Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: F. Hanke, S. Hindley, A. Jones and A. Steiner, Chem. Commun., 2016, DOI: 10.1039/C6CC05851E.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
The solid state structures of the high and low temperature phases of dimethylcadmium

Felix Hanke, a Sarah Hindley, b Anthony C. Jones, c and Alexander Steiner* c

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\(_2\)Cd, exhibits two-dimensional disorder, while the low temperature monoclinic phase, \( \beta \)-Me\(_2\)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.\(^1\) 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.\(^2\) It is an important precursor for II/VI semiconducting films and nanoparticles which find widespread applications in electronic and optoelectronic devices.\(^3\) Layered assemblies of photovoltaic CdTe and CdS, for example, are key components of solar cells.\(^4\) 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\(_2\)Zn, which undergoes a solid-solid phase transition from a disordered high-temperature \( \alpha \)-phase to an ordered low-temperature \( \beta \)-phase.\(^5,6\) Single crystals of the high temperature \( \alpha \)-phase of Me\(_2\)Cd were obtained on slow cooling of a liquid sample contained in a capillary. Due to the strong hysteresis of the phase transitions, the X-ray structure of the \( \alpha \)-phase was determined in the supercooled regime at 240 K.\(^7\) 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 molecules form stacks along c. Note that every stack can adopt one of two tilt-directions, here depicted in red and orange, respectively.

---


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_2Zn as a pseudo-merohedral twin in this spacegroup,\(^5\) the analogous twin refinement of \(\alpha\)-Me_2Cd 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\(^8\) using the CASTEP program\(^9\) provided with Materials Studio.\(^10\)

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_2Cd. 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 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 \(P2_1/c\) 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 \(P2_1/c\) 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_2Zn 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_2Cd was grown by zone-melting a polycrystalline sample at 150 K with an infrared laser.\(^11\) The X-ray structure shows that \(\beta\)-Me_2Cd crystallises in the monoclinic spacegroup \(P2_1/c\)\(^1\) and is isostructural to \(\beta\)-Me_2Zn.\(^3\) 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_2Cd 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\(^13\) shows that only an
position with no crystallographically imposed symmetry and confirms the eclipsed conformation of the methyl groups. In the α-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 β-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 Me₂Cd is very low indicating free rotation in the gas phase. 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 and computational studies of gaseous Me₂Cd. Similar Cd-C bond lengths also occur in co-crystals containing non-coordinating Me₂Cd molecules as well as those found in the gas phase structure of Et₂Cd. Diacetylcyramid compounds that exhibit a linear coordination at Cd also show comparable bonding parameters. Marginally longer Cd-C bonds were observed in adducts of Me₂Cd with donor molecules.

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 Me₂Cd 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: α-Me₂Cd: C₅H₅Cd, Mᵣ = 142.47, T = 240 K, P4₃/mnm, a = 7.195(7) Å, V = 213.2(4) Å³, Z = 2, μ = 2.22 g cm⁻³, R₁ = 0.026. β-Me₂Cd: C₅H₅Cd, Mᵣ = 142.47, T = 150 K, P2₁/n, a = 7.483(11) Å, b = 7.711(11) Å, c = 7.734(11) Å, β = 115.85(3)°, V = 401.6(10) Å³, Z = 4, μ = 2.36 g cm⁻³, R₁ = 0.072.

6 We have since discovered that the solid-solid phase transition of Me₂Zn also shows a strong hysteresis, which occurs at 180 K on cooling (α→β-phase) and 210 K on heating (β→α-phase).
16 Examination of the CIF files of the co-crystals that contain non-coordinated Me₂Cd molecules show also different conformations of methyl groups. However, no information is given about the localisation and refinement of H-atoms.