

Crystal and Molecular Structure of the Tetrameric Cd(II) Complex $(\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2\text{CdCl}_2)_2 \cdot 2\text{H}_2\text{O}$

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Abstract: The crystal and molecular structure of the tetrameric Cd(II) complex $(\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2\text{CdCl}_2)_2 \cdot 2\text{H}_2\text{O}$ has been determined from single-crystal three-dimensional x-ray data collected by counter methods. The compound crystallizes from water as pale yellow rhomboids in space group $P2_1/c$ with $Z = 2$; $a = 12.642$ (8), $b = 13.673$ (7), $c = 11.557$ (6) Å; $\beta = 124.64$ (3)°; $d_{\text{calcd}} = 2.110$, $d_{\text{obsd}} = 2.09$ (1) g/cm³. Least-squares refinement of 1252 reflections having $F^2 \geq 3\sigma(F^2)$ led to a conventional R factor of 0.053. The structure consists of centrosymmetric Cd(II) tetrameric units containing both four- and six-coordinate Cd(II) ions. The four-coordinate pseudotetrahedral CdS_2Cl_2 units show nearly equivalent Cd-S bond lengths of 2.520 (6) and 2.506 (5) Å, grossly dissimilar Cd-Cl bond lengths of 2.660 (4) and 2.413 (6) Å, and a dihedral angle of 90.5 (1)° between the CdS_2 and CdCl_2 planes. Both sulfur donors and the relatively weakly bound Cl donor bridge these pseudotetrahedral CdS_2Cl_2 units to pseudooctahedral $\text{CdS}_2\text{Cl}_2\text{N}_2$ units. The six-coordinate Cd(II) units show equal Cd-S bond distances of 2.558 (4) and 2.558 (4) Å, equal Cd-Cl bond distances of 2.946 (6) and 2.946 (5) Å, and equal Cd-N bond distances of 2.26 (2) and 2.35 (2) Å. These Cd-Cl bond distances are ~ 0.2 Å longer than those reported for other six-coordinate Cd(II) species; this effect is attributed to strain within the cluster unit. Both water molecules are lattice species which interact with the clusters via hydrogen bonding. Tetrameric units are weakly linked by hydrogen bonds between amino hydrogen atoms and triply bridging chloride ions. Structures of the title complex and of a similar zinc tetramer, $(\text{Zn}[\text{f-CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{S}]_2\text{ZnCl}_2)_2 \cdot 2\text{H}_2\text{O}$, which has been characterized previously by other workers, are compared and contrasted.

Introduction

Our recent interest in characterizing Co(II),¹ Zn(II),^{1,2} and Cu(I)/Cu(II)³ complexes of the aminomercaptide ligand $-\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ stems from their attractiveness as vehicles for investigating structural, electronic-spectral, vibrational, and related aspects of metal-mercaptide bonding. These metal ions may be naturally or artificially placed at mercaptide-containing sites in various biologically important proteins. Since $-\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ is related structurally to the chelating drug penicillamine [$\text{HSC}(\text{CH}_3)_2\text{CH}(\text{CO}_2\text{H})\text{NH}_2$], complexes of this ligand also may be relevant to the treatment of heavy metal poisoning and Wilson's disease by penicillamine therapy.

We have extended our studies of model mercaptide complexes to include those of Cd(II). Large amounts of Cd(II) (up to 6% by weight) may be bound to metallothioneins, cysteine-rich low molecular weight proteins which are present in mammalian tissue.⁴ Protein synthesis is thought to be induced by elevated tissue levels of divalent ions such as Cd(II), Zn(II), Hg(II), and Cu(II).⁵ Copper-rich metallothioneins are present in persons afflicted with Wilson's disease.⁶ The chemical basis of penicillamine therapy may in part arise from a favorable partition of copper between metallothionein sites and the soluble polynuclear complexes such as those with the ligand^{3,7} or its disulfide oxidation product.⁸

Titration studies of Cd(II)-metallothioneins suggested that an average of three mercaptide ligands may be involved with the binding of each Cd(II).⁴ However, since mercaptides exhibit a pronounced tendency to bridge Cd(II) (vide infra) as well as other metal ions, neither the coordination numbers nor coordination geometries of the protein-bound Cd(II) ions are known. Studies of various Cd(II) complexes of sulfur-donor ligands by ¹¹³Cd Fourier transform spectroscopy show that mercaptide ligation results in relatively large deshielding effects.⁹ Such data could be used advantageously to probe the nature of Cd(II)-metallothionein sites provided that the ¹¹³Cd spectra of the proteins can be obtained. A full calibration of this NMR technique has been limited by the small number of structurally characterized Cd(II)-mercaptide complexes. The three complexes of this type which have been the subject of crystallographic studies are either cluster or polymeric species

having compositions of $[\text{Cd}_{10}(\text{SCH}_2\text{CH}_2\text{OH})_{16}]^{4+}$,¹⁰ $[\text{Cd}_8(\text{SCH}_2\text{CH}_2\text{OH})_{12}\text{I}]^{3+}$,¹¹ and $[\text{Cd}(\text{SCH}_2\text{CH}_2\text{OH})_2]_n$.¹² Recently, we prepared Cd(II)-mercaptide complexes of composition $\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2$ and $(\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2\text{CdCl}_2)_2 \cdot 2\text{H}_2\text{O}$. Here, we report the crystal and molecular structure of the latter complex.

