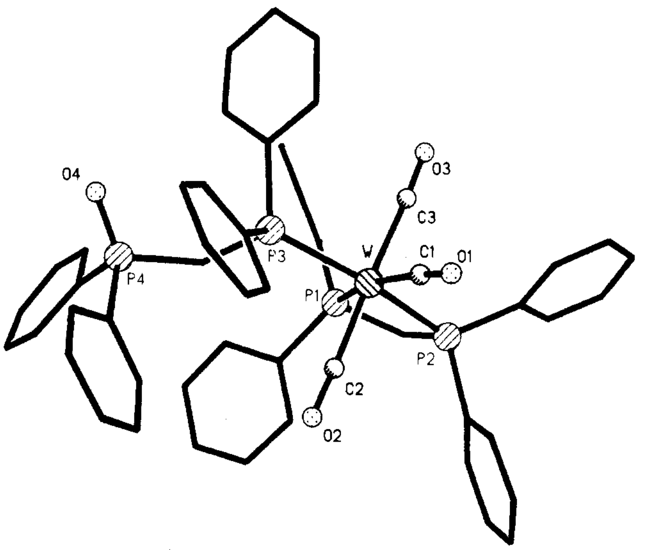

**Figure 6.** Molecular structure of the *mer*-$W(CO)_3(dppm)(Ph_2PCH_2P(O)Ph_2)$ molecule.

tensity ratio of 0.18:1.00. When a solution of *fac*-$W(CO)_3(^{13}CO)(dppm)$ is allowed to stand for approximately 2 weeks at ambient temperature, the ratio of the two $^{13}C$ signals is 0.89:1.00, indicating that reaction 3 has reached equilibrium. After the ligand rearrangement, no $^{13}CO$–$^{13}CO$ coupling was observed in the resulting $W(CO)_4(dppm)$ product, an observation consistent with an intramolecular exchange process.[11]

The reaction of *fac*-$W(CO)_3(dppm)(CH_3CN)$ with triphenylphosphine in THF at ambient temperature affords *fac*-$W(CO)_3(dppm)(PPh_3)$. However, because of the steric requirements of the $PPh_3$ ligand, when a THF solution of *fac*-$W(CO)_3(dppm)(PPh_3)$ is heated at 50 °C, isomerization to the meridional isomer readily takes place. Once formed, the meridional isomer is quite resistant to ligand dissociation; for example, it is stable to reaction with $^{13}CO$ at 50 °C for 3 days. Similarly, the reaction of *fac*-$W(CO)_3(dppm)(CH_3CN)$ with $Ph_2PCH_2PPh_2$ at ambient temperature in THF afforded what was initially assumed to be *fac*-$W(CO)_3(dppm)_2$ with a dangling phosphine ligand on the basis of the $\nu(CO)$ stretching band pattern. After prolonged standing in solution at room temperature this complex exhibited facial $\rightleftharpoons$ meridional isomerization.

More detailed examination by X-ray crystallography of crystals presumed to be *mer*-$W(CO)_3(dppm)_2$ revealed this complex to contain an uncoordinated phosphine oxide group. The coordination geometry of the complex is that of a regular octahedron (Figure 6) with a dppm bite angle of 67.2°. The three W–CO bond lengths are 1.947 (19), 2.001 (19), and 2.039 (18) Å, where the shortest distance corresponds to the carbonyl ligand located trans to the phosphine ligand. Concomitantly, the W–P bond distance trans to the carbonyl ligand is the longest at 2.500 (3) Å, with the remaining W–P distances being 2.445 (3) and 2.458 (3) Å for the dppm and $Ph_2PCH_2P(O)Ph_2$ groups, respectively. Although the origin of the phosphine oxide has not been clearly established, since we started with pure dppm, oxidation of the $PPh_2$ moiety by adventitious oxygen presumably occurred during the prolonged *fac–mer* isomerization process.

**Acknowledgment.** The financial support of the Robert A. Welch Foundation is greatly appreciated.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, hydrogen atom coordinates, and complete bond distances and angles (9 pages); listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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[11] (a) Darensbourg, D. J. *J. Organomet. Chem.* **1979**, *174*, C70. (b) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113. (c) Dobson, G. R.; Asali, K. J. *Inorg. Chem.* **1981**, *20*, 3563 and references therein.

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# Digonally Coordinated Halide within an Octametal Cage. Crystal and Solution Structures of $[XCd_8(SCH_2CH_2OH)_{12}X_3]$, X = Cl, Br, I[1]

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The complexes $[ClCd_8(SCH_2CH_2OH)_{12}Cl_3]$ (**5**) and $[BrCd_8(SCH_2CH_2OH)_{12}Br_3]$ (**6**) are formed in the reaction of 2-hydroxyethanethiol with cadmium acetate and excess sodium halide in water, similarly to the formation of $[ICd_8(SCH_2CH_2OH)_{12}I_3]$ (**2**). **5** and **6** contain $[XCd_8(SCH_2CH_2OH)_{12}X_3]$ molecules with threefold symmetry in the rhombohedral space group $R3$ with $Z = 1$ (**5**, $a = 11.700$ (1) Å, $\alpha = 103.57$ (1)°, 1594 reflections (Mo K$\alpha$), $R = 0.028$; **6**, $a = 11.681$ (1) Å, $\alpha = 102.38$ (1)°, 1587 reflections (Mo K$\alpha$), $R = 0.029$), in which an oblate $Cd_8$ hexahedron (compressed along the threefold axis) intersects an axially prolate $S_{12}$ icosahedron. Three four-coordinate ($S_3CdX$) and three five-coordinate (chelated $S_3Cd(\text{–}OH)_2$) Cd atoms lie outside the faces of the icosahedra in both structures. In **5** the other two Cd atoms on the threefold axis lie inside the faces of the icosahedron, creating symmetric linear digonal coordination of the central Cl atom (Cl–Cd = 2.69 (2), 2.69 (2) Å). In **6** only one axial Cd atom is inside the icosahedron, while the other is almost coplanar with its icosahedral face, thereby creating dissymmetric linear digonal coordination of the internal Br atom (Br–Cd = 2.754 (8), 3.008 (9) Å). $^{113}Cd$ NMR spectra (natural abundance, 66.6 MHz) of **5**, **6**, and **2** in DMF solution are in the slow-Cd-exchange regime at 220 K and reveal all distinct Cd coordination environments, without evidence of Cd–Cd coupling. At room temperature and above the Cd sites are interchanged rapidly.

## Introduction

There exists the established class of molecular aggregates $[XM_8Y_{12}]$ (**1**), in which a cube of metal atoms contains a halide ion X at or close to the body center and doubly bridging ligands across the 12 edges. The donor atoms Y of the 12 bridging ligands constitute an icosahedron. Examples are $(\mu_8\text{-}I)Cd_8(SCH_2CH_2OH)_{12}I_3$ (**2**)[2] and $[(\mu_8\text{-}Cl)M^{I}_8(L\text{---}L)_6]^z$ (**3**), in which M is Cu or Ag and L---L is a square-planar chelate moiety containing another metal M′ and providing two cis bridging sulfur

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[1] Applications of Cadmium NMR to Polycadmium Compounds. 5. Part 4: Dance, I. G.; Garbutt, R. G.; Craig, D. C. *Aust. J. Chem.* **1986**, *39*, 1449.

[2] Burgi, H. B.; Gehrer, H.; Strickler, P.; Winkler, F. K. *Helv. Chim. Acta* **1976**, *59*, 2558.

0020-1669/87/1326-3732$01.50/0

atoms.[3,4] Empty cages are known, but only when L- - -L is a rigid bidentate ligand,[5,6] and consequently it has been suggested[7] that when Y is nonchelating, incorporation of a central halide X is necessary for the mechanical stability of **1**. This has been proposed as the rationale for the existence of $[Cu_4(SPh)_6]^{2-}$ but not $[Cu_8(SPh)_{12}]^{4-}$.[8]

However, the size of the halide X may not match the size of the cavity in **1**. For instance, in **2** the ($\mu_8$-I)–Cd distances are variable and long, average 3.53 Å, ca. 0.5 Å longer than normal. An alternative mode of central stabilization can occur when there is a size disparity between X and the $M_8$ cube: four of the M atoms contract inside the $Y_{12}$ icosahedron to generate tight tetrahedral coordination of the halide. This mode also involves displacement of the other four metal atoms outside the $Y_{12}$ icosahedron and occurs in $[ClZn_8(SPh)_{16}]^-$ (**4**), which is thus *centro*-($\mu_4$-Cl)-*tetrahedro*-$Zn_4$-*icosahedro*-($\mu$-SPh)$_{12}$-*tetrahedro*-(ZnSPh)$_4$.[9]

We now report a new and unexpected stereochemistry for halide inside an octametal cage, in the compounds $[ClCd_8(SCH_2CH_2OH)_{12}Cl_3]$ (**5**) and $[BrCd_8(SCH_2CH_2OH)_{12}Br_3]$ (**6**), which are homologues of **2**. In **5** two diametrically opposed cadmium atoms are displaced inside the triangular faces of the $S_{12}$ icosahedron, creating linear two-coordination of the chloride, while the other six Cd atoms are outside faces of the icosahedron. In **6** only one Cd atom is inside the icosahedron, while the diametrically opposed Cd atom lies *within* its face of the icosahedron, such that the central Br atom has dissymmetric digonal coordination. Accordingly we recognize and consider two variables for cages of type **1**: (i) the degree of displacement of M atoms inside or outside the faces of the $Y_{12}$ icosahedron; (ii) the symmetry of the concomitant distortion of the $M_8$ cube and the $Y_{12}$ icosahedron.

