(SC(H)NMe$_2$), 59831-21-9; W(CO)$_4$(CNCH$_3$)(PPh$_3$), 59872-35-4; W(CO)$_5$(CS), 50358-92-4; [(Ph$_3$P)$_2$N][N$_3$], 38011-36-8; *trans*-W(CO)$_4$(PPh$_3$)(CNCH$_3$), 50298-29-8; cyclohexylamine, 108-91-8; *n*-BuNH$_2$, 109-73-9; *N,N*-dimethyl-1,3-diaminopropane, 109-55-7; piperidine, 110-89-4; benzylamine, 100-46-9; diethylamine, 109-89-7; *tert*-butylamine, 75-64-9; *cis*-W(CO)$_4$(CS)(PPh$_3$), 58617-28-0; *trans*-W(CO)$_4$(CS)(PPh$_3$), 50358-94-6; tributylphosphine, 998-40-3; 4-picoline, 108-89-4; DABCO, 280-57-9; pyridine, 110-86-1; 2-picoline, 109-06-8; triethyl phosphite, 122-52-1; 3-bromopyridine, 626-55-1; 2,6-lutidine, 108-48-5; tetrahydrofuran, 109-99-9; benzyldimethylamine, 28262-13-7; triethylamine, 121-44-8; diethyl ether, 60-29-7; *cis*-W(CO)$_4$(PPh$_3$)(CNC$_4$H$_9$), 59831-22-0; *trans*-W(CO)$_4$(PPh$_3$)-(CNC$_4$H$_9$), 59872-36-5; glycine methyl ester, 616-34-2; dimethylamine, 124-40-3; CH$_3$NH$_2$, 74-89-5.

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gave *trans*-W(CO)$_4$(PPh$_3$)(CNCH$_3$): ir (hexane) ν(CN) 2136 (w), ν(CO) 2059 (vw), 1912 (vs) cm^{-1}.
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Cadmium-113 Fourier Transform Nuclear Magnetic Resonance and Raman Spectroscopic Studies of Cadmium(II)–Sulfur Complexes, Including [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$]$^{4+}$

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The ^{113}Cd Fourier transform NMR and Raman spectra (1700–100 cm^{-1}) of a series of Cd(II) chelate complexes (derived from dithiocarbamate, xanthate, dithiophosphinate, and dithiolate ligands), Cd(SCH$_2$CH$_2$OH)$_2$, and [Cd$_{10}$-(SCH$_2$CH$_2$OH)$_{16}$]$^{4+}$ have been determined. Cd–S stretching vibrations have been assigned to bands in the 220–144-cm^{-1} interval. ^{113}Cd chemical shifts of chelate complexes exhibited no trend in terms of the extent of sulfur ligation, but the nuclear deshielding sequence Cd(SR)$_2$ < Cd(SR)$_3$ < Cd(SR)$_4$ is indicated by measurements on the 1:2 cadmium-(II)–glutathione complex and the decanuclear cation, which contains sites of the latter two types. The solution stability of [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$]$^{4+}$ has been investigated by ^{1}H and ^{113}Cd NMR and Raman spectroscopy from –40 to +100°C. It is concluded that small structural differences may exist between the crystalline and solution phases, arising mainly from partial rupture of CdSCH$_2$CH$_2$OH chelate rings known to be present in the crystal, and that the solution structure approaches that in the crystal as solution temperatures are lowered below ca. 20–25 °C. From data obtained in this and previous studies a provisional ^{113}Cd chemical shift scale is presented in terms of the types of ligand atoms in the primary coordination sphere of Cd(II). A conspicuous feature of this scale is the marked deshielding effect of thiolate sulfur vs. oxygen, halide, and nitrogen ligands relative to the reference zero of chemical shift, 0.1 M aqueous Cd(ClO$_4$)$_2$ at 25 °C. Possible application of the deshielding sequence to investigation of cadmium–cysteinate binding in metallothionein proteins is suggested.

Introduction

In the past direct observation of the high-resolution NMR spectra of a number of the heavier nuclei[2,3] of the metallic elements has been hampered by their low natural-abundance sensitivity (S) at constant field (S = abundance × NMR sensitivity at constant field). The inherent sensitivities of nuclei (N) such as ^{27}Al, ^{59}Co, and ^{205}Tl, for which S(N)/S(^{13}C) $\simeq$

1200, 1600, and 770,[4,5] respectively, do not normally present a problem of detection (excluding effects of quadrupolar line broadening) in conventional CW spectroscopy, accounting for the numerous NMR investigations of compounds containing these nuclei. However, reduction of the sensitivity ratio by ca. 10^2 or more renders the CW mode of detection impractical or at best possible only in large volumes of concentrated solutions. Recent developments in variable-frequency pulse Fourier transform techniques[4–7] now make practicable the

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direct observation of the spectra of the less sensitive heavier nuclides in natural abundance with a facility which promises to approach that of ^{13}C spectroscopy. Among the nuclei recently examined by FT techniques are ^{199}Hg,[4,8] ^{207}Pb,[4,9] and ^{113}Cd,[4-6,10] for which $S(N)/S(^{13}C) \simeq 6$–11.

NMR spectra of these and many other heavy nuclei are characterized by extreme sensitivity of their chemical shifts to structure and metal ligation, a behavior which is most easily observed for nonquadrupolar nuclei, among which is ^{113}Cd.[11] Relative to 0.1 M aqueous Cd(ClO$_4$)$_2$ standard a chemical shift scale of ca. 700 ppm has been established from measurements on organometallic compounds in nonaqueous media and various inorganic salt and complex systems in aqueous solution.[4,6,10,12] Included among these results are those of Kostelnik and Bothner-By,[12] who examined the effects of ligand binding on chemical shifts from CW spectra of labile species in concentrated solutions. The most comprehensive high-resolution ^{113}Cd spectroscopy reported to date is that by Cardin et al.,[6] who have provided information concerning ligand and solvent dependence of chemical shifts as well as T_1 relaxation time data. The present work was initiated in order to ascertain if a ^{113}Cd chemical shift scale could be developed involving correlations of shift with various types of coordination units, especially those containing sulfur alone or in combination with oxygen and nitrogen donors. In view of the pronounced tendency of Cd(II) to form mono- and polynuclear complexes of varying structural types with sulfur ligands (vide infra), correlation of shift with extent of sulfur ligation could be a potentially useful method for at least partial identification of coordination units. Raman spectral studies have been conducted in conjunction with NMR experiments in order to provide additional information on solution structures and to expand the limited set of data for Cd–S vibrational frequencies.

