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Crystal and Molecular Structures of Bismuth Compounds of a Spiro-σ-sulfurane Type

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Abstract

The crystal and molecular structures of [2-(2-methoxy-2-propyl)phenyl-C^1](2-phenyl-2-propanolato-C^1,O)bismuth (I), [2-(2-hydroxy-2-propylphenyl-C^1)]-(2-phenyl-2-propanolato-C^1,O)bismuth (II) and tetraethylammonium bis(2-phenyl-2-hexafluoropropanolato-C^1,O)bismuthate monohydrate (III) were determined by the X-ray method. Crystal data: (I), $[Bi(C_{19}H_{23}O_2)]$, $M_r = 492.37$, monoclinic, $P2_1/n$, $a = 11.635\,(3)$, $b = 8.837\,(2)$, $c = 18.149\,(4)$ Å, $\beta = 103.17\,(3)°$, $V = 1817.0\,(7)$ Å^3, $Z = 4$, $D_x = 1.800$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 9.680$ mm^{-1}, $F(000) = 944$, $T = 298$ K, $R = 0.046$, $wR = 0.061$ for 3033 observed reflections. (II), $[Bi(C_{18}H_{21}O_2)]$, $M_r = 478.34$, monoclinic, $C2/c$, $a = 19.902\,(4)$, $b = 18.353\,(2)$, $c = 17.303\,(2)$ Å, $\beta = 109.69\,(2)°$, $V = 5951\,(1)$ Å^3, $Z = 12$, $D_x = 1.602$, $D_m = 1.663$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 8.865$ mm^{-1}, $F(000) = 2736$, $T = 298$ K, $R = 0.070$, $wR = 0.096$ for 3609 observed reflections. (III), $[N(C_2H_5)_4][Bi(C_{18}H_8F_{12}O_2)].H_2O$, $M_r = 841.49$, monoclinic, $P2_1/n$, $a = 15.547\,(2)$, $b = 15.900\,(2)$, $c = 11.996\,(2)$ Å, $\beta = 90.19\,(2)°$, $V = 2965.4\,(8)$ Å^3, $Z = 4$, $D_x = 1.885$, $D_m = 1.896$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 6.029$ mm^{-1}, $F(000) = 1632$, $T = 298$ K, $R = 0.044$, $wR = 0.050$ for 4666 observed reflections. X-ray investigations revealed that the molecular structures of these compounds were four-coordinate distorted trigonal bipyramids with apical O—Bi—O bonds and equatorial C—Bi—C bonds. Bi—O bond lengths are 2.566 (8) and 2.134 (7) Å for (I), 2.32 (1) Å (mean value) for (II) and 2.306 (5) and 2.273 (5) Å for (III), which are longer than the normal single Bi—O and Bi—C bonds. This is the first case in which four-coordinate bismuth compounds of a spiro-sulfurane type have been observed. These apical O atoms play active roles in intermolecular interactions. In crystals of (I), the molecules form a dimer by a strong intermolecular Bi···O interaction. In crystals of (II), trimers are formed through strong intermolecular hydrogen bonds. Crystals of (III) contain water molecules as a crystal solvent, bridging two anions of (III) to form a dimer through hydrogen bonding.

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Introduction

Hypervalent sulfur compounds (Musher, 1969) such as thiathiophthenes (Hansen & Hordvik, 1973) and σ-sulfuranes (Paul, Martin & Perozzi, 1972; Kálmán, Sásvári & Kapovits, 1973; Akiba, Takee, Ohkata & Iwasaki, 1983, Iwasaki & Akiba, 1985) provide great interest in structural chemistry and organic synthesis. The characteristic features of the hypervalent bonds in these compounds are: (1) a tetravalent or divalent sulfur atom forms an X—S—X bond system with electronegative groups X; (2) these S—X bonds are longer than the usual single bond distances by about 10%, but much shorter than the sum of the van der Waals radii; (3) these bonds correspond to Pauling's bond order of 0.5 (Pauling, 1960) and are more liable to change in bond length if the molecule was perturbed to some degree; (4) X—S—X is almost linear. Recently, the concepts of hypervalent bonds have been extended to various heteroatom compounds, such as organometallic compounds of the main group (Akiba, Ito *et al.*, 1992; Akiba, Nakata, Yamamoto & Kojima, 1992).