In molecules **5** and **6** in the crystalline phase, Cd atoms are immobilized at positions inside, outside, and within the triangular $S_3$ faces of the icosahedron. The question of cage fluxionality arises, and in particular the possibility of a cage-breathing motion in which one, two, or four Cd atoms undergo concerted inversion through the faces of the icosahedron. This concept is reminiscent of Burgi's investigation of the geometry of $XCdL_3 + X' \rightarrow X + L_3CdX'$ ligand exchange through analysis of the static geometry in a sequence of sites in crystals,[10] and our data can contribute to the Burgi analysis. Intramolecular cage-breathing motions, as well as other processes causing interchange of Cd sites such as dissociative exchange of terminal ligands, can be investigated directly by Cd NMR. We report here the variable-temperature Cd NMR spectra of **2**, **5**, and **6**.

## Experimental Section

**Syntheses.** All preparations were performed under an atmosphere of dinitrogen. Laboratory grade chemicals were used as received.

**$ClCd_8(SCH_2CH_2OH)_{12}Cl_3$ (5).** A solution of 2-hydroxyethanethiol (4.13 g, 52.9 mmol) in water (20 mL) was added dropwise to a solution of $Cd(CH_3CO_2)_2(H_2O)_2$ (7.81 g, 29.3 mmol) in water (30 mL), and stirred until all precipitate had dissolved. A solution of NaCl (3.43 g, 58.7 mmol) in water (10 mL) was added, yielding a turbid solution that settled to a sticky white precipitate. This mixture was allowed to stand at room temperature for 50 h, while colorless crystals of the product grew: these crystals were separated manually from the remaining fine precipitate, washed with water, and vacuum-dried. Anal. Calcd for $Cd_8Cl_4S_{12}O_{12}C_{24}H_{60}$: C, 14.66; H, 3.08. Found: C, 14.27; H, 3.28. The microanalysis and density of these crystals indicated that they could have contained solvent water, $ClCd_8(SCH_2CH_2OH)_{12}Cl_3{\cdot}3H_2O$, but the anhydrous formulation was confirmed by the crystal structure determination.

**Table I.** Numerical Details for the Diffraction Analyses of **5** and **6**

| | **5** | **6** |
|---|---|---|
| formula | $Cd_8Cl_4S_{12}C_{24}H_{60}O_{12}$ | $Cd_8Br_4S_{12}C_{24}H_{60}O_{12}$ |
| formula mass | 1966.5 | 2144.3 |
| cryst descripn | colorless rhombohedra | |
| space group | *R*3 | |
| $a$/Å | 11.700 (1) | 11.681 (1) |
| $\alpha$/deg | 103.57 (1) | 102.38 (1) |
| $V$/Å$^3$ | 1440.5 (5) | 1462.9 (4) |
| temp/°C | 21 | |
| $d_{obsd}$/(g cm$^{-3}$) | 2.30 (1) | 2.44 (1) |
| $Z$ | 1 | |
| $d_{calcd}$/(g cm$^{-3}$) | 2.27 | 2.43 |
| radiation, $\lambda$/Å | Mo K$\alpha$, 0.7107 | |
| $\mu$/cm$^{-1}$ | 35.35 | 60.04 |
| cryst dimens/mm | 0.15 × 0.19 × 0.15 | 0.13 × 0.14 × 0.20 |
| scan mode | $\theta/2\theta$ | |
| $2\theta_{max}$/deg | 50 | |
| no. of intensity measmts | 1844 | 1874 |
| criterion for obsd rfln | $I/\sigma(I) > 3$ | |
| no. of indep obsd rflns | 1594 | 1587 |
| no. of rflns ($m$) and variables ($n$) in final refinement | 1594, 180 | 1587, 180 |
| $R = \sum^m\lvert\Delta F\rvert/\sum^m\lvert F_o\rvert$ | 0.028 | 0.029 |
| $R_w = [\sum^m w\lvert\Delta F\rvert^2/\sum^m w\lvert F_o\rvert^2]^{1/2}$ | 0.042 | 0.039 |
| $s = [\sum^m w\lvert\Delta F\rvert^2/(m-n)]^{1/2}$ | 1.75 | 1.54 |
| $R$ for other enantiomer | 0.033 | 0.033 |
| cryst decay | 1→0.95 | 1→0.93 |
| max, min transmission coeff | 0.61, 0.52 | 0.49, 0.29 |
| $R$ factor for multiply measd rflns | 0.023 | 0.011 |
| max indices in data collecn | $-21 < h, k < 21, l < 18$ | |

Crystallization of **5** without the fine precipitate has not been achieved. It is possible to dissolve the initial precipitate by cooling the preparative mixture or avoid its formation by addition of NaCl to the solution at ≤5 °C. However, subsequent warming to room temperature yields polycrystalline powders that are mixtures of variable composition.

**$BrCd_8(SCH_2CH_2OH)_{12}Br_3$ (6).** This was prepared by the same procedure, with substitution of an excess of NaBr (24.1 g, 235 mmol). The use of the ratio Br/Cd = 2 (as in the preparation of **5**) does not yield crystals of **6**. Anal. Calcd for $Cd_8Br_4S_{12}O_{12}C_{24}H_{60}$: C, 13.44; H, 2.82. Found: C, 13.39; H, 2.99. The powder diffraction patterns of **5** and **6** are very similar.[11]

Both **5** and **6** decompose when dissolved in water, yielding finely crystalline products that are the same as those obtained from preparations with a $Cd(CH_3CO_2)_2/HSCH_2CH_2OH/X^-$ ratio of 1/1/1: these products have not yet been characterized by crystal structure determination.

**$ICd_8(SCH_2CH_2OH)_{12}I_3{\cdot}H_2O$ (2).** Our procedure was similar to that of Burgi et al.[2] A solution of 2-hydroxyethanethiol (2.6 g, 33 mmol) in water (10 mL) was added slowly to a solution of $Cd(CH_3CO_2)_2(H_2O)_2$ (5.86 g, 22 mmol) in water (50 mL). Addition of a solution of sodium iodide (6.0 g, 40 mmol) in water (10 mL) yielded a fine white precipitate, which was filtered, washed with cold water, and vacuum-dried. This solid was dissolved in acetonitrile (30 mL) and reprecipitated by addition of water; yield ca. 4 g. Anal. Calcd for $Cd_8I_4S_{12}O_{13}C_{24}H_{62}$: C, 12.17; H, 2.64. Found: C, 12.18; H, 2.82. The identity of the compound was confirmed by its X-ray diffraction pattern.

**Crystal Structure Determination.** Well-formed colorless crystals were separated from the preparative mixtures and examined with a CAD4 diffractometer. Numerical details for the crystals, the collection of data, and the refinement of the structure are provided in Table I. Our crystallographic procedures have been described previously.[12] The structure of **5** was solved with MULTAN80 and Fourier methods and re-

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(3) M′ = Cu$^{II}$: (a) Birker, P. J. M. W. L.; Freeman, H. C. *J. Am. Chem. Soc.* **1977**, *99*, 6890. (b) Schugar, H. J.; Ou, C. C.; Thich, J. A.; Lalancette, R.; Furey, W., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 3407. (c) Schugar, H.; Ou, C. C.; Thich, J. A.; Potenza, J. A.; Felthouse, T. R.; Haddad, M. S.; Hendrickson, D. N.; Furey, W., Jr.; Lalancette, R. A. *Inorg. Chem.* **1980**, *19*, 543. (d) Birker, P. J. M. W. L. *Inorg. Chem.* **1979**, *18*, 3502.

(4) M′ = Ni$^{II}$: Birker, P. J. M. W. L.; Reedijk, J.; Verschoor, G. C. *Inorg. Chem.* **1981**, *20*, 2877.

(5) Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* **1977**, *99*, 6268.

(6) Birker, P. J. M. W. L.; Verschoor, G. C. *J. Chem. Soc., Chem. Commun.* **1981**, 322.

(7) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.

(8) Dance, I. G.; Bowmaker, G. A.; Clark, G. R.; Seadon, J. K. *Polyhedron* **1983**, *2*, 1031.

(9) Dance, I. G. *Aust. J. Chem.* **1985**, *38*, 1391.

(10) Burgi, H. B. *Inorg. Chem.* **1973**, *12*, 2321.

(11) See paragraph at the end of this paper regarding supplementary material.

(12) Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 2883.