Experimental Section

Preparation of Compounds. Reagent grade Cd(ClO$_4$)$_2$·6H$_2$O, Cd(NO$_3$)$_2$·4H$_2$O, CdCl$_2$·$\frac{5}{2}$H$_2$O, and anhydrous CdBr$_2$ all were used without further purification. Cd(CF$_3$SO$_3$)$_2$ was prepared by dissolving reagent grade CdO in trifluoromethanesulfonic acid and evaporating to dryness. The white solid obtained was recrystallized from hot water and dried in vacuo. ^{113}Cd used for isotope enrichment was obtained from Oak Ridge Laboratories in the form of ^{113}CdO (97.5% isotopic purity), which was converted to ^{113}Cd(ClO$_4$)$_2$·6H$_2$O for subsequent use. The following compounds were prepared by published methods: bis(N,N'-diethyldithiocarbamato)cadmium(II)[13] (Cd(Et$_2$(dtc)$_2$)), bis(O,O'-diisopropyl dithiophosphinato)cadmium(II)[14] (Cd(dpdtp)$_2$), tetraethylammonium tris(O-ethyl xanthato)cadmate(II)[15] ((Et$_4$N)[Cd(exan)$_3$]), Cd(SCH$_2$CH$_2$OH)$_2$.[16,17]

[Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$](ClO$_4$)$_4$. This compound was prepared by the method of Schwarzenbach et al.[18] and was analyzed to ensure identification. Anal. Calcd for C$_{32}$H$_{80}$Cd$_{10}$Cl$_4$O$_{32}$S$_{16}$: C, 13.95; H, 2.93; Cd, 40.79; Cl, 5.15; S, 18.62. Found: C, 14.10; H, 2.93; Cd, 40.62; Cl, 5.20; S, 18.60. The NO$_3^-$ and CF$_3$SO$_3^-$ salts were prepared by the same method.

(Et$_4$N)$_2$[Cd(S$_2$C$_2$(CN)$_2$)$_2$]. This compound, containing the Cd-(mnt)$_2^{2-}$ anion, was prepared from Na$_2$mnt[19] by a procedure analogous to that for its zinc(II) analogue[20] and was recrystallized from ethanol. Anal. Calcd for C$_{24}$H$_{40}$CdN$_6$S$_4$: C, 44.17; H, 6.13; N, 12.88. Found: C, 43.81; H, 6.20; N, 12.60.

Cd(II) complexes of EDTA and glutathione were prepared using 0.5 M Cd(NO$_3$)$_2$ solutions and 1 and 2 equiv of ligand, respectively. Final pH values were adjusted by use of potassium hydroxide or nitric acid.

Physical Measurements. ^{113}Cd NMR spectra were recorded on a Bruker HFX-90 spectrometer employing the multinuclei modification of Traficante et al.[7] and operating at 19.96 MHz with a magnetic field of ca. 21.2 kG and an rf power of 100 W. The spectrometer was locked on the ^{19}F resonance of either C$_6$F$_6$ or C$_2$F$_4$Br$_2$ contained in a 1-mm coaxial capillary for all spectra. Spectra were obtained using 10-mm o.d. tubes and are externally referenced to 0.1 M aqueous Cd(ClO$_4$)$_2$ solutions at 25 °C unless otherwise indicated. Raman

Table I. ^{113}Cd NMR Data at 25 °C

Compd	Solvent	Concn, M	$\delta,^a$ ppm	$\Delta H_{1/2}$, Hz
Cd(ClO$_4$)$_2$	H$_2$O	2.0	5.8	3
		1.0	2.2	3
		0.10	0.0	3
	MeOH	1.0	29.4	5
	DMSO	0.50	26.0	8
	DMF	1.0	45.5	8
	Pyridine	0.20	−80.2	5
Cd(NO$_3$)$_2$–imidazole (1:25)	H$_2$O, pH 5.0	0.50^d	−74.2	8
Cd(CF$_3$SO$_3$)$_2$	H$_2$O	1.0	3.0	5
	MeOH	1.0	47.0	5
CdCl$_2$	12 M HCl	1.0	−264.5	4
		0.50	−278.8	3
		0.10	−287.3	8
CdBr$_2$	9 M HBr	1.0	−167.0	3
[Cd(EDTA)]$^{2-}$	H$_2$O, pH 5	0.50	−85.2	60
Cd(II)–glutathione (1:2)	H$_2$O, pH 9.5	0.50^d	−318	70
	H$_2$O, pH 10.4	0.50^d	−317	60
Cd(SCH$_2$CH$_2$OH)$_2$	DMSO	0.20	−655	350
[Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$](ClO$_4$)$_4$^{b}	DMF	0.20	−520 (3)	105
			−387 (2)	80
[^{113}Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$](ClO$_4$)$_4$^{c}	H$_2$O	0.065	−515 (3)	45
			−382 (2)	230
[Cd(dpdtp)$_2$]$_2$	PhCH$_3$	0.50	−401	5
(Et$_4$N)$_2$[Cd(mnt)$_2$]	DMSO	0.50	−813	12
Cd(Et$_2$dtc)$_2$	DMSO	0.08	−215	45
(Et$_4$N)[Cd(exan)$_3$]	CHCl$_3$	0.50	−277	43

^{a} Referenced to external aqueous 0.1 M Cd(ClO$_4$)$_2$ at 25 °C. Shifts have been corrected for bulk diamagnetism using measured susceptibilities or published values ("Handbook of Chemistry and Physics", R. C. Weast, Ed., 54th ed, CRC Press, Cleveland, Ohio, 1973-1974). Corrections are very small, ranging from −0.44 ppm (DMF) to ~0 ppm. The numbers in parentheses indicate relative integrated intensities. ^{b} −10 °C. ^{c} 5 °C. ^{d} Cd(II) concentration.