The crystal and molecular structure of three organobismuth compounds coordinated with Martin ligands (—φ-CR_2O—), (I), (II) and (III), were determined by X-ray analysis in order to study the existence of Bi—O hypervalent bonds. (I) has a methoxy group, while (II) has a hydroxyl group. It would be interesting to investigate whether there is any interaction or not between Bi and O in these

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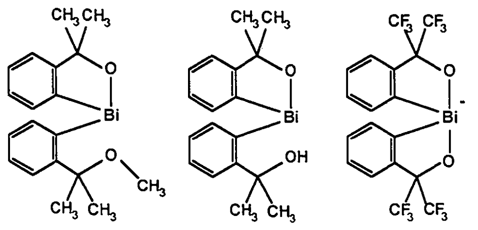
groups. (III) is an anion with a tetravalent Bi atom (Chen *et al.*, 1992).



(I) (II) (III)

Experimental

Crystals of the compounds were obtained from CH_2Cl_2–MeOH mixed solutions. Details of data collection and structure refinement are listed in Table 1. Intensity data were collected using a Rigaku AFC-4 diffractometer with a graphite monochromator. Absorption corrections were applied numerically. The structures of (I) and (III) were solved by direct methods using the program *MULTAN*78 (Main *et al.*, 1978). The structure of (II) was solved by Patterson's method using the program *SHELXS*86 (Sheldrick, 1986). The structure analysis of (II) with the space group *Cc* failed due to the strong parameter correlation between atoms related by a pseudosymmetry. Disagreement between the observed and calculated densities of (II) suggested that any crystal solvent might exist in the crystals. Assignments of some residual peaks found in the *D* maps failed, however, due to the dispersion of these peaks during the least-squares refinements. The crystal structure analysis of (III) revealed that the crystals contain water molecules as a crystal solvent. The densities of (II) and (III) were measured by flotation in potassium iodide solution and zinc bromide solution, respectively.

For all the crystals, H atoms were located from the calculation. Structures were refined by block-diagonal least squares with anisotropic temperature factors for non-H atoms and isotropic factors for H atoms. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized. $w = 1/[\sigma^2(F) + 0.00204|F_o|^2]$, $1/[\sigma^2(F) + 0.00268|F_o|^2]$ and $1/[\sigma^2(F) - 0.00243|F_o| + 0.00087|F_o|^2)$ for (I), (II) and (III), respectively. For (III), nine strong reflections, considered to be affected by extinction, were omitted during the final refinement. The final atomic parameters are given in Table 2.*

Table 1. *Details of data collection and structure refinement*

	(I)	(II)	(III)
Color	Colorless	Colorless	Colorless
Crystal shape	Prisms	Needles	Plates
Crystal size (mm)	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.225	0.30 × 0.25 × 0.30
For cell parameters			
2θ range (°)	27.2–33.4	25.0–33.4	25.3–34.0
No. of reflections	25	25	25
Scan range 2θ (°)	2–55	2–55	2–55
Scan width $\Delta\omega$ (°)	$1.2 + 0.4 \tan\theta$	$1.2 + 0.4 \tan\theta$	$1.35 + 0.4 \tan\theta$
Scan speed 2θ (° min^{-1})	4	4	4
Scan mode	2θ–ω	2θ–ω	2θ–ω
Monitored reflections (every 50 reflections)	$\bar{3}01$, $0\bar{1}5$, 027	008, 10,0,0, 060	$23\bar{6}$, 533, $22\bar{3}$
Variation of intensities	0.983–1.006	0.946–1.000	0.982–1.006
Range of h,k,l	−15–15, 0–12, 0–24	−26–26, 0–24, −23–0	−12–21, 0–21, 0–16
Time for background (s)	10	10	10
Transmission factor			
A_{max}–A_{min}	0.214–0.109	0.282–0.179	0.296–0.199
No. of reflections			
Measured	4570	7733	7896
Unique	4303	7286	7132
Observed $[\|F_o\| > 3\sigma(F)]$	3033	3609	4666
Refined	3033	3609	4656
R_{int}	0.030	0.020	0.028
R	0.046	0.070	0.044
wR	0.061	0.096	0.050
R (all observed)	0.046	0.070	0.045
$\Delta\rho_{max}$ (e Å^{-3})	1.22	1.31	1.35
$(\Delta/\sigma)_{max}$	0.069	0.056	0.085
S	0.968	1.256	1.060

Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on the IBM3090-180S Computer of the Information Processing Center of the University of Electro-Communications, using the programs *SHELXS*86 (Sheldrick, 1986), *MULTAN*78 (Main *et al.*, 1978), *UNICS*III (Sakurai & Kobayashi, 1979) and *ORTEP*II (Johnson, 1976).

