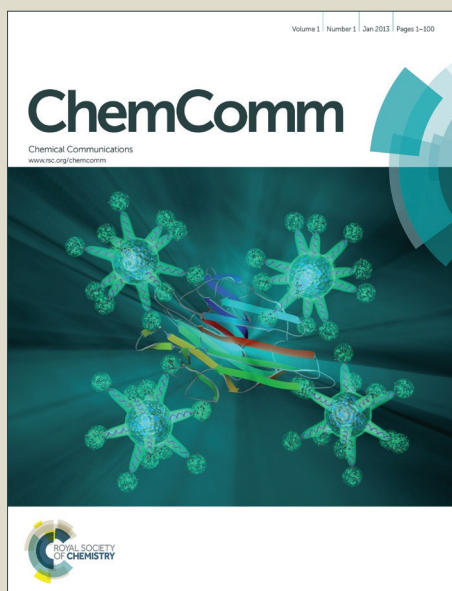


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## The solid state structures of the high and low temperature phases of dimethylcadmium

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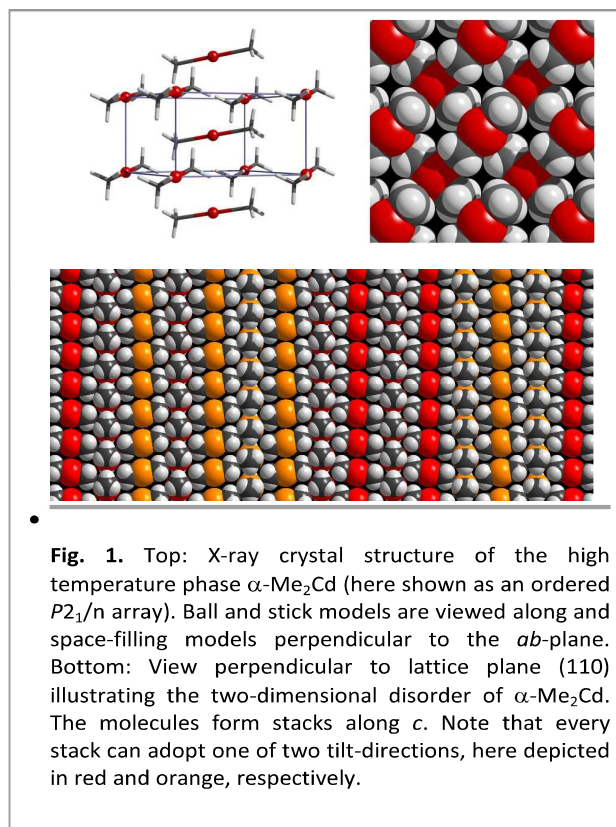
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The solid state structure of dimethylcadmium, a classic organometallic compound with a long history, has remained elusive for almost a century. X-ray crystallography and density functional theory reveal similar phase behaviour as in dimethylzinc. The high temperature tetragonal phase,  $\alpha$ -Me<sub>2</sub>Cd, exhibits two-dimensional disorder, while the low temperature monoclinic phase,  $\beta$ -Me<sub>2</sub>Cd, is ordered. Both phases contain linearly coordinated cadmium atoms. While the methyl groups are staggered in the  $\alpha$ -phase, they are eclipsed in the  $\beta$ -phase.

Dimethylcadmium is a classic organometallic compound with a long history dating back to the early 20th century.<sup>1</sup> Its high volatility makes it ideally suited for metal organic chemical vapour deposition (MOCVD) and atomic layer deposition (ALD), which produces high aspect structures with atomic level control.<sup>2</sup> It is an important precursor for II/VI semiconducting films and nanoparticles which find widespread applications in electronic and optoelectronic devices.<sup>3</sup> Layered assemblies of photovoltaic CdTe and CdS, for example, are key components of solar cells.<sup>4</sup> Here we present a combined crystallographic and computational study that elucidates the solid state structure of dimethylcadmium, which, despite its long history, has remained elusive.

