Te_2, and $[^{113}Cd_4(SePh)_x(TePh)_{10-x}]^{2-}$ (x = 7–10), produced from **1*** and Ph_2Te_2. The observed or extrapolated ^{113}Cd NMR chemical shifts of $[Cd_4(ER)_{10}]^{2-}$, in which the kernels are $(RE)Cd(\mu\text{-}ER)_3$, are close to those of $[Cd(ER)_4]^{2-}$, confirming that ^{113}Cd NMR is not very sensitive to the bridging/terminal nature of the bound groups, as found in earlier work. When mixtures of $[Cd_4(SPh)_{10}]^{2-}$ and $[Zn_4(SPh)_{10}]^{2-}$ were reinvestigated with use of ^{113}Cd enrichment, only three cadmium-containing species could be detected by ^{113}Cd NMR. These are probably $[^{113}Cd_xZn_{4-x}(SPh)_{10}]^{2-}$ (x = 2–4). The relevance of this nonstatistical metal distribution to that in zinc–cadmium metallothionein is discussed.

Introduction

The ^{113}Cd NMR spectra of ^{113}Cd-enriched cadmium and cadmium-containing mixed-metal metallothioneins have provided invaluable information about the spatial disposition of the cadmium ions in the binding sites of the cysteine-rich protein.[1,2] Thus, for intance, on this basis it is thought that mammalian cadmium metallothionein (Cd-MT) contains two types of polynuclear cadmium clusters, a three-atom cluster, $Cd_3(S\text{-}cyst)_9$, and a four-atom cluster, $Cd_4(S\text{-}cyst)_{11}$, while Cd-MT from the crab *Scylla serrata* contains two different three-atom clusters of the type $Cd_3(S\text{-}cyst)_9$.

Mammalian MT induced by administration of cadmium always contains a significant amount of zinc (see, for examples, ref 1–3). The ^{113}Cd NMR spectrum of Zn,^{113}Cd-MT is more complex than that of ^{113}Cd-MT but can be interpreted[1,2] to show that the distribution of the two metals over the seven binding sites is not random, the overwhelming majority of ^{113}Cd occupying the four-atom cluster. An assumption in this interpretation is that replacement of cadmium by zinc in a particular cluster has relatively little effect on the ^{113}Cd NMR chemical shifts of the remaining ^{113}Cd nuclei.[1]

To our knowledge there is no simple model available for the three-atom cluster of MT. However, the tetranuclear cluster $[Cd_4(SPh)_{10}]^{2-}$ is well established,[4] and the zinc analogue is also known.[5] These clusters have structures based on an adamantane-like $M_4(\mu\text{-}SPh)_6$ cage in which each metal ion is also associated with one terminal thiolate.[4,5] We[6] and others[7] have shown recently that 45-Hz two-bond $^{113}Cd\text{–}S\text{–}^{111}Cd$ nuclear spin–spin coupling is observable in the ^{113}Cd and ^{111}Cd NMR spectra of $[Cd_4(SPh)_{10}]^{2-}$, making this a good model for the 20–50-Hz $^{113}Cd\text{–}S\text{–}^{113}Cd$ couplings observed in the ^{113}Cd NMR spectra of various ^{113}Cd-MT's. In addition, the fine structure found in the $^{111/113}Cd$ NMR spectra of $[Cd_4(SPh)_{10}]^{2-}$ shows that the Cd_4 core of this species is long-lived on the $^{111/113}Cd$ NMR time scale. The ^{113}Cd NMR chemical shift of $[Cd_4(SPh)_{10}]^{2-}$ (e.g. in acetone at 295 ± 1 K, 575 ppm relative to external $Cd(ClO_4)_2(aq)$[6]) is outside the range reported for ^{113}Cd-MT, and better models for this parameter are desirable. No discrete clusters $[Cd_4(SR)_{10}]^{2-}$ (R = alkyl) have been reported, though Kurtz and co-workers[8] have drawn attention to the occurrence of related tetraatomic clusters within the structure of the decanuclear cluster $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$. In the solid-state ^{113}Cd NMR spectra of this 10-atom cluster, as the ClO_4^- and SO_4^{2-} salts, chemical shifts from 623 to 705 ppm were found for the CdS_4 kernels, depending on the particular salt and its extent of aquation, and it was concluded, inter alia, that disortions of the kernel, rather than differences in the number of bridging vs. terminal thiolates, affect the chemical shifts most significantly.[8]

In this paper we describe our ^{113}Cd NMR studies of various mixed-thiolate clusters $[Cd_4(SPh)_x(SR)_{10-x}]^{2-}$ in solution. We could find no previous report of such discrete cadmium-containing mixed-ligand clusters. As selenium has an important antagonistic effect toward cadmium toxicity,[9] we have extended our study to selenium-containing tetranuclear clusters, which we describe for

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(1) Otvos, J. D.; Armitage, I. M.. In "Biochemical Structure Determination by NMR"; Bothner-By, A. A.; Glickson, J. D.; Sykes, B. D., Eds.; Marcel Dekker: New York, 1982; Chapter 4.

(2) Armitage, I. M.; Boulanger, Y. In "NMR of Newly Accessible Nuclei"; Laszlo, P., Ed.; Academic Press: New York, 1983; Volume 2, Chapter 13.

(3) Kägi, J. H. R.; Vašák, M.; Lerch, K.; Gilg, D. E. O.; Hunziker, P.; Bernhard, W. R.; Good, M. *EHP, Environ. Health Perspect.* **1984**, *54*, 93–103.

(4) Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3171–3174.

(5) Hencher, J. L.; Khan, M.; Said, F. F.; Tuck, D. G. *Polyhedron* **1985**, *4*, 1261–1267.

(6) Dean, P. A. W.; Vittal, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 6436–6437.

(7) Dance, I. G.; Saunders, J. K. *Inorg. Chim. Acta* **1985**, *96*, L71–L73.

(8) Lacelle, S.; Stevens, W. C.; Kurtz, D. M., Jr.; Richardson, J. W., Jr.; Jacobson, R. A. *Inorg. Chem.* **1984**, *23*, 930–935.