Discussion

Molecular structures with the atomic numbering are shown in Fig. 1. Selected bond distances and bond angles are listed in Table 3. The structures of these bismuth compounds are of a four-coordinate spiro-σ-sulfurane type with a distorted trigonal bipyramid and apical O—Bi—O hypervalent bonds.

Structure of (I)

In (I), the O atom of the methoxy group coordinates to the Bi atom with a Bi(1)—O(2) distance of 2.566 (8) Å, while the length of the other Bi(1)—O(1) bond is 2.134 (7) Å, which is considered to be a normal single bond (2.08 Å). The length of the Bi(1)—O(2) bond is longer than a normal single bond and also longer than the Bi—O apical hypervalent bonds (2.3–2.4 Å) in tetra-coordinated bismuth compounds such as (II), (III), diphenyl-

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, H-atom parameters and bond lengths and angles related to the phenyl groups and the cation of (III) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71545 (69 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0619]

Table 2. *Positional parameters and equivalent isotropic temperature factors* (B_{eq}) *for non*-H *atoms*

$$B_{eq} = 4/3\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
(I)				
Bi(1)	0.50003 (3)	0.10858 (4)	0.10119 (2)	3.32 (1)
O(1)	0.5587 (6)	−0.0947 (8)	0.0579 (4)	4.4 (2)
O(2)	0.3847 (7)	0.2737 (9)	0.1757 (5)	5.5 (3)
C(11)	0.5672 (8)	−0.0279 (12)	0.2063 (6)	4.0 (3)
C(12)	0.6214 (8)	−0.1625 (12)	0.1918 (6)	3.9 (3)
C(13)	0.6713 (10)	−0.2587 (15)	0.2518 (7)	5.5 (4)
C(14)	0.6627 (10)	−0.2227 (15)	0.3260 (6)	5.4 (4)
C(15)	0.6079 (10)	−0.0916 (14)	0.3405 (6)	5.2 (3)
C(16)	0.5587 (9)	0.0053 (13)	0.2807 (6)	4.7 (3)
C(17)	0.6318 (9)	−0.1955 (11)	0.1104 (6)	4.0 (3)
C(18)	0.7616 (10)	−0.1701 (16)	0.1064 (7)	5.7 (4)
C(19)	0.5933 (13)	−0.3593 (13)	0.0850 (8)	5.9 (4)
C(21)	0.3149 (8)	0.0262 (11)	0.0913 (5)	3.5 (3)
C(22)	0.2312 (8)	0.1068 (11)	0.1201 (5)	3.6 (2)
C(23)	0.1164 (9)	0.0497 (15)	0.1079 (6)	4.8 (3)
C(24)	0.0861 (10)	−0.0893 (15)	0.0741 (7)	5.6 (4)
C(25)	0.1696 (10)	−0.1718 (14)	0.0480 (6)	5.0 (3)
C(26)	0.2839 (9)	−0.1141 (11)	0.0558 (6)	4.0 (3)
C(27)	0.2590 (9)	0.2609 (12)	0.1582 (6)	4.5 (3)
C(28)	0.2059 (15)	0.3885 (14)	0.1039 (8)	6.8 (5)
C(29)	0.2136 (11)	0.2682 (14)	0.2317 (7)	5.3 (4)