spectra were recorded with a Spex Ramalog Model 4 spectrometer equipped with a Coherent Radiation 52 G argon ion laser. Solid samples were pressed into pellet form. Solution samples were centrifuged to remove any suspended material before injection into a "Kimax" melting point capillary (No. 34507, 1.0-mm i.d.) used as a Raman cell. For recording spectra below or above room temperature, cells were placed in a massive thermostat of the design of Thomas and Barylski,[21] by means of which the temperature was controlled to better than ±1 °C. At least 15 min was allowed for the sample to reach equilibrium after the thermostat temperature had become constant at a new temperature. A mixture of dry ice and 2-propanol was used to cool the cell to −40 °C. The laser power of the 4880-Å excitation line measured at solid samples was ca. 25 mW and at solution samples ca. 75 mW. The scattered radiation was observed at 90° to the incident beam and the spectral slit width for all spectra was 6 cm^{-1}. Each spectrum was recorded in 1 h.

Results and Discussion

The complexes or solution systems for which ^{113}Cd NMR spectra have been determined are set out in Table I, in which are listed chemical shifts and line widths at signal half-heights. All shifts are relative to 0.1 M Cd(ClO$_4$)$_2$ external standard and have been corrected for the bulk diamagnetism of the various nonaqueous solvents employed. The species examined are most simply considered in terms of the types of donor atoms which are known or may reasonably be assumed to be directly ligated to Cd(II). Chemical shifts of specific complexes and ranges of shifts for different types of ligation are presented in the graphical chemical shift scale in Figure 1. Results are drawn from this investigation and those by Maciel and Borzo[10] and Cardin et al.[6] These data define a chemical shift range of ca. 850 ppm. Decreasing negative (increasing
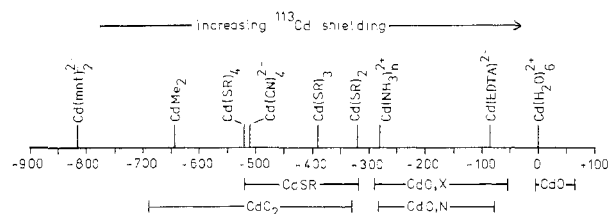
Figure 1. Schematic ^{113}Cd chemical shift scale derived from data obtained in this and other investigations.[6,10] Shifts are referenced to 0.1 M Cd(ClO$_4$)$_2$ external standard. For Cd–S species R = CH$_2$-CH$_2$OH. CdC$_2$ species are dialkyl compounds and CdPh$_2$, measured as neat liquids and in a variety of nonaqueous solvents.

positive) values denote resonances displaced in the direction of increasing shielding (higher applied field). All spectra were recorded without proton decoupling; in no case was ^{113}Cd–^{1}H coupling observed in the ^{113}Cd spectra.

Cd–O and Cd–O,X Species. A recent x-ray diffraction study[22] of aqueous Cd(ClO$_4$)$_2$ solutions has established that the solvated cation is Cd(H$_2$O)$_6^{2+}$.[23] Chemical shifts extrapolated from 3.0 M to infinite dilution for Cd(ClO$_4$)$_2$ and CdSO$_4$ solutions indicate the shift ranges 13.4 and 5.1 ppm, respectively, with less shielded resonances found in the more dilute solutions.[12] From 4.0 M Cd(NO$_3$)$_2$ the range is 65 ppm.[12] The concentration dependence of shifts may arise from inner- or outer-sphere complexation involving weakly coordinating anions which, however, must be slight in view of the small formation constants obtained for such systems.[25–27] The data in Table I and from other sources[6,10,12] reveal that in 0.015–4.5 M solutions containing predominantly or exclusively Cd(H$_2$O)$_6^{2+}$ in the presence of nitrate, perchlorate, or sulfate counterions the chemical shift range is ca. –1.4 to +65 ppm relative to the standard. Six-coordinate solvate complexes may also be expected in methanol, DMF, and DMSO solutions,[23] and in these media the shift range is 26.0–45.5 ppm (Table I), which encompasses the shifts found for CdSO$_4$ in mixed aqueous solvents containing dioxane, acetone, DMF, and DMSO.[12] Assuming Cd–DMSO species to be oxygen ligated, the data define a range of ca. –1.4 to +65 ppm over the preceding concentration limits for complexes containing Cd–O$_6$ coordination units.

The presence of halide produces a deshielding effect on ^{113}Cd resonances. In 0.1–5.0 M aqueous CdX$_2$ solutions (X$^-$ = Cl$^-$, Br$^-$, I$^-$) resonances span the interval of –55 to –131 ppm.[6,10,12] In the presence of large excesses of chloride and bromide, under which conditions concentrations of CdX$_3^-$ and CdX$_4^{2-}$ are expected to predominate,[27,28] greater downfield shifts are observed. Thus with molar ratios X:Cd ≥2 the observed shift range at the specified Cd(II) concentrations is ca. –55 to –290 ppm. In Figure 1 this range is attributed to the generalized species Cd–O,X inasmuch as the majority of data refer to solutions containing mixtures of species with both aquo and halide coordination.

Cd–O,N and Cd–N Species. It has previously been observed that in 2 M CdSO$_4$ solutions containing ligand:Cd molar ratios of 0.025–0.25 obligatory (ethylenediamine, pyridine, azide) and probable nitrogen-binding ligands (amino acids) effected small displacements of ^{113}Cd shifts to less shielded positions.[12] Oxygen-binding ligands had a similarly small but opposite chemical shift effect. A 1.0 M solution of Cd(NH$_3$)$_6$Cl$_2$ in 50:50 NH$_3$–D$_2$O exhibited a resonance at –287 ppm.[6] Substantial deshielding is observed in aqueous Cd(EDTA)$^{2-}$ (–85.2 ppm) and Cd(NO$_3$)$_2$–imidazole solutions (~–74.2 ppm) and in a solution of Cd(ClO$_4$)$_2$·6H$_2$O in neat pyridine (–80.2 ppm). Salts of [Cd(Im)$_6$]$^{2+}$ have been isolated from solutions containing a smaller Im:Cd ratio than employed here and the octahedral structure of the cation has been established by x-ray diffraction.[29] These results demonstrate that diverse nitrogen

ligands cause downfield shifts relative to the hexaaquo ion. These limited data for complexes in which two or more nitrogen atoms are bound and the remaining coordination positions (if any) are occupied by oxygen donor ligands suggest a chemical shift range of ca. –70 to –290 ppm. This range is indicated as that for Cd–O,N species in Figure 1.