(9) (a) Parízek, J.; Benes, I.; Ostâdalovâ, I.; Babickŷ, A.; Benes, J.; Pitha, J. In "Mineral Metabolism in Pediatrics"; Barltrop, D., Burland, W. L., Eds.; F. A. Davies: Philadelphia, 1969; Chapter 8. (b) Ganther, H. E. In "Selenium"; Zingaro, R. A., Cooper, W. C., Eds.; Van Nostrand-Reinhold: New York, 1974; Chapter 9. (c) Underwood, E. J. "Trace Elements in Human and Animal Nutrition", 4th ed.; Academic Press: New York, 1977; Chapters 9 and 12. (d) Odom, J. D. *Struct. Bonding (Berlin)* **1983**, *54*, 1–26. (e) Shamberger, R. J. "Biochemistry of Selenium"; Plenum Press: New York, 1983; Chapter 5. (f) Magos, L.; Webb, M. *CRC Crit. Rev. Toxicol.* **1980**, *8*, 1–42.

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the first time; these are possible ^{113}Cd NMR spectroscopic models for cadmium bound to selenium-substituted MT, which might be formed on administration of selenium.[9e] Also, for comparison with the ^{113}Cd NMR spectra of the sulfur- and selenium-containing clusters, we report ^{113}Cd NMR data for several new tellurium-containing analogues. Finally, we have examined the ^{113}Cd NMR spectra of the mixed-metal complexes $[^{113}Cd_xZn_{4-x}(SPh)_{10}]^{2-}$. An earlier study[10] of $[Cd_xZn_{4-x}(SPh)_{10}]^{2-}$ provided ambiguous results: three ^{113}Cd resonances were observed, but because natural cadmium was used, it was unclear whether these were chemically shifted resonances or a central resonance with $^{111/113}$Cd satellites.

Experimental Section

Materials and General Procedures. Cadmium metal enriched in ^{113}Cd was from Technabsexport, Moscow, USSR. Literature syntheses were used for $(Me_4N)_2[Zn_4(SPh)_{10}]$,[10] $(Me_4N)_2[Cd(SPh)_4]$,[11] natural and ^{113}Cd-enriched $(Me_4N)_2[Cd_4(SPh)_{10}]$ (**2** and **2***, respectively),[6] and Ph_2S_2 and $(2\text{-}C_6H_4Me)_2S_2$,[12] while $(Me_4N)_2[Cd_4(SePh)_{10}]$ was prepared as described below. All other chemicals were reagent grade and were used as received from commercial sources. The purity of the various disulfides was checked by ^{1}H and/or ^{13}C NMR, and ^{13}C and ^{77}Se/^{125}Te NMR was used to confirm the purity of Ph_2E_2 (E = Se or Te).

The syntheses of $(Me_4N)_2[M_4(EPh)_{10}]$ (M = Cd, E = S; M = Cd, E = Se; M = Zn, E = S) were carried out under an Ar atmosphere in a glovebag, with use of solvents that had been thoroughly deoxygenated with Ar. NMR samples were also prepared with use of deoxygenated solvents; however, the air sensitivity of the compounds $(Me_4N)_2[M_4(EPh)_{10}]$ listed above does not seem to be significant.

Carbon, hydrogen, and nitrogen microanalyses were performed by Guelph Chemical Laboratories, Ltd. Cadmium was determined by EDTA titration.[13]

Natural and ^{113}Cd-Enriched $(Me_4N)_2[Cd_4(SePh)_{10}]$. (a) The Natural Compound, 1. A 1.45-g (9-mmol) portion of PhSeH was added to an equimolar amount of sodium metal dissolved in 10 mL of methanol. The resultant solution of NaSePh was added to a stirred solution of 0.95 g (3 mmol) of $Cd(NO_3)_2\cdot 4H_2O$ in 20 mL of methanol, producing a white precipitate. Following addition, with stirring, of a solution of 0.65 g (6 mmol) of Me_4NCl in methanol and then 100 mL of water, the mixture was warmed to 80 °C and acetonitrile added in small portions until the precipitate dissolved. After hot filtration, the clear solution was left at 5 °C for crystallization to occur. The colorless crystals were separated by filtration, washed with methanol, water, and then methanol again, and finally dried under vacuum. The filtrate was concentrated to produce a second crop of crystals; yield 1.4 g (84%). Anal. Calcd for $C_{68}H_{74}Cd_4N_2Se_{10}$: C, 37.84; H, 3.46; Cd, 20.83; N, 1.30. Found: C, 37.97; H, 3.45; Cd, 21.08; N, 1.08. ^{1}H NMR (ambient probe temperature, CD_3CN): δ_H 7.45 ($H_{2,6}$), 6.82 ($H_{3,5}$), 6.98 (H_4), 2.99 ($(CH_3)_4N^+$). ^{13}C NMR (ambient probe temperature, CD_3CN): δ_C 131.5 (br, C_1), 136.3 ($C_{2,6}$), 128.8 ($C_{3,5}$), 124.9 (C_4), 56.1 ($(CH_3)_4N^+$).

The ^{113}Cd-Enriched Compound, 1*. This was prepared in the same manner as the natural compound, except that $^{113}Cd(NO_3)_2\cdot 4H_2O$, prepared by dissolution of ^{113}Cd metal in HNO_3, followed by evaporation to dryness, was used as the source of cadmium(II). At 295 ± 1 K, a 0.020 M solution of **1*** in acetone gives a single broad ^{113}Cd NMR line with $\delta_{Cd} = 519.3$ and $\Delta\nu_{1/2} \approx 65$ Hz and a single broad ^{77}Se NMR line with $\delta_{Se} = -12.0$ and $\Delta\nu_{1/2} \approx 250$ Hz.

Preparation of Samples for NMR Study. All samples for ^{113}Cd, ^{77}Se, and ^{125}Te NMR were prepared in acetone solution in 10 mm o.d. NMR tubes. Cadmium-113 concentrations used were in the approximate range 4–100 mM. In addition to the obvious advantage of shortening the time to acquire the ^{113}Cd NMR spectra, a high concentration of ^{113}Cd has the secondary advantage of reducing line broadening of ^{113}Cd resonances caused by slight changes in ambient probe temperature during spectral accumulation coupled with the appreciable temperature dependence of δ_{Cd} in many of these compounds.[6] Enrichment with ^{113}Cd was used where necessary to reduce spectral accumulation times or to simplify the ^{113}Cd NMR spectra and/or remove ambiguity by removing ^{111}Cd–^{113}Cd nuclear spin–spin coupling.