Experimental Section

1. Preparation of $(\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2\text{CdCl}_2)_2 \cdot 2\text{H}_2\text{O}$. An attempt to recrystallize $\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2$ from its mother liquor yielded the title complex as the sole (and unexpected) product. A solution of 0.283 g of $\text{HSC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2 \cdot \text{HCl}^{13}$ (2.0 mmol) and 0.228 g of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (1.0 mmol) in 100 mL of hot (85 °C) H_2O was made alkaline (pH 9–10) by the addition of 4 mL of Et_3N , filtered through a fine glass frit, and left at 25 °C for 1 day. Microscopic examination revealed that the colorless product consisted entirely of clumps of the platelike $\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2$ complex ($d = 1.68$ (2) g/cm³).¹⁴ An attempt was made to recrystallize this product by adding 100 mL of H_2O to the above mixture, heating it to boiling, and refiltering the resulting colorless solution. After remaining at 25 °C for 1 day, the solution deposited pale yellow rhomboids which were collected by filtration, washed thoroughly with water, and dried in air (yield 0.15 g or 57% based on Cd). The product has no apparent solubility in hot acetonitrile, hot *N,N*-dimethylformamide, or hot nitromethane. Although the product dissolves in hot dimethyl sulfoxide, it is not yet known if the tetrameric cluster structure is retained in solution.

Anal. Calcd for $\text{Cd}_4\text{S}_4\text{Cl}_4\text{C}_{16}\text{N}_4\text{H}_{44}\text{O}_2$: Cd, 43.06; Cl, 13.58; N, 5.36; C, 18.40; H, 4.25. Found: Cd, 43.52; Cl, 13.14; N, 5.26; C, 17.95; H, 4.28.

The title complex may also be prepared directly in approximately quantitative yield by the neutralization of equimolar aqueous solutions of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and the ligand hydrochloride with 2 equiv of Et_3N .

2. Collection of Diffraction Data. A single crystal of dimensions 0.24 × 0.10 × 0.19 mm was mounted along a in a glass capillary. Preliminary Weissenberg photographs showed systematic absences for $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, fixing the space group as $P2_1/c$. Unit cell dimensions (Table I) were determined from a least-squares analysis of the θ , χ , and ϕ values of ten reflections obtained using graphite-monochromated Mo $K\alpha$ radiation and an Enraf-Nonius CAD-3 automated diffractometer. The crystal density was measured by the gradient method¹⁵ using a mixture of CH_2Br_2 and $\text{BrCH}_2\text{CH}_2\text{Br}$ as the high-density medium and a mixture of CCl_4 and $\text{BrCH}_2\text{CH}_2\text{Br}$ as the low-density medium. KCl ($d = 1.984$ g cm⁻³),

KCNO ($d = 2.056 \text{ g cm}^{-3}$), KNO_3 ($d = 2.109 \text{ g cm}^{-3}$), and $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ($d = 2.127 \text{ g cm}^{-3}$) were used as standards.¹⁶ Observed and calculated densities (Table I) agreed well for two $(\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2\text{CdCl}_2)_2 \cdot 2\text{H}_2\text{O}$ units per unit cell.

A total of 4197 reflections were collected at room temperature ($24 \pm 1^\circ \text{C}$). Graphite-monochromated Mo $K\alpha$ radiation was detected using a scintillation counter and a pulse height analyzer set to admit approximately 95% of the $K\alpha$ peak. A θ - 2θ scan was used to collect a unique data set in the range $2 \leq \theta \leq 25^\circ$. The scan range S was set according to $S = (1.10 + 0.10 \tan \theta)^\circ$. Background measurements were made at the beginning and end of each scan with the counter stationary; the total time for background counting was equal to the scan time. The scan rate was $1/6 \text{ deg s}^{-1}$, and each reflection was scanned repeatedly to a maximum of five scans or until 8000 counts were obtained. Intensities were placed on a common scale by dividing by the number of scans. The intensity of a standard reflection, measured at 50 reflection intervals, was consistent to $\pm 2\%$ and showed no significant trend. Lorentz, polarization, and absorption¹⁷ corrections were applied to the 4197 measured intensities. Absorption factors ranged from 1.34 to 1.68 using a linear absorption coefficient of 30.9 cm^{-1} for Mo $K\alpha$ radiation. Of the measured intensities, 1252 with $F^2 \geq 3\sigma(F^2)$ were used in the structure solution and refinement; here, $\sigma(F^2) = (Lp)^{-1}(N_t + (0.02N_n)^2)^{1/2}$ is the standard deviation estimated from counting statistics, N_t is the total count (scan plus background), N_n is the net count (scan minus background), and 0.02 is an estimate of instrumental instability.

