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Carbon–Sulfur Bond Cleavage in Bis(*N*-alkyldithiocarbamato)cadmium(II) Complexes: Heterolytic Desulfurization Coupled to Topochemical Proton Transfer

Laura H. van Poppel, Thomas L. Groy, and M. Tyler Caudle*

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

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Three bis(*N*-alkyldithiocarbamato)cadmium(II) complexes $[Cd(S_2CNHR)_2]$ (**1**, R = *n*-C_3H_7; **2**, R = *n*-C_5H_{11}; **3**, *n*-$C_{12}H_{25}$) were prepared by metathesis of the corresponding lithium salt, $Li[S_2CNHR]$, with cadmium chloride. The crystal structures of **2** and **3** consist of planar molecular units of $[Cd(S_2CNHR)_2]$ connected by intermolecular Cd···S interactions to give a one-dimensional chain. The chains are connected by a network of intermolecular N–H···S hydrogen bonds between the dithiocarbamato nitrogen atom and bridging sulfur atoms in neighboring chains. In solution, the ^{113}Cd NMR spectrum of **2** is dependent on concentration and temperature, indicative of a dimerization equilibrium mediated by similar Cd···S intermolecular bridging interactions. In the solid state, thermal gravimetric analyses show that all three complexes decompose smoothly via a heterolytic C–S bond cleavage reaction to give the corresponding alkyl isothiocyanate and cadmium sulfide as the primary products, with the formation of primary amine and CS_2 as coproducts. These products can result only from the net transfer of protons between *N*-alkyldithiocarbamato ligands in the solid state. Thus, the C–S bond cleavage reaction is interpreted in terms of the topochemical arrangement of molecular units in the crystalline state, which provides a pathway for proton transfer between ligands via N–H···S hydrogen bonds. Decomposition was also initiated by addition of a tertiary amine to a solution of $[Cd(S_2CNHR)_2]$. This confirms that C–S bond cleavage must be coupled to deprotonation of the –NH group, and explains why dialkylated derivatives $[Cd(S_2CNR_2)_2]$ are inert to this particular mode of C–S bond cleavage. This system thus constitutes an unusual example of heterolytic, nonoxidative C–S bond cleavage that appears to proceed by a topochemical transfer of protons, which has implications for C–S bond cleavage processes in single-source precursors for II–VI semiconductor materials.

Introduction

A considerable body of literature exists on the preparation and structure of *N*,*N*-dialkyldithiocarbamato complexes of cadmium(II) and zinc(II) ions.[1,2] These compounds are air and moisture stable and sufficiently volatile that they readily sublime. Recently, these properties have been exploited to prepare II–VI semiconductor materials using *N*,*N*-dialkyldithiocarbamato complexes as single-source precursors. Thermolytic desulfurization of dialkyldithiocarbamato complexes of cadmium and zinc has become a method of choice for the synthesis of metal sulfide semiconductor materials by chemical vapor deposition.[3] In addition, nanoparticulate clusters of group 12 sulfides are prepared by thermolysis of $[M(S_2CNR_2)_2]$ precursors in high-boiling solvents.[4] Thermal

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* To whom correspondence should be addressed. E-mail: tcaudle@asu.edu.

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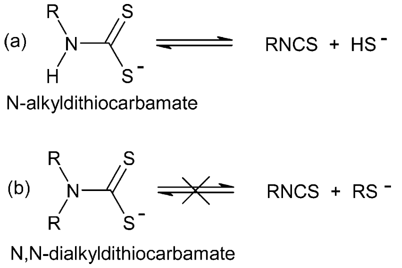
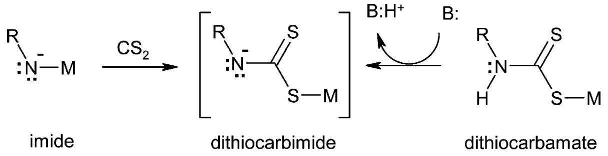
Scheme 1



Scheme 2



Scheme 3

$$MX_2 + 4\,R_2NH + CS_2 \longrightarrow M(S_2CNR_2)_2 + 2\,[R_2NH_2^+][X^-]$$

decomposition of *N*,*N*-dialkyldithiocarbamato complexes probably proceeds via free-radical decomposition of the dialkyldithiocarbamato ligand since elimination of sulfide also requires concomitant elimination of an alkyl group. Free radical decomposition is consistent with the formation of disulfide products from the thermal decomposition of *N*,*N*-dialkyldithiocarbamato complexes.[5] The C−S bond of *N*,*N*-dialkyldithiocarbamato anions can also be cleaved by oxidative addition to trivalent group 5 metal ions,[6] but this would appear to be unrelated to their thermolytic cleavage in the presence of redox-inert group 12 ions.

Given this extensive body of literature on *N*,*N*-dialkyldithiocarbamato complexes of Cd^{2+} and Zn^{2+}, it is surprising to find a substantial void concerning *N*-alkyldithiocarbamato complexes of group 12 ions. In fact, only one example of a structurally or chemically characterized *N*-alkyldithiocarbamato derivative of cadmium(II) could be located.[7] This may arise in part from the fact that such complexes are predicted to be considerably less volatile, and thus not suitable as single-source CVD precursors. However, it may also arise from different chemical reactivity of the *N*-alkyldithiocarbamato species, which makes them less stable than their *N*,*N*-dialkylated counterparts. The *N*-alkyldithiocarbamato anion is formally the product of condensation between HS^- and an alkylisothiocyanate, Scheme 1a. The presence of a dissociable proton suggests that *N*-alkyldithiocarbamato ligands might eliminate sulfide via heterolytic desulfurization, which should yield the corresponding isothiocyanate. This is not the case for *N*,*N*-dialkyldithiocarbamato derivatives, Scheme 1b, since this would require a chemically unlikely heterolytic cleavage of an $N-C_{alkyl}$ bond. There is chemical precedent for heterolytic C−S bond breaking in the desulfurization of CS_2 observed when CS_2 is reacted with imido complexes of zirconium(IV).[8] This reaction proceeds via an *N*-alkyldithiocarbimide intermediate, which is also formed by deprotonation of an *N*-alkyldithiocarbamato ligand, Scheme 2.

Group 12 *N*,*N*-dialkyldithiocarbamato complexes can be prepared by the direct reaction of a metal salt with CS_2 in the presence of a secondary amine, Scheme 3.[9] However, our attempts to prepare *N*-alkyldithiocarbamatocadmium(II) complexes by substituting a primary amine in Scheme 3 resulted instead in apparent desulfurization of CS_2 at room temperature. As the expected product was bis(*N*-alkyldithiocarbamato)cadmium(II), this led to the hypothesis that desulfurization occurs from an *N*-alkyldithiocarbamato ligand, and that the C−S bond is activated by deprotonation of the −NH group. This contrasts with the behavior of *N*,*N*-dialkyldithiocarbamatocadmium(II) derivatives which cannot form the dithiocarbimide intermediate and thus show no evidence for carbon−sulfur bond cleavage under the same conditions.

In this paper we describe the synthesis, solid state structure, and solution structure of a new class of bis(*N*-alkyldithiocarbamato)cadmium(II) complexes and show that they decompose via heterolytic desulfurization of the dithiocarbamato ligand under relatively mild conditions. Decomposition generates readily identifiable products by solid state thermolysis and base-initiated decomposition at room temperature, which both occur via a common heterolytic C−S activation process involving abstraction of the −NH proton of the *N*-alkyldithiocarbamato ligand. This reaction thus provides considerable new insight into nonoxidative C−S bond cleavage reactions and their use as a source of sulfide for the synthesis of important metal sulfide materials.