Cd–S Species. Of the various Cd(II) ligation modes those involving sulfur are of particular interest in view of the diversity and complexity of structures encountered. For those complexes in which ligation is exclusively by sulfur, approximately tetrahedral (Cd(exan)$_2$[30] and bis(O-n-butyl xanthate)[31] polymers, [Cd(dpdtp)$_2$]$_2$[32]), square-pyramidal ((Et$_4$N)[Cd-(exan)$_3$][33]), and intermediate square-pyramidal–trigonal-bipyramidal ([Cd(Et$_2$dtc)$_2$]$_2$[34]) coordination units have been established by x-ray diffraction. Polynuclear complex formation effected by thiolate sulfur bridging is a common occurrence and for Cd(II) complexes has been recognized in solution[18,35–37] and in the solid state.[16,38–40] A near limit of polynuclear complexity in any discrete sulfur-containing species is found with the decanuclear cluster cation [Cd$_{10}$-(SCH$_2$CH$_2$OH)$_{16}$]$^{4+}$, whose Cd–S framework[39] is represented in Figure 2.

(a) Cd(II) Chelates. In order to investigate the relationship, if any, between extent of sulfur ligation and ^{113}Cd shifts, complexes known to contain only Cd–S bonds in the solid state and to be soluble to the extent of ca. 0.1 M were examined (Table I). Under the experimental conditions the dimeric structure of [Cd(dpdtp)$_2$]$_2$ should be preserved in toluene.[32] Inasmuch as Cd(Et$_2$dtc)$_2$ exists as a dimer–monomer mixture in benzene,[34,41] a five- or six-coordinate structure CdS$_4$O$_{1,2}$ is anticipated in DMSO solution. One of these structures or a tetrahedral CdS$_4$ unit is likely for Cd(mnt)$_2^{2-}$ in DMSO. Earlier it had been observed that addition of thiourea to aqueous 2 M CdSO$_4$ solutions at ligand:metal molar ratios up to 0.5 produced definite deshielding effects on ^{113}Cd resonances.[12] X-ray data show that in a variety of structures thiourea binds to Cd(II) exclusively through sulfur,[42] a feature that doubtless applies to the solution state as well. Resonances of the four chelate complexes are substantially deshielded and cover the range of –215 to –813 ppm, with [Cd(mnt)$_2$]$^{2-}$ affording the lowest field signal observed in this work. Other than noting the shift order [Cd(exan)$_3$]$^-$ > Cd(Et$_2$dtc)$_2$, suggesting decreased shielding in the CdS$_5$ relative to the CdS$_4$ unit in complexes with similar ligands, no trends in chemical shift are evident. These variant values suggest that shielding effects are not simply related to the number of sulfur atoms coordinated but are also sensitive to the electronic nature of these atoms as influenced by the remainder of the ligand structure.

(b) Cadmium(II) Thiolates. The sensitivity of ^{113}Cd shifts to the extent of sulfur coordination at near parity of the remainder of the ligand structure was then examined by the use of several cadmium(II) alkylthiolate complexes which furnish cases of two (1:2 glutathione complex[43,44]) and three and four ([Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$]$^{4+}$ [18,39]) sulfur atoms bound to cadmium. The glutathione complex has been identified only in solution. The decanuclear cation, with a Cd$_{10}$S$_{16}$ core in which every sulfur atom is doubly or triply bridging (Figure 2), has overall S_4 symmetry[39] such that cadmium atoms 1–4 define a tetrahedron and members of the sets Cd$_{1–4}$, Cd$_{5,6}$, and Cd$_{7–10}$ are symmetry related. Cd$_{5,6}$ are located at tetrahedral CdS$_4$ sites (Cd–S = 2.51 Å), Cd$_{7–10}$ exhibit trigonal-bipyramidal coordination (Cd–S$_{eq}$ = 2.52 Å, Cd–S$_{ax}$ = 2.86 Å), and Cd$_{1–4}$ have distorted cis-octahedral coordination (Cd–S 2.56 Å).[39] Except for the long axial bond, Cd–S distances are normal compared with those of other structures.[30–34,42,45] Cd–O bonds (2.41, 2.46 Å) involve ligand hydroxyl groups and result in closure of five-membered chelate
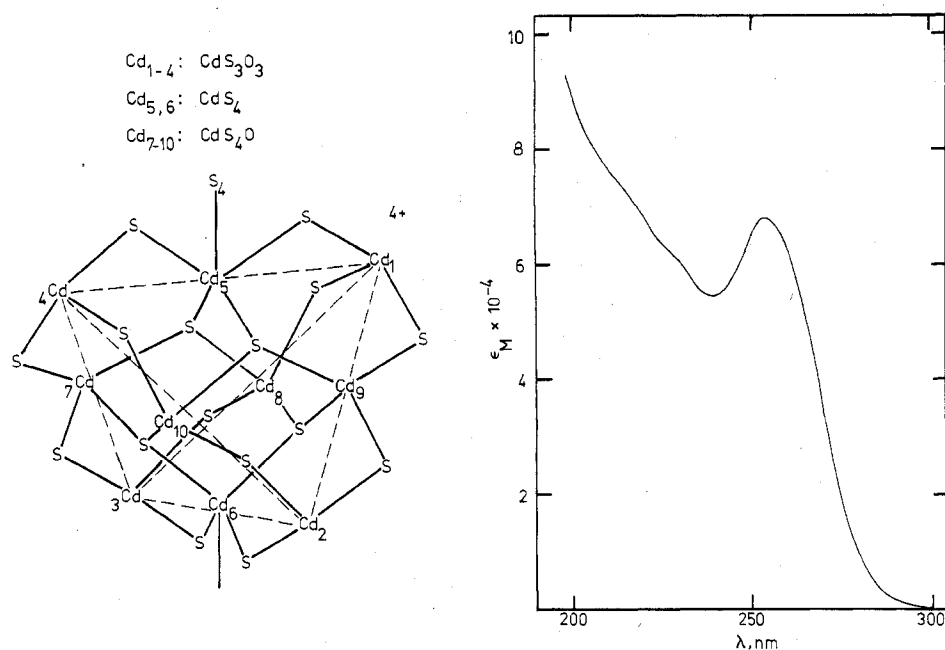
Figure 2. Left: representation of the Cd–S framework of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$. Coordination units for the three distinct types of Cd(II) sites are indicated. Depictions emphasizing the three-dimensional aspects of the structure are available elsewhere.[18,38] Right: electronic spectrum of $[Cd_{10}(SCH_2CH_2OH)_{16}](ClO_4)_4$ in aqueous solution; λ_{max} 254 nm, ϵ_M 68 700 M^{-1} cm^{-1}.
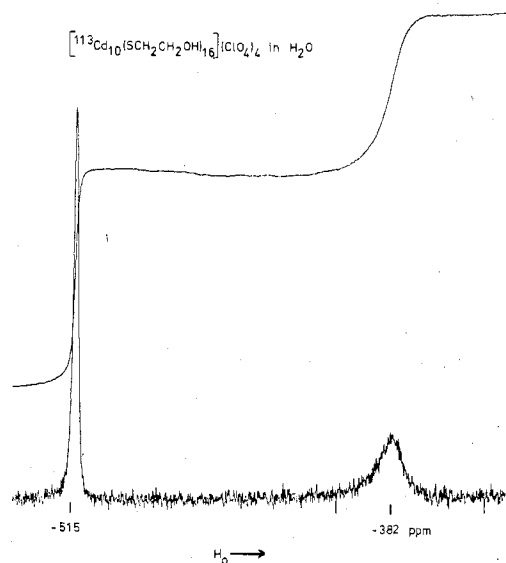
Figure 3. Cd NMR spectrum of $[^{113}Cd_{10}(SCH_2CH_2OH)_{16}](ClO_4)_4$ in 0.065 M aqueous solution: 24 000 pulses, 11-μs pulse, 0.8-s delay between pulses, 4K point transform, 9090-Hz bandwidth.