**Table II.** Fractional Atomic Coordinates for **5** and **6**[a]

| | **5**, X = Cl | | | | **6**, X = Br | | | |
|---|---|---|---|---|---|---|---|---|
| | *x/a* | *y/b* | *z/c* | $B_{eq}$ | *x/a* | *y/b* | *z/c* | $B_{eq}$ |
| Cd(1) | −0.1895 | −0.1895 | −0.1895 | 3.57 | −0.1895 | −0.1895 | −0.1895 | 3.29 |
| Cd(2) | 0.1359 (1) | −0.1698 (1) | −0.2014 (1) | 3.91 | 0.1304 (1) | −0.1712 (1) | −0.2072 (1) | 3.86 |
| Cd(3) | 0.1748 (3) | 0.1748 | 0.1748 | 4.74 | 0.1874 (4) | 0.1874 | 0.1874 | 4.43 |
| Cd(4) | 0.1927 (1) | −0.1434 (1) | 0.1569 (1) | 4.65 | 0.1933 (1) | −0.1527 (1) | 0.1483 (1) | 4.20 |
| X(1) | −0.007 (1) | −0.007 (1) | −0.007 (1) | 3.51 | −0.0094 (5) | −0.0094 (5) | −0.0094 (5) | 3.02 |
| X(2) | 0.3175 (4) | −0.2498 (4) | 0.2743 (4) | 8.59 | 0.3333 (2) | −0.2681 (2) | 0.2614 (2) | 8.77 |
| S(1) | −0.0744 (3) | −0.3324 (3) | −0.2656 (3) | 3.64 | −0.0737 (3) | −0.3320 (3) | −0.2712 (3) | 3.44 |
| S(2) | 0.2990 (3) | −0.0830 (3) | 0.0051 (3) | 3.93 | 0.2928 (3) | −0.0913 (3) | −0.0107 (3) | 3.80 |
| S(3) | 0.2437 (3) | 0.0627 (3) | 0.3215 (3) | 4.60 | 0.2370 (3) | 0.0459 (3) | 0.3105 (3) | 3.99 |
| S(4) | −0.0130 (3) | −0.2971 (3) | 0.0603 (3) | 4.36 | −0.0097 (3) | −0.3020 (3) | 0.0587 (3) | 3.99 |
| C(11) | −0.108 (1) | −0.352 (1) | −0.430 (1) | 5.49 | −0.117 (2) | −0.3446 (15) | −0.4366 (12) | 5.88 |
| C(12) | −0.245 (1) | −0.426 (1) | −0.496 (1) | 5.37 | −0.243 (1) | −0.413 (1) | −0.492 (1) | 5.92 |
| O(1) | −0.269 (1) | −0.4619 (9) | −0.6289 (8) | 7.15 | −0.278 (1) | −0.429 (2) | −0.621 (1) | 13.4 |
| C(21) | 0.391 | −0.189 (1) | −0.016 (1) | 5.14 | 0.389 (1) | −0.194 (2) | −0.036 (1) | 6.35 |
| C(22) | 0.320 (1) | −0.314 (1) | −0.088 (1) | 5.43 | 0.319 (1) | −0.321 (1) | −0.096 (1) | 5.60 |
| O(2) | 0.2488 (9) | −0.3185 (9) | −0.2080 (8) | 7.29 | 0.245 (1) | −0.3320 (9) | −0.2103 (9) | 6.68 |
| C(31) | 0.416 (1) | 0.117 (2) | 0.351 (1) | 9.70 | 0.402 (1) | 0.087 (1) | 0.346 (1) | 6.32 |
| C(32) | 0.481 (2) | 0.173 (5) | 0.448 (2) | 24.2 | 0.476 (3) | 0.152 (4) | 0.455 (3) | 13.7 |
| O(3) | 0.612 (1) | 0.197 (2) | 0.483 (1) | 17.3 | 0.444 (3) | 0.257 (3) | 0.472 (4) | 26.2 |
| C(41) | −0.016 (2) | −0.412 (1) | 0.141 (2) | 7.25 | −0.010 (1) | −0.415 (1) | 0.149 (2) | 6.83 |
| C(42) | −0.059 (2) | −0.406 (3) | 0.233 (3) | 17.9 | −0.077 (4) | −0.427 (4) | 0.209 (4) | 26.0 |
| O(4) | −0.170 (1) | −0.367 (1) | 0.222 (1) | 12.1 | −0.182 (1) | −0.380 (1) | 0.206 (1) | 10.4 |

[a] $B_{eq}$ ($=8\pi^2U^2$, $U^2$ = mean square amplitude (Å$^2$)) is the isotropic equivalent of the anisotropic temperature factor.

fined finally with anisotropic temperature factors. Hydrogen atoms were not included. Some of the pendant arms of the uncoordinated ligands were poorly defined. The structure of **6** was refined by beginning with the atomic coordinates of **5**, on the incorrect assumption that the compounds were isostructural: the Cd(3) atom moved satisfactorily to its different position in **6**, but the ligand chains on S(3) had to be repositioned by Fourier methods. Weights $w = 1/\sigma^2(F_o)$ were assigned in the least squares, where $\sigma(I_o) = [\sigma_2(I_o + (0.04I_o)^2]^{1/2}$. No corrections for extinction were made in **5** or **6**.

The molecules possess crystallographic threefold symmetry. Atom labels for **6** are the same as those for **5**, shown in Figure 1. Atomic coordinates are listed in Table II. There is no ambiguity about the positions of the X(1) atoms along the threefold axes, even though in **6** Br(1) is not midway between Cd(1) and Cd(3). Mean values of the interatomic distances in the ligands for **5** and **6** respectively are as follows: S–C = 1.84, 1.84 Å; C(p1)–C(p2) = 1.35, 1.35 Å; C(p2)–O(p) = 1.45 (1), 1.40 (4) Å. Averaged rms thermal displacements for the ligand atoms are high and range 0.24–0.54 Å and are marginally larger for the terminal atoms of the dangling ligands. Final difference maps provided no evidence of solvent molecules, hydrogen atoms, or unusual features. Although hydrogen atoms could not be located, interaggregate O- - -O distances of 2.58–2.84 Å in **5** and 2.62–2.94 Å in **6** and O- - -Cl distances of 2.96 and 3.07 Å in **5** are indicative of hydrogen bonding.

**Cd NMR.** Solutions were prepared in dry distilled DMF with the following concentrations: **5**, 0.1 g mL$^{-1}$ (ultrasound required for dissolution); **6**, 0.1 g mL$^{-1}$; **2**, 0.4 g mL$^{-1}$. $^{113}$Cd spectra were recorded, at natural abundance, on a Bruker CXP300 spectrometer at 66.6 MHz, using 2000–8000 25-μs (ca. 90° tip angle) pulses. Spectra were calculated by using exponential multiplication of the FID by a line-broadening parameter of 20–40 Hz. Temperatures in the sample tube were controlled to ±1 °C and were calibrated by replacement with a sample tube containing a platinum thermometer. Chemical shifts are referenced to external 0.1 M aqueous $Cd(NO_3)_2$, which resonates at −5 ppm relative to aqueous $Cd(ClO_4)_2$ at infinite dilution. $Bu_4NCl$ and $Bu_4NI$ were used for the solutions containing additional halide ions. All spectra were measured at least twice on different preparations.

## Results and Discussion

**Preparations.** The compounds $[ClCd_8(SCH_2CH_2OH)_{12}Cl_3]$ (**5**) and $[BrCd_8(SCH_2CH_2OH)_{12}Br_3]$ (**6**) are obtained as well-developed colorless crystals in reactions of cadmium acetate or cadmium carbonate with $HSCH_2CH_2OH$ (1.8 molar equiv) and excess (2–8 molar equiv) of the sodium halide in water. This preparative procedure is analogous to that used for **2**[2] and is equivalent to the reaction of preformed $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ (**7**) with excess halide in water. We have reported elsewhere[13] that the reaction of **7** with 4 $Cl^-$ in DMF rather than water yields $[Cd_{10}(SCH_2CH_2OH)_{16}Cl_4]$ (**8**). However, the preparations of **5** and **6** are complicated by the coprecipitation of additional products, usually as powdery or plastic solids, from which the desired crystals must be separated mechanically. Variation of the reactant proportions in the aqueous chloride system leads to the formation of at least two other products, still to be characterized unequivocally. Attempts to prepare the fluoride homologue have not been successful, nor have reactions using mixtures of $Na_2S$ and NaCl in an attempt to prepare $[SCd_8(SCH_2CH_2OH)_{12}Cl_3]^-$.

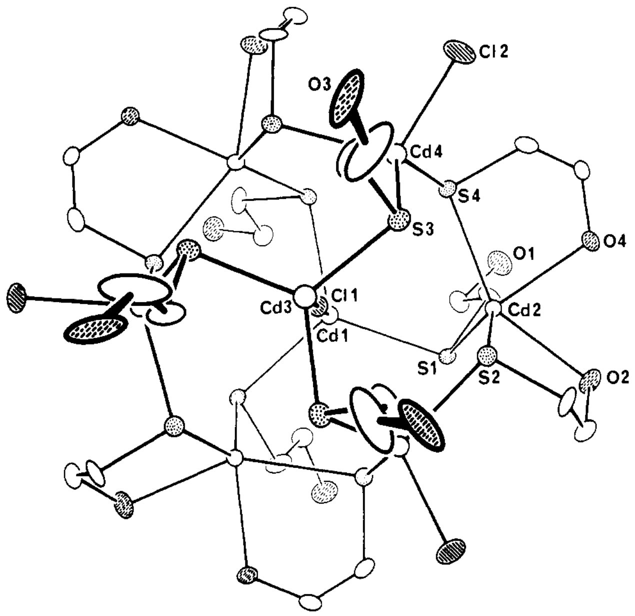

**Figure 1.** $ClCd_8(SCH_2CH_2OH)_{12}Cl_3$ (**5**) viewed 7° from the threefold axis. The outlines of the thermal ellipsoids represent the 10% probability surfaces.

**Structures of 5 and 6.** The two compounds are crystallographically isomorphous in a rhombohedral lattice, space group *R*3. In each case there is one molecule with threefold symmetry per unit cell, and hydrogen bonding between uncoordinated ligand hydroxy functions is the only intermolecular linkage. However, the molecules of **5** and **6** are not fully isostructural and differ in the coordination geometry at one Cd atom.

Figure 2 emphasizes the threefold symmetry component of the idealized *hexahedro*-$M_8$-*icosahedro*-$S_{12}$ cage skeleton in which

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

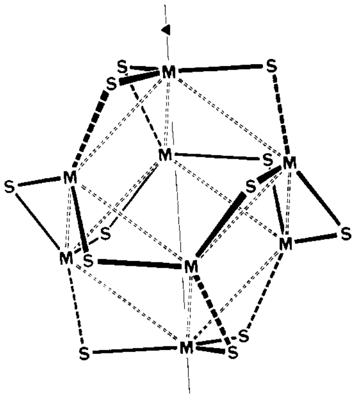


Figure 2. Diagrammatic representation of the connectivity of the *hexahedro*-$M_8$-*icosahedro*-$S_{12}$ cage skeleton, relative to a threefold axis. Two polar trigonal $\{M^{ax}(S^{ax})_3\}$ units are differentiated (by interrupted bonds) from the equatorial belt of alternating M and S atoms. The $M^{eq}$ atoms occur in two triangular sets, as do the $S^{eq}$ atoms.