3. Solution and Refinement of the Structure. The structure was solved by the heavy atom method and refined using full-matrix least-squares techniques.¹⁷ Approximate coordinates for the two unique cadmium atoms were obtained from a normal sharpened Patterson map while a series of structure factor, difference Fourier calculations revealed coordinates for all remaining atoms except hydrogen. A structure factor calculation, based on phases derived from the cadmium atoms only, gave an initial agreement factor $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.322$.

Isotropic refinement was initiated using atomic scattering factors for zerovalent Cd, Cl, S, N, and C.¹⁸ Both real and imaginary parts of the anomalous dispersion corrections were applied to Cd, Cl, and S.¹⁸ Initial refinement was based on F^2 and weights were set according to $w = 1/\sigma^2(F^2)$. Several cycles of isotropic refinement led to convergence with $R_F = 0.080$. At this point, all hydrogen atoms were located. Methyl group H atoms were located by placing tetrahedrally oriented H atoms 0.95 \AA from the appropriate C atom.¹⁹ These groups were rotated in 5° intervals until a best fit was obtained between calculated H positions and positive regions of a difference Fourier map. Methylene and amine hydrogen coordinates were calculated assuming tetrahedral geometry and an N-H distance of 0.87 \AA ;¹⁹ these atoms were also located in positive regions of the difference electron density map. Finally, the two water H atoms were found experimentally. Analysis of the difference map revealed several peaks of high electron density approximately 1 \AA from the oxygen atom. One peak, much larger than the rest, was assumed to be the first hydrogen, while a second, which showed an H-O-H angle of 108° and was located 0.96 \AA from the oxygen atom, was assumed to be the second hydrogen atom. Temperature factors for the hydrogen atoms were set according to $B_H = B_N + 1$, where N is the atom to which hydrogen is bonded; hydrogen atom parameters were not refined. Several cycles of isotropic refinement at this point reduced R_F to 0.077.

Anisotropic refinement was based on F and a weighting scheme was chosen by an analysis of variance to make $|\Delta F|/\sigma$ independent of $|F_o|$. This procedure led to the following assignments for $\sigma(F_o)$:

$$\begin{aligned}\sigma(F_o) &= 0.168 + 0.042|F_o|, & |F_o| < 14.6 \\ \sigma(F_o) &= 2.674 - 0.103|F_o|, & 14.6 < |F_o| < 17.8 \\ \sigma(F_o) &= 0.650 + 0.020|F_o|, & |F_o| > 17.8\end{aligned}$$

The anisotropic refinement did not proceed smoothly; convergence was difficult to obtain and two atoms showed slightly negative values for one cofactor of the anisotropic temperature factor matrix. Analysis of the correlation matrix revealed high $\beta_{33} - \beta_{13}$ coefficients for all atoms which we attributed to the large value of the cell angle β (124.64°).²⁰⁻²² Therefore, the cell was transformed and refinement was continued in space group $B2_1/n$ ($a = 12.642$; $b = 13.673$; $c = 19.023 \text{ \AA}$; $\beta = 88.5^\circ$; $V = 3287 \text{ \AA}^3$). This transformation to the B -centered cell resulted in a drastic reduction in the $\beta_{33} - \beta_{13}$ correlation

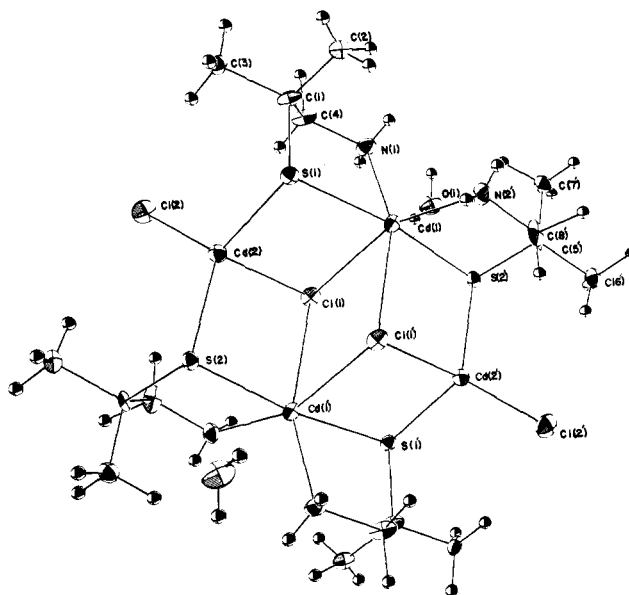


Figure 1. View of the title complex showing the atom numbering scheme.