Experimental Section

n-Pentylamine ($C_5H_{11}NH_2$) and dodecylamine ($C_{12}H_{25}NH_2$) were acquired from Aldrich and used without further purification. *n*-Propylamine ($C_3H_7NH_2$) was acquired from Aldrich and distilled from CaH_2 prior to use. $CdCl_2$ was dried overnight at 120 °C to remove any water present and then stored under N_2. Phenyllithium was obtained from Acros Organics and stored under N_2. Proton and ^{13}C NMR spectra were measured on a Varian Gemini 300 MHz spectrometer. ^{113}Cd NMR was measured on a Varian Inova 400 MHz spectrometer. Samples for infrared spectrometry were prepared as a KBr pellet, and FTIR spectra were collected on a Nicolet Avatar 360 FTIR spectrometer. TG/DTA thermal analyses were performed on a Setaram TG 92 instrument. Residual gas analysis was measured using a Stanford Research Systems RGA 200 mass spectrometer. Powder X-ray diffraction data were acquired using Rigaku D/MAX-

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II diffractometer. Compositional analyses were run in the in-house facility at the ASU Center for Solid State Science.

Li[S_2CNHR] (R = C_3H_7, C_5H_{11}, $C_{12}H_{25}$). In a typical preparation, 0.58 mL (7.1 mmol) of *n*-propylamine was carefully reacted with 1 equiv of phenyllithium in anhydrous tetrahydrofuran under an atmosphere of nitrogen. After stirring for 1 h, 0.43 mL (7.1 mmol) of carbon disulfide was carefully added to this solution. The reaction was stirred for 6 h, and then, the solvent was removed in vacuo. The residue was washed with dichloromethane, producing 0.92 g (92%) of a flocculant white powder that gave characterization data consistent with Li[$S_2CNHC_3H_7$]. Li[$S_2CNHC_5H_{11}$] (yield: 64%) and Li[$S_2CNHC_{12}H_{25}$] (yield: 82%) were prepared by similar procedure.

Li[$S_2CNHC_3H_7$]. ^{1}H NMR (ppm, DMSO-d_6): 7.89 [1H, br s, N*H*], 3.27 [2H, m, *J*(H−H) = 7 Hz, NC*H*], 1.43 [2H, m, *J*(H−H) = 7 Hz, β-C*H*], 0.79 [3H, t, *J*(H−H) = 7 Hz, CH_3]. IR (cm^{-1}, KBr): 3251 (s), 2962 (m), 2918 (s), 2847 (s), 1510 (s), 1437 (m), 1159 (w), 1061 (w), 946 (s), 869 (m). Anal. Found (Calcd) %: C, 34.2 (34.1); H, 5.6 (5.7); N, 9.8 (9.9); S, 45.3 (45.4).

Li[$S_2CNHC_5H_{11}$]. ^{1}H NMR (ppm, DMSO-d_6): 7.85 [1H, m, N*H*], 3.31 [2H, m, NC*H*], 1.42 [2H, m, *J*(H−H) = 7 Hz, β-C*H*], 1.22 (4H, m, CH_2), 0.85 [3H, t, *J*(H−H) = 7 Hz, CH_3]. IR (cm^{-1}, KBr): 3251 (s), 2956 (m), 2923 (s), 2858 (s), 1503 (s), 1470 (m), 1383 (m), 1350 (m), 1301 (w), 1142 (w), 1061 (w), 946 (s), 673 (m). Anal. Found (Calcd) %: C, 49.5 (49.6); H, 7.3 (7.1); N, 8.2 (8.3); S, 37.7 (37.9).

Li[$S_2CNHC_{12}H_{25}$]. ^{1}H NMR (ppm, DMSO-d_6): δ 7.86 [1H, m, N*H*], 3.32 [2H, m, NC*H*], 1.41 [2H, m, β-C*H*], 1.23 [18H, br s, CH_2], 0.84 [3H, t, CH_3]. IR (cm^{-1}, KBr): 3251 (s), 2962 (m), 2918 (s), 2850 (s), 1508 (s), 1470 (m), 1394 (m), 1361 (m), 1301 (w), 1110 (w), 1061 (w), 946 (s), 667 (m). Anal. Found (Calcd) %: C, 53.6 (53.8); H, 10.0 (10.1); N, 5.1 (5.2); S, 23.8 (23.9).

[Cd($S_2CNHC_3H_7$)$_2$] (1). A solution of 0.12 g (0.86 mmol) of Li[$S_2CNHC_3H_7$] in 10 mL of distilled water was combined with a solution of 0.08 g (0.43 mmol) of anhydrous $CdCl_2$ in 10 mL of distilled water to produce a white precipitate. This precipitate was recrystallized from a THF/toluene solution yielding 0.12 g (75%) of **1** as colorless crystals. Mp (decomposition): 130−133 °C. ^{1}H NMR (ppm, DMSO-d_6): 9.86 [1H, t, N*H*], 3.24 [2H, m, *J*(H−H) = 5 Hz, NC*H*], 1.51 [2H, m, *J*(H−H) = 7 Hz, β-C*H*], 0.84 [3H, t, *J*(H−H) = 7 Hz, CH_3]. ^{13}C NMR (ppm, DMSO-d_6): δ 11.26, CH_3; 21.12, CH_2CH_3; 51.67, CH_2NH. IR (cm^{-1}, KBr): 3213 (s), 3016 (m), 2962 (m), 2923 (m), 2880 (m), 1530 (s), 1459 (w), 1400 (m), 1395 (m), 1295 (m), 1153 (w), 1066 (w), 965 (m), 891 (w), 667 (m), 563 (w). Anal. Found (Calcd)% for Cd($S_2CNHC_3H_7$)$_2$: C, 25.1 (25.2); H, 4.2 (4.2); N, 7.4 (7.4); S, 33.7 (33.7).

[Cd($S_2CNHC_5H_{11}$)$_2$] (2). A solution of 0.24 g (1.42 mmol) of Li[$S_2CNHC_5H_{11}$] in 10 mL of distilled water was combined with a solution of 0.13 g (0.71 mmol) of anhydrous $CdCl_2$ in 10 mL of distilled water producing a pale yellow precipitate. This precipitate was recrystallized from a THF/CH_3CN solution yielding 0.27 g (84%) of **2** as colorless crystals. Mp (decomposition): 140−143 °C. ^{1}H NMR (ppm, DMSO-d_6): 9.88 [1H, t, *J*(H−H) = 6 Hz, N*H*], 3.26 [2H, m, *J*(H−H) = 6 Hz, NC*H*], 1.51 [2H, m, *J*(H−H) = 7 Hz, β-C*H*], 1.26 (4H, m, CH_2), 0.86 [3H, t, *J*(H−H) = 7 Hz, CH_3]. ^{13}C NMR(ppm, DMSO-d_6): δ 13.79, CH_3; 21.72, CH_2CH_3; 27.38, CH_2; 28.42, CH_2; 49.88, CH_2NH. IR (cm^{-1}, KBr): 3198 (s), 3008 (m), 2995 (s), 2922 (s), 2850 (s), 1529 (s), 1464 (m), 1418 (s), 1339 (m), 1306 (m), 1240 (w), 1142 (w), 1063 (m), 945 (s), 728 (w), 662 (s), 557 (w). Anal. Found (Calcd)% for Cd($S_2CNHC_5H_{11}$)$_2$: C, 32.5 (32.9); H, 5.3 (5.5); N, 6.0 (6.4); S, 29.0 (29.4).