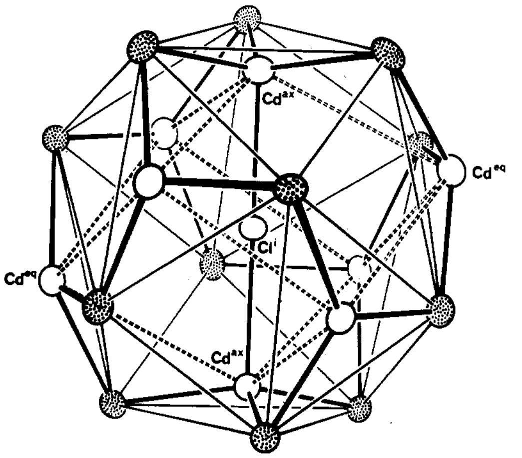
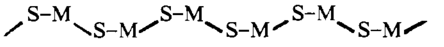


Figure 3. Side view of the $ClCd_8S_{12}$ cage skeleton of **5** (dotted ellipses are S atoms) almost normal to the vertical threefold axis, showing the inward displacements of the two $Cd^{ax}$ atoms creating digonal coordination of the central $Cl^i$ atom. The axially lengthened $S_{12}$ icosahedron and the axially compressed $Cd_8$ hexahedron are outlined.

each M atom has trigonal $S_3$ coordination. Two trigonal $MS_3$ coordination moieties are located in polar positions on the threefold axis (these atoms are denoted $M^{ax}$, $S^{ax}$), while the cycle



of $M^{eq}$, $S^{eq}$ atoms comprises the equatorial belt. The sequence of sets of metal atoms along the direction of the threefold axis is therefore $(M^{ax})(M^{eq})_3(M^{eq})_3(M^{ax})$, and the sulfur atom sets are $(S^{ax})_3(S^{eq})_3(S^{eq})_3(S^{ax})_3$. In addition to the bonds within the equatorial belt each $M^{eq}$ atom is connected to one $S^{ax}$ atom.

Displacements of Cd atoms from their $S_3$ planes are signed negative inside the icosahedron. In both **5** and **6** the six $Cd^{eq}$ atoms have positive displacements, but the two structures differ in the displacements of the $Cd^{ax}$ atoms. In **5** both of the $Cd^{ax}$ atoms (Cd(1), Cd(3)) have negative displacements and are coordinated equally to the central chloride ligand. Figure 3 shows diagrammatically the $ClCd_8S_{12}$ cage skeleton of **5**, with the two $Cd^{ax}$ atoms displaced inward to create the digonal coordination of the central $Cl^i$. However, in **6** only one $Cd^{ax}$ atom (Cd(1)) has a negative displacement similar to that in **5**, while the displacement of the opposite $Cd^{ax}$ (Cd(3)) is almost zero. Therefore, the $(Cd^{ax})_2$ coordination of the central Br(1) atom is dissymmetric. Figure 4 shows the coordination of Cd(3) in **6**, viewed normal to the threefold axis.

At both $Cd^{ax}$ atoms in **5** the ligands are nonchelating, with the hydroxy functions (O(1) and O(3)) dangling away along the trigonal axis as shown in Figure 1. In **6** the same axial dangling of unchelated $SCH_2CH_2OH$ ligands occurs around the inner $Cd^{ax}$ atom (Cd(1)), but at the unique in-plane $Cd^{ax}$ atom (Cd(3)) the OH functions of the ligands fold in toward the Cd atom, in a weakly chelating fashion. This effect, shown in Figure 4, is clearly concomitant with and in compensation of the elongated connection to the central Br ligand.

**Table III.** Bond Distances (Å) and Angles (deg) for $[XCd_8(SCH_2CH_2OH)_{12}X_3]^a$

| | **5**, X = Cl | **6**, X = Br |
|---|---|---|
| At $X^i$ | | |
| X(1)–Cd(1) | 2.694 (18) | 2.754 (8) |
| X(1)–Cd(3) | 2.685 (19) | 3.008 (9) |
| Cd(1)–X(1)–Cd(3) | 180 | 180 |
| At $Cd^i$ | | |
| Cd(1)–X(1) | 2.694 (18) | 2.754 (8) |
| Cd(1)–S(1) | 2.515 (3) | 2.520 (3) |
| X(1)–Cd(1)–S(1) | 101.7 (1) | 102.7 (1) |
| S(1)–Cd(1)–S(1) | 116.0 (1) | 115.3 (1) |
| $\Delta$Cd(1)–$[S(1)]_3$$^b$ | −0.511 | −0.553 |
| Cd(3)–X(1) | 2.685 (19) | 3.008 (9)$^c$ |
| Cd(3)–S(3) | 2.494 (3) | 2.492 (3)$^c$ |
| Cl(1)–Cd(3)–S(3) | 101.8 (1) | 93.7 (1)$^c$ |
| S(3)–Cd(3)–S(3)′ | 116.0 (1) | 119.6 (1)$^c$ |
| $\Delta$Cd(3)–$[S(3)]_3$$^b$ | −0.509 | −0.159$^c$ |
| Cd(3)- - -O(3) | 5.43 (1) | 3.78 (4)$^c$ |
| At $^4Cd^{eq}$ | | |
| Cd(4)–S(2) | 2.533 (3) | 2.541 (3) |
| Cd(4)–S(3) | 2.547 (3) | 2.534 (3) |
| Cd(4)–S(4) | 2.458 (4) | 2.477 (4) |
| Cd(4)–X(2) | 2.507 (3) | 2.648 (2) |
| $\Delta$Cd(4)–[S(2)S(3)S(4)]$^b$ | +0.608 | +0.626 |
| X(2)–Cd(4)–S(2) | 107.6 (1) | 106.0 (1) |
| X(2)–Cd(4)–S(3) | 100.9 (1) | 101.8 (1) |
| X(2)–Cd(4)–S(4) | 104.1 (1) | 105.5 (1) |
| S(2)–Cd(4)–S(3) | 102.6 (1) | 104.0 (1) |
| S(3)–Cd(4)–S(4) | 125.5 (1) | 124.5 (1) |
| S(2)–Cd(4)–S(4) | 114.4 (1) | 113.2 (1) |
| At $^5Cd^{eq}$ | | |
| Cd(2)–S(1) | 2.550 (3) | 2.546 (3) |
| Cd(2)–S(2) | 2.507 (3) | 2.489 (3) |
| Cd(2)–S(4)′ | 2.581 (3) | 2.581 (3) |
| Cd(2)–O(2) | 2.416 (7) | 2.530 (9) |
| Cd(2)–O(4)′ | 2.378 (8) | 2.357 (10) |
| S(1)–Cd(2)–S(2) | 128.9 (1) | 131.5 (1) |
| S(2)–Cd(2)–S(4)′ | 116.7 (1) | 115.9 (1) |
| S(4)′–Cd(2)–S(1) | 96.9 (1) | 98.2 (1) |
| S(1)–Cd(2)–O(2) | 94.2 (3) | 91.6 (3) |
| S(2)–Cd(2)–O(2) | 77.4 (2) | 76.3 (2) |
| S(4)′–Cd(2)–O(2) | 148.1 (2) | 149.5 (3) |
| S(1)–Cd(2)–O(4)′ | 112.9 (4) | 107.3 (5) |
| S(2)–Cd(2)–O(4)′ | 112.1 (4) | 113.6 (4) |
| S(4)′–Cd(2)–O(4)′ | 75.6 (2) | 75.7 (3) |
| O(2)–Cd(2)–O(4)′ | 72.5 (3) | 73.9 (4) |
| $\Delta$Cd(2)–[S(1)S(2)S(4)′]$^b$ | +0.608 | +0.546 |
| At Doubly Bridging Thiolate | | |
| Cd(1)–S(1)–Cd(2) | 97.1 (1) | 95.5 (1) |
| Cd(2)–S(2)–Cd(4) | 105.5 (1) | 105.7 (1) |
| Cd(3)–S(3)–Cd(4) | 95.7 (1) | 102.4 (1) |
| Cd(2)″–S(4)–Cd(4) | 107.8 (1) | 109.1 (1) |

[a] Symmetry operations: (′) *z*, *x*, *y*; (″) *y*, *z*, *x*. [b] The displacements of the Cd atom from the $S_3$ plane, negative inside the cage. [c] $Cd^p$ instead of $Cd^i$.

The terminal coordination of the positively displaced $Cd^{eq}$ atoms is shown in Figure 1 and is the same in both structures. In one set of three (Cd(4)), terminal halide ligands complete tetrahedral coordination at each Cd, while each of the other set of $Cd^{eq}$ atoms (Cd(2)) is five-coordinate due to coordination by two hydroxy functions of chelating equatorial $SCH_2CH_2OH$ ligands. This chelating coordination is shown clearly in Figure 1.