Table I. Crystal Data for $(\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2\text{CdCl}_2)_2 \cdot 2\text{H}_2\text{O}$

Mol wt 1044.20	$V = 1643.5 \text{ \AA}^3$
Space group $P2_1/c$ (no. 14)	$d_{\text{obsd}} = 2.09 (1) \text{ g/cm}^3$
$Z = 2$	$d_{\text{calcd}} = 2.110 \text{ g/cm}^3$
$a = 12.642 (8) \text{ \AA}$	$\lambda = 0.71069 \text{ \AA}$
$b = 13.673 (7) \text{ \AA}$	$T = 24 (1)^\circ \text{C}$
$c = 11.557 (6) \text{ \AA}$	$\mu = 30.90 \text{ cm}^{-1}$
$\beta = 124.64 (3)^\circ$	

coefficients and aided convergence. Several cycles of anisotropic refinement in $B2_1/n$ reduced R_F to 0.057 while two additional cycles in $P2_1/c$ gave final values of $R_F = 0.053$ and $R_{wF} = (\Sigma(w(|F_o| - |F_c|)^2)/\Sigma w F_o^2)^{1/2} = 0.061$. For the final cycle, all positional and thermal parameter changes were within their estimated standard deviation. A final difference map showed a general background of approximately $\pm 0.8 \text{ e/\AA}^3$ except in the vicinity of the heavy Cd, Cl, and S atoms where the background was $\pm 1.0 \text{ e/\AA}^3$. No positive peak on the final difference map was larger than the largest negative peak. Final atomic parameters are listed in Table II, while views of the title complex and its packing are shown in Figures 1 and 2, respectively. A list of observed and calculated structure factors is available.²³

4. Description of the Structure. The complex crystallizes as discrete centrosymmetric Cd(II) tetramers which contain both four- and six-coordinate Cd(II) ions. The former are the two crystallographically equivalent Cd(2) species which show distorted tetrahedral S_2Cl_2 ligation. Departure from idealized T_d geometry is evidenced by the marked nonequivalence of the two Cd(2)-Cl bond lengths (Table III). This departure is not reflected in the Cd(2)-S(1)-S(2)/Cd(2)-Cl(1)-Cl(2) dihedral angle ($90.5 (1)^\circ$) which is close to the ideal value of 90° . Of the four donor atoms in the Cd(2) coordination sphere, only Cl(2) is nonbridging. Bonding differences between the terminal Cl(2) and the triply bridging Cl(1) are reflected in the observed Cd(2)-Cl(2) and Cd(2)-Cl(1) bond lengths ($2.431 (6)$ and $2.660 (4) \text{ \AA}$). The sum of the effective crystal radii^{24,25} of Cl^- and four-coordinate Cd(II) is $\sim 2.61 \text{ \AA}$. Thus, the Cd(2)-Cl(2) bond is relatively robust, whereas the Cd(2)-Cl(1) bond is somewhat weak. For comparison, approximate Cd-Cl bond lengths of 2.50 \AA were reported for the $\text{CdCl}_2 \cdot 2\text{NH}_2\text{C}(\equiv\text{S})\text{NH}_2$ complex which crystallizes with discrete pseudo-tetrahedral CdCl_2S_2 units.²⁶ The Cd(2)-S(1) and Cd(2)-S(2) bond distances of $2.520 (6)$ and $2.506 (5) \text{ \AA}$, respectively, are equivalent and fall within the range (2.50 - 2.58 \AA) reported for the approximately tetrahedral mercaptide-bridged CdS_4 units present in the $[\text{Cd}(\text{SCH}_2\text{CH}_2\text{OH})_2]_n$ ¹² and $[\text{Cd}_{10}(\text{SCH}_2\text{CH}_2\text{OH})_{16}]^{4+}$ ¹⁰ structures.