Table 1. Summary of Single Crystal X-ray Diffraction Data for Compound **2**

formula	$C_{12}H_{24}CdN_2S_4$
fw	436.97
cryst syst	orthorhombic
space group	$Pca2_1$
color	colorless
a (Å)	14.6353(7)
b (Å)	4.1454(2)
c (Å)	30.3184(15)
V (Å^3)	1839.39(15)
Z	4
temp (K)	300
λ (Å)	0.71073
measured reflns	12098
indep reflns	3189
obsd reflns	3037 ($\lvert F_o \rvert > 4.0\sigma \lvert F_o \rvert$)
R	0.0640
R_w	0.1557
GOF	1.198
x^{23}	0.46(8)

[Cd($S_2CNHC_{12}H_{25}$)$_2$] (3). A solution of 0.26 g (0.96 mmol) of Li[$S_2CNHC_{12}H_{25}$] in 10 mL of THF was combined with a solution of 0.090 g (0.48 mmol) of anhydrous $CdCl_2$ in 10 mL of THF, producing a white precipitate. The solvent was reduced to yield more white precipitate. Both batches of precipitate were combined and recrystallized from a THF/toluene solution yielding 0.25 g (81%) of **3** as colorless crystals. Mp (decomposition): 135−138 °C. ^{1}H NMR (ppm, DMSO-d_6): 9.88 [1H, t, N*H*], 3.24 [2H, m, *J*(H−H) = 6.5 Hz, NC*H*], 1.51 [2H, m, β-C*H*], 1.23 (18H, m, CH_2), 0.86 [3H, t, *J*(H−H) = 6.5 Hz, CH_3]. ^{13}C NMR (ppm, DMSO-d_6): δ 14.42, CH_3; 22.56, CH_2CH_3; 26.83, CH_2; 28.28, CH_2; 29.18, CH_2; 29.47, 3C, CH_2; 29.51, 3C, CH_2; 31.75, CH_2; 49.93, CH_2NH; 206.64, CS_2. IR (cm^{-1}, KBr): 3207 (s), 3011 (w), 2956 (m), 2918 (s), 2847 (m), 1530 (s), 1470 (m), 1399 (m), 1339 (m), 1312 (m), 940 (m), 722 (m), 673 (m). Anal. Found (Calcd) % for [Cd($S_2CNHC_{12}H_{25}$)$_2$]: C, 49.3 (49.3); H, 8.2 (8.2); N,4.4 (4.4); S, 20.2 (20.3).

Single-Crystal Diffraction Studies. Single crystals of **2** and **3** were coated with mineral oil and mounted on the tip of a glass fiber. Single-crystal diffraction data were collected at ambient temperature on a Bruker SMART APEX system using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. SHELXS-97 and SHELXL-97 were used for structure solution and refinement. Refinement of F^2 data was against all reflections. The weighted *R* and goodness-of-fit are based on F^2, and conventional *R* factors are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ was used only for calculating *R* factors and is not relevant to the choice of reflections for refinement. The data set for compound **2** refined to a suitable *R*-value, and pertinent details of its data collection and refinement are provided in Table 1. Compound **3** did not yield an anisotropic refinement of publishable *R*-value, but the isotropic refinement was of sufficient quality to establish atom connectivity and packing.

Results Section

The metathesis reaction between a lithium *N*-alkyldithiocarbamato salt and cadmium chloride in neutral aqueous solution cleanly produces bis(*N*-alkyldithiocarbamato)cadmium(II) complexes **1**−**3** in good yield and purity. By contrast, condensation of the primary amine with carbon disulfide in the presence of cadmium chloride gave negligible yields of [Cd(S_2CNHR)$_2$]. Instead, the latter reaction yields cadmium sulfide in essentially quantitative yield based on

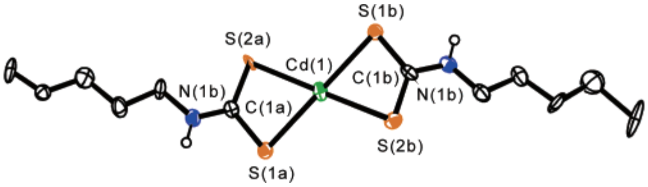

Figure 1. Molecular structure of **2** (50% probability ellipsoids). Important bond lengths (Å): Cd−S(1a), 2.674(2); Cd−S(2a), 2.592(3); Cd−S(1b), 2.672(2); Cd−S(2b), 2.648(3); C(1a)−S(1a), 1.770(10); C(1a)−S(2a), 1.698(9); C(1b)−S(1b), 1.749(10); C(1b)−S(2b), 1.686(9); C(1a)−N(1a), 1.302(12); C(1b)−N(1b), 1.308(12). Important bond angles (deg): S(1a)−Cd−S(2a), 69.19(8); S(1b)−Cd−S(2b), 68.73(7); S(1a)−Cd−S(2b), 111.38(8); S(2a)−Cd−S(1b), 110.70(8); S(1a)−C(1a)−S(2a), 119.1(5); S(1b)−C(1b)−S(2b), 121.9(5).

$CdCl_2$. The sulfide anion must arise from CS_2, and so this reaction corresponds to net desulfurization of carbon disulfide. Preparative control experiments using diethylamine under identical conditions instead gives quantitative yields of $Cd[S_2CNEt_2]_2$, the most well-known of the bis(*N*,*N*-dialkyldithiocarbamato)cadmium(II) complexes. The results from preparative experiments therefore establish either a clear difference between the reactivity of primary and secondary amines with CS_2, or a difference between the reactivity of *N*-alkyldithiocarbamato and *N*,*N*-dialkyldithiocarbamato ligands coordinated to Cd^{2+}. Since stable *N*-alkyl- and *N*,*N*-dialkyldithiocarbamatolithium salts are easily prepared by reaction of CS_2 with primary lithium amides, this would indicate that the difference lies in the comparative chemistry of $[Cd(S_2CNHR)_2]$ and $[Cd(S_2CNR_2)_2]$.

Compounds **1**−**3** all form colorless, very thin platelike crystals that are flaky and difficult to mount for X-ray studies, but otherwise stable to air and moisture. The small aspect ratio of the crystals of **2** is a result of the orthorhombic crystal system with a unit cell of dimensions $14.6 \times 4.1 \times 30.0$ Å^3 for **2**, Table 1.[10] The molecular structure of **2**, Figure 1, consists of a rhombic planar cadmium ion that results from chelation by two *N*-*n*-pentyldithiocarbamato ligands. The two large S−Cd−S angles are 111°, and the two smaller S−Cd−S angles are 69°. The four sulfur atoms reside in a perfect plane as shown by the fact that the in-plane angles add to exactly 360°. The in-plane Cd−S bond lengths are typical of dithiocarbamato complexes.[11,12] There are three long Cd−S bonds averaging 2.66 Å, and one that is somewhat shorter at 2.59 Å. The reason for this distortion is not obvious. However, the space group $Pca2_1$ lacks inversion symmetry, so the Cd^{2+} ion cannot lie on an inversion center, and this may allow one Cd−S distance to deviate. The dithiocarbamato group is in a planar configuration, which is favored by delocalization of the lone pair from the nitrogen atom into the $-CS_2$ unit. In the solid state, the alkyl groups on **2** are disposed in a *trans* configuration with respect to each other. However, this likely arises from packing phenomena since there would appear to be no obvious stability gained in the *trans* configuration relative to the *cis* configuration.

