

A New Three Dimensional Crystal Structure of a Cadmium Thiolate

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Received January 27, 1995

Introduction

X-ray structure investigations on the class of nonmolecular compounds $\text{Cd}(\text{SC}_6\text{H}_4\text{X})_2$ have revealed that the nature and position of the substituent X have a decisive influence on the crystal structure. Thus, with $\text{X} = \text{H}$, CH_3 -4, or CH_3 -2, different three dimensional structures are obtained^{1–3} whereas with $\text{X} = \text{Br}$ -4 a two dimensional crystal structure is realized.⁴ However, to the best of our knowledge, only one and two dimensional structures of cadmium thiolates with aliphatic residues have until now been described. Examples are the crystal structures of $\text{Cd}(\text{SCH}_2\text{COOCH}_2\text{CH}_3)_2$ ⁵ and $\text{Cd}(\text{SCH}_2\text{CH}_2\text{OH})_2$ ⁶ built up of linear chains or layers, respectively. In this article we present a three dimensional nonmolecular structure of a cadmium thiolate with an aliphatic ligand ($\text{Cd}(\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH})_2$, **1**) which was crystallized from an aqueous solution of cadmium perchlorate and 1-thioglycerol.

Experimental Section

General Details. All chemicals used were of analytical grade or of the highest purity available and obtained from Alfa, Fluka, and Merck. X-ray powder diffraction was carried out using a Siemens D 5000 diffractometer operating with a Cu anode. A nickel filter was used to select the $\text{K}\alpha$ lines ($\lambda = 1.506 \text{ \AA}$). ¹¹³Cd-NMR spectra were recorded with a Varian Gemini-200 BB spectrometer (4.7 T) at 44.4 MHz. As ref $\delta_{\text{CdCl}_2} = 98 \text{ ppm}$ (1.0 M aqueous solution) was taken which corresponds to $\delta_{\text{Cd}(\text{ClO}_4)_2} = 0 \text{ ppm}$ (0.1 M aqueous solution).⁷ Elemental analysis was carried out commercially at the microanalytic laboratory Pascher in Remagen-Bahndorf, Germany.

Preparation of $\text{Cd}(\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH})_2$. Two different methods were used: A) 2.0 g (4.8 mmol) of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 1 mL (11.5 mmol) of 1-thioglycerol were dissolved in 250 mL of deionized water. The solution was adjusted to pH 11.2 using 1 M NaOH and dialyzed two times against 10 L of deionized water (using spectrapor MWCO 3500 dialysis tubings). As the pH value of the solution slowly decreased, colorless crystals grow in the dialysis tubings as flat tetragonal bipyramids. These crystals were used for X-ray structure

Table 1. Crystallographic Data for **1**

formula	$\text{C}_{48}\text{H}_{112}\text{Cd}_8\text{O}_{32}\text{S}_{16}\cdot 4\text{H}_2\text{O}$
fw	2613.7
space group	$I4_1/a$ (No. 88)
a , \AA	26.434(6)
c , \AA	13.190(4)
V , \AA^3	9217(4)
Z	4
ρ_{calc} , g cm^{-3}	1.935
$\mu(\text{Mo K}\alpha)$, cm^{-1}	22.46
ψ -scan abs corr	
transm factors	0.825–1.000
T , $^\circ\text{C}$	20
λ , \AA	0.7107
$R_1(F_o)^{a,b}$	0.096
$R_2(F_o^2)^c$	0.273

^a $I \geq 2\sigma(I)$. ^b $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^c $R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$ with $w^{-1} = [\sigma(F_o^2) + (aP)^2 + bP]$, ($a = 0.194$; $b = 182.6$) and $P = (F_o^2 + 2F_c^2)/3$.

determination. In order to prepare larger amounts of the compound, a method similar to that described in ref 6 was used: (B) 4.0 g (9.5 mmol) of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 1.7 mL (19.6 mmol) of 1-thioglycerol were dissolved in 30 mL of deionized water. Using 1 M NaOH the pH was adjusted to 3.2. The reaction mixture was stored in a desiccator together with 250 mL of a 1% ammonia solution. As the pH value slowly increased a colorless crystalline precipitate was formed within a few days. After washing (with water, 2-propanol, and diethyl ether) and drying, the crystalline product was obtained as a white powder. Yield: 2.8 g (90%).