In presenting details of the coordination distances and angles in Table III and the cage dimensions in Table IV, and in analyzing

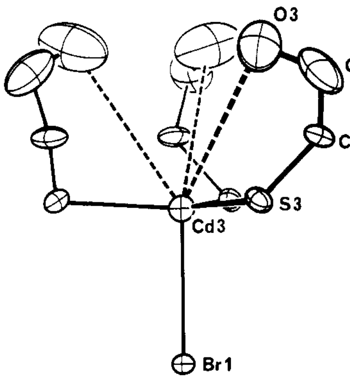


**Figure 4.** Coordination of Cd(3) in **6**, viewed normal to the threefold axis, showing the very small displacement of the Cd atom inside the $S_3$ triangle and the weak additional coordination by three O(3) atoms. Thermal ellipsoids are drawn at the 20% probability surface.

the metal coordination geometries and the aggregate structure, we use the following generic atom labels: $X^i$ for the internal halide ion; $X^o$ for the outer terminal halide ions; $^4Cd^{eq}$ and $^5Cd^{eq}$, respectively, for the four-coordinate and five-coordinate equatorial cadmium atoms; $Cd^i$ for the negatively displaced inner Cd atoms; $Cd^p$ for the in-plane Cd(3) atom of **6**. Assessment of the bonding significance of the various Cd–X distances (including those of **2**) is made with reference to the following values for different halide coordination numbers (denoted by superscripts preceding the atom): $^4Cd-^1Cl = 2.39$ Å;[14] $^4Cd-^2Cl = 2.53$ Å;[14] $^4Cd-^6Cl = 2.65$ Å;[15] $^4Cd-^1Br = 2.53$ Å;[16] $^4Cd-^2Br = 2.67$ Å;[16] $^4Cd-^6Br = 2.80$ Å;[15] $^4Cd-^1I = 2.70$ Å;[17] $^4Cd-^2I = 2.86$ Å;[17] $^4Cd-^6I = 3.04$ Å.[15]

At $^4Cd^{eq}$ the coordination is tetrahedral $CdS_3X^o$: the Cd–$X^o$ distances are slightly longer than the reference $^4Cd-^1X$ values. At $^5Cd^{eq}$ the five-coordination involving the alcohol functions of two chelating ligands has irregular stereochemistry. Both of the uncharged oxygen donor atoms are coordinated quite strongly at distances of 2.38, 2.42 Å (**5**) and 2.36, 2.53 Å (**6**), which are comparable with Cd–O distances for $CdS_4(OH)$ five-coordination in $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ [18,19] and $[Cd_{10}(SCH_2CH_2OH)_{16}Cl_4]$,[13] while the Cd(2)–S(2) bond is slightly shorter than usual. The stereochemical irregularity occurs in the angular distribution of ligands, which does not approach either of the conventional stereochemistries for five-coordination. The atoms Cd(2), S(4), O(2), and O(4) are virtually coplanar, as are the atoms Cd(2), S(1), S(2), and O(4). Three interbond angles are within 3° of 75°, namely the two intrachelate angles (this is characteristic of $CdSCH_2CH_2OH$ chelates) and O(2)–Cd–O(4).

The $X^iCd^iS_3$ coordination in both structures is essentially tetrahedral. The $X^i$–$Cd^i$–S angles (mean 102°) are slightly diminished and the $X^i$–$Cd^i$ distances are slightly elongated (by 0.15 Å in **5** and 0.08 Å in **6**) relative to above reference values. Therefore, a small additional negative displacement of $Cd^i$ could create virtually ideal tetrahedral coordination.

At Cd(3) in **6** the coordination stereochemistry is unusual (see Figure 4). The primary coordination is trigonal $CdS_3$, with short Cd–S distances (2.49 Å) and the Cd atom displaced only −0.16 Å from the trigonal plane. The next shortest bond is to the central $Br^i$ atom at 3.01 Å, 0.34 Å longer than normal for two-coordinate Br. In addition there is distant (3.78 Å) threefold coordination by the hydroxy groups of the axial ligands. The validity of $(OH)_3$ coordination at this long distance is established by comparison with the Cd(3) coordination in **5**: it is evident that as Cd(3) moves into the $S_3$ plane and away from $X^i$ the hydroxy groups provide some weak compensatory coordination on the other side of the $S_3$ plane.

**Table IV.** Cage Dimensions[a]

| | 5 | 6 |
|---|---|---|
| $X^i$- - -$Cd^{eq}$ | | |
| X(1)- - -Cd(2) | 3.583 (5) | 3.557 (2) |
| X(1)- - -Cd(4) | 3.573 (6) | 3.600 (2) |
| $X^i$- - -$S^{ax}$ | | |
| X(1)- - -S(1) | 4.042 (14) | 4.121 (7) |
| X(1)- - -S(3) | 4.021 (14) | 4.027 (7) |
| $X^i$- - -$S^{eq}$ | | |
| X(1)- - -S(2) | 3.866 (9) | 3.853 (4) |
| X(1)- - -S(4) | 3.649 (7) | 3.671 (4) |
| Cd- - -Cd, Cube Edges | | |
| Cd(1)- - -Cd(2) | 3.797 (1) | 3.750 (1) |
| Cd(3)- - -Cd(4) | 3.738 (2) | 3.918 (3) |
| Cd(2)- - -Cd(4) | 4.012 (1) | 4.010 (1) |
| Cd(2)- - -Cd(4)′ | 4.073 (1) | 4.121 (1) |
| Cd- - -Cd, Cube Diagonals | | |
| Cd(1)- - -Cd(3) | 5.38 | 5.76 |
| Cd(2)- - -Cd(4) | 7.16 | 7.16 |
| S- - -S around Cd(1) | | |
| S(1)- - -S(1)′ | 4.264 (5) | 4.259 (5) |
| S- - -S around Cd(3) | | |
| S(3)- - -S(3)′ | 4.230 (6) | 4.308 (6) |
| S- - -S around Cd(2) | | |
| S(1)- - -S(4)′ | 3.839 (4) | 3.876 (5) |
| S(4)′- - -S(2) | 4.333 (4) | 4.299 (5) |
| S(2)- - -S(1) | 4.563 (4) | 4.591 (4) |
| S- - -S around Cd(4) | | |
| S(2)- - -S(3) | 3.964 (4) | 3.998 (5) |
| S(2)- - -S(4) | 4.194 (4) | 4.190 (5) |
| S(3)- - -S(4) | 4.450 (5) | 4.436 (4) |
| Other S- - -S | | |
| S(1)- - -S(4) | 3.615 (4) | 3.689 (4) |
| S(2)- - -S(3)′ | 3.657 (4) | 3.702 (4) |

[a] Symmetry operation: (′) *z*, *x*, *y*.

In **5** the coordination of the central $Cl^i$ atom is distinctly digonal, with two diametrically opposed collinear $Cl^i$–$Cd^i$ bonds of length 2.69 Å, and the other six $Cd^{eq}$ atoms further distant at 3.58 Å, 0.9 Å longer than the normal coordinate bond length. In **6** the digonal $Br^i$–Cd distances are larger and disparate, 2.75 and 3.01 Å, but still distinctly shorter than the $Br^i$- - -$Cd^{eq}$ distances of 3.56 and 3.60 Å. This *linear* digonal coordination of a halide bridge between two metal atoms might not be regarded as abnormal in terms of bonding capabilities, but it is unusual as only a few other instances have been reported.[20] The coordination of the central halide is different in **2**, which has no crystallographically imposed molecular symmetry: two of the $I^i$–Cd distances that are separated

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(17) In $Cd_2I_6^{2-}$: Orioli, P. L.; Ciampolini, M. *J. Chem. Soc., Chem. Commun.* **1972**, 1280.

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(20) Values quoted for the following compounds are M–X–M angles (deg) and M–X distances (Å). (a) 167.4, 2.60, and 2.56 for $^{2}_{\infty}\{(\mu\text{-}Cl)_{4/2}MnCl_2\}$ in $[H_3NCH_2CH_2CH_2NH_3]^{2+}[MnCl_4]^{2-}$: Tichy, K.; Benes, J.; Kind, R.; Arend, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1355. (b) 160.8, 2.66, and 2.68 for $^{2}_{\infty}\{(\mu\text{-}Cl)_{4/2}CdCl_2\}$ in $[H_3NCH_2CH_2CH_2NH_3]^{2+}[CdCl_4]^{2-}$: Willett, R. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1641. (c) 169.5, 2.73, and 2.83 in $^{1}_{\infty}[(\mu\text{-}Cl)_{2/2}CdClH_2NCH_2CH_2NHCH_2CH_2NH_2]$: Cannas, M.; Margongiu, G.; Saba, G. *J. Chem. Soc., Dalton Trans.* **1980**, 2090. (d) 180, 2.425, and 2.941 in $^{1}_{\infty}\{(\mu\text{-}Cl)_{2/2}Ni(bzim)_4]$: Drew, M. G. B.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1968**, *7*, 2618. (e) 179.4, 2.72, and 2.97 in $[Cl_4(\mu\text{-}Cl)CuCl_4(\mu\text{-}Cl)CuCl_4]^{8-}$: Antolini, L.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1980**, *102*, 5506. (f) 180, 2.89, and 2.89 in $[ICo(CNPh)_4ICo(CNPh)_4I]^+$: Baumann, D.; Endres, H.; Keller, H. J.; Nuber, B.; Weiss, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 40. (g) 180, 2.69, and 2.69 in $[Cl_2Ag(\mu\text{-}Cl)AgCl_2]^{3-}$: Bowles, J. C.; Hall, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 2149.