C(30)	0.4405 (14)	0.4074 (14)	0.2132 (9)	6.9 (5)
(II)				
Bi(1*A*)	0.0000	0.18482 (5)	0.2500	5.00 (3)
O(1*A*)	0.1168 (6)	0.2081 (7)	0.2576 (7)	5.5 (4)
C(11*A*)	0.0433 (8)	0.2602 (10)	0.3510 (10)	4.9 (6)
C(12*A*)	0.1148 (10)	0.2847 (10)	0.3699 (11)	5.8 (6)
C(13*A*)	0.1454 (11)	0.3321 (13)	0.4374 (12)	7.3 (8)
C(14*A*)	0.1091 (12)	0.3547 (15)	0.4870 (14)	8.7 (9)
C(15*A*)	0.0388 (14)	0.3349 (16)	0.4694 (14)	10.0 (11)
C(16*A*)	0.0042 (11)	0.2874 (12)	0.4029 (13)	6.6 (7)
C(17*A*)	0.1589 (9)	0.2611 (10)	0.3168 (11)	5.5 (6)
C(18*A*)	0.1743 (13)	0.3276 (12)	0.2695 (15)	8.0 (9)
C(19*A*)	0.2270 (10)	0.2266 (11)	0.3677 (13)	6.4 (7)
Bi(1*B*)	0.09987 (4)	−0.00883 (5)	0.24710 (5)	5.36 (3)
O(1*B*)	0.1686 (7)	0.0858 (6)	0.2231 (8)	5.8 (4)
O(2*B*)	0.0666 (6)	−0.1267 (6)	0.2622 (8)	5.3 (4)
C(11*B*)	0.1192 (11)	−0.0373 (10)	0.1328 (10)	5.7 (7)
C(12*B*)	0.1593 (11)	0.0123 (11)	0.1054 (13)	6.2 (8)
C(13*B*)	0.1683 (19)	−0.0079 (12)	0.0295 (16)	9.9 (13)
C(14*B*)	0.1460 (18)	−0.0687 (15)	−0.0123 (15)	10.3 (13)
C(15*B*)	0.1089 (18)	−0.1126 (14)	0.0151 (14)	11.0 (13)
C(16*B*)	0.0963 (14)	−0.0993 (13)	0.0889 (14)	8.3 (9)
C(17*B*)	0.1937 (11)	0.0796 (10)	0.1563 (13)	6.2 (7)
C(18*B*)	0.1707 (17)	0.1454 (12)	0.1043 (15)	9.4 (12)
C(19*B*)	0.2728 (14)	0.0741 (17)	0.1871 (18)	10.6 (13)
C(21*B*)	0.1932 (9)	−0.0644 (10)	0.3346 (10)	5.1 (6)
C(22*B*)	0.1852 (9)	−0.1340 (10)	0.3545 (10)	5.1 (6)
C(23*B*)	0.2440 (11)	−0.1696 (12)	0.4144 (12)	6.5 (7)
C(24*B*)	0.3103 (11)	−0.1351 (12)	0.4502 (13)	7.2 (8)
C(25*B*)	0.3194 (12)	−0.0659 (15)	0.4306 (13)	8.1 (9)
C(26*B*)	0.2610 (12)	−0.0297 (11)	0.3729 (13)	6.4 (7)
C(27*B*)	0.1173 (10)	−0.1745 (10)	0.3175 (12)	5.7 (7)
C(28*B*)	0.1340 (13)	−0.2344 (14)	0.2675 (22)	12.6 (13)
C(29*B*)	0.0859 (13)	−0.1981 (17)	0.3816 (17)	10.4 (11)
(III)				
Bi(1)	0.56764 (2)	0.10591 (2)	0.47799 (2)	3.16 (1)
O(1)	0.6773 (3)	0.0421 (3)	0.5764 (4)	3.85 (14)
O(2)	0.4999 (3)	0.1948 (3)	0.3581 (4)	4.10 (14)
C(11)	0.6702 (5)	0.0802 (4)	0.3522 (6)	3.63 (19)
C(12)	0.7442 (5)	0.0383 (5)	0.3918 (6)	3.8 (2)
C(13)	0.8101 (5)	0.0232 (5)	0.3190 (7)	4.7 (2)
C(14)	0.8051 (6)	0.0490 (6)	0.2090 (7)	5.3 (3)
C(15)	0.7329 (6)	0.0877 (6)	0.1697 (7)	5.0 (3)
C(16)	0.6654 (5)	0.1039 (5)	0.2417 (6)	4.4 (2)
C(17)	0.7442 (5)	0.0108 (5)	0.5162 (6)	3.59 (19)
C(18)	0.8278 (5)	0.0398 (7)	0.5740 (7)	5.3 (3)