Crystal Structure Determination. A colorless crystal of approximate dimensions of $0.25 \times 0.15 \times 0.11 \text{ mm}$ was mounted in a capillary tube filled with several microliters of mother liquor to prevent the crystal from cracking. Crystallographic data are summarized in Table 1. Intensity data were collected using a Enraf-Nonius CAD-4 diffractometer with a graphite monochromator, in the range $2\theta \leq 40^\circ$ by the θ - 2θ scan technique with index ranges $0 \leq h \leq 25$, $0 \leq k \leq 25$, $0 \leq l \leq 12$. A total of 1908 independent reflections were measured of which 1507 with $I(hkl) \geq 2\sigma(I)$ were considered as observed and used for the structure determination. The data were corrected for Lorentz, polarization, and X-ray absorption effects. Systematic monitoring of three check reflections at regular intervals showed a loss in intensities of 15%. Laue symmetry $4/m$ and systematic extinctions hkl , $h + k + l = 2n$, $hk0$, $h_c(k) = 2n$, and $00l$, $l = 4n$ assigned the space group $I4_1/a$, which was confirmed by the structure analysis. Positions of Cd and S atoms were determined by direct methods using SHELX-86.⁸ By several cycles of difference Fourier synthesis and full-matrix least-squares calculations all C and O atoms could be located. For three O atoms two possible positions were found in each case ($\text{O}3$, $\text{O}3'$; $\text{O}4$, $\text{O}4'$; and $\text{O}7$, $\text{O}7'$). In order to prevent too large shifts of light atom parameters strongly weighted restraints for bond lengths and angles of the organic residues were introduced at this stage of structure refinement which was done with the program RESTRA.⁹ After the location of C and O atoms a subsequent difference electron density map showed a significant peak of 2.6 e \AA^{-3} , which was assumed to be an O atom of a water molecule bonded via two hydrogen bonds at organic residues. The final refinement (on F_o^2 data) of atomic coordinates and anisotropic thermal parameters of Cd and S atoms as well as isotropic U values of all light atoms was carried out with SHELXL-93.¹⁰ Atomic scattering factors, f' and f'' values were taken from ref 11. Because of relatively low redundancy and small contributions of C and O atoms to the reflection intensities as a

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Cd1	4357(1)	9215(1)	3030(1)	85(1)
Cd2	4885(1)	8138(1)	1318(1)	100(1)
S1	4090(2)	8385(1)	2210(3)	90(1)
S2	5255(1)	9334(1)	3591(3)	76(1)
S3	4657(2)	7481(1)	-39(3)	98(1)
S4	3701(1)	9431(2)	4337(3)	90(1)
O1	3219(4)	7674(7)	2869(14)	296(6)*
O2	3548(12)	7693(6)	4853(11)	435(10)*
O3	4642(4)	8533(10)	4763(18)	296(6)*
O3' ^b	5354(11)	8951(5)	5809(11)	296(6)*
O4	5845(4)	8118(11)	5737(30)	435(10)*
O4'	5085(11)	8010(10)	6454(11)	435(10)*
O5	3766(6)	7795(9)	-1370(8)	296(6)*
O6	3085(9)	7391(9)	-1365(10)	435(10)*
O7	4249(5)	10148(11)	6879(11)	296(6)*
O7'	3689(8)	10498(5)	5540(15)	296(6)*
O8	3796(7)	9446(7)	7043(22)	435(10)*
C1	4057(4)	7915(4)	3215(9)	123(3)*
C2	3697(4)	7474(4)	3162(8)	230(7)*
C3	3598(9)	7252(5)	4215(9)	296(6)*
C4	5442(5)	8717(4)	4116(7)	123(3)*
C5	5155(4)	8589(4)	5102(8)	230(7)*
C6	5318(5)	8070(4)	5480(10)	296(6)*
C7	3975(3)	7362(4)	143(11)	123(3)*
C8	3639(4)	7790(5)	-295(9)	230(7)*
C9	3096(4)	7581(9)	-323(10)	296(6)*
C10	4118(4)	9739(4)	5297(7)	123(3)*
C11	3884(4)	10073(4)	6086(8)	230(7)*
C12	3446(4)	9809(6)	6607(13)	296(6)*
O1W	3866(8)	8266(8)	6275(15)	263(8)*