Dimethylcadmium is a pyrophoric liquid at room temperature. It freezes at 250 K and, on further cooling, undergoes a solid-solid phase transition at 210 K. On heating the solid-solid phase transition reverses at 255 K and finally the substance melts at 270 K. Its solid state behaviour resembles that of Me<sub>2</sub>Zn, which undergoes a solid-solid phase transition from a disordered high-temperature  $\alpha$ -phase to an ordered low-temperature  $\beta$ -phase.<sup>5,6</sup> Single crystals of the high temperature  $\alpha$ -phase of Me<sub>2</sub>Cd were obtained on slow cooling of a liquid sample contained in a capillary. Due to the strong



**Fig. 1.** Top: X-ray crystal structure of the high temperature phase  $\alpha$ -Me<sub>2</sub>Cd (here shown as an ordered  $P2_1/n$  array). Ball and stick models are viewed along and space-filling models perpendicular to the  $ab$ -plane. Bottom: View perpendicular to lattice plane (110) illustrating the two-dimensional disorder of  $\alpha$ -Me<sub>2</sub>Cd. The molecules form stacks along  $c$ . Note that every stack can adopt one of two tilt-directions, here depicted in red and orange, respectively.

hysteresis of the phase transitions, the X-ray structure of the  $\alpha$ -phase was determined in the supercooled regime at 240 K.<sup>‡</sup> The tetragonal unit cell (spacegroup  $P4_2/mnm$ ) contains two linear molecules (Cd-C = 2.128(3) Å) which are centred at 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , and aligned parallel to lattice planes (110) and (1-10), respectively (Fig. 1). The linear molecules are tilted from the  $ab$ -plane by about 9° and are stacked upon each other in columns parallel to the  $c$ -axis.

Two-dimensional disorder can be found in collateral assemblies of ordered columnar structures.<sup>7</sup> Here it arises because the molecules can adopt one or the other tilt direction (+9° or -9°) with respect to the  $ab$ -plane. While all

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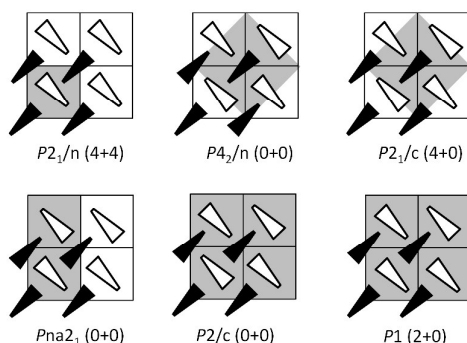
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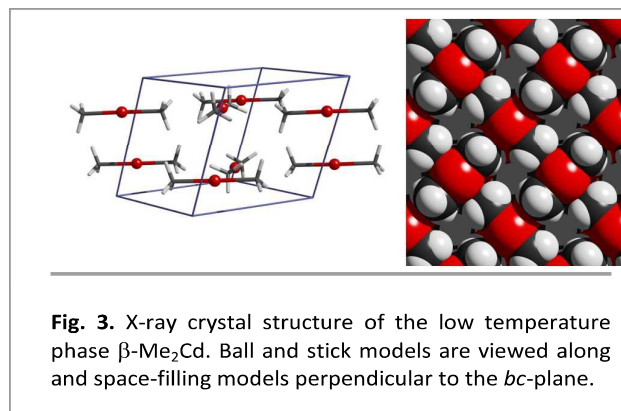
molecules of each single columnar stack exhibit the same tilt-direction resulting in one-dimensional order along  $c$ , each individual stack can display one or the other tilt direction leading to two-dimensional disorder along  $a$  and  $b$ . Diffuse scattering, which is often indicative of low-dimensional disorder, could not be detected perhaps due to the body-centred superlattice of Cd atoms, which is not affected by the disorder but dominates the reflection pattern.