Figure 4. Temperature dependence of the Cd NMR spectrum of $[^{113}Cd_{10}(SCH_2CH_2OH)_{16}](ClO_4)_4$ in 0.2 M DMF solution. Chemical shifts are in ppm. The conditions in Figure 3 apply except that 5000 pulses were used.

rings whose oxygen atoms are external to the core. Distances of Cd–O bonds in numerous structures are decidedly variable (ca. 2.2–2.8 Å) and those in the decanuclear cation lie near the center of the observed range.[46]

The ^{113}Cd NMR spectrum of isotopically enriched (~98%) $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ in aqueous solution at 25 °C is shown in Figure 3. The two signals at –515 and –382 ppm have an integrated intensity ratio of nearly 3:2. This result together with the tendency of oxygen ligands to enhance nuclear shielding (Table I) suggests the assignments of the low- and high-field signals to Cd_{5-10} and Cd_{1-4}, respectively. To examine further these assignments and to investigate the stability of the decanuclear cation in solution, studies of the ^{113}Cd NMR and Raman spectra in solutions over appreciable temperature intervals have been conducted.

^{113}Cd NMR spectra of isotopically enriched $[Cd_{10}-(SCH_2CH_2OH)_{16}]^{4+}$ were examined in 0.1 and 0.2 M DMF

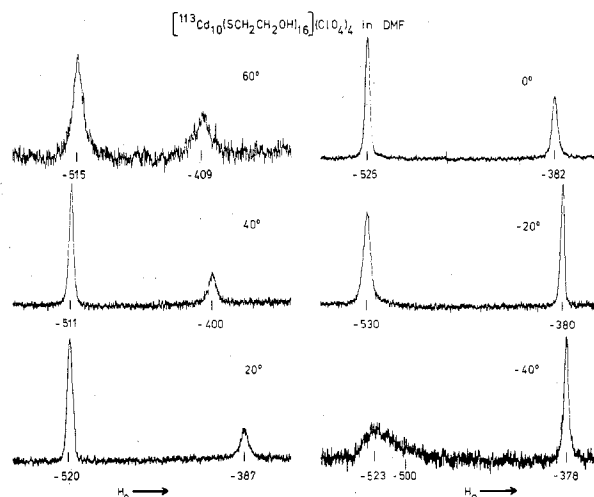solutions from –40 to +100 °C. This solvent was chosen to afford a wide temperature range; spectra of these two solutions at all temperatures were the same. Spectra at selected temperatures are shown in Figure 4 and reveal temperature dependencies of line widths and chemical shifts, with the shifts of the high-field signal exhibiting the larger dependence. In terms of signal assignment the temperature dependence of the low-field resonance line shape is the more useful. From ca. +40 to –10 °C a sharp signal with nearly constant shift and half-width (~100 Hz) is observed. At lower temperatures the line shape becomes progressively asymmetric until at –40 °C the signal broadens to the point where two signals are just resolvable, suggesting a two-site exchange process. Resolution at this temperature is limited by the high viscosity of the solution, and, possibly, the line shape is additionally broadened because the slow-exchange limit has not been attained. The two partially resolved features presumably arise from the CdS$_4$ and CdS$_4$O environments in the Cd_{5-10} sites and tend to
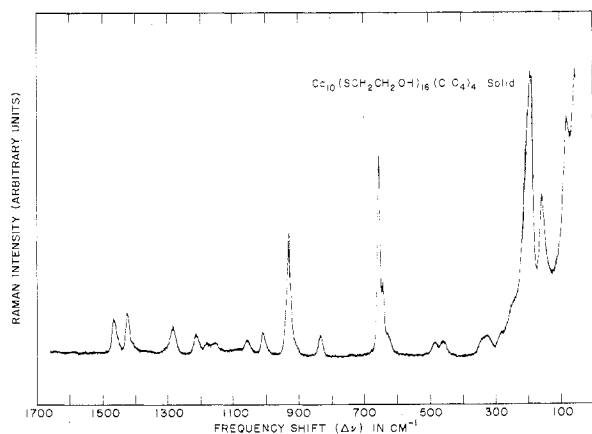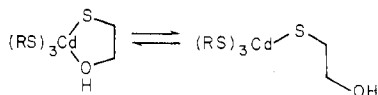
Figure 5. Raman spectrum of a solid pressed pellet of $[Cd_{10}(SCH_2-CH_2OH)_{16}](ClO_4)_4$.