NMR Spectra. Most of the ^{113}Cd NMR spectra and all of the ^{77}Se and ^{125}Te NMR spectra were obtained as outlined previously,[6,14] with a Varian XL-200 NMR spectrometer system operating at 44.37, 38.15, and 63.14 MHz for ^{113}Cd, ^{77}Se, and ^{125}Te, respectively, without field/frequency lock (field drift << 1 Hz/day). The spectra were referenced by sample interchange using 0.1 M $Cd(ClO_4)_2$(aq), neat Me_2Se, and 0.5 M Ph_2Te_2 in CH_2Cl_2, respectively, as primary references. No corrections for diamagnetic susceptibility were applied. To minimize thermal broadening,[6] usually no proton decoupling was used in collecting ^{113}Cd NMR data for samples that did not contain alkyl groups; when alkyl groups were present, gated decoupling was used to avoid any negative NOE, while ^{77}Se and ^{125}Te NMR data were collected with use of 2-W continuous decoupling via the WALTZ-16 sequence.[15]

A few ^{113}Cd NMR spectra of $[Zn_4(SPh)_{10}]^{2-}$–$[^{113}Cd_4(SPh)_{10}]^{2-}$ mixtures were measured with a Varian XL-300 spectrometer running at 66.53 MHz. Operating conditions were similar to those used on the Varian XL-200.

Results

Synthesis of $(Me_4N)_2[Cd_4(SePh)_{10}]$ (1). This compound was prepared in high yield by essentially the same direct method used for the sulfur analogue:[6,16]

$$Cd^{2+} + 2Me_4N^+ + 10SePh^- \rightarrow (Me_4N)_2[Cd_4(SePh)_{10}] \quad (1)$$

1 was the only species isolated with use of $SePh^-/Cd^{2+}$ ratios from 2.5 to 3.5; use of a slight excess of $SePh^-$ seems beneficial, perhaps because some oxidation of $SePh^-$ occurs despite the precautions taken to preclude oxygen. **1*** was prepared similarly with use of ^{113}Cd-enriched cadmium metal as the source of Cd^{2+}.

The ^{1}H and ^{13}C NMR spectra of **1** at ambient probe temperature (see Experimental Section) show one set of phenyl signals, whereas the studies described below show that **1** has the same structure as **2** and so must have bridging and terminal PhSe groups. However, the solubility of **1** in acetone is significantly less than that of **2**, precluding a variable-temperature NMR study of the terminal-to-bridging exchange process.

Synthesis and ^{113}Cd NMR Spectroscopic Characterization of the Mixed-Ligand Complexes $[Cd_4(EPh)_x(E'R)_{10-x}]^{2-}$ in Solution. The three methods used to prepare the complexes were as follows.

A. Redox of 2 with $R_2E'_2$:

$$\mathbf{2} + R_2E'_2 \rightleftarrows [Cd_4(SPh)_x(E'R)_{10-x}]^{2-} + Ph_2S_2/PhSE'R \text{ (equilibrium mixture)} \quad (2)$$

2* behaves identically.

B. Redox of 1 with $R_2E'_2$:

$$\mathbf{1} + R_2E'_2 \rightleftarrows [Cd_4(SePh)_x(E'R)_{10-x}]^{2-} + Ph_2Se_2/PhSeE'R \text{ (equilibrium mixture)} \quad (3)$$

1* behaves identically.

C. Ligand Redistribution:

$$\mathbf{1} + \mathbf{2} \rightleftarrows [Cd_4(SPh)_x(SePh)_{10-x}]^{2-} \text{ (equilibrium mixture)} \quad (4)$$

Mixtures of **1*** and **2*** behave identically.

These routes have the advantage of producing an excess of neither cadmium ion nor thiolate ion, two species that have been shown[6] to cause broadening of the ^{113}Cd resonance of $[Cd_4(SPh)_{10}]^{2-}$. Another possible method, reaction of $Cd(ER)_2$ with $Cd(E'R')_4{}^{2-}$, would require perfect control of stoichiometry, while we found that the reaction of RSH (R = alkyl) with **1** or **2** produces no mixed complex, probably because the acidity of RSH is much less than that of PhSH or PhSeH.[17]

Formation of a tetranuclear PhSe-containing iron cluster by a redox reaction like (2) has been described previously.[18]

At room temperature (ca. 23 °C), the redox reactions (2) and (3) are slow; up to 24 h is required to reach equilbrium. Therefore,

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(10) Hagen, K. S.; Stephan, D. W.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 3928–3936.

(11) Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 157–161.

(12) Field, L. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; Chapter 7.

(13) Vogel, A. I. "A Textbook of Quantitative Inorganic Analysis", 3rd ed.; Longmans Green and Co.: London, 1961; p 444.

(14) Dean, P. A. W.; Srivastava, R. S. *Inorg. Chim. Acta* **1985**, *105*, 1–7.

(15) Shaka, A. J.; Keeler, J.; Freeman, R. *J. Magn. Reson.* **1983**, *53*, 313–340.

(16) Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6285–6295.

(17) (a) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1977; Volume 3, p 355. (b) Nygård, B. *Acta Chem. Scand.* **1966**, *20*, 1710–1712.

(18) Que, L., Jr.; Bobrik, M. A.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4168–4178.