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor. An asterisk indicates isotropically refined atoms. ^b A prime indicates an additional position, due to stereochemical or rotational disorders.

consequence of rotational and stereochemical disorders, the SADI option in SHELXL-93 was used requiring similar distances for corresponding bonds within all organic residues. This refinement converged at *R*₂ (*F*_o²) = 0.274 and conventional *R*₁(*F*_o) = 0.096. The final atomic parameters are given in Table 2, and selected bond lengths and angles, in Table 3. Complete details of the data collection and refinement process are given in the supporting information or can be ordered referring to the no. CSD-401898, names of the authors, and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

Results

Irrespective of the preparation method, colorless crystals were obtained as flat tetragonal bipyramids. Upon air drying these crystals cracked and a white powder was formed, which dissolved easily in dimethyl sulfoxide (DMSO). In dimethyl formamide (DMF) dissolution was achieved only on heating to about 100 °C. The melting point of the powder was determined as 209–211 °C. The elemental analysis was in good agreement with the formula Cd(SCH₂CH(OH)CH₂OH)₂. Anal. Calcd for C₆H₁₄O₄S₂Cd: C, 22.1; H, 4.3; O, 19.6; S, 19.6; Cd, 34.4. Found: C, 21.9; H, 4.4; O, 19.9; S, 19.4; Cd, 34.4.

The atomic coordinates and the corresponding *U* values obtained from structural analysis are given in Table 2. Decreasing the temperature during data collection to 173 K did not improve the extremely high *U* values of some C and all O atoms, which is indicative of the fact that these high values are due to statistical disorders of the organic residues rather than thermal motion (see below). The crystal structure is best described as a framework built up of covalently linked Cd₈(SR)₁₆ units which belong to the pointgroup *S*₄ (Figure 1). These units are formed by eight apically linked Cd(μ -SR)_{4/2} tetrahedra located around

Table 3. Selected Bond Distances and Angles for **1**

Distances (\AA)			
Cd1–S2	2.504(4)	Cd2–S3	2.567(4)
Cd1–S4	2.511(4)	Cd2–S3 ^c	2.597(4)
Cd1–S1	2.545(4)	S2–Cd1 ^b	2.558(4)
Cd1–S2 ^a	2.558(4)	S3–Cd2 ^c	2.597(4)
Cd2–S4 ^b	2.494(4)	S4–Cd2 ^a	2.494(4)
Cd2–S1	2.495(4)		
Angles (deg)			
S2–Cd1–S4	115.04(13)	S1–Cd2–S3	107.94(13)
S2–Cd1–S1	119.73(12)	S4 ^b –Cd2–S3 ^c	104.65(13)
S4–Cd1–S1	107.24(13)	S1–Cd2–S3 ^c	105.35(14)
S2–Cd1–S2 ^a	101.63(14)	S3–Cd2–S3 ^c	96.64(13)
S4–Cd1–S2 ^a	115.58(12)	Cd2–S1–Cd1	101.10(13)
S1–Cd1–S2 ^a	96.33(13)	Cd1–S2–Cd1 ^b	105.98(13)
S4 ^b –Cd2–S1	128.12(12)	Cd2–S3–Cd2 ^c	83.36(13)
S4 ^b –Cd2–S3	109.43(14)	Cd2 ^a –S4–Cd1	109.8(2)

^a Symmetry-related atom: $y - 1/2, -x + 3/2, -z + 1/2$. ^b Symmetry-related atom: $-y + 3/2, x + 1/2, -z + 1/2$. ^c Symmetry-related atom: $-x + 1, -y + 3/2, -z + 1/4$.

the improper rotation axis. As can readily be seen from Figure 1, part A, the units are joined to one another through the four outer coordination tetrahedra by sharing an edge. The distance between the atoms Cd2 and Cd2^c (3.433(2) Å) is significantly shorter than the distances between all other neighboring Cd atoms (3.891–4.096 Å) because of the double bridging. As an alternative to the tetrahedron description, the Cd₈(SR)₁₆ units can also be considered to consist of four Cd₃S₃ six-membered rings which form a Cd₄S₄ eight-membered ring around the improper rotation axis through cyclic *spiro*-like bridges. In this description the Cd₈(SR)₁₆ units are joined via a *spiro*-bound Cd₂S₂ four-membered ring. The Cd–S bond distances and angles given in Table 3 are in the same range as for Cd–S bonds of other cadmium thiolates if the considered Cd atoms are also tetrahedrally coordinated.^{2,3,6} A whole Cd₈(SR)₁₆ unit with all carbon and oxygen atoms of the organic residues is depicted in Figure 1, part B. Also shown are the oxygen atoms OW1 of the four water molecules which are bound to hydroxyl groups of the organic residues through hydrogen bonds (see also Figure 2).

