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Cadmium Polysulfide Complexes, $[Cd(S_x)(S_y)]^{2-}$: Syntheses, Crystal and Molecular Structures, and ^{113}Cd NMR Studies

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Received August 24, 1988

Controlled methods for the formation of cadmium polysulfide complexes in nonaqueous solution, mainly DMF, have been developed. The preferred method is $CdS + Na_2S + S_8$ in DMF, which allows a wide range for the solution compositional variables $Cd^{2+} + n(S_m)^{2-}$ to be attained. ^{113}Cd NMR spectroscopy reveals the existence of the series of monocadmium complexes $[Cd(S_x)_2]^{2-}$, which are in NMR slow exchange ($<10^2$ s^{-1}) at ambient temperature. The principal Cd NMR resonances are assigned to $[Cd(S_5)_2]^{2-}$ (740 ppm), $[Cd(S_5)(S_6)]^{2-}$ (695 ppm), and $[Cd(S_6)_2]^{2-}$ (648 ppm), with $[Cd(S_6)(S_7)]^{2-}$ (616 ppm) also postulated. Crystal structures of $(Ph_4P)_2[Cd(S_6)_2]$ (**6**) and $(Ph_4P)_2[\{(S_6)_{0.56}(S_7)_{0.44}\}Cd(S_6)]$ (**7**), isolated from these solutions, reveal the variability of cadmapolysulfane ring sizes and conformations in crystals. Modifications of the cadmapolysulfane ring sizes, which occur on redissolution of **6** and on deployment of sulfur addition and abstraction reagents, were clearly evident in the Cd NMR spectra. Crystal data: **6**, space group $P\bar{1}$, a = 11.849 (6) Å, b = 11.990 (6) Å, c = 19.856 (10) Å, α = 92.05 (3)°, β = 92.88 (3)°, γ = 111.88 (2)°, V = 2610 (2) Å^3, 3561 observed reflections (Mo Kα, $I > 3\sigma(I)$), R = 0.055; **7**, space group $P\bar{1}$, a = 11.913 (5) Å, b = 12.010 (5) Å, c = 19.785 (8) Å, α = 92.01 (3)°, β = 93.05 (3)°, γ = 111.65 (2)°, V = 2623 (2) Å^3, 5211 observed reflections (Mo Kα, $I > 3\sigma(I)$), R = 0.054.

Introduction

Homoleptic metal polysulfide complexes, $[M(S_x)_w]^z$, containing polysulfide chains as chelating ligands, have been known for more than 85 years.[1] Metallapolysulfane complexes are now known to be formed in diverse reactions, which have been recently reviewed.[2-4] An important advance in the preparative and reaction chemistry of metal polysulfides was the introduction of nonaqueous and aprotic solvents, which increased the thermodynamic activities of polysulfide ions in solution and therefore expanded the range of complexes that could exist in solution equilibria. The main method for the formation of nonaqueous $(S_x)^{2-}$ has been the direct analogue of the aqueous method[5] (eq 1) applied principally by Müller et al.[6-9]

$$\text{solvent} + S_8 + NH_3(g) + H_2S(g) \rightarrow (NH_4)_2S_x(\text{solv}) \quad (1)$$

The use of gaseous reagents in this preparation has led to substantial variability of the composition of the $(NH_4)_2S_x$ solutions and can introduce difficulties in attaining reproducible metallapolysulfane stoichiometry. Therefore, we have used three alternative methods for the controlled generation of nonaqueous solutions of $(S_x)^{2-}$, for reaction with suitable metal precursors. One method is the reaction of Na_2S and S_8, mainly in DMF; a second is the partial reduction of S_8, usually with Na, again mainly in DMF. The third method involves the isolation of Bu_4N^+ and Ph_4P^+ salts of S_x^{2-}, such as $(Bu_4N)_2S_6$,[10] which can then be redissolved and deployed preparatively in solvents of interest.

An astonishing variety of structures for metal polysulfides has been revealed in the crystals of the less soluble products of preparative reactions. Key examples of this variety are $[Ag(S_9)]^-$,[7,11] $[(S_7)_2BiS_6Bi(S_7)_2]^{4-}$,[9] $[Ag_2(S_6)_2]^{2-}$,[11] $[(S_7)_4Pd_2]^{4-}$,[12] $[Cu_3(S_x)_3]^{3-}$ (x = 4,[13] 6[14]), $[Cu_4(S_5)_m(S_4)_{3-m}]^{2-}$ (m = 0–3[15]), $[Cu_6(S_5)(S_4)_3]^{2-}$,[6,16,17] and $[Re_4S_4(S_3)_6]^{4-}$.[18] However, these impressive crystal structures belie a dearth of information on the species, the reactions, and the equilibria that occur in solution, information that could be used to support rational syntheses and applications. We are undertaking a systematic investigation of metal polysulfide species and equilibria, particularly for post transition metals. We have chosen systems where the metal nucleus is amenable to NMR studies, since ^{33}S NMR spectroscopy as currently practiced is unlikely to be informative.

In this paper we report our findings on cadmium polysulfides. Amorphous CdS_5 was claimed by Schiff.[19] Coucouvanis et al.[20] used reactions of dibenzyl trisulfide with $[Zn(SPh)_4]^{2-}$ and $[Cd(SPh)_4]^{2-}$ to form the complexes $[(PhS)_2Zn(S_x)]^{2-}$ (x = 4, 5 (Ph_4P^+)), $[Zn(S_x)_2]^{2-}$ (x = 5, 6 (Ph_4P^+); x = 4 (Et_4N^+, Ph_4P^+)), $(Ph_4P)_2[(PhS)_2Cd(S_5)]$, and $(Ph_4P)_2[Cd(S_5)_2]$ (**1**) and determined the crystal structure of $(Et_4N)_2[Zn(S_4)_2]$: no evidence of other species $[Cd(S_x)_y]^{2-2y}$ was reported. Müller et al.[8] obtained $[(Ph_3P)_2N]_2[Cd(S_6)_2]CH_3CN$ (**2**) from a mixture prepared by addition of a solution of hydrated $Cd(OAc)_2$, Me_4NCl, and $[(Ph_3P)_2N]Cl$ in acetonitrile to an ethanolic ammonium polysulfide solution, $(Ph_4P)_2[Zn(S_6)_2]$ (**3**) from hydrated $Zn(OAc)_2$ with a methanolic ammonium polysulfide solution containing Ph_4PBr, $(Et_4N)_2[Hg(S_6)_2]$ (**4**) by reaction of a methanolic polysulfide solution containing Et_4NCl with mercuric acetate,[21] and $(Ph_4P)_2[Hg(S_4)_2]$ (**5**) from a solution containing Ph_4PBr. They reported the crystal structures of **2**–**5**.

This paper contains the preparations and crystal structures of $(Ph_4P)_2[Cd(S_6)_2]$ (**6**) $(Ph_4P)_2[(S_6)Cd(S_7)_{0.56}(S_6)_{0.44}]$ (**7**), the

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0020-1669/89/1328-1862$01.50/0

preparation of $(Bu_4N)(Ph_4P)[Cd(S_6)_2]$ (**8**), the methods we use for the generation of cadmium polysulfide complexes in solution, and the ^{113}Cd NMR data that reveal the range of cadmium polysulfide complexes in equilibrium in solution.

Experimental Section

Materials. $Na_2S·9H_2O$ was dehydrated by heating under a stream of N_2 at 90 °C for 6 h and finally at 120 °C to obtain a white solid. CdS was prepared by reaction of $Cd(NO_3)_2·4H_2O$ and $Na_2S·9H_2O$ in methanol, washed with methanol, and dried under dinitrogen. DMF was purified by drying with $MgSO_4$, followed by vacuum distillation, and was stored over molecular sieves.

All preparations were performed under nitrogen as inert gas. Solvents were deoxygenated before use.

$(PPh_4)_2CS_3$. A solution of KOH (20.0 g) in ethanol (200 mL) was saturated with H_2S by bubbling for 30 min. Carbon disulfide (13.6 g) in ethanol (30 mL) was added, and the solution became orange and precipitated an orange solid. Precipitation of K_2CS_3 was completed by addition of diethyl ether (250 mL). A solution of K_2CS_3 (0.5 g) in water (5 mL) was added to a hot solution of Ph_4PBr (2.2 g) in water (40 mL). The product crystallized on cooling, was washed with water, and was vacuum-dried.

Preparation of $(Bu_4N)_2S_6$. The following is a refinement of the procedure described by Teller et al.[10] $Na_2S·9H_2O$ (4.8 g, 20 mmol) was dissolved in water (10 mL) and deoxygenated. Sulfur (1.28 g, 40 mmol of S) was added and the mixture heated to 70 °C for 10 min until the sulfur dissolved to yield a dark red solution. The solution was cooled to 0 °C, diluted with water (20 mL), and treated at 0 °C with a cooled solution of Bu_4NBr (6.45 g, 20 mmol) in water (30 mL). As the solution was allowed to warm slowly to room temperature, maroon needles appeared: they were collected after 24 h, washed with water, and vacuum-dried: yield 2.7 g; mp 128–130 °C. Anal. Found: C, 54.87; H, 10.82; N, 4.14. Calcd for $C_{32}H_{72}N_2S_6$: C, 56.80; H, 10.65; N, 4.14. The identity of the compound was confirmed by diffraction measurements on single crystals. IR (cm^{-1}): 2950 (s), 2865 (s), 890 (s), 745 (m), 610 (s), 500 (s), 250 (w). Raman (cm^{-1}): 1708 (m), 1420 (m), 800 (s), 350 (w, br), 260 (w). $(Bu_4N)_2S_6$ is soluble in acetone, yielding a blue solution (due to $(S_3)^-$) that changes to red on addition of ethanol, in acetonitrile (ca. 0.7 g/10 mL at ambient temperature, dark green solution), and in DMF (ca. 0.7 g/10 mL at ambient temperature, ca. 1.4 g/10 mL at 90 °C, dark green solution).

Preparation of $(Bu_4N)(Ph_4P)[Cd(S_6)_2]$ (8). A mixture of $(Bu_4N)_2S_6$ (4.50 g, 6.6 mmol) and $CdCl_2·2.5H_2O$ (0.66 g, 3 mmol) was dissolved in deoxygenated acetonitrile (30 mL) with ultrasonication for 15 min. After an initial blue coloration a red-brown solution was obtained. A solution of Ph_4PBr (2.50 g, 6 mmol) in acetonitrile (25 mL) was added and the mixture allowed to stand while the yellow polycrystalline product separated slowly. Addition of ethanol to the cooled mother liquor yielded more product: total yield 3.2 g; mp 128 °C. Anal. Found: C, 44.30; H, 5.43; N, 1.19. Calcd for $C_{40}H_{56}NPCdS_{12}$: C, 44.56; H, 5.20; N, 1.30.

The presence of both cations was confirmed by the C–H vibrational frequencies and by the proton NMR spectrum.

All attempts to grow single crystals of this compound were unsuccessful.

