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Crystal structure of bis(µ-N-i-propyl-N-n-propyldithiocarbamato-κ³S,S':S)bis(N-i-propyl-N-n-propyldithiocarbamato-κ²S,S')dicadmium(II), C₂₈H₅₆Cd₂N₄S₈

Table 1: Data collection and handling.

<table>
<thead>
<tr>
<th>Crystal:</th>
<th>Block, pale-yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size:</td>
<td>0.16 x 0.14 x 0.10 mm</td>
</tr>
<tr>
<td>Wavelength:</td>
<td>Mo Kα radiation (0.71073 Å)</td>
</tr>
<tr>
<td>μ:</td>
<td>1.52 mm⁻¹</td>
</tr>
<tr>
<td>Diffractometer, scan mode:</td>
<td>XtaLAB Synergy, ω-scans</td>
</tr>
<tr>
<td>θmax, completeness:</td>
<td>26.4°, &gt;99%</td>
</tr>
<tr>
<td>N(hkli)_measured, N(hkli)_unique, Rint:</td>
<td>26079, 4038, 0.065</td>
</tr>
<tr>
<td>Criterion for Iobs, N(param)_refined:</td>
<td>Iobs &gt; 2σ(Iobs), 3607</td>
</tr>
<tr>
<td>Programs:</td>
<td>CrysAlisPRO [1], SHELX [2, 3], WinXG and ORTEP [4]</td>
</tr>
</tbody>
</table>

Source of material

The compound was obtained from reacting a 1:2 mixture of CdCl₂ (Acros Organic) and Na[S₂CN(i-Pr)n-Pr] [prepared from the 1:1:1 reaction of CS₂ (Panreac), N(i-Pr)n-Pr (Alfa Aesar) and NaOH (Merck) in acetone solution] in water which resulted in a white precipitate. This was extracted with CH₂Cl₂ and filtered. The filtrate was allowed to stand for slow evaporation under ambient conditions. Colourless crystals formed after a few days. M.p.: 467.5 – 468.4 K. IR (cm⁻¹): ν(C—S) 1188 (s, sh), 955 (s, br), ν(C—N) 1455 (s).

Discussion

Until 2013, the structural chemistry of the binary cadmium dithiocarbamates, Cd[S₂CNRR']₂, was dominated by a single structural motif comprising a binuclear complex with equal numbers of µ₂-bridging and chelating dithiocarbamate ligands leading to five-coordinate cadmium centres [5, 6]. Very recently, a new motif was discovered featuring µ₂-bridging dithiocarbamate ligands exclusively, resulting in linear coordination polymers and six-coordinate cadmium centres [7, 8]. It was during such crystal engineering studies that the title compound, [Cd[S₂CN(i-Pr)n-Pr]₂], with disparate R substituents, was characterised.

The molecular structure is shown in the figure (70% displacement ellipsoids) and the centrosymmetric binuclear
complex features $\mu_b$-bridging and chelating dithiocarbamate ligands, as is normal for these compounds [5, 6]. Thus, one ligand chelates one cadmium atom and simultaneously bridges the second centrosymmetrically-related cadmium atom.

The bridging S2 atom forms the longest of the Cd–S bond lengths in the structure at 2.624(6) Å, for the bridging bond (symmetry operation: $-x, 1-y, -z$), and 2.788(6) Å. The shortest bond length of 2.547(15) Å is found for the Cd–S1 bond. The other ligand is chelating with Cd–S bond lengths intermediate to those formed by the S1 and S2 atoms. The S3 donor set is highly distorted and based on the value of $\tau$ of 0.51, cf. the extreme values of 0.0 and 1.0 for ideal square-pyramidal and trigonal-bipyramidal geometries [9], respectively, the coordination geometry is intermediate between these extremes.

The aforementioned crystal chemistry studies on Cd[S2CN(iPr)CH2CH2OH]2 [6, 7] revealed the presence of supramolecular isomers for one-dimensional coordination polymers, i.e. {Cd[S2CN(iPr)CH2CH2OH]2-vent} for solvent-actonitrite [6] and ethanol [7]. This came about as all dithiocarbamate ligands in the polymers are $\mu_b$-bridging. Solvent-mediated structural transformations were also observed between the polymers and the anticipated binuclear molecules, i.e. {Cd[S2CN(iPr)CH2CH2OH]2-vent}.

The conclusion of these studies was that the polymers were kinetic outcomes of crystallisation and that the dimers were the thermodynamic products. The title structure is very similar to the zinc analogue, {Zn[S2CN(i-Pr)n-Pr]2} [10] except that the transaminal interaction is not as significant so the coordination geometry for the zinc atom is best described as being distorted tetrahedral. This difference in structure relates to the different sizes of the zinc and cadmium atoms.

Acknowledgements: Sunway University is thanked for support of biological and crystal engineering studies of metal dithiocarbamates.

References

cadmium bis(N-hydroxyethyl, N-isopropylthiocarbamate) compound: physicochemical characterization of ball (n = 2) and chain (n = ∞) forms of \( \text{[Cd(S}_2\text{CN(iPr)CH}_2\text{OH}]_2\text{solvent}} \)_n. Cryst. Growth Des. 13 (2013) 3046–3056.