Table II. Fractional Atomic Coordinates^a and Thermal Parameters^b for the Title Complex

Atom	x	y	z	β_{11} or B, Å ²	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd(1)	-5066 (1)	812 (1)	1670 (1)	35 (1)	33 (1)	62 (2)	-1 (1)	21 (1)	-6 (1)
Cd(2)	-2247 (1)	171 (1)	1703 (1)	49 (1)	29 (1)	67 (2)	-5 (1)	35 (1)	-10 (1)
Cl(1)	-4332 (4)	1121 (3)	-309 (4)	54 (3)	23 (3)	68 (6)	-2 (3)	30 (4)	6 (3)
Cl(2)	-498 (4)	1203 (4)	2166 (5)	72 (3)	40 (3)	101 (7)	-16 (3)	53 (4)	0 (4)
S(1)	-2824 (3)	120 (3)	3461 (4)	42 (2)	21 (3)	53 (6)	-3 (3)	25 (3)	-2 (3)
S(2)	-2720 (3)	-1399 (3)	374 (4)	40 (3)	20 (3)	62 (6)	-2 (2)	34 (3)	-2 (3)
O(1)	-4009 (13)	-3667 (12)	-153 (13)	91 (11)	52 (10)	73 (19)	-8 (9)	44 (12)	6 (10)
N(1)	-3957 (13)	2291 (12)	2707 (15)	50 (12)	28 (9)	70 (22)	-1 (9)	17 (14)	-16 (11)
N(2)	-3734 (13)	-357 (12)	-2562 (15)	47 (11)	25 (9)	92 (23)	10 (9)	29 (13)	2 (10)
C(1)	-2149 (15)	1270 (14)	4555 (15)	58 (14)	23 (11)	30 (22)	1 (12)	12 (15)	4 (12)
C(2)	-2612 (16)	1296 (18)	5550 (17)	71 (14)	35 (12)	50 (23)	-8 (12)	37 (15)	-21 (12)
C(3)	-685 (15)	1184 (16)	5450 (19)	30 (12)	46 (14)	55 (27)	-6 (11)	20 (15)	-8 (13)
C(4)	-2540 (17)	2173 (14)	3620 (18)	76 (17)	14 (10)	38 (24)	5 (12)	7 (17)	20 (11)
C(5)	-1946 (12)	-1338 (13)	-575 (15)	35 (10)	25 (11)	73 (24)	0 (9)	48 (13)	-5 (11)
C(6)	-463 (16)	-1317 (16)	542 (19)	42 (13)	32 (13)	83 (28)	9 (11)	34 (16)	-4 (13)
C(7)	-2303 (16)	-2233 (16)	-1472 (20)	59 (13)	28 (12)	86 (28)	15 (11)	48 (16)	3 (13)
C(8)	-2355 (16)	-340 (17)	-1469 (17)	54 (14)	70 (16)	54 (25)	14 (12)	35 (16)	52 (13)
H1(O)	-448	-381	-105	4.27					
H2(O)	-458	-363	7	4.27					
H1(N1)	-416	274	205	3.35					
H2(N1)	-421	256	321	3.35					
H1(N2)	-390	-77	-324	3.04					
H2(N2)	-395	22	-292	3.04					
H1(C2)	-308	187	544	3.61					
H2(C2)	-189	125	652	3.61					
H3(C2)	-316	74	567	3.61					
H1(C3)	-31	172	609	3.01					
H2(C3)	-38	117	487	3.01					
H3(C3)	-44	59	599	3.01					
H1(C4)	-221	210	304	3.13					
H2(C4)	-212	274	419	3.13					
H1(C6)	-22	-73	109	3.73					
H2(C6)	-2	-134	9	3.73					
H3(C6)	-20	-187	115	3.73					
H1(C7)	-207	-215	-212	3.37					
H2(C7)	-320	-235	-198	3.37					
H3(C7)	-185	-279	-90	3.37					
H1(C8)	-188	-33	-186	4.07					
H2(C8)	-213	16	-86	4.07					

^a Hydrogen coordinates are $\times 10^3$; nonhydrogen coordinates are $\times 10^4$. ^b The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Anisotropic thermal parameters are $\times 10^4$.

Bond angles within the Cd(2) S₂Cl₂ unit fall in the range of 96–120° and deviate substantially from the idealized tetrahedral value. A significant part of these angular distortions may be ascribed to effects arising from the triply bridging chlorine atom, Cl(1) (see Discussion).