Preparation of $(Ph_4P)_2[Cd(S_6)_2]$ (6). A mixture of $Na_2S·9H_2O$ (4.24 g, 17.4 mmol), S_8 (5.04 g, 157.5 mmol of S), and DMF (40 mL) was stirred at 70 °C for 10 min, under an atmosphere of dinitrogen. The color changed from green to dark red after 30 s. To the red solution was added CdS (1.7 g, 11.8 mmol), and the mixture was stirred for a further 30 min until all CdS had dissolved. After the mixture was cooled to room temperature, a solution of Ph_4PBr (10 g, 24 mmol) in acetonitrile (40 mL) was added. The large orange crystals that grew within 12 h were collected, washed with acetonitrile, and dried under N_2: yield 10.8 g (78%); mp 188–190 °C. Anal. Found: C, 48.93; H, 3.26. Calcd for $C_{48}H_{40}P_2CdS_{12}$: C, 49.02; H, 3.40.

The single crystals of $(Ph_4P)_2[Cd(S_6)_2]$ (**6**) used in the structure determination were obtained initially by the following method: $(Bu_4N)(Ph_4P)[Cd(S_6)_2]$ (0.08 g) was dissolved in acetonitrile (10 mL), and a solution of Ph_4PBr (0.06 g) in ethanol (5 mL) was added. Crystals grew during 2 days.

Preparation of $(Ph_4P)_2[Cd(S_6)(S_7)]$ (7). $Na_2S·9H_2O$ (12.5 g, 52.1 mmol) was dehydrated by heating under a stream of dinitrogen to obtain a white solid. CdS (5.0 g, 34.7 mmol) and sulfur (15.0 g, 469 mmol of S) were added, and the mixture was treated with dry DMF (175 mL) and stirred at 90 °C for 2 h, generating a very dark red solution. The small amount of solid that remained was dissolved by heating the mixture briefly to 135 °C. After the mixture was cooled, the small amount of residue (0.56 g) was removed by filtration, and a solution of Ph_4PBr (29.5 g, 70 mmol) in acetonitrile (250 mL) was added. The first rapidly precipitated product was separated and washed with acetonitrile; yield 4.4 g. Anal. Found: C, 41.54; H, 2.83. The mother liquor yielded dark red crystals of the product during 2 days: yield 27.0 g; mp 180 °C. Anal. Found: C, 47.34; H, 3.14. Calcd for $C_{48}H_{40}CdP_2S_{13}$: C, 47.72; H, 3.34.

Table I. Crystallographic Data for $(Ph_4P)_2[Cd(S_6)_2]$ (**6**) and $(Ph_4P)_2[(S_6)Cd(S_7)_{0.56}(S_6)_{0.44}]$ (**7**)

formula, fw	$C_{48}H_{40}CdP_2S_{12}$, 1175.9	$C_{48}H_{40}CdP_2S_{12.44}$, 1190.0
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.849 (6)	11.913 (5)
b, Å	11.990 (6)	12.010 (5)
c, Å	19.856 (10)	19.785 (8)
α, deg	92.05 (3)	92.01 (3)
β, deg	92.88 (3)	93.05 (3)
γ, deg	111.88 (2)	111.65 (2)
V, Å^3	2610 (2)	2623 (2)
temp, °C	21	21
Z	2	2
d_{calcd}, g cm^{-3}	1.50	1.49
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)
μ, cm^{-1}	9.71	9.66
max, min transmissn coeff	0.93, 0.84	0.91, 0.84
$R = \sum^m\lvert\Delta F\rvert/\sum^m\lvert F_o\rvert$	0.055	0.054
$R_w = [\sum^m w\lvert\Delta F\rvert^2/\sum^m w\lvert F_o\rvert^2]^{1/2}$	0.068	0.072

Reaction of $(Bu_4N)(Ph_4P)[Cd(S_6)_2]$ with Ph_3P. A solution of $(Bu_4N)(Ph_4P)[Cd(S_6)_2]$ (0.55 g) in DMF (2.5 mL) was treated with a solution of Ph_3P (0.535 g) in DMF (2 mL) at room temperature. An immediate green coloration developed, fading slowly, until a very pale yellow crystalline precipitate began to form, when further intense green coloration occurred. The crystalline product was isolated and confirmed to be Ph_3PS by its melting point and IR spectrum.

Vibrational Spectroscopy. IR spectra were measured on a Perkin-Elmer 580B spectrometer, as halocarbon and paraffin mulls. Raman spectra were obtained on a Cary 82 spectrometer, using an Ar laser.

IR spectrum of **6** (cm^{-1}): 3055 (w; Ph_4P^+), 1585 (w; Ph_4P^+), 1370 (sh), 1340 (w), 1315 (m), 1190 (m; Ph_4P^+), 1165 (m; Ph_4P^+), 1110 (s), 1085 (w), 1075 (w), 1030 (w; Ph_4P^+), 1000 (s; Ph_4P^+), 975 (w), 930 (w; Ph_4P^+), 850 (w; Ph_4P^+), 765 (m, sh), 755 (m), 725 (s; Ph_4P^+), 690 (s; Ph_4P^+), 620 (w; Ph_4P^+), 540 (s, sh), 525 (s), 500 (m), 455 (m), 350 (w), 245 (m), 205 (m), 190 (m).

IR and Raman spectra of **8** (cm^{-1}; IR = infrared, R = Raman): 3055 (w, IR; s, R; Ph_4P^+), 2960 (m, R; Bu_4N^+), 2920 (m, R; Bu_4N^+), 2860 (m, R; Bu_4N^+), 1585 (w, IR; s, R; Ph_4P^+), 1190 (m, R; Ph_4P^+), 1170 (w, R; Ph_4P^+), 1100 (s, R), 1110 (ms, IR), 1030 (w, IR; s, R; Ph_4P^+), 1000 (m, IR; s, R; Ph_4P^+), 800 (w, IR; w, R), 495 (m, IR; m, R), 455 (m, IR; s, R), 405 (s, R), 295 (w, R), 265 (m, R), 220 (s, R), 190 (m, IR; s, R).

Crystal Structure Analyses. Crystallographic examinations of single crystals were made with a Nonius CAD4 diffractometer. Reflections with high 2θ values and moderate intensity were accurately centered to yield the unit cell dimensions. Intensity data were measured as follows: (i) aperture width $(1.00 + 1.00 \tan\theta)$°; (ii) maximum scan time 60 s; (iii) intensity standard measured after 2000 s; (iv) orientation control checked every 200 reflections. Absorption corrections were calculated by numerical integration over a 6 × 6 × 6 grid oriented approximately parallel to the crystal morphology. Other procedures were as previously described.[22] Details of the crystal lattices, diffraction data, and least-squares refinement are included in Table I.

$(Ph_4P)_2[Cd(S_6)_2]$ (6) is not crystallographically isomorphous with the Zn homologue **3**.[8] With use of direct methods (MULTAN2) the positions of the Cd atom and of 10 of the S atoms could be determined. A Fourier map phased on these 11 atoms yielded the positions of all the remaining non-hydrogen atoms, and isotropic refinement led to $R = 0.117$. Anisotropic refinement including all hydrogen atoms in calculated positions gave $R = 0.067$, but there were residual peaks in a difference map of up to 2.6 e Å^{-3} in the vicinity of the sulfur atoms of one of the hexasulfide rings, indicating that the ring may have been disordered. A program for constrained least-squares refinement (RAELS[23]) was used to continue the refinement. The phenyl rings of the Ph_4P^+ cations were treated as rigid groups with fixed $mm2$ geometry. Thermal parameters of the atoms of the rings were refined by using a 12-parameter TL model with the origin for each ring fixed on the appropriate P atom.

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Table II. Parameters for Non-Hydrogen Atoms of $(Ph_4P)_2[Cd(S_6)_2]$ (**6**)

atom	*x/a*	*y/b*	*z/c*
Cd	0.15129 (7)	0.46105 (7)	0.23811 (4)
S1A	0.3682 (3)	0.6001 (3)	0.2754 (2)
S2A	0.4393 (3)	0.5086 (3)	0.3381 (1)
S3A	0.5032 (3)	0.4051 (3)	0.2803 (1)
S4A	0.3782 (3)	0.2306 (3)	0.2781 (1)
S5A	0.2417 (3)	0.2068 (3)	0.2054 (1)
S6A	0.1055 (2)	0.2402 (2)	0.2501 (1)
S1B	0.1139 (5)	0.5389 (6)	0.1242 (2)
S2B	−0.0654 (4)	0.4690 (5)	0.0864 (3)
S3B	−0.1614 (7)	0.3257 (4)	0.1418 (3)
S4B	−0.2367 (3)	0.3818 (4)	0.2213 (2)
S5B	−0.1327 (3)	0.3769 (3)	0.3065 (2)
S6B	0.0230 (3)	0.5297 (3)	0.3172 (2)
S1B′	0.1667 (12)	0.5074 (13)	0.1134 (2)
S2B′	0.0326 (10)	0.5777 (11)	0.1070 (8)
S3B′	−0.1387 (14)	0.4444 (15)	0.1031 (9)
S4B′	−0.1721 (23)	0.3283 (18)	0.1806 (9)
S5B′	−0.1872 (20)	0.3993 (24)	0.2744 (11)
S6B′	−0.0095 (16)	0.4802 (26)	0.3141 (10)
S1B″	0.1558 (18)	0.5821 (19	0.1341 (8)
S2B″	−0.0212 (17)	0.5623 (24)	0.1084 (15)
S3B″	−0.1619 (32)	0.4083 (25)	0.0696 (17)
S4B″	−0.1799 (63)	0.2898 (43)	0.1453 (19)
S5B″	−0.1807 (47)	0.3638 (46)	0.2405 (23)
S6B″	−0.0291 (28)	0.4742 (49)	0.2992 (20)
PA	0.2876 (2)	1.1155 (2)	0.4913 (1)
PB	−0.3219 (2)	0.8480 (2)	0.0811 (1)
C1A	0.2425 (3)	1.0026 (3)	0.4240 (2)
C2A	0.2798 (4)	0.9054 (5)	0.4286 (2)
C3A	0.2463 (5)	0.8156 (4)	0.3765 (3)
C4A	0.1754 (5)	0.8229 (4)	0.3197 (2)
C5A	0.1382 (5)	0.9202 (5)	0.3151 (2)
C6A	0.1717 (5)	1.0100 (5)	0.3672 (3)
C7A	0.1961 (3)	1.2043 (2)	0.4934 (2)
C8A	0.1921 (4)	1.2725 (4)	0.4384 (2)
C9A	0.1209 (5)	1.3426 (5)	0.4390 (3)
C10A	0.0536 (4)	1.3446 (4)	0.4945 (3)
C11A	0.0577 (5)	1.2763 (5)	0.5494 (3)
C12A	0.1289 (5)	1.2061 (4)	0.5489 (2)
C13A	0.4386 (2)	1.2103 (4)	0.4747 (2)
C14A	0.4891 (4)	1.3241 (5)	0.5081 (3)
C15A	0.6072 (5)	1.4010 (4)	0.4964 (3)
C16A	0.6749 (3)	1.3642 (5)	0.4513 (3)
C17A	0.6243 (4)	1.2503 (5)	0.4178 (3)
C18A	0.5062 (4)	1.1734 (4)	0.4295 (3)
C19A	0.2865 (5)	1.0530 (4)	0.5714 (1)
C20A	0.3891 (4)	1.0915 (4)	0.6169 (3)
C21A	0.3840 (5)	1.0400 (5)	0.6791 (2)
C22A	0.2762 (6)	0.9500 (5)	0.6960 (2)
C23A	0.1735 (5)	0.9115 (5)	0.6505 (3)
C24A	0.1787 (4)	0.9630 (5)	0.5882 (2)
C1B	−0.2603 (5)	0.7900 (2)	0.1487 (2)
C2B	−0.3235 (4)	0.7562 (5)	0.2068 (3)
C3B	−0.2746 (6)	0.7107 (6)	0.2596 (2)
C4B	−0.1624 (6)	0.6989 (5)	0.2543 (3)
C5B	−0.0993 (5)	0.7327 (7)	0.1962 (3)
C6B	−0.1482 (5)	0.7783 (6)	0.1434 (2)
C7B	−0.3777 (5)	0.7365 (3)	0.0132 (2)
C8B	−0.3207 (5)	0.6550 (6)	0.0023 (3)
C9B	−0.3638 (8)	0.5673 (5)	−0.0509 (4)
C10B	−0.4640 (8)	0.5611 (5)	−0.0933 (3)
C11B	−0.5210 (8)	0.6426 (7)	−0.0823 (3)
C12B	−0.4778 (7)	0.7303 (6)	−0.0291 (4)
C13B	−0.4364 (4)	0.8928 (5)	0.1141 (1)
C14B	−0.5491 (5)	0.8063 (4)	0.1272 (3)
C15B	−0.6385 (4)	0.8419 (5)	0.1533 (3)
C16B	−0.6152 (5)	0.9640 (6)	0.1663 (3)
C17B	−0.5025 (6)	1.0505 (4)	0.1531 (3)
C18B	−0.4131 (4)	1.0149 (5)	0.1270 (3)
C19B	−0.2090 (4)	0.9791 (3)	0.0522 (3)
C20B	−0.2183 (5)	1.0055 (5)	−0.0153 (3)
C21B	−0.1312 (6)	1.1080 (6)	−0.0393 (3)
C22B	−0.0347 (5)	1.1840 (4)	0.0041 (3)
C23B	−0.0254 (4)	1.1575 (5)	0.0716 (3)
C24B	−0.1126 (5)	1.0551 (5)	0.0956 (2)