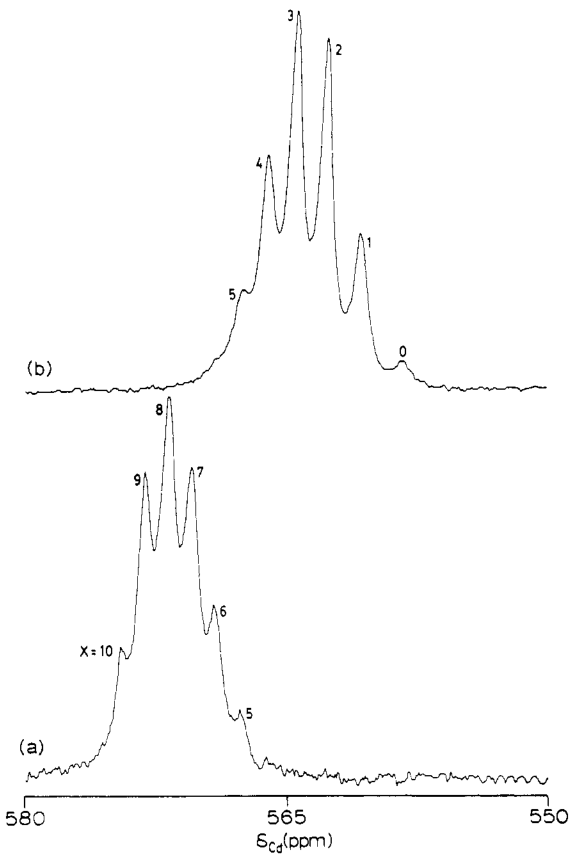

Figure 1. ^{113}Cd NMR spectra at 44.37 MHz and 295 K of equilibrated $[^{113}Cd_4(SPh)_{10}]^{2-}$ (**2***)-$(2\text{-}C_6H_4Me)_2S_2$ ($otol_2S_2$) mixtures in acetone, showing the formation of $[^{113}Cd_4(SPh)_x(Sotol)_{10-x}]^{2-}$. For (a), **2***/$otol_2S_2$ = 1/2; this spectrum was collected without proton decoupling and results from accumulation of transients from 3000 54° (12 μs) pulses applied at 3-s intervals with a 1-s acquisition time. A 4-Hz line broadening has been used. For (b), **2***/$otol_2S_2$ = 1/32; this spectrum results from accumulation of 15 000 transients obtained and processed as in (a). For both (a) and (b), $[^{113}Cd_4]_{total}$ = 0.025 M.

after some exploratory measurements, samples were kept at room temperature for 24 h prior to ^{113}Cd NMR spectral measurements. The redistribution (4), however, is complete within the time taken to obtain preliminary spectra (ca. 1 h); in fact, the redistribution is probably complete within the time of mixing.

The ^{113}Cd NMR chemical shifts for the various new species found are given in Table I, and representative spectra are shown in Figures 1–3. Each mixed species is characterized by a single line, and assignments are made readily with use of the order of appearance of the lines as the EPh/E′R ratio is changed, together with the systematic change in ^{113}Cd chemical shift caused by replacing one ligand by another in each series (see Table I, Figures 1–3, and Discussion below). As can be seen from Figures 1 and 2, the ligands that are coordinated are distributed among the various members of a series in a near-statistical manner,[19] to give an approximately binomial population distribution of the various Cd_4 clusters.

When the system **2**–$(4\text{-}C_6H_4Me)_2S_2$ (=$ptol_2S_2$) was examined by ^{13}C NMR, clear evidence for redox as in (2) was found: in the region δ_C = 129.5–131.0, which is free from overlap with resonance due to the clusters, two signals from $C_{3,5}$ of *ptol*SSR and two from $C_{3,5}$ of *Ph*SSR, at 130.77, 130.72, and 130.10, 130.05 ppm, respectively, were found, with the intensity ratio $I(Ph)_{total}/I(ptol)_{total} \approx 1$. Clearly Ph_2S_2, ptolSSPh, and $ptol_2S_2$ are present in solution. However, we could find no new ^{113}Cd resonances and we conclude that the new ptol complexes that are formed accidentally have chemical shifts isochronous with that of **2**. Accordingly, we switched to $(2\text{-}MeC_6H_4)_2S_2$ ($otol_2S_2$) as a second representative diaryl disulfide: the otol moiety is known to produce more marked changes in the NMR properties of attached groups than ptol (see for example, ref 21). In **2**–$otol_2S_2$

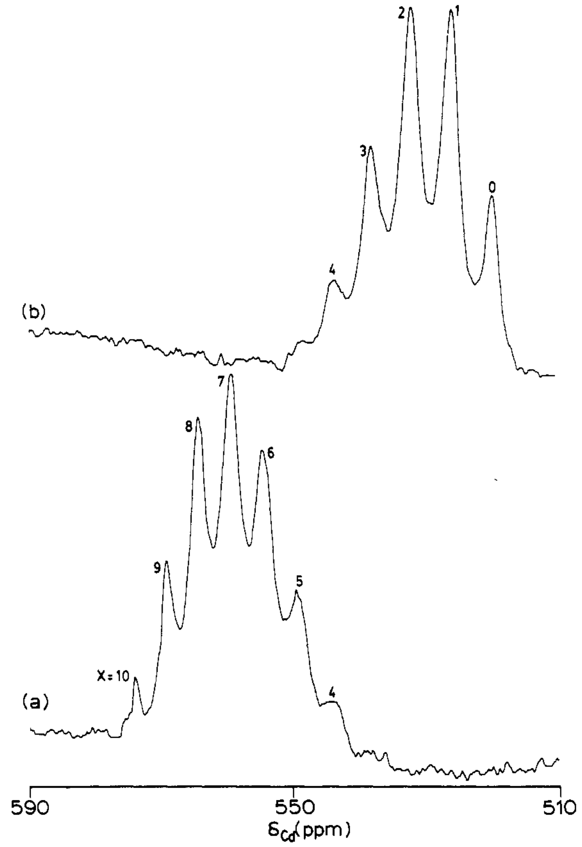

Figure 2. ^{113}Cd NMR spectra at 44.37 MHz and 295 K of equilibrated $[^{113}Cd_4(SPh)_{10}]^{2-}$ (**2***)-$[^{113}Cd_4(SePh)_{10}]^{2-}$ (**1***) mixtures in acetone, showing the formation of $[^{113}Cd_4(SPh)_x(SePh)_{10-x}]^{2-}$. For (a), **2***/**1*** = 2/1 and $[^{113}Cd_4]_{total}$ = 0.025 M; this spectrum was collected with 2-W gated broad-band proton decoupling and results from accumulation of transients from 16 500 50° (11 μs) pulses applied at 3-s intervals with a 0.5-s acquistion time. A 20-Hz line broadening has been used. For (b), **2***/**1*** = 1/4.4 and $[^{113}Cd_4]_{total}$ = 0.031 M; this spectrum results from accumulation of 19 250 transients obtained and processed as in (a).

