Crystal and Molecular Structure of Bismuth(III) 2,2-Dimethylpropanoate

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X-Ray investigations of single crystals of bismuth(III) 2,2-dimethylpropanoate (pivalate), obtained by sublimation *in vacuo*, reveal its structure to consist of isolated tetrameric units $[Bi(O_2CCMe_3)_3]_4$; each of the twelve crystallographically inequivalent Bi atoms has practically the same coordination environment of nine O atoms at distances of 2.24–3.27 Å.

The discovery of oxide superconductors has favoured the synthesis and study of new volatile bismuth complexes with oxygen-donor ligands, which could be applied in superconducting film manufacture *via* chemical vapour deposition techniques. Along with alkoxides[1] and β-diketonates[1,2] Bi^{III} carboxylates[3] are also promising precursors.

In this connection the investigation of the crystal structures of such compounds seems to be of particular importance since it accounts for the volatility dependence on the nature of the ligand. It is to be noted that only two structures of Bi tris-carboxylates have been determined so far: the formate $Bi(O_2CH)_3$[4] and acetate $Bi(O_2CMe)_3$.[5] The present study concerns bismuth 2,2-dimethylpropanoate $Bi(O_2CCMe_3)_3$ **1** which displays the greatest volatility compared with other bismuth carboxylates.

Compound **1** was obtained through a ligand exchange reaction between bismuth acetate and 2,2-dimethylpropanoic acid as described previously.[3] Single crystals were grown by slow sublimation in a vacuum-sealed tube placed in a furnace with a temperature gradient of 160–120 °C, which is below the melting point of **1** (164 °C).

The crystal structure of **1** consists of isolated tetrameric units $[Bi(O_2CCMe_3)_3]_4$ (Fig. 1).[†] Although these units are crystallographically inequivalent, they have practically the same geometry. Furthermore, the coordination environment of Bi atoms in each unit, and hence all twelve inequivalent Bi atoms, were shown to be essentially the same.

In each tetrameric unit (Fig. 2) tetrahedrons of Bi atoms are flattened so that the four Bi–Bi distances are 4.1 Å, while the remaining two Bi–Bi distances are 5.0 Å. (Interatomic distances given here and below are averaged for all 12 Bi atoms.)

The coordination mode of the ligands by Bi atoms allows three types of carboxylic groups to be distinguished. The first group with O(*n*1) and O(*n*2) donor atoms asymmetrically chelates with only one Bi atom (with number *n*); Bi–O distances are 2.24 and 2.50 Å, respectively. Apart from chelating its 'own' Bi atom, [Bi(*n*)–O(*n*3) and Bi(*n*)–O(*n*4) are 2.25 and 2.73 Å, respectively) the O(*n*4) atom of the second carboxylic group is additionally coordinated by the two nearest neighbouring Bi atoms at distances of 2.87 and 3.16 Å. The third carboxylic group bridges two neighbouring Bi atoms corresponding to the short edges of the Bi_4 tetrahedron while O(*n*6) is coordinated by both Bi atoms at distances of 3.27 and 2.50 Å; O(*n*5) is coordinated by one Bi atom at 2.30 Å. Such inequivalence of carboxylic groups also results in several

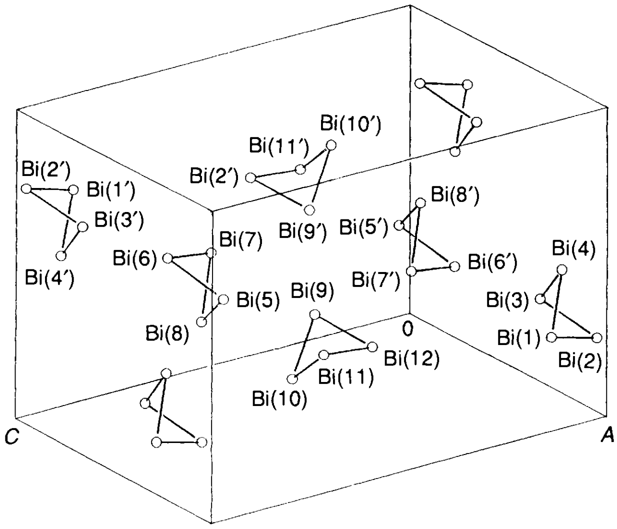

Fig. 1 Arrangement of $[Bi(O_2CCMe_3)_3]_4$ groups in the unit cell of Bi pivalate (only Bi atoms are shown)