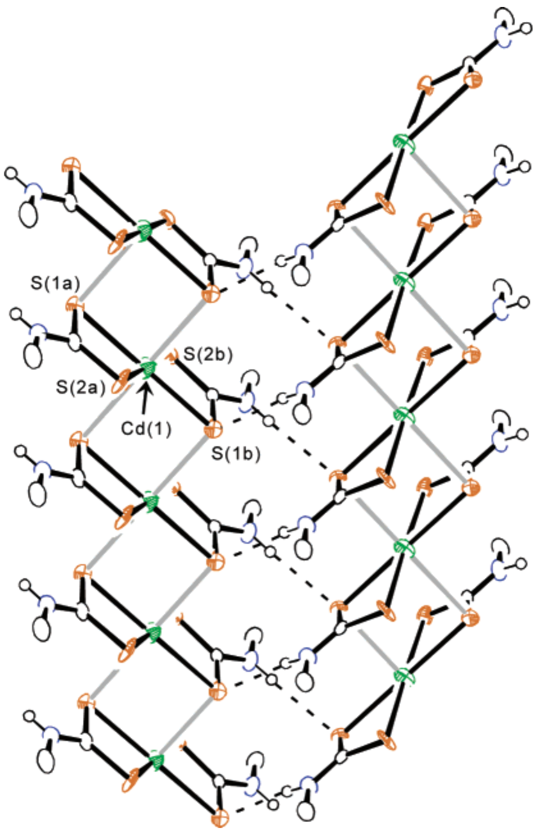

Figure 2. Intermolecular interactions in **2**. *n*-Pentyl groups have been truncated for clarity. Cadmium (green), sulfur (orange), nitrogen (blue), carbon (white). Shaded lines indicate intermolecular Cd···S interactions. Cd···S = 2.93 Å, Cd···Cd = 4.14 Å. Dashed lines indicate intermolecular N−H···S hydrogen bonding interactions. N···S distance = 3.43 Å.

In the crystalline solid state, complex **2** forms a one-dimensional polymer via intermolecular Cd···S interactions orthogonal to the intramolecular CdS_4 plane, Figure 2. This gives an infinite linear chain of $[Cd(S_2CNHC_5H_{11})_2]$ molecules canted such that the cadmium ion of one molecular unit is situated directly above a sulfur of the previous unit.

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(10) The atoms C(5a), C(6a), C(5b), and C(6b) were refined isotropically, since all four atoms became nonpositive definite when refined anisotropically. The anomolous thermal behavior in these atoms arises from the presence of two enantiomorphs cocrystallizing in an acentric space group $Pca2_1$, which made it difficult to accurately model empirical absorption corrections for the irregular crystal dimensions. The large ratio of predicted to reported transmission factors, $(T_{max}/T_{min})_{exp}/(T_{max}/T_{min})_{rep} = 1.42$, is also a result of the difficulty in determining absorption corrections for these crystal dimensions. A TWIN refinement gave a Flack parameter $x = 0.46(8)$, indicating that the crystal is composed of 54(8)% of the molecule as illustrated and 46(8)% of the inverted form.

(11) Glinskaya, L. A.; Zemskova, S. M.; Klevtsova, R. F. *Zh. Strukt. Khim.* **2000**, *40*, 979−983. Zemskova, S. M.; Glinskaya, L. A.; Klevtsova, R. F.; Fedotov, M. A.; Larionov, S. V. *Zh. Strukt. Khim.* **1999**, *40*, 284−292. Cox, M. J.; Tiekink, E. R. T. *Z. Kristallogr.* **1999**, *214*, 670−676. Jian, F.; Wang, Z.; Bai, Z.; You, X.; Fun, H.-K.; Chinnakali, K. *J. Chem. Crystallogr.* **1999**, *29*, 227−231. Jian, F.-F.; Wang, Z.-X.; Fun, H.-K.; Bai, Z.-P.; You, X.-Z. *Acta Crystallogr., Sect. C* **1999**, *C55*, 174−176. O'Brien, P.; Walsh, J. R.; Watson, I. M.; Motevalli, M.; Henriksen, L. *J. Chem. Soc., Dalton Trans.* **1996**, 2491−2496. Baggio, R.; Garland, M. T.; Perec, M. *Acta Crystallogr., Sect. C* **1996**, *C52*, 823−826. Glinskaya, L. A.; Zemskova, S. M.; Klevtsova, R. F.; Larionov, S. V.; Gromilov, S. A. *Polyhedron* **1992**, *11*, 2951−2956. Casas, J. S.; Sanchez, A.; Bravo, J.; Garcia-Fontan, S.; Castellano, E. E.; Jones, M. M. *Inorg. Chim. Acta* **1989**, *158*, 119−126. Agre, V. M.; Shugam, E. A. *Kristallogr.* **1972**, *17*, 303−308. Agre, V. M.; Shugam, E. A.; Rukhadze, E. G. *Zh. Strukt. Khim.* **1966**, *7*, 897−898. Malissa, H.; Kolbe-Rohde, H. *Talanta* **1961**, *8*, 841−845. Albano, V.; Domenicano, A.; Vaciago, A. *Gazz. Chim. Ital.* **1966**, *96*, 922−934.

(12) Dee, C. M.; Tiekink, E. R. T. *Z. Kristallogr.* **2002**, *217*, 85−86.

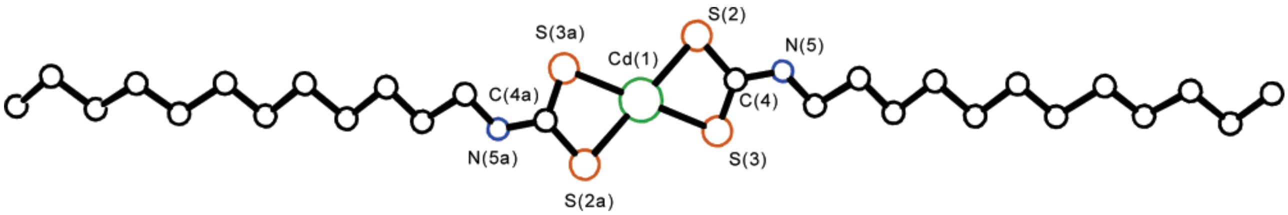
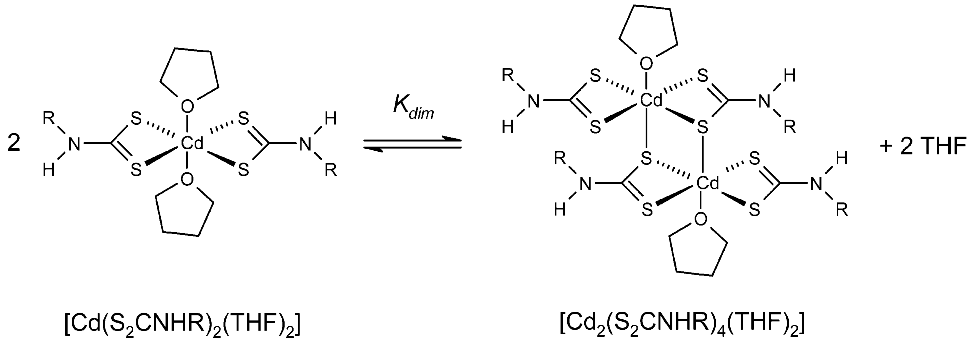


Figure 3. PLUTO diagram of **3** derived from isotropic refinement of X-ray diffraction data.