substantiate the low-field signal assignment to these sites. The exchange process most likely proceeds via the labile equilibrium

which is shifted to the right with increasing temperature. The high-field signal progressively broadens and shifts to lower field as the temperature is increased. These changes within the interval of −40 to ca. +40 °C are interpreted in terms of a similar equilibrium between chelated and nonchelated forms at the Cd_{1-4} sites, with the fully chelated limit approached or achieved at −40 °C and fast exchange operative at higher temperatures. It is probable that chelate ring rupture at Cd_{1-4} and Cd_{7-10} sites is accompanied by some extent of DMF solvation. Whatever may be the coordination arrangement around cadmium as a result of hydroxyl group detachment, the effect on Cd_{1-4} shielding should be larger than for Cd_{7-10}, as observed. Consistent with the proposal of a rapid equilibrium of the above type at these two types of sites is the temperature dependence of the hydroxyl proton NMR spectra in DMF-d_7. From −27 to +39 °C two signals with invariant 3:1 integrated intensities are observed, arising from the twelve and four hydroxyl groups associated with sites Cd_{1-4} and Cd_{7-10}, respectively. The more intense signal shifts from 5.98 to 5.57 ppm and the less intense signal from 6.82 to 6.44 ppm, i.e., toward the more shielded values of the free ligand itself (4.44 ppm at −40 °C, 3.94 ppm at 25 °C in DMF-d_7).

At temperatures above ca. 50 °C both [113]Cd resonances broaden markedly and coalesce to a single broad line (200-Hz half-width) at 100 °C. Line shape changes are suggestive of an additional dynamic process whose NMR kinetic range partially overlaps that of processes observed at lower temperatures. While spectra obtained up to 70 °C in both DMF and aqueous solution are fully reversible with temperature, those obtained at higher temperatures were accompanied by precipitate formation and substantial departures from 3:2 intensity ratios when remeasured at those temperatures (−20 to +20 °C in DMF, 5–20 °C in H_2O) at which the intensity ratio found with unheated solutions is exactly 3:2. Until conditions are found which afford spectra fully reversible with temperature, we refrain from attempting an interpretation of the high-temperature spectra.

The Raman spectra of $[Cd_{10}(SCH_2CH_2OH)_{16}](ClO_4)_4$ in the solid state, in H_2O and D_2O solutions, and in DMF solution at temperatures ranging from −40 to +60 °C are set out in Figures 5–7, respectively. Of principal interest are the Cd–S vibrations. Frequencies and proposed assignments are listed in Table II for this compound and for $Cd(SCH_2C-$
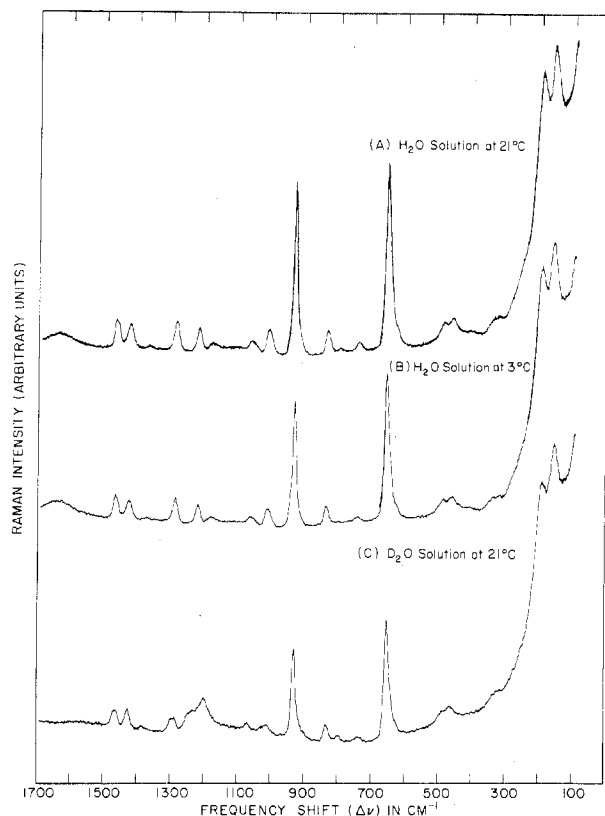

Figure 6. Raman spectra of $[Cd_{10}(SCH_2CH_2OH)_{16}](ClO_4)_4$ in H_2O and D_2O solutions at 21 °C and in H_2O solution at 3 °C.

Table II. Raman Frequencies of Cadmium(II) β-Hydroxyethanethiolate Complexes

Compd	Conditions	Freq, cm⁻¹	Assignment
$[Cd_{10}(SCH_2CH_2-OH)_{16}](ClO_4)_4$	Solid[b]	160, 197	Cd–S
		~250 sh, 330	Cd–O?
		644, 658	C–S
	$D_2O, H_2O, 21$ °C	160, 197	Cd–S
		330[a]	Cd–O
		660	C–S
	DMF, 21 °C[a]	160, 193	Cd–S
		660	C–S + DMF
	DMSO, 21 °C[a]	160, 193	Cd–S
		672	C–S + DMSO
$Cd(SCH_2CH_2-OH)_2$[c]	Solid	168, 190 sh	Cd–S
		~250 sh, 314	Cd–O?
		658	C–S

[a] Poorly defined shoulder near 250 cm⁻¹ may be a Cd–O vibration. [b] Additional bands: 84 (lattice), 462 (ClO_4^-, E), 488, 630 (ClO_4^-, F_2), 834 (C–C), 932 (ClO_4^-, A_1), 1012 (C–O), 1060 (ClO_4^-, F_2), 1154, 1180, 1214, and 1284 (CH deformations), 1427 and 1469 cm⁻¹ (CH_2 scissors). [c] Additional bands: 404, 484, 743, 812 (C–C), 944, 1012 (C–O), 1056, 1154, 1180, 1214, and 1284 (CH deformations), 1427 and 1469 cm⁻¹ (CH_2 scissors).