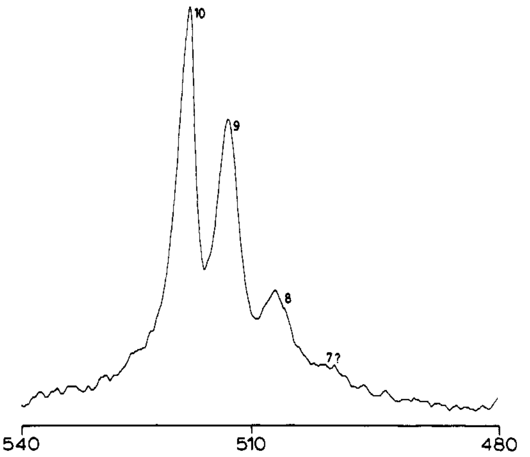

Figure 3. ^{113}Cd NMR spectrum at 44.37 MHz and 295 K of an equilibrated mixture of $[^{113}Cd(SePh)_{10}]^{2-}$ **1***-Ph_2Te_2 (1/10) in acetone, with [**1***] = 0.020 M, showing the formation of $[^{113}Cd_4(SePh)_x(TePh)_{10-x}]^{2-}$. This spectrum was obtained without proton decoupling and results from accumulation of transients from 15 520 54° (12 μs) pulses applied at 3-s intervals with a 1-s acquisition time. A 25-Hz line broadening has been used.

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(19) Calingaert, G.; Beatty, H. A. *J. Am. Chem. Soc.* **1939**, *61*, 2748–2754.

(20) (a) Pinnell, R. P.; Megerle, C. A.; Mannatt, S. L.; Kroon, P. A. *J. Am. Chem. Soc.* **1973**, *95*, 977–978. (b) Dean, P. A. W. *Can. J. Chem.* **1978**, *57*, 754–761. (c) Allman, T.; Goel, R. G. *Can. J. Chem.* **1984**, *62*, 621–627.

Table I. Cadmium-113 NMR Chemical Shifts[a] in Equilibrium Mixtures Containing $[Cd_4(EPh)_x(E'R)_{10-x}]^{2-}$ at 295 ± 1 K[b]

E in EPh	E'R[c]	method used[d]	overall EPh/E'R in soln	10^3 × $[Cd_4]$, M	δ_{Cd}										
					x										
					0	1	2	3	4	5	6	7	8	9	10
S	S(otol)	A[e]	2.5[f]	2.5						567.7 ± 0.2	569.2 ± 0.1	570.5 ± 0.1	571.8 ± 0.1	573.2 ± 0.1	574.3 ± 0.2
S	S(otol)	A[e]	0.16[f]	2.5	558.3 ± 0.2	560.6 ± 0.2	562.6 ± 0.1	564.4 ± 0.1	566.0 ± 0.1	567.4 ± 0.1	~569				
S	SBu	A[g]	2.5	5.0									596.1 ± 0.1	586.7 ± 0.1	577.4 ± 0.1
S	SBu	A[g]	0.13	5.0						621.4 ± 0.4	613.0 ± 0.1	603.9 ± 0.1	594.9 ± 0.2	585.4 ± 0.2	
S	SBu	A[e,g]	0.011	0.74					630.6 ± 0.1	622.2 ± 0.1	613.3 ± 0.1				
S	SCH_2Ph	A	1.7	5.0									588.8 ± 0.2	582.1 ± 0.2	574.5 ± 0.1
S	SCH_2Ph	A	0.25	5.0								597.1 ± 0.2	589.7 ± 0.1	582.0 ± 0.1	574.4 ± 0.1
S	SMe	A[g]	2.5	5.0									~598	588.2 ± 0.1	578.1 ± 0.1
S	SePh	C[e,h,i]	2.0[j]	2.5				~538	543.8 ± 0.4	548.8 ± 0.4	554.0 ± 0.2	559.1 ± 0.2	563.9 ± 0.2	568.8 ± 0.1	573.5 ± 0.2
S	SePh	C[e,h,i]	0.23[j]	3.1	519.1 ± 0.2	525.4 ± 0.2	531.4 ± 0.2	537.0 ± 0.2	542.6 ± 0.4	~547					
S	TePh	A[e]	0.50	2.0								~552	~558	567.2 ± 0.2	574.1 ± 0.1
Se	SBu	B	0.83	2.0								~571	553.3 ± 0.1	536.3 ± 0.1	518.9 ± 0.1
Se	SBu	B	0.083	2.0						~605	588.1 ± 0.2	571.6 ± 0.1	553.6 ± 0.1	535.1 ± 0.2	~517
Se	TePh	B[i]	0.50	2.0[k]								~500	507.1 ± 0.2	513.9 ± 0.2	519.1 ± 0.1

[a] Relative to external 0.1 M $Cd(ClO_4)_2(aq)$; estimated errors are given. [b] Sample temperature when no proton decoupling is used. The sample temperature will be slightly higher in solutions containing alkane- or α-toluenethiolates, for which proton decoupling was used. [c] otol = $2-C_6H_4Me$. [d] See text; in acetone unless specified otherwise. [e] ^{113}Cd enrichment used; 91.7 atom % ^{113}Cd in $(Me_4N)_2[^{113}Cd_4(SPh)_{10}]$. [f] See Figure 1. [g] In MeCN. [h] Can also be prepared by methods A and B; separate ^{77}Se NMR signals could not be observed for $[Cd_4(SPh)_x(SePh)_{10-x}]^{2-}$. [i] ^{113}Cd enrichment used; 95.8 atom % ^{113}Cd in $(Me_4N)_2[^{113}Cd_4(SePh)_{10}]$. [j] See Figure 2. [k] See Figure 3.

Table II. Cadmium-113 NMR Chemical Shifts of $[Cd_4(ER)_{10}]^{2-}$ and $[Cd(ER)_4]^{2-}$

RE[a]	δ_{Cd}[b]		RE[a]	δ_{Cd}[b]	
	$[Cd_4(ER)_{10}]^{2-}$	$[Cd(ER)_4]^{2-}$		$[Cd_4(ER)_{10}]^{2-}$	$[Cd(ER)_4]^{2-}$
PhS	575,[c,d] 576[e]	573,[f] 583[g]	BuS	666,[h,i] 692[h,j]	644[g]
otolS	558[c]	558[f]	$PhCH_2S$	650[c,k]	646[g]
ptolS	575[c]	571[f]	PhSe	519	538[l]