The disordered (B) rings of S atoms were treated as follows: three different disorder components were allowed for each S atom; the occupancies of the atoms in each disordered ring were held equal, and the sum of the three components was maintained at 1; S–S distances were slack-constrained to be equal; the atoms of the major component (labeled B) were refined anisotropically in the normal way along with the Cd, P, and S atoms of the A ring; the atoms of the two minor components (B′ and B″) were refined with isotropic temperature factors, the temperature factors of corresponding disorder "pairs" being kept equal. At convergence, $R = 0.055$, with the refined values of the occupancies being 0.768, 0.150 (4), and 0.082 (3), respectively, for the B, B′, and B″ components. The largest peak in the difference map was 0.85 e Å^{-3}. Atom labeling is given in Figure 1.

$(Ph_4P)_2[(S_6)Cd(S_7)_{0.56}(S_6)_{0.44}]$ (7). The similarity of the cell dimensions of **6** and **7** led to the expectation that there would be only minor differences in conformation of the S_6 chains. The final parameters for **6** were therefore taken as the starting point for the refinement of **7**. It was quickly obvious that one of the S_6 rings in **7** was different from that in **6**, and so it was removed from the structure factor calculation; a map revealed the S_7 ring in its place. Refinement of this model led to $R = 0.072$ for data with $(\sin \theta)/\lambda > 0.3$. A difference map showed disorder in the vicinity of the S_7 ring, so refinement was continued by using rigid-body least squares, with the cations being treated exactly as described above for **6**. It was found that not only were there S_7 components in the disordered chelate ligand but also the chelate was in fact a mixture of S_7 and S_6 rings. In place of three atoms (S1B, S2B, S3B) at one end of the S_7 ring, there were only two (S1B′, S2B′) in the weaker component. The other end of the S_7 chain was found to be almost identical with the corresponding end of the S_6 chain in **6**. Atoms labeled S4B, S5B, and S6B in **6** recur in **7** as S5B, S6B, and S7B, respectively, with S3B (**6**) and S4B (**7**) being nearly identical. For the sake of consistency with the previously completed structure of **6**, these atom labels were maintained when the S_6 component of the ring was fitted on the other end. The atom connectivity in this S_6 ring is therefore S2B′–S3B′–S4B′–S5B–S6B–S7B. A second complete S_6 ring was also included in the model (labeled S1B″ to S6B″). The proportions of the rings were varied, with their sum being held at 1. The Cd, P, and S atoms of the ordered S_6 (A) ring and the S_7 (B) ring were refined anisotropically. All the smaller components were refined with isotropic temperature factors, except for S4B′, whose thermal parameters were kept the same as those for S4B. The final residual was 0.054. On the final difference map the largest peaks were in the vicinity of one of the phenyl rings, which may be very slightly disordered, but this was not modeled, as it would contribute nothing to the information required from this structure. The values of the occupancies are 0.561 (6), 0.338 (6) and 0.101 for the S_7, S_6 (B′) and S_6 (B″) rings, respectively. Atom labeling is given in Figure 2.

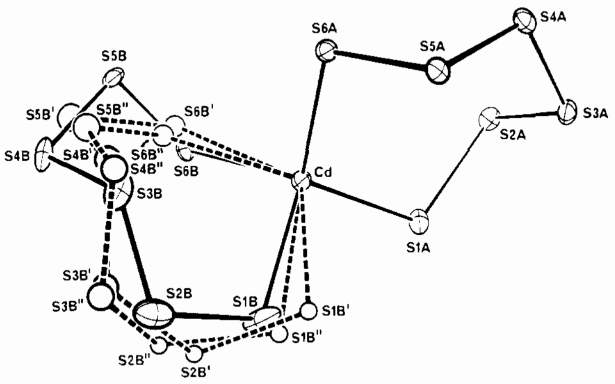

Figure 1. Structure of the $[Cd(S_6)_2]^{2-}$ ion in **6**, showing the major (B, 77%, full bonds) and two minor conformations (B′, 15%; B″, 8%; broken bonds) of one chelate ring. Thermal ellipsoids (and spheres for the disorder components) are drawn at the 5% probability level.

No atom in either structure is unusually anisotropic or has unusually high thermal vibration parameters. The most anisotropic atoms are in fact those of the ring B in **6**. Atomic coordinates for the two structures are contained in Tables II and III. Full listings of atomic parameters and structure factors for both structures are included with the supplementary material.[24]

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[24] See paragraph at end of paper about supplementary material.

Table III. Parameters for Non-Hydrogen Atoms of $(Ph_4P)_2[Cd(S_6)(S_7)]$

atom	*x/a*	*y/b*	*z/c*
Cd	0.15148 (4)	0.46096 (4)	0.23723 (2)
S1A	0.3669 (2)	0.5988 (2)	0.2756 (1)
S2A	0.4372 (2)	0.5059 (2)	0.3389 (1)
S3A	0.5004 (2)	0.4023 (2)	0.2805 (1)
S4A	0.3758 (2)	0.2284 (2)	0.2777 (1)
S5A	0.2396 (2)	0.2067 (2)	0.2048 (1)
S6A	0.1046 (1)	0.2403 (1)	0.2506 (1)
S1B	0.1491 (3)	0.5062 (3)	0.1123 (1)
S2B	0.0177 (4)	0.5726 (3)	0.1107 (2)
S3B	−0.1388 (5)	0.4384 (5)	0.0775 (3)
S4B	−0.1692 (21)	0.3113 (7)	0.1483 (6)
S5B	−0.2384 (2)	0.3796 (2)	0.2254 (2)
S6B	−0.1297 (2)	0.3797 (2)	0.3074 (1)
S7B	0.0210 (2)	0.5279 (2)	0.3145 (1)
S2B′	0.1101 (9)	0.5443 (11)	0.1258 (5)
S3B′	−0.0635 (8)	0.4671 (8)	0.0899 (5)
S4B′	−0.1733 (36)	0.3295 (10)	0.1400 (14)
S1B″	0.1240 (24)	0.5872 (21)	0.1405 (10)
S2B″	−0.0090 (18)	0.4693 (22)	0.0765 (12)
S3B″	−0.1676 (24)	0.4438 (26)	0.1184 (14)
S4B″	−0.1810 (23)	0.3190 (20)	0.1891 (11)
S5B″	−0.1869 (23)	0.4048 (24)	0.2797 (12)
S6B″	−0.0123 (19)	0.4650 (40)	0.3144 (15)
PA	0.2876 (1)	1.1159 (1)	0.4914 (1)
PB	−0.3226 (1)	0.8455 (1)	0.0816 (1)
C1A	0.2427 (2)	1.0031 (2)	0.4237 (1)
C2A	0.2796 (3)	0.9058 (3)	0.4280 (2)
C3A	0.2459 (4)	0.8166 (3)	0.3755 (2)
C4A	0.1751 (3)	0.8246 (3)	0.3187 (2)
C5A	0.1382 (3)	0.9219 (3)	0.3144 (1)
C6A	0.1719 (3)	1.0112 (2)	0.3669 (2)
C7A	0.1965 (2)	1.2048 (2)	0.4931 (1)
C8A	0.1935 (3)	1.2740 (3)	0.4383 (1)
C9A	0.1227 (3)	1.3443 (3)	0.4388 (2)
C10A	0.0548 (3)	1.3454 (3)	0.4941 (2)
C11A	0.0579 (3)	1.2761 (3)	0.5489 (2)
C12A	0.1287 (3)	1.2059 (3)	0.5484 (1)
C13A	0.4375 (1)	1.2102 (2)	0.4748 (1)
C14A	0.4879 (3)	1.3241 (3)	0.5078 (2)
C15A	0.6051 (3)	1.4000 (2)	0.4959 (2)
C16A	0.6721 (2)	1.3621 (3)	0.4510 (2)
C17A	0.6217 (2)	1.2482 (3)	0.4179 (2)
C18A	0.5044 (3)	1.1722 (2)	0.4298 (2)
C19A	0.2868 (3)	1.0534 (2)	0.5718 (1)
C20A	0.3892 (3)	1.0914 (3)	0.6172 (2)
C21A	0.3847 (3)	1.0401 (3)	0.6798 (1)
C22A	0.2778 (4)	0.9508 (3)	0.6969 (1)
C23A	0.1754 (3)	0.9128 (3)	0.6513 (2)
C24A	0.1799 (3)	0.9641 (3)	0.5888 (1)
C1B	−0.2635 (3)	0.7883 (2)	0.1511 (1)
C2B	−0.3289 (3)	0.7537 (3)	0.2083 (2)
C3B	−0.2818 (4)	0.7088 (4)	0.2623 (2)
C4B	−0.1691 (4)	0.6985 (3)	0.2592 (2)
C5B	−0.1037 (3)	0.7332 (4)	0.2019 (2)
C6B	−0.1509 (3)	0.7780 (4)	0.1479 (2)
C7B	−0.3759 (3)	0.7343 (2)	0.0131 (1)
C8B	−0.3221 (3)	0.6497 (4)	0.0053 (2)
C9B	−0.3628 (5)	0.5622 (3)	−0.0481 (2)
C10B	−0.4573 (5)	0.5594 (3)	−0.0939 (2)
C11B	−0.5111 (5)	0.6441 (4)	−0.0862 (2)
C12B	−0.4704 (4)	0.7316 (3)	−0.0327 (2)
C13B	−0.4379 (2)	0.8906 (3)	0.1130 (1)
C14B	−0.5509 (3)	0.8046 (2)	0.1241 (2)
C15B	−0.6408 (2)	0.8401 (3)	0.1489 (2)
C16B	−0.6178 (3)	0.9617 (4)	0.1626 (2)
C17B	−0.5048 (3)	1.0477 (3)	0.1514 (2)
C18B	−0.4149 (2)	1.0122 (3)	0.1266 (2)
C19B	−0.2092 (2)	0.9750 (2)	0.0521 (2)
C20B	−0.2133 (3)	0.9975 (3)	−0.0166 (2)
C21B	−0.1254 (4)	1.0986 (4)	−0.0405 (2)
C22B	−0.0334 (3)	1.1772 (3)	0.0042 (2)
C23B	−0.0294 (3)	1.1546 (3)	0.0729 (2)
C24B	−0.1173 (3)	1.0535 (3)	0.0968 (1)