As mentioned in the Experimental Section, the localization of the C and O atoms was complicated by rotational and stereochemical disorders. This feature is visualized in Figure 2, where two possible positions for the oxygen atoms 3, 4, and 7 are given (O3, O3', O4, O4', and O7, O7'). In the case of oxygen atom 4, the two positions are related by a rotation around the C5–C6 axis of 108 °, whereas the different positions of the other two oxygen atoms are explained by either the *R*- or *S*-enantiomer of the 1-thioglycerol ligand. It should be noted that, in contrast to Cd(SCH₂CH₂OH)₂,⁶ no additional coordination of Cd atoms by hydroxyl O atoms is observed. However, the distances between Cd1 and O3 (3.01(1) Å) as well as Cd2^a and O7' (3.02(1) Å) are indicative of weak interactions and might be regarded as a secondary coordination.

Figure 3 shows how the nonmolecular network of the structure is formed. The way the Cd₈(SR)₁₆ units are connected with each other leads to the formation of helices around the 4-fold screw axis of the spacegroup *I*4₁/*a*. By the fusion of neighboring helices expanded oval cavities are created, which are penetrated by the organic residues of the 1-thioglycerol. Due to the numerous hydroxyl groups, a hydrophilic environment is provided and many hydrogen bonds are formed. At least four water molecules per Cd₈(SR)₁₆ unit are incorporated during crystal growth as described above.

Although the crystals cracked upon air drying, some small crystals remained which were suitable for an additional structure

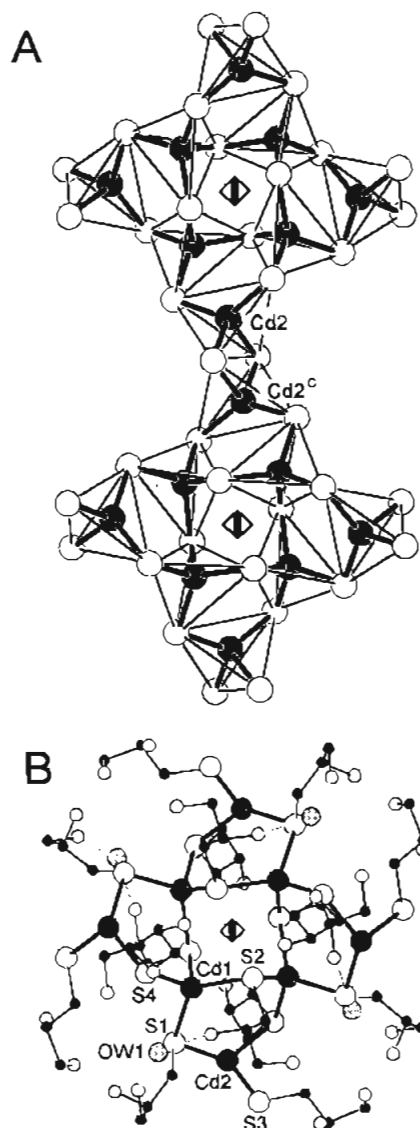


Figure 1. Structure of the $\text{Cd}_8(\text{SR})_{16}$ units:¹⁹ ●, cadmium; ○, sulfur; ●, carbon; ○, oxygen; stippled circle, oxygen of water. (A) Units built up of eight apically linked $\text{Cd}(\mu\text{-SR})_{12}$ tetrahedra which form a ring around the S_4 axis (tilted square with vertical bar). Neighboring units are linked by the outer tetrahedra sharing an edge. The distance between the atoms Cd2 and Cd2^c (3.433(2) Å) is significantly shorter than between all other neighboring Cd atoms (3.891–4.096 Å). (B) All non-hydrogen atoms of the $\text{Cd}_8(\text{SR})_{16}$ unit and the four hydrogen-bonded water molecules. For the atomic coordinates and Cd–S bond distances and angles, see Table 2 and 3, respectively. Only one position is depicted for the disordered O atoms (see text).