[a] otol = $2-C_6H_4Me$; ptol = $4-C_6H_4Me$. [b] Relative to external 0.1 M $Cd(ClO_4)_2(aq)$; this work at 295 ± 1 K unless specified otherwise. [c] In acetone. [d] Reference 6. [e] In MeCN.[10] [f] In an MeOH solution where [Cd] = 0.05 M and $RS^-/Cd^{2+} = 12$. [g] In H_2O at 308 K.[24] [h] In MeCN. [i] Extrapolated from data for $[Cd_4(SPh)_x(SBu)_{10-x}]^{2-}$ (x = 4–10) (see text and Table I). [j] Extrapolated from data for $[Cd_4(SePh)_x(SBu)_{10-x}]^{2-}$ (x = 5–10) (see text and Table I). [k] Extrapolated from data for $[Cd_4(SPh)_x(SCH_2Ph)_{10-x}]^{2-}$ (x = 7–10) (see text and Table I). [l] In H_2O at 306 K.[21]

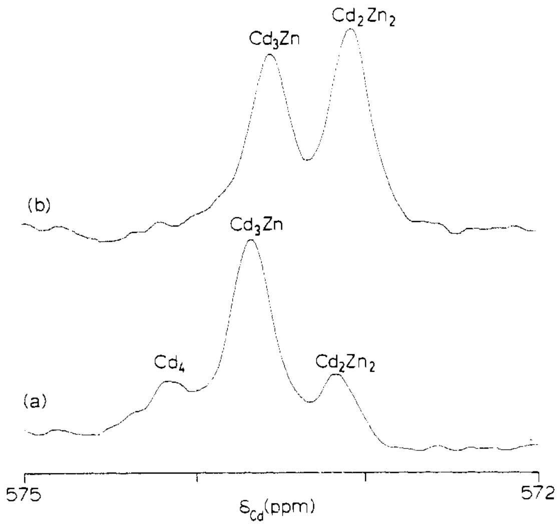

Figure 4. ^{113}Cd NMR spectra at 44.37 MHz and 295 K of equilibrated $[^{113}Cd_4(SPh)_{10}]^{2-}$–$[Zn_4(SPh)_{10}]^{2-}$ mixtures in acetone, showing the formation of $[^{113}Cd_{4-x}Zn_x(SPh)_{10}]^{2-}$. For (a), $^{113}Cd/Zn \approx 2.7/1$ and $[^{113}Cd_4]_{initial} = 0.0014$ M; this spectrum was collected without proton decoupling and results from accumulation of transients from 10 000 45° (10 μs) pulses applied at 3-s intervals with a 1-s acquisition time. A 5-Hz line broadening has been used. For (b), $^{113}Cd/Zn \approx 1.2/1$ and $[^{113}Cd_4]_{initial} = 0.0013$ M; this spectrum results from accumulation of 17 404 transients obtained and processed as in (a).

mixtures at equilibrium, separate ^{113}Cd NMR signals *are* observed for the various clusters present (Figure 1); coordination of PhS$^-$ over otolS$^-$ is slightly but definitely preferred in **2**–otol$_2$S$_2$ mixtures, with the most intense ^{113}Cd NMR signal found for a mixture with otol$_2$S$_2$/**2** = 5 being that of $[Cd_4(SPh)_6(otolS)_4]^{2-}$.

Similarly, in equilibrated **2**–Ph$_2$Se$_2$ or **1**–Ph$_2$S$_2$ mixtures, coordination of PhS$^-$ over PhSe$^-$ is favored slightly, if at all: in both cases, when $Ph_2E'_2/[Cd_4(EPh)_{10}]^{2-} = 5$, the major species present is $[Cd_4(SPh)_5(SePh)_5]^{2-}$. However, when dialkyl disulfides are used, **1**–R$_2$S$_2$ and **2**–R$_2$S$_2$ mixtures require a large excess of R$_2$S$_2$ to push the equilibria (2) and (3) toward the right-hand side (Table I), and in no case was the all-alkyl $[Cd_4(SR)_{10}]^{2-}$ formed.

Cadmium-113 NMR Spectra of Cd(SR)$_4^{2-}$ (R = otol or ptol). For comparison with the ^{113}Cd NMR spectra of **2**–C$_6$H$_4$Me- and **4**–C$_6$H$_4$Me-containing tetranuclear clusters, we have measured δ_{Cd} for the corresponding 1/4 mononuclear complexes prepared from Cd^{2+} and excess thiolate in MeOH as reported earlier;[6,21] these data are included in Table II, as is the result of a remeasurement of δ_{Cd} for $Cd(SPh)_4^{2-}$. We find here that the presence of a significant excess of SR$^-$ is necessary to obtain sharp ^{113}Cd NMR signals for species of this type: for instance, at 295 K in 1/1 (v/v) MeCN–MeOH, a 0.05 M solution of an analytically pure sample of $(Me_4N)_2[Cd(SPh)_4]$[11] gives a broad ($\nu_{1/2} \approx 130$ Hz) ^{113}Cd resonance with $\delta_{Cd} \approx 571$. This salt is incompletely soluble in MeOH but dissolves in the presence of excess SPh$^-$: in a 0.4 M solution of NaSPh in MeOH, a 0.05 M solution of the salt gives a sharp ($\nu_{1/2} \approx 5$ Hz) ^{113}Cd signal with $\delta_{Cd} = 577$.

Cadmium-113 NMR Spectra of $[^{113}Cd_4(SPh)_{10}]^{2-}$–$[Zn_4(SPh)_{10}]^{2-}$ Mixtures. A careful ^{113}Cd NMR spectroscopic study of the incremental addition of $(Me_4N)_2[Zn_4(SPh)_{10}]$ to $(Me_4N)_2[^{113}Cd_4(SPh)_{10}]$ (or vice versa) in acetone demonstrates that redistribution occurs rapidly, confirms Holm's observation[10] that only three ^{113}Cd NMR signals are observed in this system, and now shows unambiguously that these are from chemically distinct species. The first new species, **3***, gives a ^{113}Cd resonance that is shielded by 0.45 ± 0.01 ppm relative to the resonance of **2*** and reaches its maximum relative intensity at Cd/Zn ≈ 2.7, as shown in Figure 4a. The second new species, **4***, gives a signal shielded by 0.92 ± 0.02 ppm relative to the resonance of **2*** that becomes the major signal when Cd/Zn $\lesssim$ 1.2. (See Figure 4b.) No fourth resonance could be observed up to Zn/Cd ≈ 2.1,[22] at which point a 1.2×10^{-3} M solution of **2*** is saturated with $(Me_4N)_2[Zn_4(SPh)_{10}]$. (The zinc salt is significantly less soluble than its cadmium analogue.)