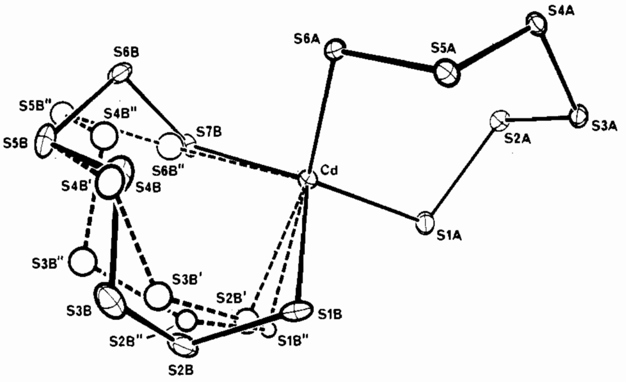

Figure 2. Structure of the $[(S_6/S_7)Cd(S_6)]^{2-}$ ion in **7**, showing the S_7 ring (B, 56% occurrence, full bonds) and the two conformations (B′, 34%; B″, 10%; broken bonds) of the S_6 ring at the same location. Thermal ellipsoids are drawn at the 5% probability level.

Cadmium NMR Spectroscopy. The ^{113}Cd spectra were measured at 66.6 MHz with a Bruker CXP300 spectrometer, fitted with a 10-mm multinuclear probe or a 10-mm Cd probe, locked to acetone-d_6 in an insert. Solutions were deoxygenated by sparging with nitrogen. Temperatures in the sample tube were controlled to ±1 °C and were calibrated by replacement with a sample tube containing a platinum thermometer. Spectra typically required 4000 pulses (20 μs, ca. 75° tip angle). Approximate measurements of relaxation times for resonances in solutions of $Cd/(S_x)^{2-}$ species indicated that T_1 values are ca. 1 s at low temperatures (ca. 230 K) but at least several seconds at 300 K. There were also indications that the T_1 values were different for the various species responsible for the different observed lines. In general, spectra were not recorded with allowance for full relaxation, and the relative intensities reported are approximate, although all spectra where relative intensities are compared were run under the same conditions. Chemical shifts are referenced to 0.1 M aqueous $Cd(NO_3)_2$, which resonates at −5 ppm relative to infinitely dilute aqueous $Cd(ClO_4)_2$. Lines are identified by their chemical shift value at 220 K. Changes in chemical shift (ppm) with temperature are as follows: "740", 740 (220 K), 733 (260 K), 727 (300 K); "695", 695 (220 K), 686 (260 K), 678 (300 K); "648", 648 (220 K), 638 (260 K), 630 (300 K); "616", 616 (220 K), 606 (260 K), 598 (300 K); "546", 546 (220 K), 537 (260 K), 530 (300 K).

Preparations of Solutions. Solutions containing cadmium polysulfide species for NMR measurements were generated by the following methods, with use of appropriate deoxygenation. The variables *m* and *n* represent the nominal composition $Cd^{2+} + n[(S_m)]^{2-}$ of these solutions.

(I) In the reactions of CdS, $Na_2S{\cdot}9H_2O$, and S_8 in DMF, the Na_2S (q_1, mmol) was dehydrated by heating to 140 °C under a stream of dinitrogen, the CdS (q_2, mmol), S_8 (q_3, mmol of S), and DMF were added, and the mixture was heated to 110 °C until a red solution was obtained and then cooled and decanted if necessary: $n = (q_1 + q_2)/q_2$; $m = (q_1 + q_2 + q_3)/(q_1 + q_2)$. Ultrasonication was found to be less satisfactory than heating for dissolution of CdS. All solutions were heated to ca. 120 °C to achieve solution, and when they were cooled, small amounts of solids precipitated, which were not identified. The cadmium concentrations achieved in these solutions were in the range 0.1–0.3 mmol mL^{-1}.

(II) S_8 in DMF was heated with Na to generate a stock solution of sodium polysulfide, which was then treated with CdS and S_8, heated to obtain solution, cooled, and decanted if necessary.

(III) $(Ph_4P)_2[Cd(S_6)_2]$ (**6**) or $(Ph_4P)(Bu_4N)[Cd(S_6)_2]$ (**8**) was dissolved by ultrasonication in DMF, yielding bright red solutions (ca. 0.17 M).

(IV) Solutions of $(Ph_4P)(Bu_4N)[Cd(S_6)_2]$ (**8**) in DMF were (i) subjected to aerial oxidation, (ii) treated with solid Ph_3P, which quickly dissolved, yielding paler yellow and green solutions, (iii) treated with $PhCH_2SSCH_2Ph$ and ultrasonicated, (iv) treated with S_8, which required heating to dissolve, (v) treated with $PhCH_2SSSCH_2Ph$ and ultrasonicated, without color change, or (vi) treated with $(Ph_4P)_2CS_3$, all in appropriate molar proportions.

(V) Solid $(Bu_4N)_2S_6$ and solid $CdCl_2{\cdot}2.5H_2O$ in various proportions were dissolved together in DMF or CH_3CN at 20 °C. In a typical reaction $CdCl_2{\cdot}2.5H_2O$ (0.128 g, 0.56 mmol) and $(Bu_4N)_2S_6$ (1.52 g, 2 mmol) were treated with DMF (3 mL) and ultrasonicated for 30 min to yield a very dark red solution. With CH_3CN as solvent and low $(Bu_4N)_2S_6/CdCl_2$ ratios, undissolved solids were present after ultrasonication, and the solutions were less intensely red.

(VI) $2(Bu_4N)_2S_6 + 1CdCl_2{\cdot}2.5H_2O + {}^1/_4S_8$ were dissolved together in DMF by ultrasonication to yield a dark red solution with a cadmium concentration of 1 mmol/3 mL.

(VII) A stock solution of Na_2S_m in DMF was treated with $Cd(NO_3)_2{\cdot}4H_2O$ or $CdCl_2{\cdot}2.5H_2O$ in DMF.

The achievable concentration of cadmium polysulfide complexes in DMF solution is maximized for $m \approx 5$, $n \approx 2.5$ and decreases appreciably when $m < 4$ or $m > 8$ ($2 \leq n \leq 3$).

Addition of a solution of $Cd(NO_3)_2{\cdot}4H_2O$ in DMF to a green solution of $(Bu_4N)_2S_6$ in DMF generated dark red solutions of cadmium polysulfide complexes until the Cd/S_6 ratio reached 0.5, after which the color rapidly diminished to pale yellow, and sulfur soon crystallized on standing. The amount and rate of sulfur crystallization appeared to be proportional to the excess of $Cd(NO_3)_2$. Similar experiments in acetonitrile gave the same result. Reactions in which $Cd(NO_3)_2$ was added to Na_2S_x solutions in DMF also yielded sulfur, more rapidly on heating. All of these solutions were protected from aerobic oxidation, and therefore it is concluded that the nitrate ion is a fairly rapid oxidant of polysulfide ions in nonaqueous solvents.

Solutions of $[Cd(edt)_2]^{2-}$ and $[Cd(pdt)_2]^{2-}$ ($edt^{2-} = {}^-SCH_2CH_2S^-$; $pdt^{2-} = {}^-SCH_2CH_2CH_2S^-$) in DMF were prepared by treatment of a mixture of excess NaOH(s) and deoxygenated DMF with the dithiol, followed by addition of solid $Cd(NO_3)_2$ to give a dithiolate/Cd ratio of 3 and ultrasonication for 1 h to yield a clear solution over the excess NaOH(s), which was separated. The solution of $[Cd(edt)(pdt)]^{2-}$ was obtained by mixing equimolar proportions of $[Cd(edt)_2]^{2-}$ and $[Cd(pdt)_2]^{2-}$. Weak NMR resonances, additional to the principal lines, were observed at 679 and 665 ppm for solutions containing pdt^{2-} and at 730 ppm for the mixed solution.

Results

Syntheses. We have improved the preparation[10] of $(Bu_4N)_2S_6$, obtained by crystallization from an aqueous solution of nominal composition Na_2S_3: control of the concentration and the temperature of this aqueous solution is important to avoid the formation of other products. $(Bu_4N)_2S_6$ is soluble in acetone, acetonitrile, and DMF, yielding blue ($(S_3)^-$) or dark green solutions that change to red on addition of ethanol. We have also prepared $(Ph_4P)_2S_6{\cdot}2H_2O$ by addition of Ph_4P^+ to a solution of Na_2S_3 in water. The preparations of $(Ph_4P)(NH_4)S_7$ and $(Ph_4P)_2S_7$ by reaction of CH_3CN, NH_3, Ph_4PBr, S_8, and H_2S[11] are known.[25]

We have deployed the reactions $Na_2S + S_8$ and $Na + S_8$ as the principal means of generation of polysulfides in DMF solution.[26] Cadmium can be introduced as $CdCl_2$ or $Cd(NO_3)_2$, but the best source is CdS, which does not introduce unnecessary anions. The variables *m* and *n*, which describe the nominal composition $Cd(S_m)_n$ of the solution, take account of the S^{2-} introduced by dissolution of CdS. CdS does not react with Na_2S alone in DMF (as does HgS) but dissolves rapidly in the presence of S_8 due to the formation of the polysulfide complexes (eq 2).[27]

$$CdS + (n - 1)Na_2S + (n(m - 1)/8)S_8 \rightarrow [Cd(S_m)_n]^{2-2n}(solv) + (2n - 2)Na^+(solv) \quad (2)$$

In fact a solid mixture of Na_2S, CdS, and S_8 when heated to ca. 140 °C forms red cadmium polysulfide complexes, which can then be extracted readily into DMF solution. CdS did not react with a solution of $(Bu_4N)_2S_6$ in DMF.

