

# Solid-State $^{13}\text{C}$ NMR Determination of Methyltin(IV) Structure. Crystal and Molecular Structure of Dimethyltin(IV) Bis(1-pyrrolidinecarbodithiate)

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**Abstract:** Solid-state  $^{13}\text{C}$  NMR and X-ray crystallographic studies of the title compound,  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ , are reported. The magnitude of  $^1J(^{119}\text{Sn},^{13}\text{C})$ ,  $|^1J|$ , measured for a polycrystalline sample, is 705 Hz. When a previously described relationship between  $|^1J|$  and the Me-Sn-Me angle was used, an angle of  $138.6^\circ$  was predicted for the molecule. The discrepancy between this result and the published X-ray structure [Me-Sn-Me angle =  $130(2)^\circ$ ] led to a redetermination of the crystal structure by X-ray. Solution of the structure of the orthorhombic crystals in the *Pmnm* space group yielded a chemically reasonable structure ( $R = 0.029$ ,  $R_w = 0.038$ ) in which the pyrrolidine carbons C3 and C4 are disordered across the mirror plane at  $y = 1/4$ . Similar to other dimethyltin(IV) bis(dithiocarbamates),  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  adopts a distorted octahedral geometry: the Me-Sn-Me angle is  $137.3(3)^\circ$ , and the dithiocarbamate ligands are coplanar with tin but adopt an anisobidentate coordination geometry (Sn-S = 2.518, 2.938 Å). The presence of two mirror planes results in a simple solid-state  $^{13}\text{C}$  NMR spectrum. In contrast to the accurate NMR-derived prediction, published Mössbauer data led to a predicted Me-Sn-Me angle ( $123.5^\circ$ )  $14^\circ$  in error.

X-ray crystallography enjoys the position of being the most accurate method of determining molecular structure in the crystalline state, and it has profoundly influenced our understanding of molecular structure and bonding. Structural data determined for a crystalline solid generally influence considerations of its molecular structure in other environments, as well, because of the general lack of methods capable of providing comparably detailed structural information for compounds in other phases. Few other methods are sufficiently sensitive to structural features to be capable even of questioning X-ray-determined structures. Consequently, X-ray structures are generally accepted as correct unless challenged by a new X-ray structure determination or a re-solution of the original diffraction data set.<sup>2</sup>

Recently, we have explored<sup>3,4</sup> the possibility that by studying structurally characterized substrates by solid-state NMR, new, accurate relationships between NMR and structural parameters might be discovered. Examination<sup>4</sup> of numerous X-ray characterized methyltin(IV) compounds by solid-state  $^{13}\text{C}$  NMR has revealed that the magnitude of the tin-carbon  $J$  coupling,  $|^1J(^{119}\text{Sn},^{13}\text{C})|$  ( $|^1J|$ ), is linearly related to the size of the Me-Sn-Me bond angle. The close adherence of the  $|^1J|/\text{angle}$  data to the empirical line suggested that the relationship may provide a new, quantitative method for estimating Me-Sn-Me angles of methyltin(IV)'s in the solid-state. Because  $|^1J|$  can also be measured in solution NMR spectra, it may provide a means of accurately determining methyltin(IV) molecular structures in solution, as well.<sup>3,5</sup>

In this study, we report solid-state NMR data for the title compound,  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ . Conflict between the structure predicted from the NMR data and that in a published<sup>6</sup> X-ray diffraction study has led us to redetermine the x-ray structure of the molecule; the accuracy of the NMR relationship is strongly supported by the results. The structural analysis using solid-state NMR is compared to that using the widely employed  $^{119}\text{mSn}$  Mössbauer spectroscopy.

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(2) Jones, P. G. *Chem. Soc. Rev.* **1984**, 13, 157.

(3) Manders, W. F.; Lockhart, T. P. *J. Organomet. Chem.*, in the press.

(4) Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1985**, 107, 4546.

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(6) (a) Malik, K. M. A.; Lindley, P. F.; Jeffery, J. W. *J. Bangladesh Acad. Sci.* **1981**, 5, 53. (b) Original citation: Lindley, P. F.; Carr, P. *J. Cryst. Mol. Struct.* **1974**, 4, 173.