Table 2 (*cont.*)

	x	y	z	B_{eq} (Å^2)
C(19)	0.7400 (6)	−0.0857 (5)	0.5176 (8)	5.2 (3)
C(21)	0.6165 (5)	0.2356 (5)	0.5182 (6)	3.53 (19)
C(22)	0.5761 (5)	0.3015 (5)	0.4645 (6)	3.8 (2)
C(23)	0.6010 (6)	0.3834 (5)	0.4895 (7)	4.7 (2)
C(24)	0.6665 (7)	0.4000 (6)	0.5626 (8)	6.0 (3)
C(25)	0.7076 (6)	0.3349 (6)	0.6176 (7)	5.0 (3)
C(26)	0.6814 (5)	0.2525 (5)	0.5956 (6)	4.3 (2)
C(27)	0.5058 (5)	0.2792 (5)	0.3779 (6)	3.8 (2)
C(28)	0.5246 (5)	0.3216 (5)	0.2642 (7)	4.7 (2)
C(29)	0.4176 (5)	0.3099 (5)	0.4219 (7)	4.7 (2)
F(1)	0.8273 (4)	0.0269 (4)	0.6830 (4)	7.4 (2)
F(2)	0.8997 (3)	0.0048 (5)	0.5369 (5)	8.1 (2)
F(3)	0.8374 (4)	0.1242 (4)	0.5618 (5)	7.04 (19)
F(4)	0.6644 (4)	−0.1101 (3)	0.4710 (5)	7.12 (19)
F(5)	0.7397 (4)	−0.1162 (3)	0.6219 (5)	7.3 (2)
F(6)	0.8027 (4)	−0.1249 (3)	0.4653 (6)	8.0 (2)
F(7)	0.6043 (3)	0.3047 (4)	0.2318 (4)	7.09 (19)
F(8)	0.5171 (4)	0.4052 (3)	0.2644 (5)	6.88 (19)
F(9)	0.4722 (4)	0.2929 (4)	0.1832 (4)	6.58 (18)
F(10)	0.4000 (4)	0.2729 (3)	0.5180 (4)	6.13 (16)
F(11)	0.4130 (4)	0.3927 (3)	0.4397 (6)	7.16 (19)
F(12)	0.3529 (3)	0.2918 (4)	0.3513 (5)	6.95 (19)
N(1*E*)	0.4621 (4)	0.1945 (4)	−0.1368 (5)	3.98 (17)
C(1*E*)	0.5426 (6)	0.1522 (6)	−0.1817 (8)	5.5 (3)
C(2*E*)	0.6227 (7)	0.1597 (9)	−0.1108 (12)	9.4 (5)
C(3*E*)	0.4352 (6)	0.1548 (7)	−0.0267 (8)	5.9 (3)
C(4*E*)	0.4039 (7)	0.0673 (7)	−0.0350 (10)	7.2 (4)
C(5*E*)	0.3932 (6)	0.1821 (6)	−0.2241 (7)	5.4 (3)
C(6*E*)	0.3056 (6)	0.2173 (7)	−0.1922 (11)	7.6 (4)
C(7*E*)	0.4789 (7)	0.2872 (6)	−0.1132 (8)	6.0 (3)
C(8*E*)	0.5107 (7)	0.3382 (6)	−0.2110 (10)	6.9 (4)
O(3)	0.5750 (5)	−0.0490 (5)	0.7437 (5)	6.7 (2)

bismuth *N*-benzoylglycinate (Huber, Domagala & Preut, 1988) and diphenylbis(trifluoroacetato)-bismuthate (Barton *et al.*, 1984). The O(1)—Bi(1)—O(2) angle is 157.3 (3)°. Non-linear O—Bi—O is ascribed to the normal bond lengths of the spiro-benzyl groups, such as C—C and C—O, of the ligand framework. In diphenylbis(trifluoroacetato)-bismuthate, where the ligands are not of the spiro type, the O—Bi—O angle is 171.8°. The C(11)—Bi(1)—C(21) angle is 92.1°, which is smaller than the corresponding C—S—C angle of sulfuranes of 100–110°. The molecular structure is a distorted trigonal biyramid about Bi with an apical O—Bi—O bond and an equatorial C—Bi—C bond. The torsion angles of the five-membered spiro rings in Table 4 show larger deviations from the planar structure for molecules of (I) rather than those of (II) and (III).