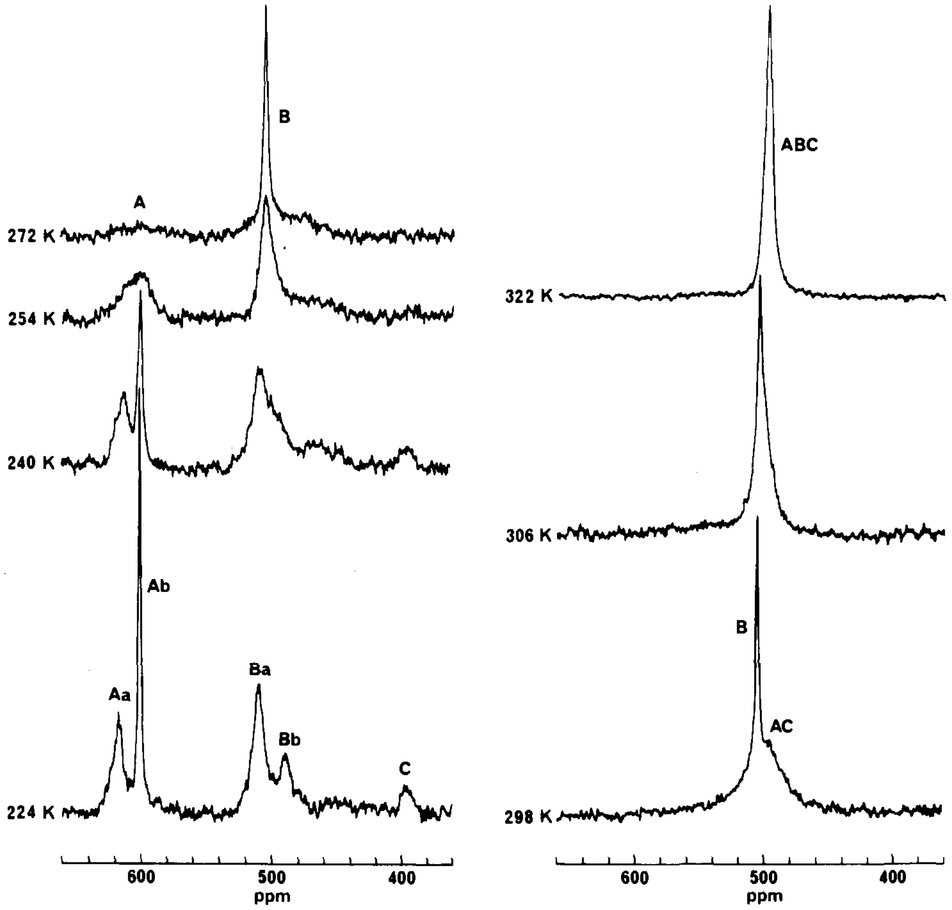

**Figure 5.** $^{113}$Cd NMR spectra of [$ClCd_8(SCH_2CH_2OH)_{12}Cl_3$] (**5**) in DMF at the temperatures marked. The letters identify resonances separate and coalesced.

by ca. 90° rather than 180° are shorter (3.08, 3.17 Å) than the remainder, which range 3.50–3.86 Å.

Dimensions of the $XCd_8S_{12}$ cages, presented in Table IV, elicit the following comments: (i) The size of the central halide has little influence on the size of the $Cd_8$ or the $S_{12}$ polyhedra. (ii) The $X^i$- - -$S^{ax}$ distances are distinctly longer than the $X^i$- - -$S^{eq}$ distances, and the $S_{12}$ icosahedron is prolate. (iii) In contrast the $Cd_8$ hexahedron is oblate, with the axial diagonal $Cd^{ax}$- - -$Cd^{ax}$ shorter than the $Cd^{eq}$- - -$Cd^{eq}$ diagonal by 1.78 Å in **5** and by 1.40 Å in **6**. (iv) The triangular faces of the $S_{12}$ icosahedron are distinctly scalene around the $Cd^{eq}$ atoms, and the S- - -S edges which are not part of Cd coordination are shorter than those that are.

Some appreciation of the possibilities and the constraints for structures in which metal atoms are displaced inside or outside the faces of a $S_{12}$ icosahedron comes from analysis of idealized structures. If the edge length of a regular icosahedron is $e$, the distance from the body center to a face center is $0.75576e$, and the displacement of a tetrahedrally coordinated metal atom from the face is $\pm 0.20412e$. Assuming $e = 4.20$ Å at the upper end of the pertinent range,[21] the idealized $X^i$–M distances are calculated to be $X^i$–$M^i$ = 2.32 Å, $X^i$–$M^p$ = 3.17 Å, and $X^i$- - -$M^o$ = 4.03 Å. This calculated $X^i$–$M^i$ distance is too short to accommodate $M^i$ = Cd and $X^i$ = Cl (or S, or larger atoms) without distortion: it is however an appropriate distance for tetrahedral $Cl^i$–$Zn^i$ coordination, as has already been observed in **4**. In order to incorporate $Cl^i$ and $Cd^i$, this cage skeleton must be distorted in a manner that increases the distance of the pertinent $S_3$ faces from the cage center without increasing S- - -S distances. A tetrahedral expansion of four $S_3$ faces cannot satisfy these requirements,[22] but increased diametrical separation of two faces is possible and is in fact what is observed in **5**.

The idealized $X^i$–$Cd^p$ distance of 3.17 Å is appropriate for $X^i$ = I, and this geometry is similar to that observed at the two trigonal-bipyramidal sites of **2** where the Cd atom is close to the $S_3$ plane. In **6** an intermediate mode of accommodation of $Br^i$–Cd bonds into the $S_{12}$ polyhedron is found: the $S_{12}$ icosahedron is prolengthened, as in **5**, with one $Cd^i$ and one $Cd^p$ atom.

We have previously expounded the theme of geometrical congruence between molecular and nonmolecular structures, particularly between metal thiolate cluster molecules and metal chalcogenides in the crystalline phase.[7,23] Another instance of this congruence occurs between the molecular structures of **5** and **6** and the crystal structures of a group of ternary and quaternary metal chalcogenides. The compound $Cd_{13}P_4S_{22}I_2$ (**9**),[24] a good example of the nonmolecular group, contains an anion ($S^{2-}$, $I^-$) lattice composed of interpenetrating centered icosahedra. Cadmium atoms are distributed statistically among sites of two types: one with tetrahedral coordination corresponds to the positions inside and outside the faces of the icosahedra (i.e. corresponds to all of the Cd atoms in **5** and all except one in **6**); the other site in **9** is within the trigonal planar faces of the icosahedron and corresponds to the $Cd^p$ atom of **6**. The details of the triangular-pyramidal coordination of this latter site in **9** (Cd–S(I) distances 2.40–2.46 Å in the triangular plane and Cd- - -S 3.14 Å to the central $S^{2-}$ atom) are close to those for Cd(3) in **6**. Other metal chalcogenides with centered icosahedral sublattices are listed in ref 24 and 25.

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[21] The mean S- - -S distances in **5**, **6**, and **2** are 4.13, 4.16, and 4.20 Å, respectively, and in **4** the S- - -S distances range 3.71–4.24 Å with a mean value of 3.92 Å.[9]

[22] We note that a *centro*-($\mu_4$-X)-*tetrahedro*-($Cd^i$)$_4$-*icosahedro*-($\mu$-SR)$_{12}$-*tetrahedro*-($Cd^o$)$_4$ cage skeleton is geometrically possible for X = $F^-$ or $O^{2-}$.

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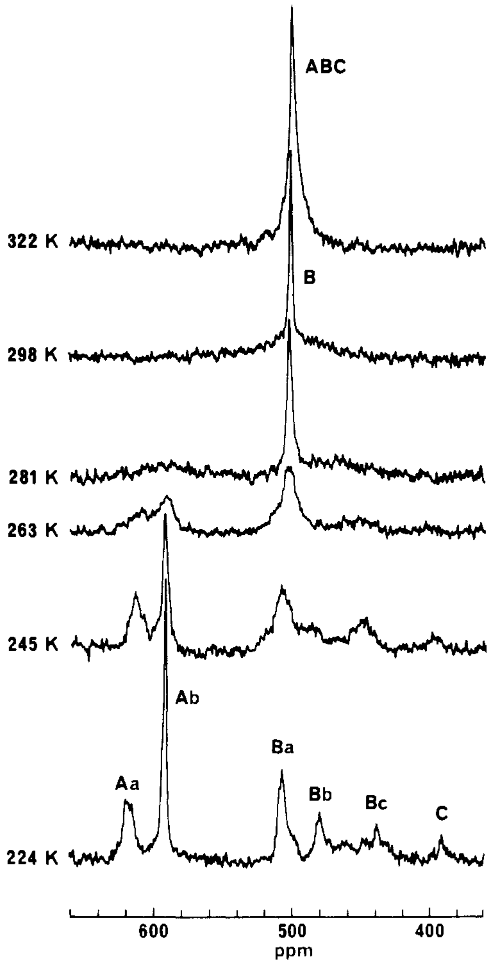