determination.¹² Despite the inferior quality of these crystals, this analysis revealed that the Cd_8S framework of the structure remained almost unchanged upon drying. However, the unit cell volume clearly decreased (8983 Å³ as opposed to 9217 Å³), most probably due to the loss of incorporated water, which could no longer be located. The comparison of the two calculated

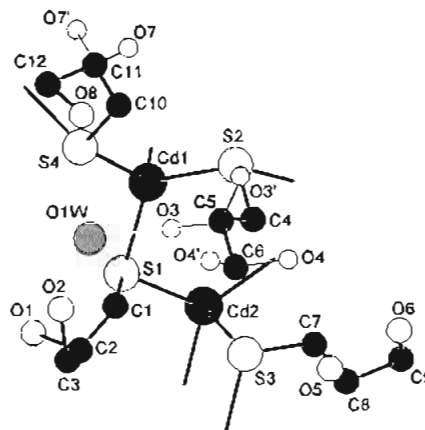


Figure 2. Asymmetric unit. The water molecule (OW1) is bound by hydrogen bonds to O atoms O2 and O3 (2.55(3) and 2.95(3) Å). For three O atoms two different positions were located, which are explained by stereochemical or rotational disorders (O3, O3'; O7, O7'; and O4, O4', respectively).

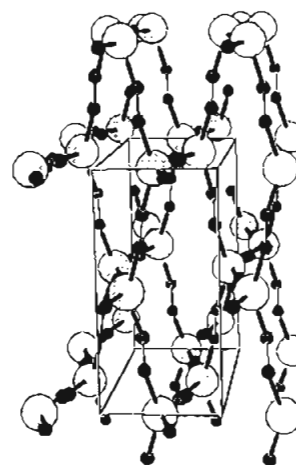


Figure 3. Framework structure of **1** projected in the x -direction: Stippled circle, inner part of the $\text{Cd}_8(\text{SR})_{16}$ units; ●, cadmium. Only the Cd2 atoms of the outer, edge-sharing $\text{Cd}(\mu\text{-SR})_{12}$ tetrahedra are explicitly depicted. The tetragonal cell dimensions are $a = b = 26.434(6)$ Å and $c = 13.190(4)$ Å.

powder diffractograms¹³ (using the parameters of the crystal structure determinations) with the diffractogram obtained from a powdered sample which was stored several weeks under air (Figure 4) visualizes that the structure changed only slightly upon air drying and that the dried crystal investigated was representative for the whole powdered sample.

The ¹¹³Cd-NMR spectrum of a 1 M solution of $\text{Cd}(\text{SCH}_2\text{-CH}(\text{OH})\text{CH}_2\text{OH})_2$ in DMSO displayed a broad signal between 400 and 600 ppm ($\nu_{1/2} = 2200$ Hz) at room temperature. With increasing temperature this signal changed into a sharp peak at 515 ppm ($\nu_{1/2} = 260$ Hz at $T = 383$ K).

Discussion

As described in the Experimental Section, there are two possible ways of crystal formation. Following route A, the crystals were formed by decreasing the pH value of the alkaline reaction mixture. At pH 11.2 cadmium thiolato complexes are formed which are probably stabilized in solution by (co-)coordinating hydroxyl ions. These complexes are assumed to form larger aggregates and so do not pass through the dialysis tubings. During dialysis the concentration of the stabilizing OH^- ions is decreased and the aggregates slowly precipitate as a crystalline solid. Following route B, crystallization was achieved by slowly increasing the pH value of an acidic reaction

(12) The data of the structural analysis are also included in the supplementary material or can be ordered referring to the no. CSD-401052, names of the authors, and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The space group for this structure was determined as $I4_1/a$ (No. 82), but due to the poor quality of the collected data, the higher symmetry of space group $I4_1/a$ could not be excluded. The tetragonal cell dimensions were determined as $a = b = 26.181(5)$ Å, and $c = 13.105(3)$ Å.