**Table I.** Summary of Crystallographic Data for Dimethyltin Bis(1-pyrrolidinecarbodithiate)<sup>a</sup>

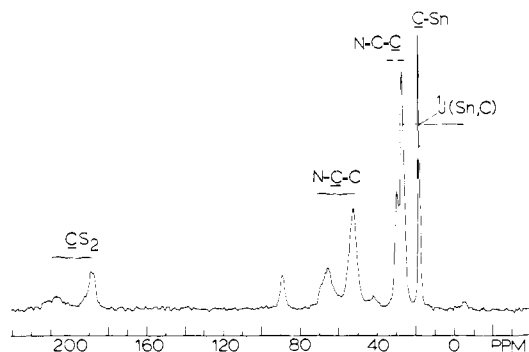
<i>a</i> , Å	17.493 (3)	scan method	$\theta - 2\theta$ step
<i>b</i> , Å	7.920 (2)	scan range ( $\theta$ )	$0.75 + 0.35 \tan \theta$
<i>c</i> , Å	6.632 (2)	scan time	to achieve 3% counting statistics (120 s max)
<i>v</i> , Å <sup>3</sup>	918.8 (4)		
formula	$\text{SnS}_4\text{N}_2\text{C}_{12}\text{H}_{22}$	$2\theta$ range, deg	4-50
fw	441.3	<i>hkl</i> range	<i>hkl</i> and <i>hkl</i>
$D_x$ , g/cm <sup>3</sup>	1.595 (3)	$\mu$ , cm <sup>-1</sup>	18.2
<i>Z</i>	2	absorption correction method	empirical ( $\psi$ scan)
crystal dimensions, mm	$0.45 \times 0.34 \times 0.35$	rel transmission range	88-99%
space group	<i>Pmnm</i>	ext. correction factor	$g = 2.7 \times 10^{-7}$
wavelength	Mo K $\alpha$ (0.7107 Å)	$R^b$	0.029
monochromator	graphite	$R_w^c$	0.038
no. of refl. measd	3097	goodness of fit	2.15
no. of ind. refl.	1172	max shift/error	0.03
no. of ind. refl. above $3\sigma$	983	max difference density, e/Å <sup>3</sup>	$0.5 \text{ e}/\text{Å}^3$
		$w^{-1}$	$[\sigma_{\text{counting}}^2 + (0.02F_o^2)^2]/4F_o^2$
		function minimized	$\sum w( F_o  -  F_c )^2$

<sup>a</sup> Estimated standard deviations in parentheses. <sup>b</sup>  $R = \sum ||F_o| - F_c| / \sum |F_o|$ . <sup>c</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ .

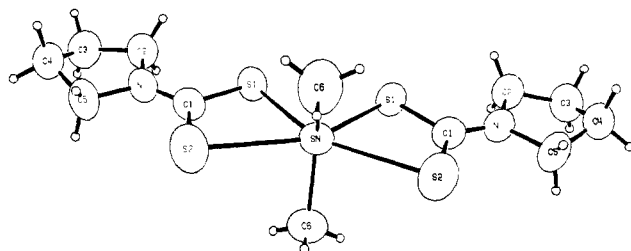
## Experimental Section

$\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  was prepared as described in the literature<sup>7</sup> except that the commercially available 1-pyrrolidinecarbodithioic acid ammonium salt,  $\text{NH}_4\text{S}_2\text{CN}(\text{CH}_2)_4$ , was used in place of the sodium salt. Large, colorless crystals (mp above 220 °C, discoloration at 210 °C) were obtained upon recrystallization from a  $\text{CHCl}_3$ /ethanol solution.

(7) Fitzsimmons, B. W.; Owusu, A. A.; Seeley, N. J.; Smith, A. W. *J. Chem. Soc. A* **1970** 935.



**Figure 1.** Solid-state  $^{13}\text{C}$  NMR spectrum of polycrystalline  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ .  $^{117,119}\text{Sn}$  satellites of  $\text{Me}_2\text{Sn}$  resonance are indicated in spectrum. Broad, unsymmetrical doublets observed for the other (pyrrolidine)  $^{13}\text{C}$ 's are due to coupling to  $^{14}\text{N}$ . Delrin, internal standard, at 89.1 ppm.



**Figure 2.** View of  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  showing atom numbering scheme. Thermal ellipsoids enclose 50% of the electron probability; hydrogen atoms were assigned a small thermal parameter.