A hypothetically ordered structure that contains two molecules per cell ( $Z = 2$ ) would exhibit spacegroup symmetry  $P2_1/n$ . While it was possible to refine  $\alpha$ -Me<sub>2</sub>Zn as a pseudomerohedral twin in this spacegroup,<sup>5</sup> the analogous twin refinement of  $\alpha$ -Me<sub>2</sub>Cd was hampered by the ordered superstructure of the heavier Cd atoms. To shed more light on the detailed structure including the positions of hydrogen atoms and the underlying disorder, we have carried out calculations based on density functional theory (DFT) with many-body dispersion corrections<sup>8</sup> using the CASTEP program<sup>9</sup> provided with Materials Studio.<sup>10</sup>

In order to model the disorder and assess the relative stabilities of various ordered arrays, we have performed DFT calculations for all possible arrangements of 2x2 supercells ( $2a, 2a, c$ ;  $Z = 8$ ) of  $\alpha$ -Me<sub>2</sub>Cd. Altogether there are  $2^8 = 256$  combinations of tilt directions for a set of eight molecules. Elimination of redundant combinations gives 11 arrangements of unique symmetry (Fig. 2 sketches six of the eleven tilt combinations; see SI for the complete set). The study shows very similar cohesive energies per molecule for the various arrangements ranging from 0.60 to 0.64 eV (see SI for full list of data obtained from DFT calculations, incl. cohesive energies and structural parameters). The molecular structures are virtually identical in the various arrangements; all show a linear coordination with staggered methyl groups and narrow



**Fig. 2.** Six of the eleven unique combinations of tilt directions for a 2x2 cell of  $\alpha$ -Me<sub>2</sub>Cd that have been studied by DFT (see SI for complete set). Black and white wedges indicate tilt directions for the two sets of molecules aligned parallel to (110) (Cd at  $z = 0$ ) and (1-10) (Cd at  $z = \frac{1}{2}$ ). Grey shaded areas show the corresponding unit cells. Numbers in brackets refer to a surplus of one tilt direction over the other for either set.



**Fig. 3.** X-ray crystal structure of the low temperature phase  $\beta$ -Me<sub>2</sub>Cd. Ball and stick models are viewed along and space-filling models perpendicular to the  $bc$ -plane.

ranges of Cd-C bond lengths (2.151 to 2.154 Å) which are in good agreement with the experimental values.

The DFT study shows that there are very subtle variations between the different 2x2 cells. Cell parameters of arrangements that contain a surplus of one tilt direction show some deviation from an ideal tetragonal lattice. This is most pronounced for  $P2_1/n$  where the molecules are all tilted in the same direction resulting in a monoclinic distortion with a  $\beta$ -angle of 93.1°. On the other hand, arrangements without a surplus of one tilt direction over the other such as  $P2/c$  exhibit cell parameters that are virtually tetragonal. This suggests that an evenly balanced distribution of tilt directions is required to stabilise the tetragonal lattice. Hence, a statistically disordered crystal of randomly distributed tilts should equally reinforce a tetragonal lattice. Corresponding DFT calculations for 2x2 cells of  $\alpha$ -Me<sub>2</sub>Zn show the same trend (see SI).

We have also probed whether disorder can occur along the columnar stacks. However, DFT studies indicate that disordered stacks in which molecules exhibit two different tilt directions have noticeably lower cohesive energies than ordered stacks with only one tilt direction (see SI). The calculations also suggest that dynamic disorder featuring unhindered 'free' rotations of methyl groups is less likely, since methyl groups of neighbouring molecules are interlocked. Hence, full rotations would require a concerted mechanism by which the rotation of methyl groups and the tilting of all neighbouring molecules are suitably synchronised. This would be energetically unfavourable as large numbers of molecules had to be dislodged from their equilibrium positions simultaneously.