**Figure 6.** $^{113}Cd$ NMR spectra of $[BrCd_8(SCH_2CH_2OH)_{12}Br_3]$ (**6**) in DMF at the temperatures marked.

**NMR Spectra of $[XCd_8(SCH_2CH_2OH)_{12}X_3]$.** The $^{113}Cd$ NMR spectra of the three compounds dissolved in DMF in the temperature range 207–322 K are presented in Figures 5–7. Chemical shift and intensity data are tabulated in Table V. The spectra of all three compounds approach a slow-exchange regime at the lowest temperatures,[26] with 6–10 resonance lines spread from 625 to 390 ppm. In the intermediate-temperature ranges these spectra are exchange-broadened, and at the top of the temperature range they approach a fast-exchange regime with two resonances each. The thermal changes are reversible, and there is no evidence that the $XCd_8S_{12}$ cage skeletons are disrupted or lose their central halide ligation. Therefore, we presume that the exchange is due to stereochemical flexibility in the cages and variable terminal ligation. We reason from the range and variability of Cd coordination sites observed in crystalline **5**, **6**, and **2** and from the structure of **4**. Fifteen ligands ($X_3$ + $(OH)_{12}$) are available for terminal coordination of Cd atoms, and possible Cd coordination environments are as follows: α, tetrahedral $X^iCd^iS_3$, externally void, as in **5** and **6**; β, tetrahedral $S_3Cd^{eq}X^o$; γ, trigonal-bipyramidal $X^i$–$CdS_3$–$X^o$; δ, trigonal-bipyramidal $X^i$–$CdS_3$–(OH); ε, five-coordinate $S_3Cd^{eq}(OH)_2$; η, octahedral $S_3Cd^{eq}(OH)_3$; θ, trigonal-pyramidal four-coordination plus weak three-coordination, $X^i$–$Cd^pS_3$–$(OH)_3$, as at Cd(3) in **6**. The 15 external ligands allow the following combinations of these coordination environments in molecular cages: $[(\alpha)_2]^{ax}[(\beta)_3(\epsilon)_3]^{eq}$ + dangling $(OH)_6$, trigonal symmetry, as in $\mathbf{5}_{cryst}$; $[(\alpha)(\theta)]^{ax}[(\beta)_3(\epsilon)_3]^{eq}$ + dangling $(OH)_6$, trigonal symmetry, as in $\mathbf{6}_{cryst}$; $[(\alpha)(\eta)]^{ax}[(\eta)_3(\beta)_3]^{eq}$, trigonal symmetry; $[(\gamma)_3]^{ax}[(\epsilon)_6]^{eq}$, trigonal symmetry; $(\alpha)_4(\eta)_4$ + uncoordinated $(X^-)_3$, tetrahedral symmetry; $(\alpha)_4(\beta)_3(\eta)$ + dangling $(OH)_9$, pseudotetrahedral symmetry.

**Slow-Exchange Spectra, Ca. 220 K.** We discuss first the assignments of the lines in the slow-exchange spectra. Three chemical shift regions are distinguished, as in the interpretations of the spectra of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ (**7**) and $[Cd_{10}(SCH_2CH_2OH)_{16}Cl_4]$ (**8**):[13,19,27] region A, above 560 ppm; region B, principally 510–480 ppm, but with additional lines down to 430 ppm in X = I; region C, ca. 395 ppm. The fact that the low-temperature spectral patterns of **5** and **6** are very similar, with fewer lines than the spectrum of **2**, correlates with the higher threefold symmetry of **5** and **6** and the asymmetry of **2** in the crystalline phase.

The resonances in region A are due to Cd with $S_3CdX$ coordination. The principal line, labeled Ab, at 599 (**5**), 591 (**6**), and 572 (**2**) ppm is halide-dependent in the normal fashion,[28] and there is exact correspondence with the 600 ppm resonance of **8**, which is assigned as a tetrahedral $S_3Cd^{eq}Cl$ site (β).[13] Therefore, the lines Ab of **5** and **6** are assigned unequivocally as type β sites, as observed in the crystals. In **2** an additional but minor resonance occurs at 580 ppm: both of the Ab resonances are assigned to Cd with terminal I coordination, in sites that are better described as pseudo trigonal bipyramidal, type γ, such as are observed in the crystal phase. Strong additional support for this assignment comes from the spectra of mixtures of **2** with $I^-$: on addition of 5 $I^-$, sufficient to provide terminal $I^-$ coordination at all eight Cd atoms, the spectrum (at 240 K) reduces to a single line at 574 ppm.

Each of the three compounds shows an additional (split) resonance Aa at higher frequency (Table V). We propose that this region corresponds to type α sites, with $X^iCdS_3$ coordination and no terminal ligands. The two distinctive properties of this resonance, namely its chemical shift higher than that of Ab and the negligible influence of the halide on chemical shift, can be rationalized in terms of the lesser contribution of $X^i$ relative to that of $X^o$ to the tetrahedral coordination: it is expected that $X^i$–$Cd^i$ bonds, being longer than $Cd^{eq}$–$X^o$ bonds, induce stronger $CdS_3$ coordination and hence higher chemical shift. Our assignment of resonance Aa at >600 ppm as not due to a $S_3Cd^{eq}X^o$ (β) site is supported by the complete absence of resonances >600 ppm in spectra of mixtures of **2** + $Cl^-$ (see below).[29]

Spectral region B extends from 510 down to 430 ppm and in addition to the principal resonance at the high end of the range contains more minor resonances (some poorly defined) as the halogen size increases. The B resonances for each compound coalesce at higher temperature. It is now established that $CdS_4(OH)$ and $CdS_4(OH)_2$ sites with four thiolate ligands resonate in this region,[13,19,27] and we propose that for the present compounds the $CdS_3$ sites with one or two OH ligands terminally coordinated also resonate here. The major resonance Ba at 509 (**5**) and 508 (**6**) ppm is assigned to the five-coordinate $CdS_3(OH)_2$ (ε) site, which occurs without halide influence in both crystalline compounds. The minor resonance Bb is probably a variant on this coordination, present only in solution. In $\mathbf{6}_{soln}$ there are also very weak lines around 440 ppm, while in $\mathbf{2}_{soln}$ well-defined but weak lines occur at 472, 452, and 431 ppm. The $S_3Cd^{eq}(OH)_3$ (η) site in $\mathbf{2}_{cryst}$ has two short Cd–OH bonds (2.45 Å) and one long Cd–OH bond (2.72 Å): a site with geometry of this type would be expected to resonate in the 430–470 ppm range. We note that in the $\mathbf{2}_{soln}$ spectrum there are more lines than Cd atoms in the molecule, and it is probable that the aggregate exists in solution with more than one low-symmetry structure. One of the lines in region B of the spectrum of $\mathbf{2}_{soln}$ is likely to be due to the trigonal-bipyramidal $I^iCdS_3(OH)$ (δ) site that occurs in the crystal, and we intend to obtain solid-state Cd NMR spectra of **5**, **6**, and

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[26] However, the residual stereochemical nonrigidity even at the lowest temperatures is too great to allow line narrowing sufficient for resolution of any satellite lines due to Cd–Cd scalar coupling.

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[28] Chemical shifts for X = Br, I in $(\mu\text{-SPh})_3CdX$ sites are reduced by 16 and 44 ppm, respectively, relative to that for X = Cl: Dance, I. G.; Garbutt, R.; Craig, D.; Scudder, M. L., submitted for publication in *Inorg. Chem.* Dean, P. A. W.; Vittal, J. J. *Inorg. Chem.* **1985**, *23*, 3722.

[29] A terminally void $I^iCd^iS_3$ site does not occur in *crystalline* **2**, where interaggregate I bridges provide additional terminal ligands.

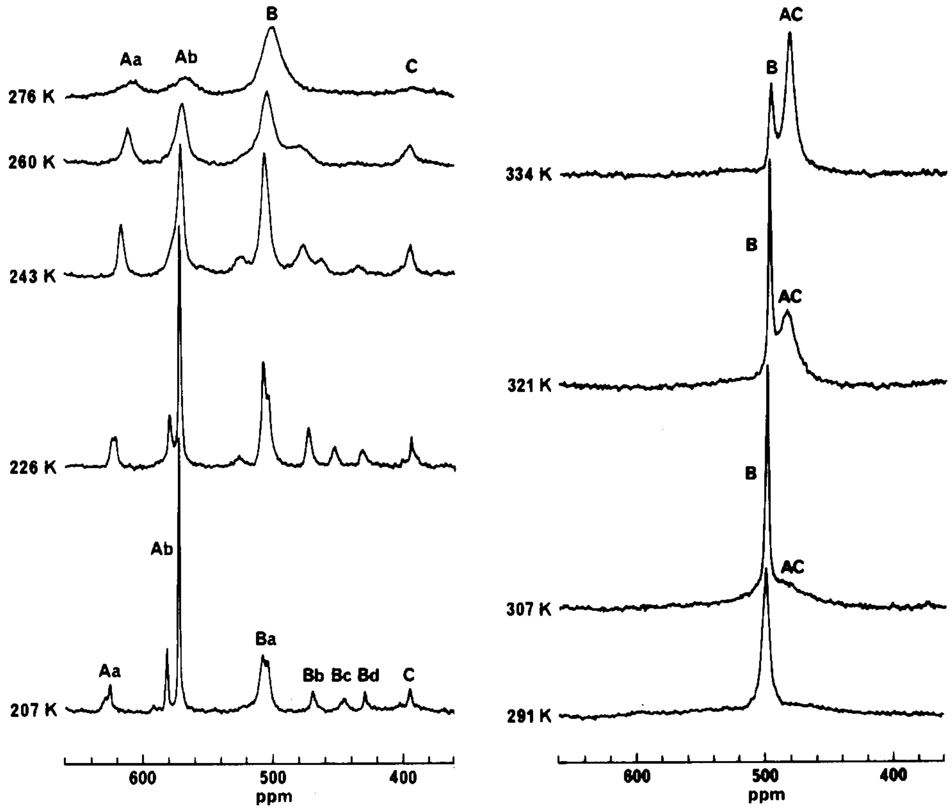

**Figure 7.** $^{113}$Cd NMR spectra of $[ICd_8(SCH_2CH_2OH)_{12}I_3]$ (**2**) in DMF at the temperatures marked.

**Table V.** Tabulation of Cd NMR Data for $[XCd_8(SCH_2CH_2OH)_{12}X_3]$ in DMF Solution

| | chem shifts[a-c] for **5**, X = Cl | | | | |
|---|---|---|---|---|---|
| temp, K | [Aa][b] | [Ab] | [Ba] | [Bb] | [C] |
| 224 | 614 (1.7)[c] | 600 (2.3) | 510 (2.5) | 488 (1.0) | 394 (0.5) |
| 240 | 613 (1.6) | 600 (1.8) | 507 (4.2) | | 393 (0.5) |
| 254 | 601 (3.3) | | 504 (4.7) | | |
| 272 | | | 504 | | |
| 298 | | | 504 [B], 496 [AC] | | |
| 306 | | | 503 [B] | | |
| 322 | | | 498 [ABC] | | |