$(Bu_4N)_2S_6$ and $CdCl_2{\cdot}2.5H_2O$ dissolve together in CH_3CN, acetone, and DMF to yield solutions of higher concentration than can be obtained for the separated reagents. The colors of these solutions depend on the S_6^{2-}/Cd ratio, varying from dark green when the ratio is 4, through dark red when it is 2, and then changing quite sharply to lighter amber colors as the ratio falls below 2. There is evidence (see Experimental Section) that NO_3^- oxidizes polysulfide ions in DMF and CH_3CN, and therefore nitrates have been avoided. The cadmium polysulfide complex **8** with mixed cations was the first we isolated, by reaction of $(Bu_4N)_2S_6$ and $CdCl_2{\cdot}2.5H_2O$ in acetonitrile with addition of Ph_4PBr. Being unable to grow suitable crystals of **8**, we treated solutions of it with further Ph_4PBr to crystallize **6**. The better synthesis of **6** is by direct reaction of Na_2S, S_8, CdS, and Ph_4PBr in a mixture of DMF and acetonitrile, but the crystallization from these solutions of **6** or **7** with very slightly different cadmium polysulfide complexes in almost the same crystal lattice is not easily controlled. ^{113}Cd NMR shows that the solutions contain several such complexes in equilibrium. It is quite likely that other crystals obtained from these solutions will contain other slightly different $[Cd(S_x)(S_y)]^{2-}$ complexes.

Table IV. Coordination Bond Lengths (Å) and Angles (deg) for **6** and **7**

		6	
Cd–S1A	2.541 (3)	Cd–S6A	2.520 (3)
Cd–S1B	2.557 (2)	Cd–S6B	2.556 (2)
Cd–S1B′	2.557 (2)	Cd–S6B′	2.559 (3)
Cd–S1B″	2.557 (2)	Cd–S6B″	2.562 (4)
S1A–Cd–S6A	115.1 (1)	S1A–Cd–S6B′	114.1 (6)
S1A–Cd–S1B	102.9 (1)	S6A–Cd–S1B′	109.8 (6)
S1B–Cd–S6B	103.9 (2)	S6A–Cd–S6B′	97.5 (6)
S1A–Cd–S6B	103.1 (1)	S1B″–Cd–S6B″	103.4 (13)
S6A–Cd–S1B	120.8 (2)	S1A–Cd–S1B″	90.4 (5)
S6A–Cd–S6B	109.1 (1)	S1A–Cd–S6B″	120.5 (10)
S1B′–Cd–S6B′	125.9 (6)	S6A–Cd–S1B″	131.7 (6)
S1A–Cd–S1B′	95.6 (3)	S6A–Cd–S6B″	97.8 (13)
		7	
Cd–S1A	2.544 (2)	Cd–S2B′	2.551 (2)
Cd–S6A	2.526 (2)	Cd–S1B″	2.563 (5)
Cd–S1B	2.550 (2)	Cd–S6B″	2.553 (4)
Cd–S7B	2.547 (2)		
S1A–Cd–S6A	115.1 (1)	S1A–Cd–S2B′	103.4 (2)
S1A–Cd–S1B	99.6 (1)	S6A–Cd–S2B′	123.0 (3)
S1A–Cd–S7B	104.0 (1)	S1B″–Cd–S6B″	102.0 (13)
S6A–Cd–S1B	110.9 (1)	S1A–Cd–S1B″	95.9 (5)
S1B–Cd–S7B	118.9 (1)	S1A–Cd–S6B″	115.9 (7)
S6A–Cd–S7B	108.2 (1)	S6A–Cd–S1B″	135.2 (6)
S2B′–Cd–S7B	100.8 (4)	S6A–Cd–S6B″	92.8 (11)

The color of a solution of $[Cd(S_6)_2]^{2-}$ (anion of **8**) in DMF is temperature dependent, changing from brighter orange at ca. 60 °C to pale yellow at ca. −60 °C. Treatment of this solution with Ph_3P in DMF, in order to shorten the polysulfide chains by abstraction of S atoms as in eq 3, causes an immediate color change

$$[Cd(S_6)_2]^{2-} + Ph_3P \rightarrow [Cd(S_6)(S_5)]^{2-} + Ph_3PS \quad (3a)$$

$$[Cd(S_6)_2]^{2-} + 2Ph_3P \rightarrow [Cd(S_5)_2]^{2-} + 2Ph_3PS \quad (3b)$$

$$[Cd(S_x)_2]^{2-} + {}^1/_8S_8 \rightarrow [Cd(S_x)(S_{x+1})]^{2-} \quad (4)$$

$$[Cd(S_x)_2]^{2-} + PhCH_2SSSCH_2Ph \rightarrow [Cd(S_x)(S_{x+1})]^{2-} + PhCH_2SSCH_2Ph \quad (5)$$

to green, which reverts to yellow within a few minutes at room temperature, and a crystalline compound precipitates from the solution after the cadmium polysulfide conversion is complete. Other reagents that were codissolved with **8** in DMF in reactions to modify the composition of the $[Cd(S_x)(S_y)]^{2-}$ complexes were S_8 (eq 4) and $PhCH_2SSSCH_2Ph$ (eq 5) to elongate the polysulfide chains and $PhCH_2SSCH_2Ph$ (reverse of eq 5) to shorten the chains. These reactions were monitored by Cd NMR (see below).

Crystal Structure Results. Crystallographic disorder of metallasulfane ring conformation and ring size is characteristic of homoleptic metal polysulfide complexes crystallized with Ph_4P^+. By use of the versatile program RAELS[23] for constrained refinement we have been able to achieve precise refinement of the disorder components that occur in low proportion in both crystals. Cadmium coordination dimensions for **6** and **7** are reported in Table IV, chelate ring dimensions for **6** in Table V, and chelate ring dimensions for **7** in Table VI. Cation dimensions and relatively short cation–anion contacts are contained in the supplementary

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(25) $(Ph_4P)_2S_7$ has also been formed from $[(S_4)_2MoS]^{2-}$: Kanatzidis, M. G.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1983**, *22*, 290.

(26) The solubility of Na_2S_x in DMF is approximately 1 mmol/mL when *x* is in the range 4–8 and drops to <0.5 mmol/mL when $x > 8$. When $x < 3$, the DMF appears not to be immune to reaction, because the solutions slowly gel.

(27) There was no evidence for reaction when we heated CdS and S_8 together in DMF.

Table V. Chelate Ring Dimensions (Distances in Å and Angles in deg) for $(Ph_4P)_2[Cd(S_6)_2]$ (**6**)

	n = A	n = B	n = B′	n = B″
		Bond Distances		
S1n–S2n	2.036 (4)	2.061 (3)	2.058 (3)	2.057 (6)
S2n–S3n	2.029 (4)	2.064 (4)	2.059 (3)	2.063 (6)
S3n–S4n	2.062 (4)	2.063 (4)	2.066 (4)	2.068 (6)
S4n–S5n	2.043 (4)	2.058 (3)	2.064 (4)	2.061 (6)
S5n–S6n	2.037 (4)	2.054 (3)	2.063 (4)	2.061 (7)
		Bond Angles		
Cd–S1n–S2n	107.4 (2	114.2 (2)	97.0 (5)	107 (1)
S1n–S2n–S3n	108.1 (2)	108.9 (3)	111.6 (9)	127 (2)
S2n–S3n–S4n	107.5 (2)	110.9 (3)	115.9 (11)	103 (2)
S3n–S4n–S5n	109.6 (2)	105.7 (3)	116.2 (14)	114 (3)
S4n–S5n–S6n	107.7 (2)	110.0 (2)	104.0 (14)	126 (3)
S5n–S6n–Cd	105.4 (1)	98.0 (1)	115.1 (11)	104 (2)
		Torsional Angles		
S6n–Cd–S1n–S2n	−20.4 (2)	−61.4 (4)	6.7 (11)	−31 (2)
Cd–S1n–S2n–S3n	83.7 (2)	−12.5 (5)	−76.1 (9)	−69 (2)
S1n–S2n–S3n–S4n	−102.8 (2)	91.7 (5)	54.7 (15)	62 (3)
S2n–S3n–S4n–S5n	83.6 (2)	−105.9 (4)	70.8 (19)	46 (4)
S3n–S4n–S5n–S6n	−92.7 (2)	81.5 (3)	−84.5 (19)	−79 (5)
S4n–S5n–S6n–Cd	91.3 (2)	−83.4 (2)	−0.7 (20)	−11 (5)
S5n–S6n–Cd–S1n	−50.1 (2)	92.9 (2)	49.5 (18)	73 (3)

Table VI. Chelate Ring Dimensions (Distances in Å and Angles in deg) for $(Ph_4P)_2[Cd(S_6)(S_7)]$ (**7**)

	n = A	n = B	n = B′	n = B″
		Bond Distances		
S1n–S2n	2.048 (3)	2.002 (3)		2.031 (9)
S2n–S3n	2.033 (2)	2.021 (4)	2.006 (3)	2.027 (6)
S3n–S4n	2.065 (3)	2.055 (5)	2.022 (4)	2.055 (4)
S4n–S5n	2.049 (2)	2.055 (4)	2.056 (4)	2.054 (5)
S5n–S6n	2.044 (2)	2.022 (4)		2.007 (5)
S6n–S7n		2.002 (3)		
		Bond Angles		
Cd–S1n–S2n	107.3 (1)	98.3 (2)		104.5 (10)
Cd–S2n–S3n			112.4 (4)	
S1n–S2n–S3n	107.8 (1)	107.7 (2)		106.7 (18)
S2n–S3n–S4n	107.5 (1)	105.6 (7)	117.5 (15)	104.8 (15)
S3n–S4n–S5n	109.5 (1)	103.1 (4)	114.9 (6)[a]	104.5 (16)
S4n–S5n–S6n	107.6 (1)	103.0 (7)	109.2 (13)[a]	101.1 (15)
S5n–S6n–Cd	104.5 (1)			120.9 (13)
S5n–S6n–S7n		110.8 (1)	110.8 (1)	
S6n–S7n–Cd		100.0 (1)	100.0 (1)	
		Torsional Angles		
S6n–Cd–S1n–S2n	−19.4 (1)			−84.8 (17)
S7n–Cd–S1n–S2n		−6.3 (2)		
S7n–Cd–S2n–S3n			−64.4 (8)	
Cd–S1n–S2n–S3n	83.5 (1)	−96.6 (2)		77.7 (17)
Cd–S2n–S3n–S4n			−5.3 (11)	
S1n–S2n–S3n–S4n	−102.9 (1)	62.7 (4)		−81.8 (19)
S2n–S3n–S4n–S5n	83.3 (1)	79.1 (10)	80.7 (22)[a]	119.5 (17)
S3n–S4n–S5n–S6n	−92.8 (1)	−126.5 (8)	−94.6 (20)[a]	−95.7 (21)
S4n–S5n–S6n–S7n		83.4 (3)	78.6 (5)[a]	
S4n–S5n–S6n–Cd	92.3 (1)			12.2 (29)
S5n–S6n–S7n–Cd		−85.3 (1)	−85.3 (1)	
S5n–S6n–Cd–S1n	−51.4 (1)			58.0 (27)
S6n–S7n–Cd–S1n		92.4 (2)		
S6n–S7n–Cd–S2n			95.0 (2)	

[a] Involves bond S4B′–S5B.