The chemical shifts of **2***–**4*** vary slightly from sample to sample because of the effect of changing composition, slight temperature variations, or both. (The ^{113}Cd chemical shifts of **2** and **2*** are highly temperature sensitive.[6]) Therefore, to be quite certain of the presence of three species only, the mixture was cycled over the composition range several times with small incremental changes in composition. In this way the spectra for adjacent compositions can be correlated even if there are slight shifts of the individual spectra.

The similarity of the increments in δ_{Cd} on a change from **2*** to **3***, and from **3*** to **4*** (see above), makes it almost certain that **3*** and **4*** are $[^{113}Cd_3Zn(SPh)_{10}]^{2-}$ and $[^{113}Cd_2Zn_2(SPh)_{10}]^{2-}$, respectively, with the reasonable assumption that zinc substitution produces near-additive effects on δ_{Cd} in the series $[^{113}Cd_{4-x}Zn_x(SPh)_{10}]^{2-}$. We conclude that no detectable amount of the ^{113}CdZn$_3$ cluster is formed even where Zn/Cd ≈ 2.1.

Discussion

The position of equilibrium in the redox reactions (2) and (3) should be determined mainly by the relative reproducibilities to the corresponding chalcogenate anions of Ph$_2$S$_2$/Ph$_2$Se$_2$ vs. R$_2$E'$_2$ and the relative stabilities of the bonds between cadmium and PhS$^-$, PhSe$^-$, and RE'$^-$ in the Cd$_4$ cluster. From polarographic measurements[17b,23] is is known that the ease of reduction of R$_2$E$_2$ to RE$^-$ follows the order Ph$_2$S$_2$ ≈ otol$_2$S$_2$ ≈ ptol$_2$S$_2$ > Ph$_2$Se$_2$ >> (PhCH$_2$)$_2$S$_2$ > R$_2$S$_2$ (R = alkyl).[24] In previous ^{113}Cd NMR studies[21,25] it has been shown that, in mononuclear $Cd(ER)_4^{2-}$, ligands bind in the order PhSe$^-$ > PhS$^-$ and PhCH$_2$S$^-$ > PhS$^-$, and the same order will probably hold in the clusters. Our results for **2***–otol$_2$S$_2$ mixtures (see Table I, Figure 1, and above) are consistent with approximately equal stabilities for the Cd–SPh and Cd–S(otol) linkages, as expected; the very slight preference noted for PhS$^-$ over otolS$^-$ may be a steric effect. For the systems **2**–Ph$_2$Se$_2$ and **1**–Ph$_2$S$_2$, the order of reducibility, Ph$_2$S$_2$ > Ph$_2$Se$_2$, appears counterbalanced by the stability order Cd–SePh > Cd–SPh, so that at equilibrium the average PhS/PhSe ratio in the clusters approximates the PhS/PhSe ratio in the mixture (see above). However, it seems that the stability order Cd–SCH$_2$Ph > Cd–SPh is not enough to compensate for the order of ease of reduction Ph$_2$S$_2$ >> (PhCH$_2$)$_2$S$_2$, and we could not approach complete displacement of PhS$^-$ in **2**–(PhCH$_2$)$_2$S$_2$ mixtures. The difficulty in reducing (alkyl)$_2$S$_2$ must also account for the absence of $[Cd_4(S(alkyl))_{10}]^{2-}$ in **1**– and **2**–(alkyl)$_2$S$_2$ mixtures. We could find no quantitative data for the reduction of Ph$_2$Te$_2$, but this is almost certainly harder to reduce than Ph$_2$Se$_2$. Therefore, the formation of PhTe$^-$-containing clusters in **1***–Ph$_2$Te$_2$ (see Figure 3) and **2***–Ph$_2$Te$_2$ mixtures appears to indicate a relatively high stability for Cd^{2+}–PhTe$^-$ complexes. We are not aware of any other evidence for such species, though PhTe$^-$ complexes of Hg(II) are well established.[26]

In **1***–**2*** mixtures, the formation of a total of 11 different species (see Table I and Figure 2) confirms that **1** has the same type of tetranuclear cluster as **2**. The absence of resolvable separate signals for PhSe$_t$ and PhSe$_{br}$ in the ^{1}H and ^{13}C NMR spectra of **1** (see Experimental Section) is consistent with rapid intramolecular exchange of terminal and bridging ligands like that demonstrated earlier[10] for **2**. Rapid intramolecular interchange of bridging and terminal ligands of both types must occur in $[^{113}Cd_4(SPh)_x(SePh)_{10-x}]^{2-}$ (x = 1–9) and all of the other tetra-

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(21) Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 37–39.

(22) The results of ^{113}Cd NMR spectroscopy at 44.37 MHz (Figure 4) were confirmed at 66.53 MHz.

(23) Chambers, J. Q. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1978; Volume 3, Chapter XII-3, Table 2.4.2.

(24) These results are complicated by the possible occurrence of preequilibria at the Hg electrode.[17b]

(25) Carson, G. K.; Dean, P. A. W.; Stillman, M. J. *Inorg. Chim. Acta* **1981**, *56*, 59–71.

(26) (a) Liesk, J.; Klan, G. *Z. Anorg. Allg. Chem.* **1977**, *435*, 103–112. (b) Behrens, H.; Hoffman, K.; Klar, G. *Chem. Ber.* **1977**, *110*, 3672–3677.

nuclear mixed ligand complexes to account for the consistent observation of just one ^{113}Cd NMR signal for each individual species in the various equilibrium mixtures.