$H_2OH)_2$. The latter compound is polymeric and contains tetrahedral Cd–S_4 (Cd–S = 2.56 Å) and trigonal-bipyramidal (Cd–S_{eq} = 2.54 Å, Cd–S_{ax} = 2.69 Å, Cd–O_{ax} = 2.62 Å) coordination units.[16] Assignments of C–S frequencies are compatible with those of Bellamy[47] for aliphatic sulfur compounds. Systematic studies of Cd–O and Cd–S vibrations leading to secure identification of stretching frequencies are very limited. Examination of literature data suggests the approximate range of 240–390 cm⁻¹ for Cd–O stretches. Raman studies of $Cd(H_2O)_6{}^{2+}$ place $\nu_3(F_{1u})$ at 348–356
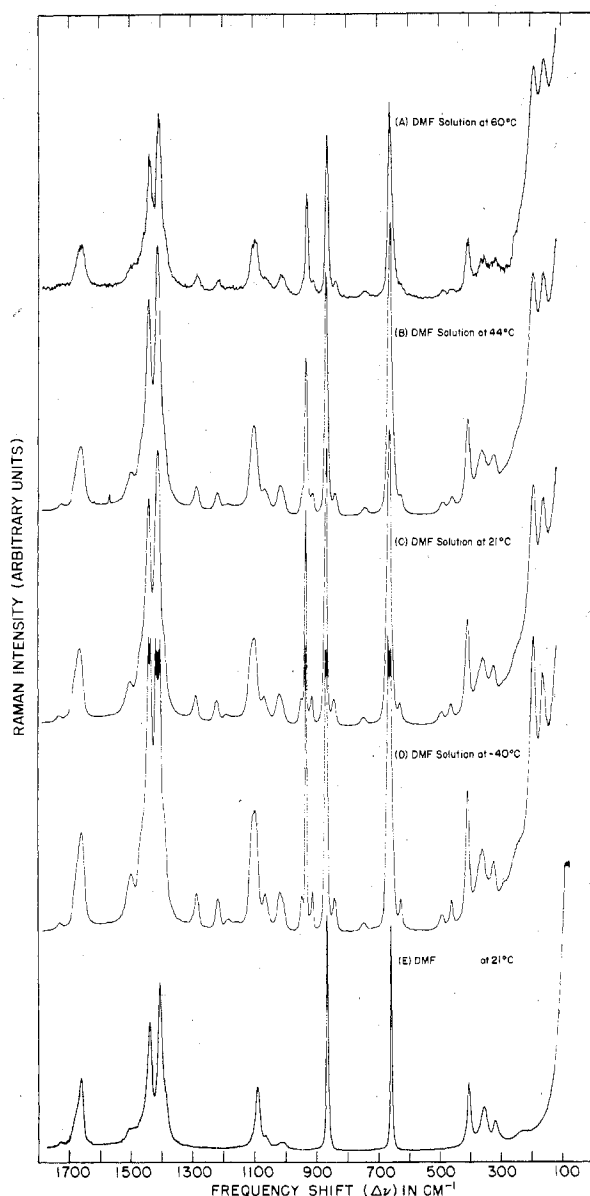
of bis(monothioacetylacetonato) complexes, bands at 245 and 180 cm^{-1} have been assigned to Cd–S stretches.[49] Other assignments of Cd–S vibrations fall in the range of ca. 400–200 cm^{-1}.[15,50]

The Raman spectra of [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$](ClO$_4$)$_4$ in the solid state and in H$_2$O and D$_2$O reveal no observable frequency shifts of the two bands assigned to Cd–S stretching vibrations. However, the intensity ratio $I(160)/I(197)$ increased from 0.52 in the solid to 1.06 in H$_2$O and 1.17 in D$_2$O at 21 °C (Figures 5 and 6). This behavior was further examined over a wider temperature range in DMF solution (Figure 7). The intensity ratio increased monotonically from 0.83 at –40 °C to 1.03 at +60 °C (0.91 at +21 °C) and changed reversibly with temperature. Other than intensity changes the spectra at 1700–100 cm^{-1} were unaltered over the temperature range. These results in conjunction with ^{113}Cd NMR data lead to the following conclusions: (i) upon passing from the crystalline to the solution state [Cd$_{10}$-(SCH$_2$CH$_2$OH)$_{16}$]$^{4+}$ undergoes a structural change, which is presumably small and involves wholly or partly rupture of Cd–O bonds; (ii) based on Raman intensity ratios the solution structure approaches that in the solid as the solution temperature is decreased; (iii) below 20–25 °C in aqueous and DMF solutions the presence of two ^{113}Cd signals with a constant 3:2 intensity ratio is consistent with (ii), and the lack of appearance of Raman bands not found in the solid-state spectrum (unless obscured by solvent) indicates appreciable stability of the decanuclear cation at these temperatures.[51]

To obtain additional information concerning the effect of thiolate sulfur ligation on ^{113}Cd nuclear shielding, aqueous solutions of Cd(NO$_3$)$_2$ and glutathione (H$_2$N-Glu-Cys-Gly-CO$_2$H) were examined under conditions (Table I) where mononuclear 1:2 complexes predominate.[43,44] Based on ^{1}H and ^{13}C NMR results,[43,52] Cd(II) is ligated most strongly to two cysteinate sulfur atoms with possible additional coordination involving peptide nitrogen and/or carboxylate.[43] The observed shift of –318 ppm at pH 9.5 is downfield of the currently known shift range for Cd–O,N species (Figure 1), again indicating that thiolate sulfur coordination causes marked deshielding relative to Cd(H$_2$O)$_6$$^{2+}$.[53]