Both crystallographically equivalent Cd(1) species have S₂N₂Cl₂ ligand sets which are severely distorted from idealized O_h geometry. The Cd(1)–S(1) and Cd(1)–S(2') bond lengths are identical (2.588 (4) Å) within experimental error, and are comparable to the average Cd–S distance of 2.56 Å reported for the CdS₃O₃ units in [Cd₁₀(SCH₂CH₂OH)₁₆]⁴⁺.¹⁰ The Cd(1)–N(1) and Cd(1)–N(2') bond lengths (2.36 (2) and 2.35 (2) Å) are comparable to those reported (2.34 (3) Å) for the centrosymmetric CdS₂N₂Cl₂ unit of Cd[S=C(NHNH₂)₂]₂Cl₂.²⁷ Cd(1)–Cl(1) and Cd(1)–Cl(1') bond distances (2.946 (6) and 2.946 (5) Å) substantially exceed the sum (~2.78 Å) of the crystal radii^{24,25} for Cl⁻ and six-coordinate Cd(II), and fall outside the range of Cd–Cl distances (2.60–2.73 Å) reported for other chloro-bridged complexes of six-coordinate Cd(II).²⁸ However, these distances are significantly shorter than the sum (~3.21 Å) of the van der Waals radius of chlorine and the metallic radius of cadmium, and are, therefore, consistent with weak Cd(1)–Cl(1) and Cd(1)–Cl(1') bonding interactions. Ligation of Cl(1) and Cl(1') to Cd(1) is also implied by the Cl(1)–Cd(1)–N(2'), Cl(1')–Cd(1)–N(1), and Cl(1)–Cd(1)–Cl(1') angles, which were observed to be 160.8 (3), 159.7 (5), and 79.3 (2)°, respectively. Substantial angular departures of the CdS₂N₂Cl₂ units from O_h symmetry are evidenced by the angles from Cd(1) to adjacent vertices of the CdS₂N₂Cl₂ pseudooctahedron; these range from 79.3 to 110.2° (ideal value, 90°). Lastly, the distorted

nature of the CdS₂N₂Cl₂ units is also reflected by atom deviations from least-squares planes²³ containing Cd and the various (pseudo)-square-planar arrays of ligating atoms formed from the S₂N₂Cl₂ units.

Structural parameters of the two crystallographically different –SC(CH₃)₂CH₂NH₂ ligands are nearly identical and agree well with values reported for Co[SC(CH₃)₂CH₂NH₂]₂ and Zn[SC(CH₃)₂CH₂NH₂]₂.^{1,2}

The water molecules are lattice species which fill space and are joined to the tetramers by hydrogen bonds. The structural parameters listed in Table IV suggest a hydrogen bond between the amino hydrogen atom H1(N2) and the water oxygen atom O(1), and possibly two additional bonds involving H1(N1) and H1(O1). Finally, we note that tetrameric units appear to be weakly linked by a hydrogen bond between H1(N1) and the triply bridging chlorine atom Cl(1).

Discussion

The structure of the title complex resembles that reported for (Zn \ddagger CH₂NH(CH₃)CH₂CH₂S)₂ZnCl₂)₂·2H₂O.²⁹ To facilitate structural comparisons between these clusters, a view of the Zn(II) complex, prepared from the published atomic coordinates,²⁹ is included as Figure 3. Both structures contain M₄S₄ rings with sulfur atoms alternately above and below the strictly coplanar²³ Zn₄ or Cd₄ units. Both clusters contain pseudotetrahedral MS₂Cl₂ units which differ in interesting ways. For example, both Zn(2)–Cl bond distances are nearly equivalent whereas the corresponding bond distances in the