The crystal structure of (I) viewed along the *b* axis is shown in Fig. 2. In the crystals, the molecules form a dimer *via* the strong intermolecular Bi···O interaction. The Bi(1)···O(1^{i}) distance, 2.814 (7) Å, is far shorter than the sum of the van der Waals radii. The intermolecular angles related to Bi(1)···O(1^{i}) are listed in Table 5. The Bi atom can also be regarded as being loosely five-coordinate, although the geometry is not the trigonal bipyramid typical of five-coordinate bismuth compounds. In tetra-phenylbismuth tosylate crystals, one of the O atoms

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for non*-H *atoms*

	(I)	(II*A*)	(II*B*)	(III)
Bi(1)—O(1)	2.134 (7)	2.323 (12)	2.334 (13)	2.306 (5)
Bi(1)—O(2)	2.566 (9)		2.303 (12)	2.273 (5)
Bi(1)—C(11)	2.242 (10)	2.168 (17)	2.20 (2)	2.237 (8)
Bi(1)—C(21)	2.241 (9)		2.210 (16)	2.249 (7)
O(1)—C(17)	1.434 (11)	1.46 (2)	1.41 (3)	1.361 (9)
C(11)—C(12)	1.399 (15)	1.42 (3)	1.40 (3)	1.410 (10)
C(12)—C(17)	1.537 (15)	1.53 (3)	1.54 (3)	1.555 (11)
C(17)—C(18)	1.545 (16)	1.56 (3)	1.48 (3)	1.542 (11)
C(17)—C(19)	1.554 (15)	1.49 (2)	1.49 (3)	1.535 (11)
O(2)—C(27)	1.429 (13)		1.43 (2)	1.367 (9)
O(2)—C(30)	1.442 (15)			
C(21)—C(22)	1.401 (14)		1.35 (3)	1.379 (10)
C(22)—C(27)	1.528 (14)		1.48 (2)	1.546 (11)
C(27)—C(28)	1.533 (16)		1.50 (4)	1.550 (11)
C(27)—C(29)	1.543 (17)		1.51 (4)	1.550 (11)
O(1)—Bi(1)—O(2)	157.3 (3)	158.8 (4)	158.1 (5)	159.7 (2)
O(1)—Bi(1)—C(11)	77.4 (3)	73.6 (6)	74.1 (7)	74.8 (2)
O(2)—Bi(1)—C(11)	88.9 (3)	92.7 (6)	91.3 (6)	91.0 (2)
O(1)—Bi(1)—C(21)	94.5 (3)		93.3 (6)	92.6 (2)
O(2)—Bi(1)—C(21)	67.6 (3)		72.3 (6)	73.8 (2)
C(11)—Bi(1)—C(21)	92.1 (4)	100.7 (7)	98.4 (7)	94.1 (3)
Bi(1)—O(1)—C(17)	118.0 (6)	119.3 (10)	118.4 (12)	117.0 (4)
Bi(1)—C(11)—C(12)	112.5 (7)	118.8 (14)	116.3 (16)	116.2 (5)
Bi(1)—C(11)—C(16)	128.1 (8)	124.3 (14)	125.1 (17)	124.1 (6)
C(11)—C(12)—C(17)	118.7 (9)	120.3 (17)	122 (2)	117.0 (7)
C(13)—C(12)—C(17)	121.6 (10)	119.6 (18)	124 (2)	124.4 (7)
O(1)—C(17)—C(12)	110.9 (8)	107.5 (15)	108.8 (17)	114.1 (6)
O(1)—C(17)—C(18)	108.5 (9)	108.8 (16)	108 (2)	107.2 (6)
O(1)—C(17)—C(19)	107.1 (9)	109.0 (16)	109.7 (19)	109.2 (6)
C(12)—C(17)—C(18)	108.0 (9)	110.3 (17)	109 (2)	110.1 (7)
C(12)—C(17)—C(19)	112.4 (9)	111.0 (17)	111 (2)	107.0 (6)
C(18)—C(17)—C(19)	109.9 (10)	110.1 (18)	110 (2)	109.2 (7)
Bi(1)—O(2)—C(27)	118.0 (6)		119.1 (11)	118.0 (4)
Bi(1)—O(2)—C(30)	118.8 (8)			
C(27)—O(2)—C(30)	119.8 (10)			
Bi(1)—C(21)—C(22)	122.8 (7)		117.9 (14)	116.3 (5)
Bi(1)—C(21)—C(26)	117.7 (7)		123.6 (14)	124.2 (6)
C(21)—C(22)—C(27)	121.9 (9)		122.3 (18)	117.4 (7)
C(23)—C(22)—C(27)	119.3 (9)		119.1 (18)	123.7 (7)
O(2)—C(27)—C(22)	105.8 (8)		108.4 (16)	112.9 (6)
O(2)—C(27)—C(28)	109.1 (10)		108 (2)	106.7 (6)
O(2)—C(27)—C(29)	109.8 (9)		107.1 (18)	108.0 (6)
C(22)—C(27)—C(28)	110.6 (10)		106 (2)	110.9 (6)
C(22)—C(27)—C(29)	110.5 (9)		111.7 (19)	108.9 (6)
C(28)—C(27)—C(29)	111.0 (10)		116 (2)	109.4 (7)