Summary

The principal aims of this work have been to provide additional cases of the detection of ^{113}Cd NMR resonances by pulse FT techniques, and to commence the definition of a ^{113}Cd chemical shift scale, indexed in terms of the number and types of ligand atoms in the primary coordination sphere of Cd(II), using previous[6,10,12] and present data with particular reference to the influence of sulfur ligands on relative nuclear shielding. The shift scale in Figure 1 must be considered *provisional* because of the limited data available and the uncertainty in structure and ligation of a number of Cd(II) species examined, especially in aqueous solution. Revisions in the scale are to be expected as additional chemical shift data become available. As already emphasized Cd–S complexes with different chelating ligands display no systematic trends in chemical shifts. A discernible trend has been found only with alkylthiolate complexes, derived from glutathione and β-hydroxyethanethiol, and, in terms of sulfur ligation only, the following deshielding sequence (also in Figure 1) is indicated: Cd(SR)$_2$ (–318 ppm) < Cd(SR)$_3$ (–380 ppm) < Cd(SR)$_4$ (–520 ppm). In assessing this sequence it should be borne in mind that, with the apparent exception of the first member, the inherent shielding propensity of thiolate sulfur is doubtless modified by its bridging function between two or three Cd sites in [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$]$^{4+}$ (Figure 2) as well as by the influence of additional ligation by other atoms. Unfortunately, no other structurally defined cadmium(II) alkylthiolate complexes are currently available which would allow further

Figure 7. Temperature dependence of the Raman spectrum of [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$](ClO$_4$)$_4$ in DMF solution from +60 to –40 °C (A–D) and the Raman spectrum of neat DMF (E).

cm^{-1};[26,48] in this work we find this band at 350 cm^{-1} for [Cd(H$_2$O)$_6$](ClO$_4$)$_2$ in the solid state and in aqueous solution. While plausible assignments of Cd–O vibrations can be made for the two thiolate compounds in the solid state, the feature near ~250 cm^{-1} is not resolved in solution and the relatively weak 330-cm^{-1} band is obscured by solvent in DMSO and DMF solutions. Consequently, the frequencies assigned to Cd–O vibrations are of little value in examining solution structures.

Both [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$](ClO$_4$)$_4$ and Cd(SCH$_2$-H$_2$OH)$_2$ exhibit two prominent bands in the 160–197-cm^{-1} region. Primarily on the basis of their relatively large intensities these bands are associated with Cd–S vibrations, which are expected to involve substantial bond polarizability changes compared with Cd–O vibrations. Further indications that Cd–S vibrations occur near or below 200 cm^{-1} are obtained from the Raman spectra of the following compounds, which show bands of moderate to strong relative intensities in the solid state at the indicated frequencies: [Cd(Et$_2$dtc)$_2$]$_2$, 212, 162, 111 cm^{-1}; [Cd(dpdtp)$_2$]$_2$, 220, 151 cm^{-1}; (Et$_4$N)-[Cd(exan)$_3$], 217, 144 cm^{-1}. From a detailed vibrational study

assessment of the sequence. Nonetheless, the results presented here reveal that, with the exception of organometallic compounds, *thiolate sulfur among common ligands affords the largest relative deshielding of the* ^{113}Cd *nucleus*. A final case in point is $Cd(SCH_2CH_2OH)_2$ in DMSO solution, which exhibits a shift of -655 ppm. The above sequence would suggest a structure in which at least four sulfur atoms are coordinated to Cd(II); the solution structure of this compound has not been investigated by other means.

Last, because of the inertness of Cd(II) toward two common physical probes of structure, ligand field optical and EPR spectroscopy, the structural utility of ^{113}Cd NMR and vibrational spectroscopy assumes added importance. An interesting biological application of the latter methods would involve the mammalian proteins, metallothioneins,[54] which generally contain six or seven Zn + Cd atoms per molecule. For proteins containing appreciable amounts of Cd(II), ^1H NMR spectral[52] and chemical results[54] indicate metal-(II)–cysteinate binding with an average of three Cys residues per metal atom available.[54] There is no further information available concerning Cd(II) coordination or possible oligomerization of binding sites by sulfur bridging. The Raman frequencies in Table II should be of value in confirming Cd–S binding, which is also supported by spectral comparison of the Cd(II) charge-transfer chromophore in the protein[54a] (pronounced shoulder at 250 nm) and $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ (Figure 2, λ_{max} 254 nm, ϵ 68 700 M^{-1} cm^{-1}). The near identity of transition energies suggests that the paramagnetic nuclear shielding terms[55] (proportional to $1/\Delta E$) in the protein and decanuclear cation may be sufficiently similar to justify utilization of the ^{113}Cd–S shielding sequence reported here,[56] or a further elaboration thereof, as a means of identifying the extent of sulfur ligation in the protein. However, as yet the detection of ^{113}Cd signals in any protein has not been reported.

Registry No. $Cd(ClO_4)_2$, 13760-37-7; $[Cd(Im)_6](NO_3)_2$, 34630-06-3; $Cd(CF_3SO_3)_2$, 29105-03-1; $CdCl_2$, 10108-64-2; $CdBr_2$, 7789-42-6; $[Cd(EDTA)]^{2-}$, 36077-58-4; Cd(II)–glutathione (1:2), 59991-75-2; $Cd(SCH_2CH_2OH)_2$, 28218-09-9; $[Cd_{10}(SCH_2CH_2O-H)_{16}](ClO_4)_4$, 60019-04-7; $[^{113}Cd_{10}(SCH_2CH_2OH)_{16}](ClO_4)_4$, 60019-05-8; $[Cd(dpdtp)_2]_2$, 34383-75-0; $(Et_4N)_2[Cd(mnt)_2]$, 59982-87-5; $Cd(Et_2dtc)_2$, 14239-68-0; $(Et_4N)[Cd(exan)_3]$, 39043-89-5; ^{113}Cd, 14336-66-4.

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