A single crystal of the low temperature  $\beta$ -phase of Me<sub>2</sub>Cd was grown by zone-melting a polycrystalline sample at 150 K with an infrared laser.<sup>11</sup> The X-ray structure shows that  $\beta$ -Me<sub>2</sub>Cd crystallises in the monoclinic spacegroup  $P2_1/n$ <sup>†</sup> and is isostructural to  $\beta$ -Me<sub>2</sub>Zn.<sup>5</sup> The unit cell contains four molecules that are arranged orthogonal to each other in square grid type layers parallel to (100) (Figure 3). The C-Cd-C coordination is virtually linear (178.79(8)°) exhibiting Cd-C bond lengths of 2.130(3) and 2.134(3) Å.

The positions of hydrogen atoms for  $\beta$ -Me<sub>2</sub>Cd could not be determined from difference Fourier maps. However, a detailed analysis of the solid-state structure with various conformations of methyl groups using Hirshfeld surfaces<sup>12</sup> shows that only an

eclipsed arrangement is generating suitable intermolecular distances (see SI). The DFT study of the  $\beta$ -phase of  $\text{Me}_2\text{Cd}$  is in good agreement with the X-ray structure (Cd-C 2.151, 2.153 Å; C-Cd-C 179.0°). It indicates a binding energy of 0.59 eV per molecule and confirms the eclipsed conformation of the methyl groups.

In the  $\alpha$ -phase the molecule lies on an inversion centre and so by symmetry is strictly linear and has staggered methyl groups. By contrast, the molecule in the  $\beta$ -phase occupies a general position with no crystallographically imposed symmetry and displays an eclipsed arrangement. The change of conformation from staggered to eclipsed between the two phases seems unusual. On the other hand, the energy difference between conformers of gaseous  $\text{Me}_2\text{Cd}$  is very low indicating free rotation in the gas phase.<sup>13</sup> This suggests that the arrangements in the solid state are a result of crystal packing that is mostly driven by non-bonded Van-der-Waals interactions which consistently account for more than 80% of the cohesive energy (see SI).

The molecular structures of the two solid-state phases of dimethylcadmium compare well with those derived from rotational spectra<sup>14</sup> and computational studies of gaseous  $\text{Me}_2\text{Cd}$ .<sup>13</sup> Similar Cd-C bond lengths also occur in co-crystals containing non-coordinating  $\text{Me}_2\text{Cd}$  molecules<sup>15</sup> as well as those found in the gas phase structure of  $\text{Et}_2\text{Cd}$ .<sup>16</sup> Diarylcadmium compounds that exhibit a linear coordination at Cd also show comparable bonding parameters.<sup>17</sup> Marginally longer Cd-C bonds were observed in adducts of  $\text{Me}_2\text{Cd}$  with donor molecules.<sup>18</sup>

In summary, we have determined the crystal structures of the high- and low-temperature phases of dimethylcadmium. These are very similar to those of dimethylzinc exhibiting analogous phase behaviour. Likewise, the high temperature phase of  $\text{Me}_2\text{Cd}$  is affected by a two-dimensional disorder which stabilises the tetragonal lattice. The two phases show different conformers, staggered in the high temperature phase and eclipsed in the low temperature phase.

## Notes and references

‡ Crystal data:  $\alpha$ - $\text{Me}_2\text{Cd}$ :  $\text{C}_2\text{H}_6\text{Cd}$ ,  $M_r = 142.47$ ,  $T = 240$  K,  $P4_2/mnm$ ,  $a = 7.195(7)$ ,  $c = 4.118(4)$  Å,  $V = 213.2(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho = 2.22$  g cm<sup>-3</sup>,  $R1 = 0.026$ .<sup>19</sup>  $\beta$ - $\text{Me}_2\text{Cd}$ :  $\text{C}_2\text{H}_6\text{Cd}$ ,  $M_r = 142.47$ ,  $T = 150$  K,  $P2_1/n$ ,  $a = 7.483(11)$ ,  $b = 7.711(11)$ ,  $c = 7.734(11)$  Å,  $\beta = 115.85(3)^\circ$ ,  $V = 401.6(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho = 2.36$  g cm<sup>-3</sup>,  $R1 = 0.072$ .<sup>19</sup>

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