Scheme 4



This results in a nominal six-coordinate environment of sulfur atoms around each cadmium ion with two long axial Cd···S interactions at 2.93 Å. Packing diagrams of **2** also reveal the existence of close contacts between the sulfur atom of one molecule and a carbamato nitrogen atom of a neighboring molecule, Figure 2. The N···S distance for these interactions is about 3.4 Å. This value is within the range of N−H···S hydrogen bonding interactions, which typically have N···S distances between 3.3 and 3.6 Å.[13] These hydrogen bonding interactions serve two functions in the solid state structure of **2**. First, they connect one stack to another and thereby support the formation of the three-dimensional crystal structure. Second, the CdS_4 planes in one stack are oriented normal to the CdS_4 planes in the neighboring stack. In this way, each molecule of $[Cd(S_2CNHR)_2]$ is hydrogen bonded to two different molecules of $[Cd(S_2CNHR)_2]$ in the neighboring stack. The result is that each molecule of $[Cd(S_2CNHR)_2]$ is joined to one above it by two Cd···S interactions and two N−H···S hydrogen bonds. These important structural features of **2** appear to be general for this class of compounds. Compound **3** consists of a molecular unit similar to that of **2**, Figure 3, and was solved in a similarly flattened $P2_1/c$ unit cell. Compound **3** also exhibits an identical network of intermolecular Cd···S and N−H···S interactions as **2**, although the crystalline structure of **3** is slightly different from **2** in regards to the disposition of the *N*-alkyl groups.

The presence of hydrogen bonding to the −NH group is also supported by infrared spectroscopy. The infrared spectra of **1**−**3** give a single sharp absorption peak near 3206 cm^{-1} that is assigned to an N−H stretching mode. The N−H stretching vibration occurs 45 cm^{-1} toward higher energy (3251 cm^{-1}) in the corresponding *N*-alkyldithiocarbamatolithium salts. The decreased N−H frequency observed in the cadmium complexes supports the hypothesis that the N−H···S interaction arises from a weak hydrogen bond. The dithiocarbamato group in **1**−**3** also gives an asymmetric NCS_2 stretching frequency at 1530 cm^{-1}, but the lithium dithiocarbamate salts, $Li[S_2CNHR]$, give stretching frequencies at 23 cm^{-1} lower in energy at 1507 cm^{-1}. This would seem to suggest that the average C−S bond order increases upon coordination to the cadmium ion. However, shifts in the vibrational energies of the dithiocarbamato group may also be influenced by the extensive intermolecular contacts in the solid state.

The polymeric solid state structure of **1**−**3** is consistent with the general observation that the compounds are highly insoluble in noncoordinating solvents but are soluble in coordinating solvents such as tetrahydrofuran. At low concentrations in THF, the complexes exhibit a single ^{113}Cd NMR signal at approximately 270 ppm versus external aqueous cadmium sulfate ($\delta = 5$ ppm). This signal arises from the solvated molecular unit $[Cd(S_2CNHR)_2(THF)_2]$. However, the chemical shift is dependent on the concentration of the complex, Figure 4, which we interpret to arise from dimerization of the molecular unit, Scheme 4. The probable structure of the dimer, involving intermolecular Cd···S interactions, is consistent with the dimeric structure of bis(diethyldithiocarbamato)cadmium(II),[2,12] and with the polymeric structure of **2** and **3** in the solid state. The concentration dependence results from a rapid chemical exchange rate between the monomer and dimer so that the ^{113}Cd chemical shift is a concentration-weighted average of the chemical shifts of the monomer and dimer. As the concentration of the cadmium *N*-alkyldithiocarbamate complex is increased, the ^{113}Cd NMR signal shifts downfield, suggesting that the Cd nucleus becomes less shielded upon dimerization. The observation that the dimer resonates downfield of the monomer implies considerable ionic

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(13) Lynch, D. E.; McClenaghan, I.; Light, M. E.; Coles, S. J. *Cryst. Eng.* **2002**, *5*, 79−94. Lynch, D. E.; McClenaghan, I. *Acta Crystallogr., Sect. E* **2001**, *57*, 26−27. Lynch, D. E.; McClenaghan, I. *Acta Crystallogr., Sect. E* **2001**, *57*, 11−12. Lynch, D. E.; McClenaghan, I. *Acta Crystallogr., Sect. C* **2000**, *56*, 587. Lynch, D. E.; McClenaghan, I. *Acta Crystallogr., Sect. C* **2003**, *59*, 53−56.

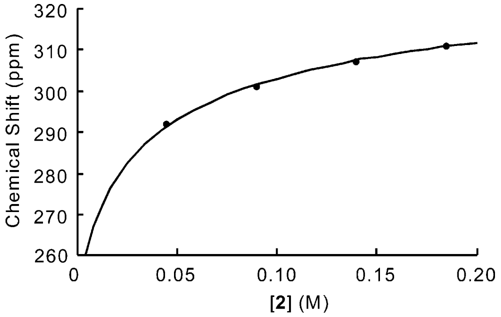

Figure 4. ^{113}Cd NMR shift for **2** dissolved in THF as a function of the concentration of **2**. Chemical shift is referenced against an internal capillary containing 3 M $CdSO_4$ in D_2O ($\delta = 5$ ppm). Solid line is a fit of eq 1 to the data with $K = 2500$ M.

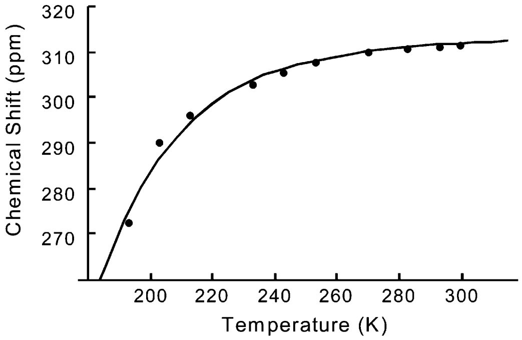

Figure 5. ^{113}Cd NMR shift for **2** dissolved in THF as a function of temperature. Chemical shift is referenced against an internal capillary containing 3 M $CdSO_4$ in D_2O ($\delta = 5$ ppm). [**2**] = 0.185 M. Solid line is a fit to eq 2 to with $\Delta H° = 28(2)$ kJ/mol and $\Delta S° = 160(8)$ J/mol.

character to the intermolecular Cd···S interaction and would be consistent with the long intermolecular Cd···S bond observed in the X-ray structure. The binding isotherm relating observed chemical shift, δ, to the total concentration of **2**, a_0, is given in eq 1.[14] It gives an acceptable fit to the data in Figure 4, yielding an estimate for $K_{dim} = 2500$ M, where $K_{dim} = [\text{dimer}][\text{THF}]^2/[\text{monomer}]^2$, and $\delta_{monomer}$ and δ_{dimer} are the chemical shifts of the monomer and dimer, respectively.

$$\delta = \left(1 - \frac{1 + \frac{4a_0K_{dim}}{[\text{THF}]^2} - \sqrt{1 + \frac{8a_0K_{dim}}{[\text{THF}]^2}}}{\frac{4a_0K_{dim}}{[\text{THF}]^2}}\right)\delta_{monomer} + \left(\frac{1 + \frac{4a_0K_{dim}}{[\text{THF}]^2} - \sqrt{1 + \frac{8a_0K_{dim}}{[\text{THF}]^2}}}{\frac{4a_0K_{dim}}{[\text{THF}]^2}}\right)\delta_{dimer} \quad (1)$$