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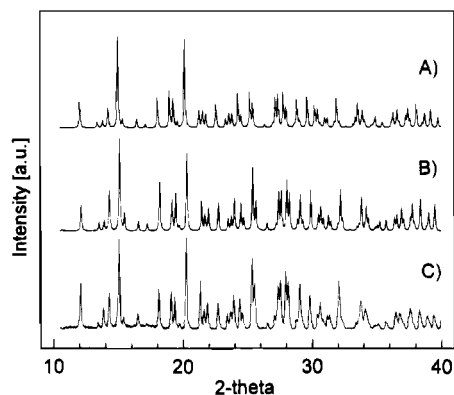


Figure 4. Comparison of X-ray powder diffractograms. A and B were calculated using the parameters of the crystal structure determinations referring to a crystal maintained in mother liquor or a dried one, respectively (Bragg–Brentano geometry, pseudo-Voigt profile function, $\text{fwhm} = 0.1^\circ$ for 2θ). Diffractogram C was measured with a powdered sample which was kept under air for several weeks. Only small changes of the diffraction pattern are observed, but due to the shrinkage of the dried crystals the reflections in B and C are slightly shifted to higher angles.

mixture. This was done by storing the solution under an NH_3 -containing atmosphere. In acidic solution the sulfur atom of the 1-thioglycerol is protonated and not available for the formation of μ -SR bridges between the Cd atoms. However, as the pH value increases, the thiolate group coordinates with Cd^{2+} ions under deprotonation; this is followed by the formation of μ -SR bridges between Cd atoms. Finally, this process leads to the buildup of the described crystal structure.

As shown in Figure 2, stereochemical disorders were located for the organic residues which are bound to sulfur atoms S2 and S4. In contrast, no different positions of any atom could be located for the other two residues, suggesting that only residues with the *R*-configuration are bound to atom S1, whereas the residues bound to sulfur atom S3 have the *S*-configuration. Due to the extremely high *U* values (Table 2), this conclusion can only be drawn speculatively. The interesting question, however, of how the crystal structure depends on whether a racemic mixture of 1-thioglycerol or only one enantiomeric form is used for the preparation remains to be decided. It is noted that, in our description of the structure, we regarded the residues bound to S2 and S4 as statistically disordered in agreement with space group $I4_1/a$ (No. 88). However, there might be an ordered stereochemistry in a manner that alternating $\text{Cd}_8(\text{SR})_{16}$ units have definite configurations. In this case the space group would be $I4$ (No. 82).

The shrinkage (and destruction) of the crystals upon drying is attributed to the loss of water which is incorporated into the expanded hydrophilic cavities. An analysis of the spatial possibilities for the incorporation of water molecules shows that a maximum of 10 water molecules can be bound per $\text{Cd}_8(\text{SR})_{16}$ unit.¹⁴ Structural analysis confirmed four of the possible positions being occupied when the crystals are stored in their mother liquor. The shrinkage during air drying indicates that the water is only weakly bound and easily leave the porous lattice framework.

It is most likely that, besides the described structure, there exists another modification of **1**. Encouraged by UV/vis spectroscopy, X-ray powder diffraction, and elemental analysis as described in ref 15, we are convinced that in a manner analogous to $\text{Cd}_{10}(\text{SCH}_2\text{CH}_2\text{OH})_{20}$ ¹⁶ compound **1** also exists as $\text{Cd}_{10}(\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH})_{20}$ clusters. These clusters, readily soluble in water, are built up of four fused adamantanoid-like cages, which approximately form a tetrahedral fragment of the cubic CdS solid state phase.¹⁷ However, the mechanism which determines the realized modification remains to be unraveled. The temperature dependency of the ¹¹³Cd-NMR spectrum of **1** in DMSO is similar to that observed previously for $\text{Cd}(\text{SPh})_2$ in DMF by Dance and co-workers.¹⁸ The rather broad signal detected at room temperature suggests that the structure of the $\text{Cd}_8(\text{SR})_{16}$ units is disrupted by the strongly coordinating solvent and an equilibrium of different aggregated cadmium thiolate species is realized.

Supporting Information Available: Complete tables of crystallographic details, atomic coordinates, bond lengths and angles, and isotropic and anisotropic displacement parameters of structure determinations labeled with code names HM88 and HMI242, which refer to the structure determinations carried out with a crystal maintained in mother liquor or a dried one, respectively (10 pages). Ordering information is given on any current masthead page.

IC9500974

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