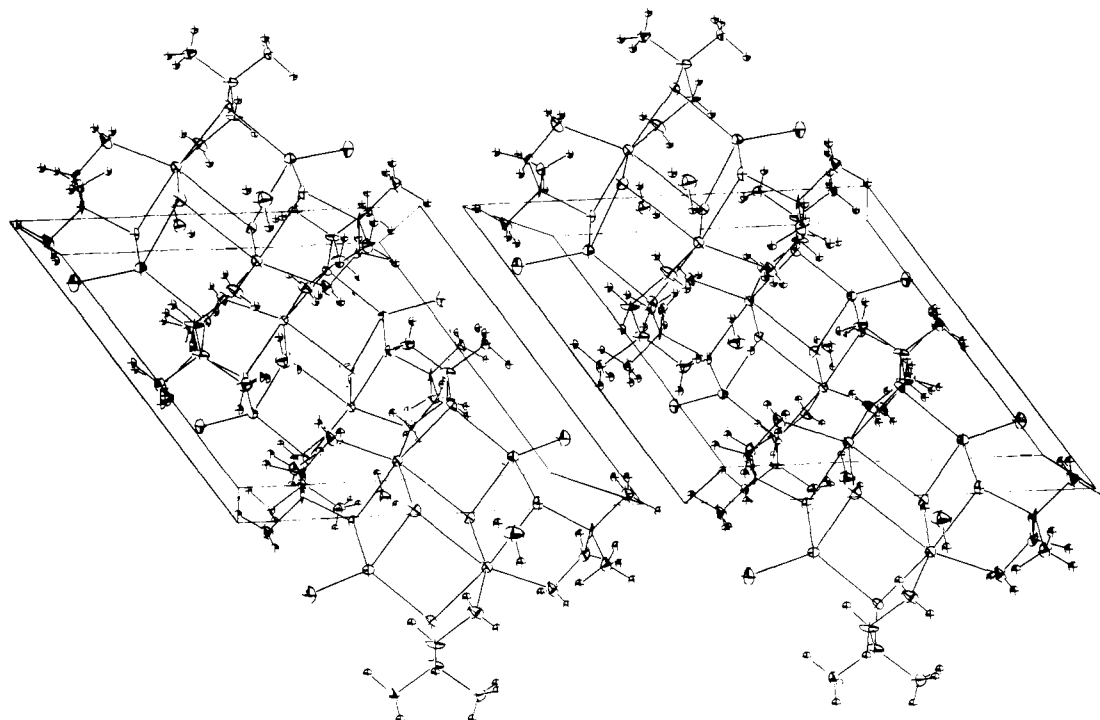


Figure 2. Stereoscopic view of the unit cell contents along b . The c axis is horizontal.

Table III. Interatomic Distances (Å) and Angles (deg) for $(\text{Cd}[\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_2\text{CdCl}_2 \cdot 2\text{H}_2\text{O})$

Distances			
Cd(1)···Cd(2)	3.648 (3)	S(1)–C(1)	1.89 (2)
Cd(1)···Cd(2')	3.672 (2)	N(1)–C(4)	1.49 (2)
Cd(1)···Cd(1')	4.537 (4)	C(1)–C(2)	1.56 (3)
Cd(2)···Cd(2')	5.745 (5)	C(1)–C(3)	1.53 (2)
Cl(1)···Cl(1')	3.76 (1)	C(1)–C(4)	1.53 (3)
Cd(1)–Cl(1)	2.946 (6)		
Cd(1)–Cl(1')	2.946 (5)	S(2)–C(5)	1.84 (2)
Cd(1)–S(1)	2.558 (4)	N(2)–C(8)	1.46 (2)
Cd(1)–S(2')	2.558 (4)	C(5)–C(6)	1.56 (2)
Cd(1)–N(1)	2.36 (2)	C(5)–C(7)	1.50 (3)
Cd(1)–N(2')	2.35 (2)	C(5)–C(8)	1.54 (3)
Cd(2)–Cl(1)	2.660 (4)		
Cd(2)–Cl(2)	2.413 (6)		
Cd(2)–S(1)	2.520 (6)		
Cd(2)–S(2)	2.506 (5)		
Angles			
S(1)–Cd(1)–S(2')	172.3 (2)	Cd(1')–S(2)–C(5)	96.3 (4)
S(1)–Cd(1)–Cl(1)	89.3 (1)	Cd(2)–S(2)–C(5)	107.7 (6)
S(1)–Cd(1)–Cl(1')	86.1 (1)	S(2)–C(5)–C(6)	107.6 (13)
S(1)–Cd(1)–N(1)	80.9 (4)	S(2)–C(5)–C(7)	108.8 (15)
S(1)–Cd(1)–N(2')	104.0 (3)	S(2)–C(5)–C(8)	110.3 (14)
Cl(1)–Cd(1)–Cl(1')	79.3 (2)	C(6)–C(5)–C(7)	109.6 (15)
Cl(1)–Cd(1)–N(1)	85.0 (5)	C(6)–C(5)–C(8)	109.2 (15)
Cl(1)–Cd(1)–N(2')	160.8 (3)	C(7)–C(5)–C(8)	111.2 (14)
Cl(1')–Cd(1)–N(2')	87.8 (4)	C(5)–C(8)–N(2)	113.2 (17)
Cl(1')–Cd(1)–S(2')	88.5 (1)	C(8)–N(2)–Cd(1')	111.1 (14)
N(1)–Cd(1)–S(2')	102.8 (3)	Cd(1)–S(1)–C(1)	96.0 (5)
N(2')–Cd(1)–S(2')	89.9 (2)	Cd(2)–S(1)–C(1)	106.8 (7)
N(2')–Cd(1)–N(1)	110.2 (7)	S(1)–C(1)–C(2)	107.2 (14)
N(1)–Cd(1)–Cl(1')	159.7 (5)	S(1)–C(1)–C(3)	107.6 (14)
Cl(2)–Cd(2)–Cl(1)	103.6 (2)	S(1)–C(1)–C(4)	111.0 (11)
Cl(2)–Cd(2)–S(1)	119.1 (2)	C(2)–C(1)–C(3)	108.7 (14)
Cl(2)–Cd(2)–S(2)	120.4 (2)	C(2)–C(1)–C(4)	113.4 (19)
S(1)–Cd(2)–S(2)	113.2 (2)	C(3)–C(1)–C(4)	108.8 (17)
S(1)–Cd(2)–Cl(1)	97.0 (2)	C(1)–C(4)–N(1)	111.5 (18)
S(2)–Cd(2)–Cl(1)	96.3 (1)	C(4)–N(1)–Cd(1)	113.3 (12)
		Cd(1)–S(1)–Cd(2)	91.8 (1)
		Cd(1')–S(2)–Cd(2)	93.0 (2)
		Cd(1')–Cl(1)–Cd(1)	100.7 (2)