The ^{113}Cd chemical shift is also dependent on the absolute temperature, as shown in Figure 5. As the temperature is lowered from ambient to 190 K, the ^{113}Cd NMR signal moves upfield, which means that the dimerization equilibrium is shifted toward the left as the temperature is decreased. Inserting the Gibbs free energy expression $-RT \ln K_{dim} = \Delta H° - T\Delta S°$ into eq 1 gives the temperature dependence of the chemical shift in terms of the standard enthalpy and entropy of dimerization, eq 2.[14] Fitting this expression to the data in Figure 5 gives $\Delta H° = 28(2)$ kJ/mol and $\Delta S° = 160(8)$ J/mol·K. The unfavorable enthalpy for dimerization means that the Cd−O_{THF} interaction is stronger than the Cd···S interaction, although this is almost entirely offset by a favorable entropy term at 298 K. This suggests that the entropy associated with liberation of solvent molecules provides a substantial contribution to the free energy of dimerization in solution.

$$\delta = \left(1 - \frac{1 + \frac{4a_0}{[\text{THF}]^2}e^{[(\Delta S°/R)-(\Delta H°/RT)]} - \sqrt{1 + \frac{8a_0}{[\text{THF}]^2}e^{[(\Delta S°/R)-(\Delta H°/RT)]}}}{\frac{4a_0}{[\text{THF}]^2}e^{[(\Delta S°/R)-(\Delta H°/RT)]}}\right)\delta_{monomer} + \left(\frac{1 + \frac{4a_0}{[\text{THF}]^2}e^{[(\Delta S°/R)-(\Delta H°/RT)]} - \sqrt{1 + \frac{8a_0}{[\text{THF}]^2}e^{[(\Delta S°/R)-(\Delta H°/RT)]}}}{\frac{4a_0}{[\text{THF}]^2}e^{[(\Delta S°/R)-(\Delta H°/RT)]}}\right)\delta_{dimer} \quad (2)$$

Upon heating to 500 °C, all three compounds give a yellow residue whose X-ray powder diffraction pattern is consistent with cadmium sulfide. Heating the complexes to 195 °C for 1 h in sealed tubes permitted collection of the volatile thermolysis products. GC/mass spectra of these products showed the presence of the alkyl isothiocyanate[15] in which the alkyl group was derived from the dithiocarbamato ligand. Residual gas analysis shows that CS_2 is also eliminated, which implies elimination of the primary amine as well. The NMR spectrum of the involatile products shows broad peaks consistent with amine that is probably coordinated with the solid CdS under constant volume conditions of the sealed tube experiments. However, these data do not permit us to entirely rule out the presence of some corresponding *N,N′*-dialkylthiourea in the involatile products. Symmetric *N,N′*-disubstituted ureas and thioureas are formed in thermal decompositions of certain *N*-alkyl- or *N*-arylcarbamato compounds,[16] but these have been shown to be secondary products arising from condensation of an alkyl isothiocyanate and amine, which are the primary products. Furthermore, symmetric *N,N′*-dialkylureas and *N,N′*-dialkylthioureas reversibly dissociate under thermal conditions to give alkyl isocyanates or alkyl isothiocyanates.[16] Therefore, we conclude that the alkyl isothiocyanate and corresponding amine

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(14) Derivation of this equation is deposited in Supporting Information.

(15) Table is deposited in Supporting Information.

(16) Daly, N. J.; Ziolkowski, F. *Int. J. Chem. Kinet.* **1980**, *12*, 241−252. Drozdov, N. S. *Zh. Obshch. Khim.* **1936**, *6*, 1368−1374.

represent primary products of the thermal decomposition of [Cd($S_2CNHR)_2$], although we do not preclude the possibility that a fraction may be condensed as an involatile *N*,*N*′-dialkylthiourea under the applied thermolysis conditions.

Thermolysis of **1** under constant pressure conditions occurs in a single resolvable step at 140−200 °C, Figure 6a, leaving 38(1)% of the original mass, as expected for stoichiometric formation CdS from **1**. Compound **2** shows two resolvable thermal steps in the TGA and DTA profiles, and these occur at 110−150 and 180−240 °C, Figure 6b. If the temperature of the sample is poised at 110 °C for 30 min, a thermally stable material is formed corresponding to 62(2)% of the original mass. The IR and proton NMR spectra of this material show that the only residual organic material consists of unreacted dithiocarbamato ligand. This intermediate must therefore correspond to a material of composition $CdS_n(S_2CNHR)_{2(1-n)}$, where $n = 0.56$. This indicates that, under constant pressure conditions of the TGA experiment, all neutral organic species are volatilized. Heating this same sample to 500 °C reproducibly gives a new material containing 39(2)% of the initial mass, giving $n = 0.91$. For complete decomposition to CdS, $n = 1$, so this final material corresponds to decomposition of 91% of the original dithiocarbamato ligand in **2**. Heating compound **3** from 15 to 500 °C gives two weight loss steps occurring at 115−150 and 200−300 °C. These are each associated with unique DTA endotherms. A third DTA endotherm occurs at 110°C but is not associated with any loss in weight and probably corresponds to a solid−solid phase change. We ascribe the stepwise weight loss in Figure 6c to initial decomposition of a fraction of the *N*-dodecyldithiocarbamato ligand, giving a thermally stable intermediate consisting of 85(3)% of the original mass, so that $n = 0.19$. This intermediate showed only the *N*-dodecyldithiocarbamato ligand by IR and proton NMR spectroscopy. Heating this sample to 500 °C gives a final material with 26(2)% of the original mass, giving $n = 0.93$. This indicates that the product stabilizes after decomposition of 93% of the dithiocarbamato ligand. The thermolysis data for **1**−**3** are summarized in Table 2.

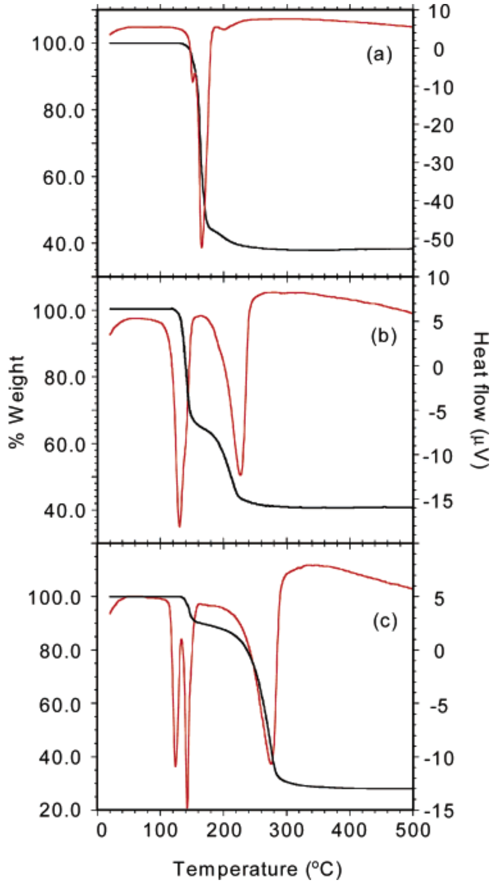

Figure 6. Thermal gravimetric profiles (black) and differential thermal analysis profiles (red) for decomposition of **1** (a), **2** (b), and **3** (c) under N_2, $T = 15-500$ °C, 10 °C/min.