**NMR Spectroscopy.** Magic-angle spinning, cross-polarization solid-state  $^{13}\text{C}$  NMR spectra were recorded on a homebuilt instrument at 15.08 MHz with high-power proton decoupling. Samples of polycrystalline  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  (0.4 g) were run in Andrew-type rotors with ca. 5 mg of Delrin added as the internal secondary chemical shift standard (89.1 ppm). Spectra with good signal/noise were acquired in 5–10K scans (repetition rate = 20 s). Other parameters have been described elsewhere.<sup>8</sup>

**Crystal Structure Determination and Refinement.** X-ray studies were done with an EnrafNonius CAD4 diffractometer. Details of the data collection, cell parameters, and refinement results are included in Table I. First, we undertook an independent solution of the structure, but the centric-acentric statistics were inconclusive. When Patterson and Fourier methods were used to obtain a model, refinement in the  $Pn2_1$  space group reported by Malik et al.<sup>6a</sup> led to final  $R$  and  $R_w$  factors of 0.029 and 0.036 (149 variables). The  $y$  coordinates of all dithiocarbamate non-hydrogen atoms were near 0.250. The resulting structure gave chemically unreasonable Sn–C and C–C distances (Sn–C6 = 2.07 Å, Sn–C7 = 2.15 Å, and C6–Sn–C7 = 136°). Moving into  $Pm\bar{m}n$  and averaging Friedel reflections (internal agreement = 0.025) gave  $R$  = 0.029 and  $R_w$  = 0.038 (92 variables including anisotropic thermal parameters for non-hydrogen atoms) with C3 and C4 disordered across the mirror plane at  $y = 1/4$ . Atomic scattering factors included  $f_0$ ,  $f'$ , and  $f''$  values for all atoms. This, of course, required two equally occupied sets of idealized positions (not refined) for all hydrogen atoms on the pyrrolidine ring. The resulting structure was chemically reasonable; details are shown in Tables I–III and Figure 2. Tables of anisotropic thermal parameters and  $F_0$  and  $F_c$  ( $\times 10$ ) values are available as supplementary material.

## Results

The solid-state NMR spectrum of  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  is shown in Figure 1;  $|J|$  = 705 Hz. The  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellites are not well-resolved in the solid-state spectra of  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ , so  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  was calculated from the distance separating the centers of the fused  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellites  $\times 1.023$ .<sup>9</sup>

**Table II.** Positional Parameters and Their Estimated Standard Deviations<sup>a</sup>

atom	$x$	$y$	$z$	$B(\text{Å}^2)$
Sn	0.250	0.250	0.151 62 (5)	4.688 (7)
S1	0.346 57 (5)	0.250	0.433 3 (1)	4.69 (2)
S2	0.410 13 (7)	0.250	0.018 0 (2)	7.70 (3)
N	0.493 3 (2)	0.250	0.349 2 (4)	4.77 (6)
C1	0.424 4 (2)	0.250	0.269 2 (6)	4.55 (7)
C2	0.509 4 (2)	0.250	0.565 1 (6)	5.35 (8)
C3	0.594 0 (3)	0.225 (1)	0.578 1 (9)	6.5 (1)
C4	0.625 1 (3)	0.2852 (8)	0.378 6 (9)	6.7 (2)
C5	0.563 8 (2)	0.250	0.228 8 (8)	6.4 (1)
C6	0.250	0.4985 (7)	0.036 (1)	8.1 (1)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $1/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab \cos \gamma B(1,2) + ac \cos \beta B(1,3) + bc \cos \alpha B(2,3)]$ .

**Table III.** Interatomic Distances and Bond Angles for Dimethyltin Bis(1-pyrrolidinedicarbodithiate)<sup>a</sup>

Bond Distances, Å			
Sn–S1	2.518 (1)	N–C1	1.317 (4)
Sn–S2	2.938 (1)	N–C2	1.459 (4)
Sn–C6	2.112 (4)	N–C5	1.469 (4)
S1–C1	1.743 (3)	C2–C3	1.496 (6)
S2–C1	1.685 (3)	C3–C4	1.508 (9)
		C4–C5	1.489 (6)
Bond Angles, deg			
S1–Sn–S1	84.23 (3)	C1–N–C5	123.3 (3)
S1–Sn–S2	65.43 (2)	C2–N–C5	111.8 (3)
S1–Sn–S2'	149.68 (2)	S1–C1–S2	120.1 (2)
S1–Sn–C6	105.6 (1)	S1–C1–N1	117.6 (2)
S2–Sn–S2'	144.88 (4)	S2–C1–N1	122.3 (2)
S2–Sn–C6	83.70 (4)	N–C2–C3	104.4 (3)
C6–Sn–C6	137.3 (3)	C2–C3–C4	105.4 (6)
C1–N–C2	124.9 (2)	C3–C4–C5	105.4 (4)
		N–C5–C4	104.0 (3)

<sup>a</sup> Estimated standard deviations in parentheses.