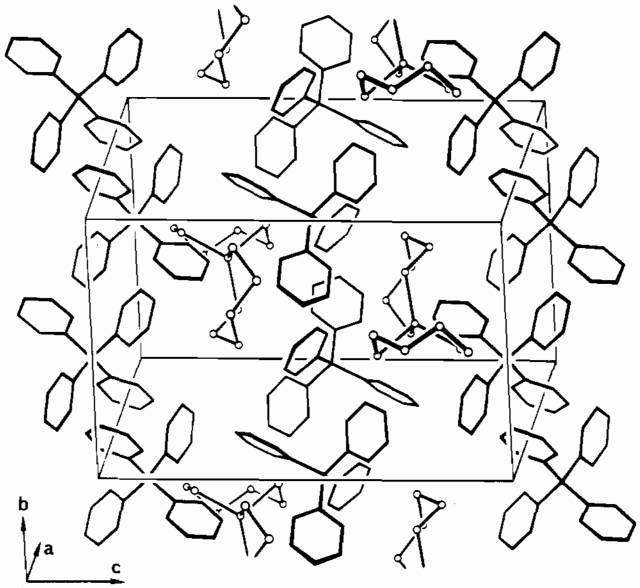

Figure 3. Crystal lattice packing for **6**, showing only the major conformation of the disordered S_6 ring.

material. The crystal packing is virtually the same for **6** and **7** and is shown in Figure 3.

Chelated polysulfide rings occur in both **6** (Figure 1) and **7** (Figure 2): one ring (A) of each is ordered CdS_6, while the other chelate is disordered in both compounds, with three distinct CdS_6 rings in **6** in the proportions 77% (B), 15% (B′), 8% (B″) and in **7** one CdS_7 ring (B, 56%) and two CdS_6 rings (B′, 34%, B″, 10%). The S_7 ring and one of the S_6 rings in **7** share the common atoms S5B, S6B, and S7B. MS_7 rings have been found previously only in $(PMe_3)_3OsS_7$[28] and $[(S_7)_2BiS_6Bi(S_7)_2]^{4-}$ (**9**)[9] and in a nonchelating mode in $[(S_7)_4Pd_2]^{4-}$.[12]

The Cd–S distances in both **6** and **7** hardly deviate from the mean of 2.54 [1] Å.[29] However, the S_4 coordination of Cd manifests substantial variations in S–Cd–S angles. In **6** the S–Cd–S angles within the CdS_6 rings are 115° (ring A), 104° (ring B), 126° (ring B′), and 103° (ring B″), while in **7** the corresponding intrachelate S–Cd–S angles are 115° (A), 102° (B″), and 101° (B′) for the CdS_6 rings and 119° for the CdS_7 ring (B). The angle appears to depend on ring conformation more than ring size. The interchelate S–Cd–S angles are wide-ranging from 90 to 132° in both structures.

Crystals of both **6** and **7** contain the anions packed in gaps between layers of cations (see Figure 3). Figure 2 shows that the CdS_7 ring in **7** is composed of two sections, S1B to S4B and S4B to S7B, with atoms in positions that are comparable with those of atoms in sections of the CdS_6 B, B′, and B″ rings in both **6** and **7**. In this way the CdS_7 ring does not occupy appreciably more volume than the CdS_6 rings.

Dimensions and Conformations of the Polysulfide Rings. In the polysulfide chain, bonds labeled α, β, and γ from the chain ends have mean S-S bond lengths of 2.036 [22] (α), 2.040 [16] (β), and 2.060 [5] Å (γ).[29] Although there is variability of cadmasulfane ring conformation, the figures show that there are patterns in all or parts of the rings in **6** and **7**, and the torsional angles presented in Table VII show the detailed correspondences that extend also to the rings in **2**. Ring A of **6** and **7** is very similar to one of the rings in **2**. The other ring of **2** is virtually the enantiomorph of ring B in **6**.

The torsional angles in the CdS_7 ring of **7** are similar to those in **9**,[9] as shown in Table VII (ring S8–S14 of **9** is the enantiomorph of the others). The conformation of the CdS_7 ring as shown in Figure 2 is reminiscent of the OsS_7 ring in $(Me_3P)_3OsS_7$. In this compound the central S atom of the chelated ring is also tightly bound to the metal atom (the central S–Os distance is shorter than the terminal S–Os distances), and the S_7 ligand is tridentate.[28] However, in **7** there is no bonding interaction between S4B and Cd.

In the crystals of **6** and **7** there are some nonbonded distances between cadmasulfane sulfur atoms and atoms of the Ph_4P^+ ions less than the sum of the van der Waals radii. In fact there are S---C distances as short as 3.07 Å, compared with a van der Waals radii sum of ca. 3.5 Å.[30] Close nonbonded contacts of this type and length are found in the crystals of all other Ph_4P^+ salts of

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(28) Gotzig, J.; Rheingold, A. L.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 814.

(29) Means taken over major component only in each position. Values in brackets are esd's of the sample.

(30) The short anion–cation contacts are tabulated with the supplementary material.

Table VII. Comparison of CdS_6 and CdS_7 Ring Torsional Angles (deg)

CdS_6 Rings

compd (ring)	Cd–S1	S1–S2	S2–S3	S3–S4	S4–S5	S5–S6	S6–Cd
2 (S1–S6)	–27.6	87.9	–97.9	79.9	–100.1	95.2	–44.6
6 (A)	–20.4	83.7	–100.2	83.6	–92.7	91.3	–50.1
7 (A)	–19.4	83.5	–102.9	83.3	–92.8	92.3	–51.4
6 (B)	–61.4	–12.5	91.7	–105.9	81.5	–83.4	92.9
7 (B′)	–64.4	–5.3	80.7	–94.6	78.6	–85.3	95.0
2 (S7–S12)	68.3	5.9	–87.0	106.6	–79.9	74.9	–90.7
7 (B″)	58.0	12.2	–95.7	119.5	–81.8	77.7	–84.8
6 (B′)	49.5	–0.7	–84.5				
6 (B″)	73	–11	–79				
7 (B)[a]			79.1	–126.5	83.4	–85.3	92.4

CdS_7 Rings

compd (ring)	Cd–S1	S1–S2	S2–S3	S3–S4	S4–S5	S5–S6	S6–S7	S7–Cd
7	–6.3	–96.6	62.7	79.1	–126.5	83.4	–85.3	92.4
9 (S1–S7)	–4	–1.7	70	77	–113	89	–106	98
9 (S21–S27)	–45	–72	78	64	–124	87	–90	120
9 (S28–S34)	–14	–89	66	71	–114	95	–102	105
9 (S8–S14)	33	85	–75	–57	113	–92	104	–111

[a] This is part of the CdS_7 ring.

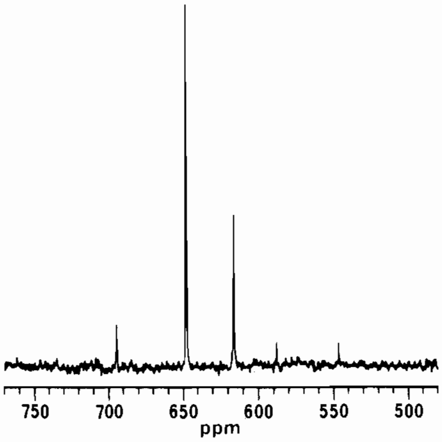

Figure 4. ^{113}Cd NMR spectrum, at 220 K, of $(Bu_4N)(Ph_4P)[Cd(S_6)_2]$ (**8**) in DMF.

metal polysulfides that we have investigated.[31] They are considered to be not anomalous and to be indicative of soft van der Waals repulsive potentials for these ions.

Vibrational Spectroscopy. Vibrational frequencies in the range 190–500 cm^{-1} can be assigned to coordinated polysulfide ligands.[32] The particularly responsive region of the spectrum is ca. 400–500 cm^{-1}, in which frequencies at ca. 495 and 455 cm^{-1} are characteristic of the metallahexasulfane ring. In **6** there are IR absorptions at 455, 500, and 525 cm^{-1}; in **8** IR and Raman frequencies occur at 455 and 495 cm^{-1}, with a Raman band also at 405 cm^{-1}. In **2** the principal Raman bands are at 397, 458 (464), and 494 cm^{-1}.[8]

^{113}Cd NMR Results. The various ^{113}Cd resonances to be described and discussed in the following are each labeled by the value of their chemical shift at 220 K. The spectrum of $(Bu_4N)(Ph_4P)[Cd(S_6)_2]$ (**8**) dissolved in DMF is shown in Figure 4: the spectrum of **6** is very similar. This spectrum is unchanged by heating at 60 °C for 100 min or by dilution. There occur four sharp ($\Delta w_{1/2}$ = ca. 20–30 Hz) resonances, "695", "648", "616", and "546". Multiple resonances such as these were observed for all other solutions containing cadmium and polysulfide ligands. The relative intensities of all lines varied independently, indicating that there occurred in these solutions equilibrium mixtures of

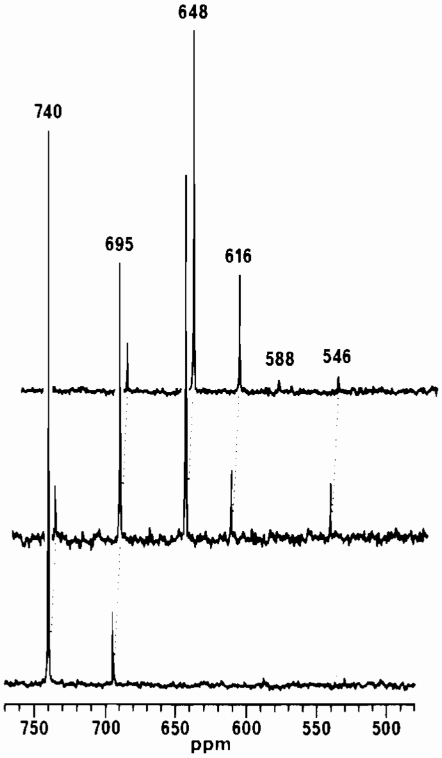

Figure 5. ^{113}Cd NMR spectra, at 220 K, of cadmium polysulfide solutions in DMF. The nominal compositions are $Cd^{2+} + 3[S_m]^{2-}$, m = 4–6, from the bottom to the top. The spectra have been displaced slightly on the chemical shift scale for clarity, and resonances are labeled as in the text. The spectrum of the solution with m = 8 is indistinguishable from that with m = 6.

Table VIII. ^{113}Cd NMR Spectra of Cadmium Polysulfide Solutions:[a] Approximate Relative Intensities[b] of Resonances in Solutions of Composition $Cd^{2+} + n[S_m]^{2-}$

m	n	"740"	"695"	"648"	"616"	"588"	"546"
4	3	89	11				
5	3	6	34	45	9		
6	3		8	64	23	3	3
7	3		7	70	19	2	3
8	3		6	67	22	2	3
6	2		6	66	25	2	3
6	4		6	66	23	5	3

[a] Solutions prepared by the reaction S_8 + Na + CdS: spectra at 220 K. [b] Relative intensities are approximate as the resonances were not fully relaxed.

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[31] Herath Banda, R. M.; Dance, I. G.; Bailey, T. D.; Craig, D. C.; Cusick, J.; Ma, I. N. L.; Scudder, M. L. Manuscript in preparation.