Table 2. Thermolysis Data for **1**−**3**

compd	thermolysis temp (°C)	% wt[a]	n	nominal composition[b]
1	140−200	38(1)[c]	1	CdS
2	110−150	62(2)[d]	0.56	$Cd_5S_3(S_2CNHC_5H_{11})_4$
	180−240	39(2)[c]	0.91	$Cd_{10}S_9(S_2CNHC_5H_{11})_2$
3	115−150	85(3)[e]	0.19	$Cd_5S(S_2CNHC_{12}H_{25})_8$
	200−300	26(2)[c]	0.93	$Cd_{10}S_9(S_2CNHC_5H_{11})_2$

[a] For remaining solid residue. [b] Smallest stoichiometric unit. [c] After heating to 500 °C. [d] After poising temperature at 110 °C for 30 min. [e] After poising temperature at 115 °C for 30 min.

The products formed in the thermal studies require that C−S bond activation be coupled to proton transfer. However, it is not obvious from solid state thermolysis experiments whether −NH proton transfer is required to initiate C−S bond cleavage or whether it occurs after C−S bond cleavage. To address this question, we examined the reaction of **1**−**3** with a Brønsted base in solution. Figure 7a shows the proton NMR spectrum of **2** in DMSO-d_6, which exhibits a splitting pattern for the α-CH_2 protons at 3.26 ppm (M) that is consistent with coupling to the β-CH_2 protons at 1.51 ppm (X) and the −NH proton at 9.88 ppm (A, not shown). Simulation of the α-CH_2 signal using a first-order AM_2X_2 coupling scheme gives $J_{MA} = 5.5$ Hz and $J_{MX} = 7.5$ Hz. This split α-CH_2 signal is characteristic of the *N*-alkyldithiocarbamato ligand in all three complexes we studied. When triethylamine is added to the solution of **2**, we observe slow precipitation of cadmium sulfide, indicating that C−S bond cleavage has occurred. In the proton NMR spectrum, the signal at 3.26 ppm is decreased, and it is replaced by a new triplet signal centered at 3.64 ppm, Figure 7b. This change is associated with a decrease in intensity of the −NH signal at 9.88 ppm (not shown), and concomitant loss of the J_{MA} coupling to the α-CH_2 protons. These changes indicate formation of *n*-pentylisothiocyanate in situ. This was confirmed by a solution infrared spectrum of the product, which exhibits the strong isothiocyanate band at 2100 cm^{-1}. There is no evidence from IR or NMR spectroscopy for formation of the corresponding *N*,*N*′-dialkylthiourea. Control experiments show that reaction of $C_5H_{11}NH_2$ with $C_5H_{11}NCS$ in DMSO-d_6 does give *N*,*N*′-di-*n*-pentylthiourea. Furthermore, even upon complete decomposition, approximately half of the original *N*-alkyldithiocarbamato ligand remains intact. These observations indicate that primary amine is not eliminated in the solution decomposition reaction, suggesting that the second equivalent of dithiocarbamato anion is a spectator ligand that is not decomposed in the base-catalyzed

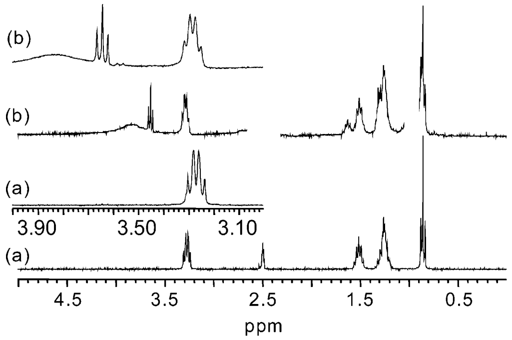

Figure 7. (a) 300 MHz proton NMR spectrum (DMSO-d_6) of **2**. The expanded inset shows the methylene region. (b) Spectrum of a sample of **2** after addition of excess triethylamine and aging for 1 h. The expanded inset shows changes in the methylene region. The excised portions at 0.9 and 2.5 ppm are where the triethylamine protons resonate.

reaction. This was demonstrated by adding triethylamine to a solution containing Li[S_2CNHR] and $CdCl_2$ in a 1:1 ratio, which results in decomposition of all of the $RHNCS_2^-$ ligand and precipitation of [Et_3NH^+][Cl^-]. This experiment shows that only 1 equiv of the dithiocarbamato complex is desulfurized to isothiocyanate for every CdS produced, and that inert spectator anions can substitute for the second equivalent of dithiocarbamato ligand. While the fate of the organic products is different for the thermal and base-initiated decomposition reactions, both reactions are consistent with a chemical mechanism whereby reversible proton transfer precedes irreversible C−S bond breaking. In both cases, proton transfer is a critical element for the activation of the C−S bond in this system.

Discussion Section

The most pertinent features in the structure of bis(*N*-alkyldithiocarbamato)cadmium(II) complexes **1**−**3** are the intermolecular Cd···S and N−H···S interactions. The Cd···S interaction is reminiscent of that observed in dimeric bis(*N*,*N*-dialkyldithiocarbamato)cadmium(II) complexes,[2,12] although the geometry about cadmium is distorted square pyramidal in the latter cases. Each [Cd(S_2CNHR)$_2$] molecular unit in the crystal is bridged to two others in the same chain by Cd···S interactions, and any two adjacent molecular units in the same chain are bridged to each other by N−H···S hydrogen bonding interactions with molecular units in the neighboring chain. These weak but complementary individual interactions result in a stronger net intermolecular interaction than is possible when the −NH proton is substituted by another alkyl group. Although N−H···S hydrogen bonds are considerably weaker than corresponding N−H···O hydrogen bonds, their ability to support a polymeric structure in the solid state structure does suggest some practical significance in crystal engineering.[13] Hydrogen bonds to metal-coordinated sulfur atoms are also commonly observed in sulfur metalloproteins such as rubredoxins[17] and ferrodoxins,[18] although the preorganization afforded by the protein's secondary and tertiary structures probably provides much of the stability for these interactions.

The coordination geometry about the bridging sulfur atoms is highly distorted from that predicted on the basis of valence bond approximations. Figure 2 shows that the intermolecular Cd(1)···S(1a) vector is very nearly perpendicular to the CdS_4 plane, as shown by the C(1a)−S(1a)···Cd(1) and Cd(1)−S(1b)···Cd(1) angles of 96° and 95°, respectively. As a result, the Cd···S interaction must have a minimal contribution from the filled sp^2 orbital on sulfur, which is in the CdS_4 plane, and must occur primarily via one of the delocalized π-type ligand orbitals orthogonal to the CdS_4 plane. This has the effect of polarizing the electron density toward the bridging sulfur atom, S(1a) or S(1b), and thereby decreasing the C−$S_{bridging}$ bond order. This is consistent with the longer C(1a)−S(1a) and C(1b)−S(1b) distances (1.76 Å) compared with the nonbridging C(1a)−S(2a) and C(1b)−S(2b) distances (1.68 Å). The hydrogen bonding occurs to the bridging sulfur atoms S(1a) and S(1b) and has an N−H···S vector that is almost perpendicular to the CdS_4 plane. This means that the hydrogen bonding must also involve the delocalized π-orbitals of the ligand and probably contributes also to the longer C−$S_{bridging}$ bond distance. These compounds therefore fit generally with the trend showing that noncovalent interactions to sulfur tend to have a more orthogonal geometry than corresponding interactions with oxygen atoms.[19]