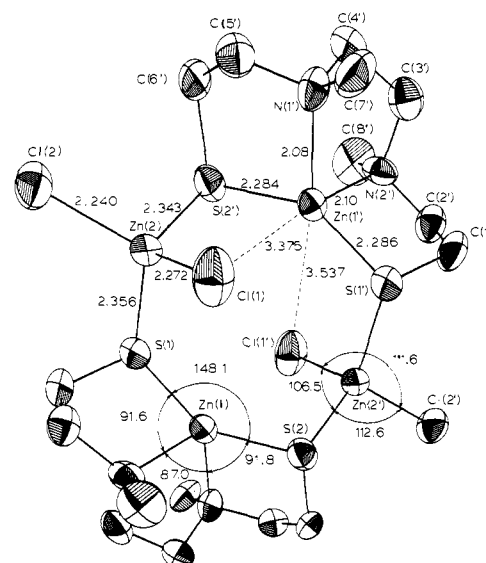


Figure 3. View of the tetrameric zinc cluster, $(\text{Zn}\{\text{CH}_2\text{NH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{S}\}_2\text{ZnCl}_2 \cdot 2\text{H}_2\text{O})$, showing the atom numbering scheme and selected bond distances and angles.

$\text{Cd}(\text{II})$ analogue are grossly dissimilar. Further, bond angles within the $\text{Zn}(2)\text{S}_2\text{Cl}_2$ units fall within the range 106.5 – 112.6° and show only small deviations from the tetrahedral angle. Corresponding angles in the $\text{Cd}(2)\text{S}_2\text{Cl}_2$ units (96 – 120°) suggest considerably more distortion. This additional distortion in the Cd complex may, in part, be related to the bridging chloride ions $\text{Cl}(1)$ which appear to form weak bonds with $\text{Cd}(1)$.

In further contrast to the title complex, the $\text{Zn}(1)$ atoms are four coordinate and exhibit no obvious bonding interactions with the Cl atoms in the center of the cluster. As evidenced by the large $\text{S}(1)\text{--Zn}(1)\text{--S}(2)$ angle (148.1°), the $\text{Zn}(1)$ coordination polyhedron has an open face which, in principle, could accommodate $\text{Zn}(1)\text{--Cl}$ bonding. That such additional

Table IV. Possible Hydrogen Bonding Contacts

Donor (D)	Hydrogen (H)	Acceptor (A)	D-H...A	D...A	H...A	D-H
N	H2(N1)	Cl(1)(i) ^a	160	3.38 (2)	2.60	0.81
N	H1(N2)	O(1)(i)	160	3.11 (3)	2.29	0.85
N	H1(N1)	O(1)(ii)	137	3.20 (2)	2.51	0.86
O	H1(O1)	N(1)(ii)	110	3.20 (2)	2.76	0.92

$$^a i = x, -1/2 - y, 1/2 + z; ii = -1 - x, \bar{y}, \bar{z}.$$

bonding does not occur may be attributed to steric restraint imposed by the tetradentate ligand. For example, in order for the Zn(1) atoms to accommodate a full S₂N₂Cl₂ ligand set, the N(1)-Zn(1)-N(2) angle presumably must increase from the observed value of 87.0° to about the value of 110.2° found for the N(1)-Cd(1)-N(2') angle in the Cd(1)Cl₂S₂N₂ unit. Relaxation of this restraint by cleavage of the C(3)-C(4) ethylene bridge might allow the coordination polyhedron of Zn(1) to increase. However, the restraint against formation of Zn(1)Cl₂S₂N₂ coordination may include strain within the cluster as well. Although localized ligand strain of the above type is absent in the Cd(II) cluster and bonding between the Cd(1) atoms and Cl atoms has become stronger, the Cd(1)-Cl bond lengths nevertheless are ~0.2 Å longer than normal (vide supra). Presumably, a full Cd(1)-Cl bonding interaction has been prevented by residual strain within the cluster structure.

Packing of the Zn tetramers is mediated by hydrogen bonding between the lattice water molecule and Cl(2) atoms of adjacent clusters. As noted above, the hydrogen bonding network in the title complex is different; this difference probably arises because the tetradentate ligand in the zinc complex has no N-H bonds. As evidenced by their respective cell volumes (1588.0 and 1643.5 Å³), the Zn and Cd clusters are about the same size.

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Supplementary Material Available: Table of least-squares planes and structure factor table (8 pages). Ordering information is given on any current masthead page.

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