[32] (a) Janz, G. J.; Coutts, J. W.; Downey, J. R.; Roduner, E. *Inorg. Chem.* **1976**, *15*, 1755. (b) Janz, G. J.; Downey, J. R.; Roduner, E.; Wasilczyk, G. J.; Coutts, J. W.; Eluard, A. *Inorg. Chem.* **1976**, *15*, 1759.

species $[Cd(S_x)_y]^{2-2y}$, each with different cadmium coordination, rather than multiple Cd sites in one complex. There is no independent data that will permit unequivocal assignment of any of these resonances. Therefore, in order to investigate these equilibria further, we have examined various solutions prepared in DMF from mixtures of Na_2S (or Na), S_8, and CdS, in proportions that yield different values of m and n in the *total* solution stoichiometry $Cd^{2+} + n[S_m]^{2-}$. Figure 5 contains spectra for DMF solutions prepared as S_8 + Na + CdS, with $n = 3$ and $m = 4$–6, and Table VIII contains approximate relative intensities of the resonances in the full series with variable m and n. Resonances "740" and "588" are now added to the previous four. Over the full range of solutions the three higher frequency resonances "740", "695", and "648" are dominant, while "588" and "546" are always minor. Variations in the compositional variable m (but not n) cause major changes in the relative intensities of the three dominant resonances: a decrease in m increases the relative intensities of the lines at higher chemical shift.

We propose that the three dominant lines correspond to the monometallic species $[Cd(S_x)_2]^{2-}$, $[Cd(S_x)(S_{x-1})]^{2-}$, and $[Cd(S_{x-1})_2]^{2-}$. These assignments are consistent with the observation that increase in the compositional variable n from 2 to 4 does not introduce new lines which could be assigned to tris(polysulfide) complexes $[Cd(S_x)_3]^{4-}$. In view of the established existence of $[Cd(S_6)_2]^{2-}$ and (almost certainly[20]) $[Cd(S_5)_2]^{2-}$ in the solid state, the most probable species and resonance assignments are

"740"	$[Cd(S_5)_2]^{2-}$
"695"	$[Cd(S_5)(S_6)]^{2-}$
"648"	$[Cd(S_6)_2]^{2-}$

Note that the chemical shift of the mixed-ligand complex $[Cd(S_5)(S_6)]^{2-}$ is almost midway between those of the parent species.

This interpretation of the spectrum of **8** in solution requires partial ligand disproportionation on dissolution (eq 6). This requirement, and data provided below, lead us to assign the "616" resonance to $[Cd(S_6)(S_7)]^{2-}$.

$$2[Cd(S_6)_2]^{2-} \rightleftharpoons [Cd(S_5)(S_6)]^{2-} + [Cd(S_6)(S_7)]^{2-} \qquad (6)$$

These assignments are supported but not confirmed by comparison with those of $[Cd(edt)_2]^{2-}$, $[Cd(pdt)_2]^{2-}$, and $[Cd(edt)(pdt)]^{2-}$, which were measured for DMF solutions at 260 K (exchange broadening is apparent at 300 K). The $[Cd(edt)_2]^{2-}$ resonance occurs at 793 ppm, that of $[Cd(pdt)_2]^{2-}$ at 689 ppm, and that of $[Cd(edt)(pdt)]^{2-}$ at 742 ppm. The first two values compare well with measurements of 794 and 691 ppm, respectively (at 193 K),[33] for the same species generated in methanol solution.[34] For both series of complexes, $[Cd\{S(S)_pS\}_2]^{2-}$ and $[Cd\{S(CH_2)_qS\}_2]^{2-}$, resonances at higher δ_{Cd} are assigned to smaller chelate rings, and $\Delta\delta_{Cd}$ is ca. 50 ppm for a decrement of one atom in one chelate ring. Although the magnitude of the effect of ring size on δ_{Cd} in both series indicates that the geometrical influence is substantial, there is no evidence of this in the distances and angles around Cd in the polysulfide complexes. Shortened polysulfide chains might have been expected to have increased charge density at the donor S atoms and, consequently, a larger δ_{Cd}, but the general similarities of the spectra indicate that the $(S)_p$ connector is electronically similar to the $(CH_2)_q$ connector. In general, the $[Cd\{S(CH_2)_qS\}_2]^{2-}$ resonances support our general assignments for the $[Cd\{S(S)_pS\}_2]^{2-}$ series but do not permit unambiguous definition of the metallapolysulfane ring sizes for each resonance. We note that as the polymethylenedithiolate ring size q increases the magnitude of $\Delta\delta_{Cd}$ decreases, which would be consistent with our assignment of the polysulfide "616" resonance to $[Cd(S_6)(S_7)]^{2-}$.

Table IX. ^{113}Cd NMR Spectra of Reaction Products of **8**: Approximate Relative Intensities of the Resonances[a]

	"740"	"695"	"648"	"616"	"546"
8		14	58	20	8
8 + $1Ph_3P$	18	36	30	5	10
8 + $2Ph_3P$	36	41	16		7
8 + $3Ph_3P$	87	11			
8 + $4Ph_3P$	100				
8 + $4PhCH_2SSCH_2Ph$	18	38	28	4	6
8 + $8PhCH_2SSCH_2Ph$	31	42	17	2	3
8 + S		4	58	33	6
8 + $4PhCH_2SSSCH_2Ph$[b]		5	52	19	3
8 + $8PhCH_2SSSCH_2Ph$[c]		8	49	15	

[a] Solvent DMF; spectrum taken at 220 K. [b] Resonance "604" 21%. [c] Resonance "604" 29%.

Modification of Polysulfide Chain Lengths. To confirm this proposal that the major species in solution are bis(polysulfide) complexes with variable chain length, solutions were treated with reactants capable of changing the chain lengths by oxidative elongation, reductive shortening, or the abstraction or addition of sulfur atoms. The simplest procedure for elongation of chain length is aerial oxidation. Thus, exposure to atmospheric dioxygen of a $Na_2S/S_8/CdS/DMF$ solution with $m = 6$ and $n = 3$ caused a shift in resonance intensity from "740" and "695" and "648", consistent with the occurrence of the reaction $6(S_5)^{2-} \rightarrow 5(S_6)^{2-} + 2e^-$. Reactions of **8** with Ph_3P (which generate yellow-green solutions, containing polysulfide radicals) are complete within 1 h at room temperature and yield spectra in which the higher δ_{Cd} lines gain intensity as expected, due to S abstraction as Ph_3PS (eq 3). These results are included in Table IX. Treatment with excess Ph_3P leads to a spectrum containing only the "740" line. Addition of dibenzyl disulfide to a solution of **8** in DMF also shifts relative intensity from the "648" to the "695" and "740" resonances, consistent with the occurrence of the chain-shortening reactions (eq 7). Addition of a solution of $(Ph_4P)_2CS_3$, which can function as a source of S^{2-} and was expected to shorten the polysulfide chains, had little effect.

$$[Cd(S_6)_2]^{2-} + PhCH_2SSCH_2Ph \rightarrow [Cd(S_6)(S_5)]^{2-} + PhCH_2SSSCH_2Ph \qquad (7a)$$

$$[Cd(S_6)(S_5)]^{2-} + PhCH_2SSCH_2Ph \rightarrow [Cd(S_5)_2]^{2-} + PhCH_2SSSCH_2Ph \qquad (7b)$$

Sulfur atom addition reactions were partially successful in elongating the hexasulfide chains of $[Cd(S_6)_2]^{2-}$. Substantial heating was required to dissolve S_8 in a DMF solution of **8**, and the resulting spectrum showed a small decrease in the intensity of "695" and small increase in "616", consistent with a small increase in the proportion of $[Cd(S_6)(S_7)]^{2-}$. Sulfur does dissolve readily in a DMF solution of $(Bu_4N)_2S_6$, but treatment with $CdCl_2$ yielded a spectrum identical with that of dissolved **8**. Addition of excess dibenzyl trisulfide to solutions of **8** had little effect on the relative intensities of the polysulfide resonances but introduced a new resonance at 604 ppm (220 K), which is probably due to a complex with $Cd-SCH_2Ph$ coordination because the same resonance occurs very weakly in the solutions treated with dibenzyl disulfide.

Dynamics of Cd–S_x Coordination. A significant property of the spectra of $[Cd(S_x)_2]^{2-}$ species is that the resonance lines remain narrow up to 300 K, indicating an order of magnitude for the rates of dissociation of polysulfide ligands as less than ca. 10^2 s^{-1} at ambient temperatures and ca. 0.1 M Cd concentration. This is in contrast with cadmium complexes with monodentate thiolate ligands, such as $[Cd_x(SPh)_y]^{2x-y}$, which exchange cadmium sites at $\geq 10^3$ s^{-1} below 270 K.[35,36] Dissociative exchanges of cadmium sites in polymetallic aggregates with chelating SCH_2CH_2OH ligands can occur at $>10^4$ s^{-1} at 300 K.[37,38] Evidently the com-

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[33] Carson, G. K.; Dean, P. A. W.; Stillman, M. J. *Inorg. Chim. Acta* **1981**, *56*, 59.

[34] The resonances for the species $[Cd\{S(CH_2)_qS\}_2]^{2-}$ are appreciably solvent dependent: δ_{Cd} values in water for $p = 2$, 3, and 4 are 829, 663, and 648 ppm, respectively.[33]

[35] Dance, I. G. *Inorg. Chim. Acta* **1985**, *108*, 227.

[36] $[CdCl_xBr_{4-x}]^{2-}$ complexes exchange ligands at ca. 10^3 s^{-1} at −45 °C in CH_2Cl_2: Colton, R.; Dakternieks, D. *Aust. J. Chem.* **1980**, *33*, 2405.

[37] Dance, I. G.; Garbutt, R. G.; Craig, D. C. *Aust. J. Chem.* **1986**, *39*, 1449.

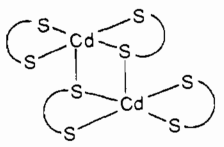
plexes of dianionic polysulfide ligands are tightly chelated, and polysulfide exchange reactions are slow. Indeed it appears that the broadening of "740", "695", and "648" which occurs at >340 K is progressing toward increased separation rather than coalescence of these lines. There is no evidence of the line broadening expected at moderate temperatures if variable solvation was prevalent.

The effect of temperature increase on solutions containing $[Cd(S_x)_2]^{2-}$ species is to increase the relative intensities of the lower δ_{Cd} lines. Thus in a $m = 6$, $n = 2$ mixture the relative intensities of "740", "695", and "648" are 35/54/11 at 220 K but 13/38/49 at 300 K. The equilibria (8) shift in favor of complexes with longer polysulfide chains at higher temperature.

$$[Cd(S_5)_2]^{2-} + (S_x)^{2-} \rightleftharpoons [Cd(S_5)(S_6)]^{2-} + (S_{x-1})^{2-} \quad (8a)$$

$$[Cd(S_5)(S_6)]^{2-} + (S_x)^{2-} \rightleftharpoons [Cd(S_6)_2]^{2-} + (S_{x-1})^{2-} \quad (8b)$$

Assignments of Weak Lines. The minor resonances "588" and "546" occur in the various $Cd^{2+}/(S_x)^{2-}$ solutions, with relative intensities that are always very low and that are less responsive to changes in solution composition than are the major lines. It is possible that the complexes responsible for these lines are associated forms of the major species, in which sulfide donor atoms bridge two Cd atoms, which would then be five-coordinate. Complexes such as **10**, with chain lengths S_5 or S_6, would probably have marginally less electron density transferred from S to Cd due to the bridging, and this would be consistent with the slightly lower δ_{Cd} of the minor resonances. The effect of coordination number on δ_{Cd} in complexes of this type is not yet established in sufficient detail to be certain of this assignment. Attempts to test the association hypothesis by examination of the concentration dependence of the spectra were inconclusive.