The intermolecular interactions observed in **2** and **3**, and their apparent impact on the C−S bond order, suggest a connection between the specific topochemical arrangement observed in the crystal and the type of decomposition we observe in neat **1**−**3**. The thermal decomposition reaction requires proton transfer from one dithiocarbamato ligand to another. The network of N−H···S hydrogen bonds suggests a potential pathway for proton transfer between dithiocarbamato ligands. This idea is supported by the observation that decomposition can be initiated directly in the solid state at modest temperatures, so that it must involve a minimum of molecular rearrangement. Such a reaction will be favored by a preorganized and concerted proton transfer pathway directed along the N−H···S vector. The intermolecular Cd···S interactions may also assist in the activation of the C−$S_{bridging}$ bond by decreasing the bond order as described above. Scheme 5 shows a proposed mechanism for the initial decomposition steps in **1**−**3** that is consistent with our experimental evidence. Interactions between one [Cd(S_2CNHR)$_2$] unit and the neighboring stack are shown in gray. Concerted proton transfer along this particular hydrogen bonding pathway forms a tautomeric dithiocarbimido intermediate **X**, which undergoes spontaneous C−S bond breaking to give the alkyl isothiocyanate and the intermediate **Y**. Compound **Y** rearranges to **Z** via either intermolecular or

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[17] Bougault, C. M.; Eidsness, M. K.; Prestegard, J. H. *Biochemistry* **2003**, *42*, 4357−4372. Sieker, L. C.; Holmes, M.; Le Trong, I.; Turley, S.; Liu, M. Y.; LeGall, J.; Stenkamp, R. E. *J. Biol. Inorg. Chem.* **2000**, *5*, 505−513. Dauter, Z.; Wilson, K. S.; Sieker, L. C.; Moulis, J.-M.; Meyer, J. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8836−8840.

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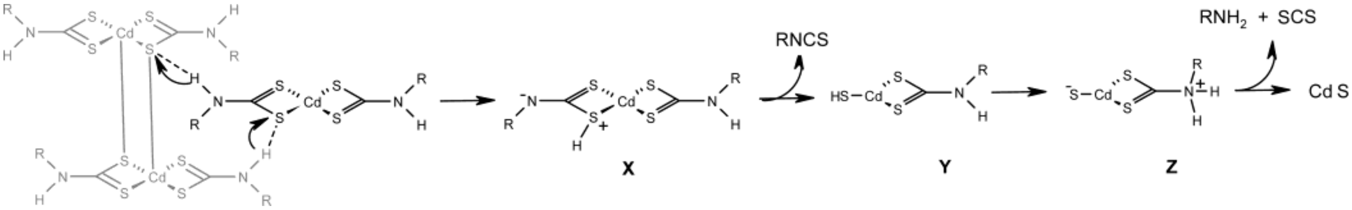
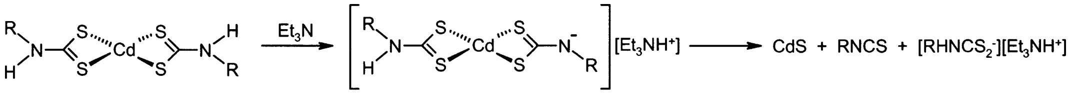
[19] Platts, J. A.; Howard, S. T.; Bracke, B. R. F. *J. Am. Chem. Soc.* **1996**, *118*, 2726−2733.

Scheme 5



Scheme 6



intramolecular proton transfer. This gives the zwitterionic $RNH_2^+CS_2^-$ species that rapidly cleaves the $N-CS_2$ bond to eliminate CS_2 and RNH_2.[20] It is important that protonation of the *N*-alkyldithiocarbamato ligand leads to irreversible $N-CS_2$ cleavage since this minimizes the problem of N···H recombination and resulting unproductive proton transfer. The large lattice energy of CdS also provides a considerable thermodynamic driving force for the overall reaction, and is consistent with prior reports on the use of thiophilic metal ions as desulfurizing agents for thiocarbamates.[21]

Decomposition is initiated for **1**−**3** in a narrow temperature range between 110 and 140 °C. However, complete decomposition of **2** and **3** requires higher temperatures than for **1**, Table 2. This may be reflective of the difficulty of accomplishing intramolecular proton transfer in the later stages of the decomposition process, where the long-range hydrogen bond network is broken down. This is apt to be more problematic for the bulkier dithiocarbamato ligands, and so explains why **1** decomposes quantitatively to CdS by 280 °C whereas **2** and **3** show residual ligand even at 500 °C.

In solution, triethylamine probably serves to deprotonate an *N*-alkyldithiocarbamato ligand to give the dithiocarbimido complex, Scheme 6, which is followed by C−S bond cleavage to give the alkyl isothiocyanate, CdS, and unreacted carbamato salt. This scheme is supported by previous work showing that group 10 *N*-alkylcarbamato complexes are deprotonated by strong bases,[22] although they are not reported to undergo subsequent C−S bond cleavage in solution. The C−S bond cleavage step is most reminiscent of the pathway taken upon insertion of CS_2 into group 4 metal amide bonds, which also result in C−S bond cleavage of a putative dithiocarbimido intermediate.[8] Scheme 6 explains why direct condensation of a primary amine, CS_2, and $CdCl_2$ does not give $[Cd(S_2CNHR)_2]$ complexes. Any *N*-alkyldithiocarbamatocadmium(II) complexes that do initially form are deprotonated by unreacted primary amine, culminating in irreversible cleavage of the C−S bond. Although it is not clear whether intermolecular interactions play a role in the decomposition reaction in solution, formation of Cd···S adducts in solution, inferred from the ^{113}Cd NMR experiments, suggests that those interactions may provide a degree of C−S bond activation. Such interactions may also assist in Cd−S bond formation and nucleation of cadmium sulfide.

This desulfurization reaction gives consistent stoichiometric yields of products specific to heterolytic C−S bond cleavage, suggesting no competing homolytic or oxidative pathways. Furthermore, identical products are obtained upon thermolysis or base-initiated cleavage in nitrogen or in air, where oxygen would be expected to scavenge free radical intermediates and yield oxygenated products. The reaction thus appears to be distinct from reports on thermolysis of *N*,*N*-dialkyldithiocarbamato complexes of other redox-inert metal ions,[5] and from the oxidative addition of the C−S bond observed in some redox-active species.[6] This work suggests that *N*-alkyldithiocarbamato complexes have potential as precursors for the preparation of metal sulfide materials, and have a number of advantages over *N*,*N*-dialkyldithiocarbamato complexes that are presently employed. We have shown that the *N*-alkyldithiocarbamatocadmium(II) complexes decompose according to a well-defined chemical process to yield characterized products under moderate conditions. Furthermore, the decomposition can be initiated chemically by addition of base, and can thereby be controlled in ways that the thermolysis of *N*,*N*-dialkyldithiocarbamato complexes cannot. The topochemical aspects of this system are also related to the general problem of chemical reactivity in condensed phases or on surfaces, where the static molecular orientation is important to chemical reactivity. As a result, the chemical mechanism for this unusual heterolytic C−S bond cleavage reaction is of considerable interest, and is the subject of our continuing work in this area.

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Supporting Information Available: Crystallographic data files for **2** (CIF format) and **3** (TXT format), derivation of eqs 1 and 2, and table of mass spectrometry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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