A remarkable feature of the ^{113}Cd NMR spectra of each series of mixed-ligand complexes $[Cd(EPh)_x(E'R)_{10-x}]^{2-}$ is the small range of the incremental shifts $\Delta\delta_{Cd}$ produced by incremental change in x. This is quite evident in Figures 1–3. The full ligand environment of the Cd$_4$ core averages at a rate fast on the NMR time scale (see above), and the near-statistical distribution of individual species (see above) suggests no marked preference of any of the ligands studied for either terminal or bridging positions. From the values of $\Delta\delta_{Cd}$(av) (i.e. with the crude approximation[27] made that $\Delta\delta_{Cd}$ does not depend on x in $[Cd_4(EPh)_x(E'R)_{10-x}]^{2-}$) values of δ_{Cd} can be estimated for some of those parent complexes for which direct spectral data were inaccessible. These are included in Table II, together with the data that could be measured directly, and values of δ_{Cd} for the corresponding mononuclear complexes, $Cd(ER)_4^{2-}$. Except for the cases where E'R = SBu, there is close agreement between the δ_{Cd} values of $Cd(ER)_4^{2-}$ and the corresponding results for $[Cd_4(ER)_{10}]^{2-}$, considering that data for different solvents, temperatures, and concentrations are compared in some instances. Therefore, we conclude that δ_{Cd} shows little sensitivity to the terminal or bridging nature of the ligand bound to cadmium. The same conclusion has been reached by Kurtz and co-workers[8] from the solid-state ^{113}Cd NMR spectra of salts of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$. At present we cannot account for the discrepancy found for the SBu complexes, but even in this case a relatively small change, 16 ppm or less, is projected for one terminal to bridging conversion.

Substitution of Zn for ^{113}Cd in $[^{113}Cd_4(SPh)_{10}]^{2-}$ produces a shielding of 0.46 ppm/Zn, confirming the assumption of Armitage and co-workers[1] that the ^{113}Cd NMR spectral result of such a change is small. The distribution of species in **2***–$[Zn_4(SPh)_{10}]^{2-}$ mixtures is not statistical, though: the equilibrium (5) lies well

$$2[^{113}CdZn_3(SPh)_{10}]^{2-} \rightleftarrows [^{113}Cd_2Zn_2(SPh)_{10}]^{2-} + [Zn_4(SPh)_{10}]^{2-} \quad (5)$$

to the right. The instability of the CdZn$_3$ species may have its origin in a mismatch of the sizes of the $(PhS_t)Cd(SPh_{br})_3$ and $(PhS_t)Zn(SPh_{br})_3$ groupings.[4,5] However, models show no evidence for a severe misfit in the CdZn$_3$ cluster, and $[Zn_4(SPh)_{10}]^{2-}$ apparently contains no unusual steric features;[5] in addition, we note that CdS and ZnS are miscible over the whole range of composition.[28] Whatever the origin of the effect, our results for the model heterometallic clusters resemble those found for Zn,Cd-MT, in that no ^{113}Cd NMR evidence was found[1] for the CdZn$_3$ combination in the four-atom cluster of the protein either. For the protein, the absence of the zinc-rich clusters CdZn$_3$ and Zn$_4$ has been attributed to increased steric hindrance between the residues when the smaller zinc ions predominate.[1]

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Registry No. **1**, 98541-30-1; **3**, 99725-82-3; **4**, 99706-35-1; $[Cd_4(S(otol))_{10}]^{2-}$, 99688-14-9; $[Cd(SPh)_4]^{2-}$, 66281-85-4; $[Cd(S(otol))_4]^{2-}$, 99688-15-0; $[Cd(S(ptol))_4]^{2-}$, 99688-16-1; $[Cd_4(S(ptol))_{10}]^{2-}$, 99706-32-8; $[Cd_4(SBu)_{10}]^{2-}$, 99706-33-9; $[Cd_4(SCH_2Ph)_{10}]^{2-}$, 99706-34-0; $(Me_4N)_2[Zn_4(SPh)_{10}]$, 76915-21-4; Ph_2S_2, 882-33-7; Ph_2Se_2, 1666-13-3; ^{113}Cd, 14336-66-4.

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(27) Using the assumption that $\Delta\delta_{Cd}$ is linearly dependent on x, to allow for possible curvature of the plot of δ_{Cd} vs. x, produces little change in the extrapolated values.

(28) Vankar, V. D.; Das, S. R.; Prem Nath; Chopra, K. L. *Phys. Status Solidi A* **1978**, *45*, 665–669 and references therein.

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EPR Spectrum of Tetragonally Compressed CuF_6^{4-}: Ligand and Metal Hyperfine Parameters

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The metal and ligand hyperfine splittings observed in the low-temperature EPR spectrum of ~1% copper(II) doped into single crystals of K_2ZnF_4 are reported. The splitting parameters of the axial ligands in the compressed tetragonal CuF_6^{4-} guest species are ~2.5 times those of the in-plane fluorines. The overall unpaired spin density on the metal is ~0.77, the bulk of which resides in the 3d$_{z^2}$ orbital, though with a minor contribution, ~0.03, in the metal 4s orbital.

Introduction

Analysis of the hyperfine coupling between electronic and nuclear spins provides a powerful method of investigating the ground-state wave function of a transition-metal complex.[1] The interaction with the metal nucleus depends upon the unpaired spin density in the metal d and s orbitals, the latter contribution apparently varying significantly as a function of the stereochemistry of the complex and the nature of the ground state.[2,3] The superhyperfine coupling involving ligand nuclear spins on the other hand allows the covalency of a complex to be quantified and this has provided a reasonably self-consistent picture of the unpaired spin density transferred to the ligands in a wide range of octahedral fluoride complexes.[4]

Recently, we reported the powder EPR spectra of copper(II)-doped K_2ZnF_4, this lattice being unusual because at low Cu^{2+} concentrations the comparatively rare tetragonally compressed geometry is stabilized for the guest CuF_6^{4-} species.[5] The g shifts and temperature dependence of the g values suggest that while the d$_{z^2}$ orbital is the most important component of the ground-state wave function, vibronic coupling causes significant admixtures of d$_{x^2-y^2}$ at higher temperatures and this aspect is the subject of a separate publication.[6] At low temperature, the spectra show

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(1) Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Ions"; Clarendon Press: Oxford, 1970; Chapter 17.

(2) Bencini, A.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1980**, *102*, 5234.

(3) Bertini, I.; Canti, G.; Grassi, R.; Scozzafava, A. *Inorg. chem.* **1980**, *19*, 2198.

(4) Owen, J.; Thornley, J. M. H. *Rep. Prog. Phys.* **1966**, *29*, 675.

(5) Reinen, D.; Krause, S. *Inorg. Chem.* **1981**, *20*, 2750.

(6) Riley, M.; Hitchman, M. A.; Reinen, D. *Chem. Phys.*, in press.

0020-1669/86/1325-0519$01.50/0