The  $^{13}\text{C}$  resonances of carbons bonded to, or one bond removed from, nitrogen are significantly broadened and unsymmetrically split owing to dipolar coupling with the  $^{14}\text{N}$  nucleus (Figure 1).<sup>10</sup>

Atomic coordinates and equivalent isotropic thermal parameters from the X-ray structure determination are given in Table II. Pertinent bond distances and angles are in Table III and the structure of  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  is illustrated in Figure 2.

## Discussion

**Description of the X-ray Structure.** Our examination and solution of the X-ray crystal structure of  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  has shown that the crystalline modification of our sample (orthorhombic) is the same as that previously studied.<sup>6</sup> The incorrect space group assignment in the earlier study coupled with the relatively poor refinement ( $R$  = 0.11) led to significant inaccuracies in that structure determination. Most notably from the perspective of the present study, our value for the Me–Sn–Me angle, 137.3 (3)°, differs significantly from the previous value, 130 (2)°.

The molecule has  $mm2$  symmetry, the methyls lying on one of the mirrors, and the dithiocarbamates on the other.<sup>11</sup> As in the other known dimethyltin(IV) bis(dithiocarbamate) structures, the octahedral coordination in  $\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$  is badly distorted: (1) The Me–Sn–Me angle, 137.3°, is intermediate between cis and trans and quite similar to those of  $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2$  (136°)<sup>12</sup> and  $\text{Me}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$  (three different crystalline modifications containing four independent molecular structures are known, Me–Sn–Me angle range 135.6–142.8°).<sup>5,13</sup>

(10) Wasylshen, R. E.; Fyfe, C. A. *Ann. Rep. NMR Spectrosc.* **1982**, *12*, 31–35 and references cited therein.

(11) This picture is complicated somewhat by the fact that the pyrrolidine carbons C3 and C4 are disordered across the mirror plane through the dithiocarbamate ligands.

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(13) Morris, J. S.; Schlemper, E. O. *J. Cryst. Mol. Struct.* **1979**, *9*, 13.

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(9) Because the natural abundances of  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  are similar (7.6% and 8.6%, respectively) the difference between the separation of the centers of the unresolved satellites and  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  is closely approximated by multiplying the separation, in hertz, by one-half the ratio of the gyromagnetic ratios of  $^{119}\text{Sn}$  and  $^{117}\text{Sn}$ .

(2) The dithiocarbamate S and C atoms are coplanar with Sn but are highly distorted from square-planar geometry (S–Sn–S angles range from 65.4° to 149.7°). Also in common with other organotin dithiocarbamates<sup>14</sup> is the pronounced asymmetry of the binding of the ligand to Sn (anisobidentate coordination); two distinctly different Sn–S interactions are indicated for each dithiocarbamate ligand in Me<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> (Sn–S distances = 2.518, 2.938 Å). Electronic<sup>12</sup> and steric<sup>6b,15</sup> arguments have been invoked to account for the distortion of diorganotin(IV) dithiocarbamates from regular octahedral geometry.

**Solid-State NMR and Mössbauer Structures.** Solid-state NMR studies<sup>4</sup> with a variety of structurally characterized methyltin(IV) compounds have shown that  $|^1J|$  is linearly related to the Me–Sn–Me angle according to eq 1 where  $|^1J|$  is the magnitude of

$$|^1J| = 11.4\theta - 875 \quad (1)$$

$^1J$  (<sup>119</sup>Sn, <sup>13</sup>C), in hertz, and  $\theta$  is the Me–Sn–Me angle, in degrees. With reference to this equation,  $|^1J|$  values measured in either solid-state or solution NMR experiments can be used to deduce the Me–Sn–Me angle of tetra-, penta- and hexacoordinated dimethyltin(IV)s.<sup>4,5</sup>

Analysis of the solid-state <sup>13</sup>C NMR spectrum of Me<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> ( $|^1J| = 705$  (10) Hz<sup>16</sup>) indicated a Me–Sn–Me angle of 138.6 (1.0)°, in significant disagreement with the angle [130 (2)°] reported in the published<sup>6</sup> X-ray diffraction study. Our subsequent X-ray analysis (vide supra) showed that the earlier structural study was in error; the Me–Sn–Me angle in the re-determined X-ray structure, 137.3 (3)°, agrees closely with that deduced from the NMR measurements. To our knowledge, *this is the first time that NMR spectroscopy has been used to correct structural (bond angle) data obtained in a modern single-crystal X-ray diffraction study.*<sup>17</sup>

Examination of the solid-state <sup>13</sup>C NMR spectra of numerous structurally characterized methyltin(IV) compounds has revealed<sup>3</sup> the sensitivity of <sup>13</sup>C chemical shifts to slight differences in magnetic environment (i.e., slight differences in distances to neighboring atoms). For this reason, in few dimethyltin(IV)'s have we observed a single resonance for the methyls bonded to tin. The narrow, single dimethyltin resonance observed for Me<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> (Figure 1) reflects the presence of a mirror plane, revealed in the X-ray analysis, through tin and the dithiocarbamate ligands, which interconverts the two methyls.