| | chem shifts for **6**, X = Br | | | | | |
|---|---|---|---|---|---|---|
| temp, K | [Aa] | [Ab] | [Ba] | [Bb] | [Bc] | [C] |
| 224 | 620, 615 (1.6) | 592 (2.7) | 507 (2.0) | 480 (1.0) | 439 (0.5) | 391 (0.3) |
| 245 | 613 | 592 | 507 | | 449 | 397 |
| 263 | 608 | 590 | 502 | | | |
| 281 | | | 501 [B] | | | |
| 298 | | | 501 [B] | | | |
| 322 | | | 500 [ABC] | | | |

| | chem shifts for **2**, X = I | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| temp, K | [Aa] | [Ab] | | [Ba] | [Bb] | [Bc] | [Bd] | [C] |
| 207 | 629.3, 625.4 (0.7) | 581.5 (0.7), 572.3 (2.6) | | 507.5, 503.6 (2.4) | 469.3 (0.4) | 445.4 (0.3) | 429.1 (0.3) | 394 (0.5) |
| 226 | 623, 621 (0.7) | 580 (0.7), 572 (2.3) | | 507, 503 (2.5) | 473 (0.6) | 453 (0.4) | 432 (0.3) | 394 (0.5) |
| 243 | 617 (0.7) | 570 (2.4) | 525? (0.4) | 506 (2.7) | 477 (0.8) | 463 (0.3) | 435 (0.2) | 395 (0.6) |
| 260 | 612 (1.0) | 570 (2.0) | | 505 (3.4) | | 480 (0.9) | | 396 (0.7) |
| 276 | 606 | 566 | | 501 [B] | | | | 395 |
| 291 | | | | 499 [B] | | | | |
| 307 | | | | 499 [B] | | | | |
| 321 | | | | 498 [B], 484 [AC] | | | | |
| 334 | | | | 497 [B], 482 [AC] | | | | |

[a] In ppm, referenced to 0.1 M aqueous $Cd(NO_3)_2$. [b] Line labels are in brackets. [c] Relative intensities normalized to a sum of 8 are given in parentheses.

**2** to confirm assignments in region B.

The one resonance in region C is due to a halide-independent six-coordinate $S_3Cd^{eq}(OH)_3$ site ($\eta$).[13,19,27] It occurs very weakly in the low-temperature spectra only of $\mathbf{5}_{soln}$ and $\mathbf{6}_{soln}$ but with more intensity and persistence at higher temperatures in $\mathbf{2}_{soln}$.

**Intermediate- and Fast-Exchange Spectra.** As the temperature increases above 230 K, all resonances in the spectra of the three compounds broaden, a consequence of the blurring of Cd coordination environments due to processes such as terminal ligand exchange and stereochemical nonrigidity of the cage skeleton. The general characteristics of the temperature dependence are the same for all three compounds: (i) broadening and coalescence of the B resonances, followed by narrowing (>280 K) to the only single sharp resonance in the spectrum at 300 K; (ii) broadening and intensity loss at the A resonances; (iii) broadening and intensity loss at the C resonance; (iv) above 300 K reappearance of the A and C intensity as a single narrowing line, AC, at intermediate chemical shift. The chemical shift of the fast-exchanging B resonance is almost halide-independent. The spectra of **2** in the temperature range 243-276 K show also that there is not interchange of the sites responsible for the Aa and Ab lines but rather separate exchange of each of them with the type ($\eta$) site, line C.

Therefore, it appears that the Cd site interconversion processes occurring in **5**, **6**, and **2** in solution are as follows: (1) The $S_3Cd^{eq}(OH)$ ($\delta$) and $S_3Cd^{eq}(OH)_2$ ($\epsilon$) sites average their stereochemistries without interchange with sites of other types. (2) $X^iCd^iS_3$ ($\alpha$) sites interchange with $S_3Cd^{eq}(OH)_3$ ($\eta$) sites. The geometry of Cd(3) in $\mathbf{6}_{cryst}$ demonstrates clearly the geometry intermediate in this interconversion. (3) The $S_3Cd^{eq}X^o$ ($\beta$) sites interchange with $S_3Cd^{eq}(OH)_3$ ($\eta$) sites. (4) The $S_3Cd^{eq}X^o$ ($\beta$) and $X^iCd^iS_3$ ($\alpha$) sites do not interchange in the temperature range studied; that is, the $\alpha \leftrightarrow \beta$ interchange is not faster than the separate $\alpha \leftrightarrow \eta$ and $\beta \leftrightarrow \eta$ exchanges.

We have examined the spectra of mixtures of **2** with $Cl^-$ in DMF in the slow-exchange temperature regime. At a molar ratio $Cl^-/\mathbf{2}$ of 3 the Aa resonance is very weak, all B and C lines have disappeared, and the major resonance is a series of at least five sharp lines in the Ab region, 573-599 ppm. At a ratio of 5 there are six sharp lines in this region only. These lines are due to Cd atoms with terminal halide coordination, types $\beta$ and $\gamma$. It is not possible to assign individual resonances unequivocally, but it is clear that they arise from different combinations of Cl and I as $X^i$ and $X^o$ in the sites $S_3CdX^o$ ($\beta$) and $X^iCdS_3X^o$ ($\gamma$). Evidently halide ions displace terminal OH ligands, exchange (slowly) into the central position, and reduce the rate of exchange of Cd sites. At $Cl^-/\mathbf{2}$ ratios $\geq 8$ additional resonances appear at higher chemical shift, indicative of cage fragmentation and the formation of species such as $[Cd(SCH_2CH_2OH)_3Cl]^{2-}$.

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**Registry No.** **2**, 61251-21-6; **5**, 110142-48-8; **6**, 110142-49-9; $^{113}Cd$, 14336-66-4.

**Supplementary Material Available:** Tabulations of *d* spacings in the powder diffraction patterns and of all atomic parameters (5 pages); tabulations of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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# Synthetic, Structural, and Physical Studies of Tris(2,4-pentanedionato)vanadium(IV) Hexachloroantimonate(V) and Tris(1-phenyl-1,3-butanedionato)vanadium(IV) Hexachloroantimonate(V)

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The complexes $[V(acac)_3][SbCl_6]$ (**1**) and $[V(bzac)_3][SbCl_6]\cdot CH_2Cl_2$ (**2**) have been prepared by reaction of $[V(acac)_2Cl_2]$ and $[V(bzac)_2Cl_2]$, respectively, with $SbCl_5$ in acetic acid solution. Their crystal structures are described. Crystals of **1** are orthorhombic, space group *Pcab*, with $a = 14.167$ (9) Å, $b = 18.774$ (3) Å, $c = 19.670$ (6) Å, $Z = 8$, and $R_w = 3.3\%$. Crystals of **2** are triclinic, space group $P\bar{1}$, with $a = 12.070$ (6) Å, $b = 14.110$ (4) Å, $c = 15.792$ (2) Å, $\alpha = 66.46$ (2)°, $\beta = 69.08$ (2)°, $\gamma = 65.90$ (2)°, $Z = 2$, and $R_w = 5.6\%$. The geometry about vanadium in each structure approximates octahedral with trigonal twist angles of 51.9 and 52.3°, respectively. The chelate rings are not planar, with two chelate rings in each complex possessing boat conformations. Corresponding hexafluorophosphates were also prepared. The results of optical and infrared spectroscopy, magnetic susceptibility, conductance, and electrochemical studies are reported.

## Introduction

The chemistry of vanadium(IV) is dominated by the vanadyl ion, $VO^{2+}$.[2] Many complexes have been structurally and spectroscopically characterized with square-pyramidal or trigonal-bipyramidal five-coordination or distorted-octahedral six-coordination.[2] In contrast, only a few non-vanadyl vanadium(IV) species are well-characterized. These include complexes with dithiolenate,[3] 2,4-pentanedione benzoylhydrazonate,[4] catecholate,[5] bis(salicylaldehyde)ethylenediiminate,[6,7] and cagelike hexaamine ligands.[8]

Von Dreele and Fay have reported the preparation of $[V(acac)_3][SbCl_6]$ by reaction of $[V(acac)_2Cl_2]$ with $SbCl_5$ in dichloromethane.[9,10] However, the reported synthesis could not be repeated successfully in this laboratory, but, with acetic acid as solvent, pure products were obtained in excellent yield for the 2,4-pentanedionato and 1-phenyl-1,3-butanedionato complexes. The molecular structures of $[V(acac)_3][SbCl_6]$ and $[V(bzac)_3][SbCl_6]\cdot CH_2Cl_2$ are described and various spectroscopic and physical properties presented.

## Experimental Section

**Materials.** Oxobis(2,4-pentanedionato)vanadium(IV), $[VO(acac)_2]$,[11] and oxobis(1-phenyl-1,3-butanedionato)vanadium(IV), $[VO(bzac)_2]$,[12] were prepared by the literature procedures and recrystallized twice from chloroform. Triethylammonium tris(catecholato)vanadate(IV)-acetonitrile, $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$, was prepared by the method of Cooper and coworkers.[5] The three complexes gave satisfactory C, H, N, and V analyses. 1-Phenyl-1,3-butanedione was recrystallized twice from ethanol. 2,4-Pentanedione was dried by refluxing over $P_4O_{10}$ for 24 h and distilled under reduced pressure. All solvents were reagent grade. Dichloromethane and acetonitrile were refluxed for at least 24 h with

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