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$Cd^{2+}/Cl^-/(S_x)^{2-}$ Complexes. The solutions formed in the mutual solubilization of $CdCl_2$ and $(Bu_4N)_2S_6$ in DMF or CH_3CN have been investigated by Cd NMR. With CH_3CN as solvent some unidentified insoluble solids were removed prior to measurement of the spectra. Again multiple resonances that are narrow at 220 and 300 K appear, with intensities dependent on the $(Bu_4N)_2S_6/CdCl_2$ molar ratio (n), as plotted in Figure 6. When $n \geq 2$, the spectra in DMF are very similar to those already described for these values of n, but the spectra at $n = 1.5$, 1.0, 0.5 in either solvent are dominated by new resonances labeled "538" and "443", according to their chemical shifts at 220 K. The spectrum of the CH_3CN solution with $n = 0.5$ at low temperature contains only the "443" resonance. Clearly two new chloro complexes are responsible for these resonances, but assignment of them is not definite. We suggest that "538" is due to $[CdCl_2(S_x)]^{2-}$ and "443" to $[CdCl_2(S_{x+1})]^{2-}$, where x is probably 5. Further experiments will be necessary to confirm these assignments.

Finally we observe that the three principal NMR resonances "740", "695", and "648" appear when nonaqueous polysulfide solutions are added to the complexes $[Cd(SPh)_4]^{2-}$, $[Cd_4(SPh)_{10}]^{2-}$, and $[S_4Cd_{10}(SPh)_{16}]^{4-}$,[39] indicating the thermodynamic stability of the species $[Cd(S_x)_2]^{2-}$ with chelating ligands relative to that of nonchelating cadmium thiolate complexes. This result is consistent with, although different from, that of Coucouvanis et al.[20] in which $[Cd(SPh)_4]^{2-}$ yielded $[(PhS)_2Cd(S_5)]^{2-}$ or $[Cd(S_5)_2]^{2-}$ when treated with small or large amounts of the oxidant $PhCH_2SSSCH_2Ph$.

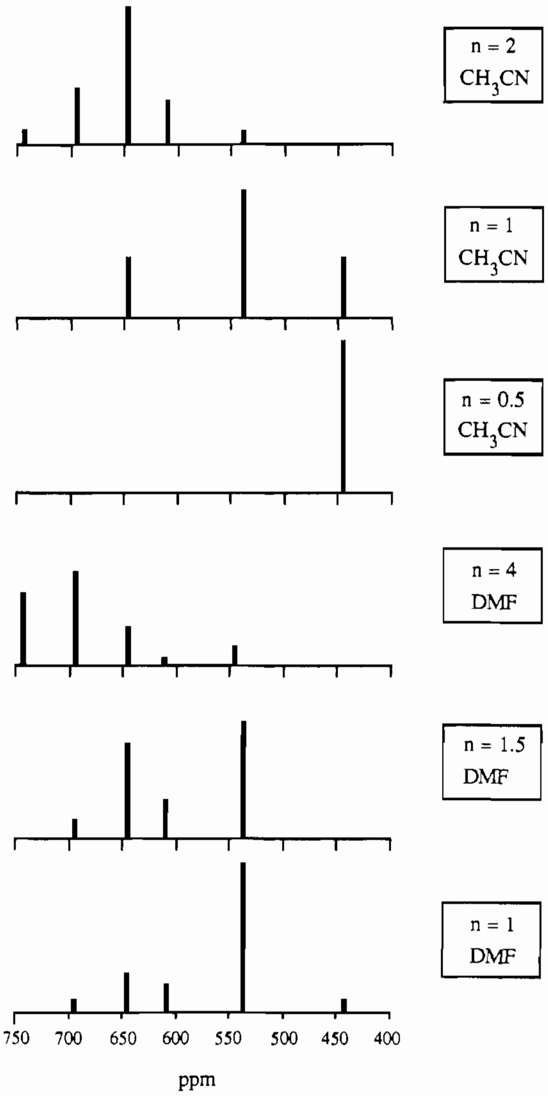

Figure 6. Diagram of the ^{113}Cd NMR lines appearing in solutions of $CdCl_2$ and $(Bu_4N)_2S_6$ in DMF (220 K) and CH_3CN (240 K). n is the molar ratio $(Bu_4N)_2S_6/CdCl_2$. The intensities are approximate and relative, both within and between solutions. The chemical shifts marked are those at 220 K. The line at 538 ppm for n = 1, 1.5 (DMF) is distinctly different from "548", which appears for n = 4 (DMF).

Discussion

We have established clean and easily reproducible procedures for the preparation of cadmium polysulfides in nonaqueous solution and in crystals. The use of CdS as cadmium precursor avoids complications caused by anions that in aprotic solvents would be activated as competitive ligands and complications due to anions such as NO_3^-, which are oxidizing in aprotic solvents. Mixed chlorocadmium polysulfide complexes are formed with $CdCl_2$ in CH_3CN.

Our data on crystals and solutions confirm what had been suspected from previous work, namely that the complexes which crystallize are not necessarily representative of the complexes in solution but are dominated by crystal lattice factors.

We summarize our knowledge of the dynamics and structure of homoleptic cadmium polysulfide complexes as follows:

(1) CdS_x rings of different sizes occur, in solution and in crystals, for x = 5–7. The CdS_4 ring is not yet confirmed but is expected by analogy with the established structures of $[Zn(S_4)_2]^{2-}$,[20] $[Hg(S_4)_2]^{2-}$,[8] and $[Cd(SCH_2CH_2S)_2]^{2-}$.[40]

(2) It is probable that CdS_5, CdS_6, and CdS_7 rings are of comparable thermodynamic stability, at least in DMF solution.

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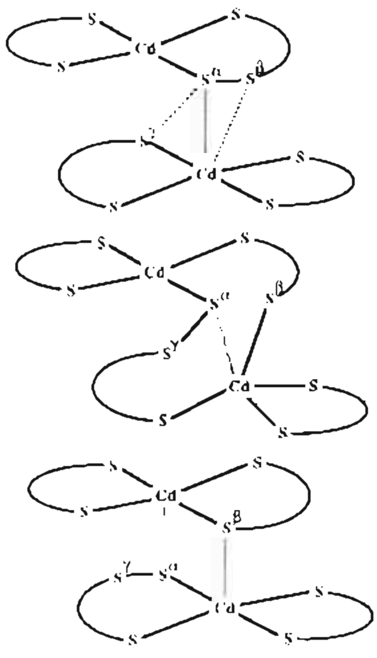

Figure 7. Proposed mechanism for the redistribution of sulfur atoms in cadmapolysulfane rings.

Interchange of cadmapolysulfane rings is a facile process in DMF at 300 K.

(3) Association of $[(S_x)Cd(S_y)]^{2-}$ complexes may occur by secondary Cd- - -S bridging in DMF solution and provide a low-energy mechanism for exchange of chelating polysulfide ligands.

(4) Redistribution of sulfur atoms in cadmapolysulfane rings is also facile, as revealed by the equilibrium distribution of ring sizes on redissolution of crystalline $[(S_x)Cd(S_y)]^{2-}$ complexes. A possible associative mechanism for this redistribution is shown in Figure 7. The molecular structure of $[Cu_6(S_5)(S_4)_3]^{4-}$ [6,16,17] confirms the ability of polysulfide ligands to coordinate and bridge through nonterminal atoms of the polysulfide chain, as required for this mechanism.

(5) The coordination geometry at Cd is relatively invariant in bond length but is angularly unrestricted.

(6) The free energy surface for the conformations of cadmahexasulfane and cadmaheptasulfane rings in solution is evidently fairly flat, on the basis of the absence of any NMR indication of conformational isomers at 220 K, and the variability of conformations observed in the crystals. This is clearly a property of the large chelate rings and contrasts with ΔG barriers of 49–73 kJ mol^{-1} for conformational interchange of MS_5 rings in Cp_2MS_5 (M = Ti, Zr, Hf)[41] and the conformational stability of $[Pt(S_5)_3]^{2-}$, which permits its resolution.[42]

(7) Precipitation of complexes from cadmium polysulfide solutions with the Ph_4P^+ cation yields crystal lattices that are cation dominated, in that the metal polysulfide anions are relatively small and occupy cavities between the cations. The crystals select and include from solution the cadmium polysulfide complexes that fit the cavity, and CdS_6 and CdS_7 cadmapolysulfane rings can have almost the same size, due to conformational flexibility.

Analogies between polysulfide ligands $[S(S)_pS]^{2-}$ and α,ω-alkanedithiolate ligands $[S(CH_2)_qS]^{2-}$ are sustained by our results and by results for the comparable complexes $\{Cu_3(S_4)_3\}^{3-}$ [6,13] and $[Cu_3(SCH_2CH_2S)_3]^{3-}$.[40]

The distribution of known crystal structures of metal polysulfides, and in particular the characterization of $[M(S_4)_2]^{2-}$ and $[M(S_6)_2]^{2-}$ for both Zn and Hg,[6,20,21] has led to the observation that MS_x rings are preferred for x even when M is a closed-shell metal ion.[2] Our results with Cd^{2+}, and others to be reported for Sn^{4+} [43] and other metals,[31] do not support this contention.

Acknowledgment. This research is supported by the Australian Research Grants Scheme. R.M.H.B. thanks the Australian Development Assistance Bureau for financial support. We acknowledge the assistance of Dr. A. D. Rae with the use of the program RAELS and I. Ma for calculations of ion volumes. Professor A. Müller is thanked for sending us a copy of ref 2 prior to publication.

Registry No. **6**, 119747-27-2; **8**, 119747-30-7; $(PPh_4)_2CS_3$, 119747-34-1; H_2S, 7783-06-4; $(Bu_4N)_2S_6$, 85533-96-6; Na_2S, 1313-82-2; Ph_3PS, 3878-45-3; $[Cd(S_6)_2]^{2-}$, 93714-67-1; $[Cd(S_5)(S_6)]^{2-}$, 119747-31-8; $[Cd(S_6)(S_7)]^{2-}$, 119747-28-3; $[Cd(edt)_2]^{2-}$, 79717-68-3; $[Cd(pdt)_2]^{2-}$, 119747-32-9; $[Cd(edt)(pdt)]^{2-}$, 119747-33-0; ^{113}Cd, 14336-66-4; S_6^{2-}, 12597-13-6; $[Cd(S_8)_2]^{2-}$, 99919-09-2; carbon disulfide, 75-15-0; sulfur, 7704-34-9.

Supplementary Material Available: Table S1, listing short nonbonding contacts in **6**, Tables S2 and S3, listing atomic coordinates, thermal parameters, and distances and angles for **6** and **7**, respectively, and Table S6, listing crystallographic details pertaining to data collection, processing, and refinement of the structures of **6** and **7** (24 pages); Tables S4 and S5, listing observed and calculated structure factors for **6** and **7**, respectively (38 pages). Ordering information is given on any current masthead page.

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