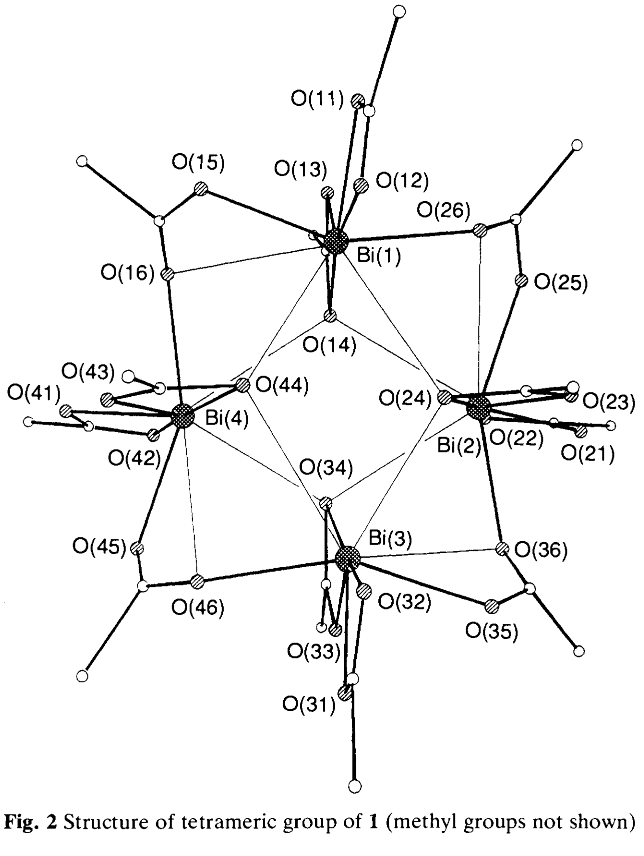

Fig. 2 Structure of tetrameric group of **1** (methyl groups not shown)

[†] *Crystal structure* determination of **1** (T = 295 K, Enraf-Nonius CAD-4 diffractometer, Mo-Kα, graphite monochromator, θ_{max} = 22°): $C_{15}H_{27}BiO_6$ M = 512.36, triclinic, space group $P\bar{1}$, a = 16.243(4), b = 23.348(4), c = 34.488(10) Å, α = 71.12(2), β = 86.64(2), γ = 83.65(2)°, V = 12295.6 $Å^3$, Z = 24, D_c = 1.661 g cm^{-3}, μ = 85.9 cm^{-1}. A colourless transparent crystal *ca.* 0.2 × 0.2 × 0.3 mm was mounted in a Pyrex capillary. 30 579 row data intensity corrected for decomposition (15%) during the exposure and for absorption (ψ-scanning of 6 reflections), 9105 unique observed reflections with $F^2 > 3\sigma(F^2)$. The structure was solved (SDP)[7] by a combination of direct methods (12 Bi atoms) and Fourier difference techniques. The full-matrix least-square refinement could be performed for all Bi atoms (anisotropically), all 72 O atoms and 104 C atoms, including carboxylic, quaternary and some methyl (isotropically). Owing to insufficient spacing in SDP we could obtain the positions of 40 methyl carbons from difference Fourier synthesis, while the coordinates of the remaining C atoms were calculated. The residuals obtained for the refined 188 atoms were R = 0.087, R_w = 0.091. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ν(CO) bands in the IR spectrum. It should be mentioned that following Davidovitch and Buslaev[6] we included in the coordination environment of Bi atoms all O atoms within the sphere of 3.47 Å which corresponds to the sum of the Bi and O Van der Waals radii.

Thus, each Bi atom is surrounded by nine O atoms as in the structures of Bi formate and acetate. The irregular shape of the coordination polyhedron can be accounted for by the stereochemically active lone electron pair. Calculation of trihedral angles corresponding to the faces of the BiO_9 polyhedron allows us to suppose that the lone pair is oriented in a direction between the O(n2), O(n5) and O(n + 1 4) atoms [*e.g.* O(12), O(15) and O(24) in the case of Bi(1)].

The number of O atoms involved in additional coordination by Bi atoms decreases, along with the lengthening of the Bi···O–Bi bridges. Such a reduction in intermolecular interaction results in the transformation from three-dimensional framework in $Bi(O_2CH)_3$ to endless layers in $Bi(O_2CMe)_3$ and to isolated $[Bi(O_2CCMe_3)_3]_4$ units. Whereas bismuth formate is not volatile and the acetate sublimes with partial decomposition, only **1** vaporizes quantitatively at a comparatively low temperature. Mass-spectral investigation of bismuth carboxylates displays only ions with one or two Bi atoms due to depolymerization in the gas phase. The relatively greater stability of bismuth 2,2-dimethylpropanoate to hydrolysis and thermolysis results from the shielding of the central atom by the bulky ligands.

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