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A low-temperature refinement of tris[\(N,N'-\text{bis}(2\text{-hydroxyethyl})\text{dithiocarbamato-}\kappa^2S,S']\text{antimony}(\text{III})

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A low-temperature refinement of tris[N,N′-bis(2-hydroxyethyl)dithiocarbamato-κ²S,S’]-antimony(III)

The title compound, [Sb(C₇H₁₀NO₂S₂)₃], has been redetermined at 93 K, allowing a detailed analysis of the crystal packing, which is dominated by O—H···O hydrogen bonding. Each terminal hydroxyl group participates in a 12-membered [···O—H]₆ ring, leading to a three-dimensional array.

Comment

The binary antimony(III) dithiocarbamates, Sb(S₂CNR₂)₃, usually associate into dimers via Sb···S interactions (Liu & Tiekink, 2005). Exceptions to this behaviour are found only when the steric bulk of the R groups precludes close association, such as in the example where NR₂ = N(CH₃)₂ (Liu & Tiekink, 2005). Indeed, steric bulk in remote substituents has been found to be an important factor in supramolecular aggregation in these and related systems (e.g. Lai et al., 2002, 2004; Tiekink, 2003, 2006a,b). In the Sb(S₂CNR₂)₃ structures for which hydrogen-bonding functionality exists in one of the R groups, the same principle of steric control holds (Liu & Tiekink, 2005). However, in the case of Sb(S₂CN(CH₃)₂CH₂OH)₃, (I), no Sb···S interactions were evident, despite being present in the n-propyl analogue Sb(S₂CN(CH₃)₂CH₂OH)₃ (Kavounis et al., 1982). In the original crystallographic analysis of (I) (Venkatachalam et al., 1997), there were ambiguities in the positions of the –OH groups. Here, a new analysis of (I) is reported from data measured at 93 K.

The molecular structure of (I) (Fig. 1 and Table 1) shows the expected features for compounds of this type (Liu & Tiekink, 2005). The molecule has non-crystallographic symmetry, at least in terms of the S₂CN₂ residues, so that the S₁S₂-dithiocarbamate ligand defines an approximate mirror plane. This ligand forms the most asymmetric chelate of the three dithiocarbamate ligands and this is reflected in the associated C—S distances (Table 1). The coordination geometry is based on a pentagonal bipyramid, with atoms S₂/S₃–S₆ defining a distorted pentagon and with atom S₁ and the lone pair of electrons occupying axial positions. This conformation allows
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Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Figure 2
Hydrogen-bonding interactions in (I) mediated by \( \text{O} \cdot \cdot \cdot \text{H} \cdot \cdot \cdot \text{O} \) interactions, shown as dashed lines; see Table 2 for symmetry operations. Colour code: Sb orange, S yellow, O red, N blue, C grey and H green.

for the formation of intermolecular Sb \( \cdot \cdot \cdot \) S interactions in many related systems, but no such interaction is present in (I).

Details of the hydrogen-bonding parameters are summarized in Table 2, from which it can be seen that each OH group functions as a hydrogen-bonding donor and acceptor. As shown in Fig. 2, each hydroxyl group is associated with an essentially planar 12-membered \([\cdot \cdot \cdot \text{O} \cdot \cdot \cdot \text{H}]_6\) ring. Those rings, highlighted with blue dashed lines in Fig. 2, involve atoms O1, O3 and O6. The net result of these interactions is the formation of a three-dimensional array, as shown in Fig. 3. Also shown in this figure is the relative disposition of a pair of centrosymmetric molecules which are aligned so as to form, potentially, the commonly observed dimeric motif. In Fig. 3, a potential point of aggregation is indicated with an asterisk, but the intermolecular Sb \( \cdot \cdot \cdot \) S separation is greater than 5.7 Å. Association via Sb \( \cdot \cdot \cdot \) S interactions leading to dimers is precluded in (I) due to the intervention of the hydrogen-bonded residues.

Experimental

Compound (I) was prepared in a manner that differed from the literature procedure (Venkatachalam et al., 1997). A suspension of ammonium bis(hydroxyethyl)dithiocarbamate (5.94 g, 3.0 mmol), prepared after the procedure of Ramos et al. (2005), in methanol (200 ml) was added to a solution of SbCl₅ (Acros Organics, 2.29 g, 1.0 mmol) in methanol (30 ml) with stirring. The ligand dissolved and the solution turned iridescent yellow. The product was filtered off and recrystallized from an ethanol solution to provide 3.78 g (65.1%) of (I) [m.p. 413.5–414.5 K; literature 403–405 K (Venkatachalam et al., 1997)].

Crystal data

\[
\begin{align*}
\text{[Sb(C}_5\text{H}_7\text{NO}_3\text{S}_2]_2} \\
M_r &= 662.53 \\
\text{Triclinic, P\bar{T}} \\
a &= 9.942 (2) \text{ Å} \\
b &= 11.011 (2) \text{ Å} \\
c &= 12.458 (3) \text{ Å} \\
\alpha &= 104.422 (4)^\circ \\
\beta &= 105.294 (4)^\circ \\
\gamma &= 94.445 (3)^\circ \\
\end{align*}
\]

\[V = 1258.9 (5) \text{ Å}^3\]

\[Z = 2\]

\[D_x = 1.748 \text{ Mg m}^{-3}\]

Mo Ka radiation

\[\mu = 1.63 \text{ mm}^{-1}\]

\[T = 93 (2) \text{ K}\]

Block, yellow

0.20 \times 0.20 \times 0.20 \text{ mm}
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The methylene H atoms were included in a riding-model approximation, with C—H = 0.99 Å and with $U_{eq}(H) = 1.2U_{eq}(C)$. The hydroxyl H atoms were located in a difference map and treated as riding, with O—H = 0.84 Å and $U_{eq}(H) = 1.5U_{eq}(O)$.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare et al., 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Crystal Impact, 2006); software used to prepare material for publication: *SHELXL97*.

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References