It is instructive to compare the structural analysis of methyltin(IV)'s by solid-state NMR with the routinely employed <sup>119</sup>mSn Mössbauer technique. Mössbauer isomer shift and quadrupole

splitting (QS) parameters are used to obtain information about the coordination number and bonding geometry of organotin<sup>18</sup>; the temperature dependence of the recoil-free fraction gives information about the lattice binding strength and can indicate the presence of strong intermolecular (polymeric) interactions.<sup>19</sup> The derivation<sup>20</sup> 10 years ago of an expression relating the QS of hexacoordinated dimethyltin(IV)'s to the Me–Sn–Me angle has been employed as an adjunct to X-ray diffraction for analyzing these structures.

Two features of the Mössbauer QS/angle relationship, however, call for considerable caution in its application: (1) The theoretical curve<sup>20</sup> of QS vs. the Me–Sn–Me angle flattens out at angles <100° and >160°, so the QS parameter is an unreliable indicator of Me–Sn–Me angles in these regions. (2) The experimental data used to support the correlation showed significant scatter.<sup>20</sup> Although the Mössbauer QS/angle correlation has been applied successfully in methyltin(IV) structure determinations,<sup>21</sup> the large deviations found for dimethyltin monothiophosphate esters,<sup>19b</sup> oxyphosphorus acid derivatives,<sup>22</sup> and other dimethyltin(IV)'s<sup>23</sup> emphasize the great sensitivity of the QS parameter to substituent effects. Application of the QS/angle relationship<sup>20</sup> to the Mössbauer data for Me<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> (QS = 2.85 mm s<sup>-1</sup>)<sup>7</sup> leads to a predicted Me–Sn–Me angle of only 123.5°, 14° at variance with the correct structure.

## Conclusions

The accuracy of eq 1, which relates  $|^1J|$  to the Me–Sn–Me angle of methyltin(IV)'s, has been demonstrated for Me<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>:  $|^1J|$ , measured on a crystalline sample by solid-state NMR, indicated an error in the reported X-ray structure; re-determination of the X-ray structure showed the size of the Me–Sn–Me angle to be in close agreement with the NMR estimate. By comparison, <sup>119</sup>mSn Mössbauer spectroscopy is shown to be much less accurate as an indicator of the organotin(IV) molecular structure. This result confirms the utility of using solid-state NMR to develop new NMR-structure correlations and argues strongly in favor of the wider application of solid-state NMR methods to structural problems in organotin and organometallic chemistry. By providing such accurate estimates of molecular structure, solid-state NMR can serve to screen and identify compounds, with unusual structural features meriting full X-ray crystallographic study.

**Supplementary Material Available:** Tables of anisotropic thermal factors and  $F_o$  and  $F_c$  ( $\times 10$ ) values (8 pages). Ordering information given on any current masthead page.

(14) A bibliography of methyltin structural studies is given in: Smith, P. J. *J. Organomet. Chem. Libr.* **1981**, 12, 97.

(15) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, 23, 1. Kepert, D. L. *J. Organomet. Chem.* **1976**, 107, 49. Tse, J. S.; Sham, T. K.; Bancroft, G. M. *Can. J. Chem.* **1979**, 57, 2223.

(16) In CDCl<sub>3</sub> solution,  $|^1J| = 665$  Hz corresponding to a Me–Sn–Me angle of 134° and indicates a slight change in structure relative to the solid state.

(17) An apparent inconsistency between an early film X-ray structure for 3CdSO<sub>4</sub>·8H<sub>2</sub>O [Lipson, H. *Proc. R. Soc. London, Ser. A* **1936**, 156, 462] and solid-state <sup>113</sup>Cd NMR data [Murphy, P. D.; Gerstein, B. C. *J. Am. Chem. Soc.* **1981**, 103, 3282] led to a refinement and correction of the crystal structure.

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