of the tosylate anion is placed at a distance of 2.77 Å from the Bi atom (Barton *et al.*, 1984).

Structure of (II)

There are one and a half molecules, *A* and *B*, in an asymmetric unit of (II), with *A* having a crystallographic twofold axis. Molecule *B* also has pseudo-twofold symmetry. The corresponding bond lengths and angles in the two molecules are chemically equivalent. The apical Bi—O bond lengths (mean value 2.32 Å) are longer than a single bond length (2.08 Å) and also longer than Bi—C bonds (2.19 Å). Thus, these Bi—O bonds of (II) are considered to be hypervalent bonds. The O—Bi—O angles are 158.8 (4) and 158.1 (5)° for *A* and *B*, respectively.

Trimers are formed in the crystals through strong intermolecular hydrogen bonds, as shown in Fig. 3. The O···O distances are: 2.62 (2) Å between molecules *A* and *B* and 2.54 (3) Å between molecules *B* and B^{i} [(i) $-x, y, \frac{1}{2}-z$]. The Bi—O···O angles are 107.0 (6), 107.3 (6) and 107.7 (6)° for Bi(1*A*)—O(1*A*)···O(1*B*), Bi(1*B*)—O(1*B*)···O(1*A*) and Bi(1*B*)—O(2*B*)···O(2B^{i}), respectively. Accurately speaking, the molecules do not have an exact twofold symmetry since each molecule has one O—H bond. Therefore, other structural possibilities should be considered; for example, with the space group *Cc* or disordered *C*2/*c*. However, structure analysis with the space group *Cc* failed because of the strong parameter correlation between atoms related with a pseudo-symmetry. Clear evidence of the disordered structure has not been observed during the structure analysis, such as from the difference maps and shapes of the ellipsoids of the anisotropic temperature factors of the Bi atoms. If the crystal structure is disordered, the deviations from the exact twofold symmetry would then be very small. Therefore, the hydroxyl H atoms may be considered to be near the mid-point of the short O···O hydrogen bonds. However, the possibility that the H atom attaches to Bi directly to form a five-coordinate trigonal bipyramidal structure can be denied from the crystal structure with hvdrogen bondings.

Structure of (III)

(III) is a distorted trigonal bipyramid with apical O—Bi—O bonds. Two C atoms bonded to a Bi atom and the lone pair of electrons of Bi occupy the equatorial positions. The Bi—O lengths of (III) are 2.306 (5) and 2.273 (5) Å, which are similar to those of (II) and longer than a single bond. The anionic 10-Bi-4 compound with hypervalent Bi—O apical bonds is confirmed. (The *N*-*X*-*L* system is applicable when *N* electrons are involved in the bonding of *L* ligands to a main group element *X*; Perkins *et al.*, 1980.) The only example of a four-coordinate anionic bismuth compound whose structure has been reported is diphenyl-bis(trifluoroacetato)bismuthate, which is not a spiro type. The distances of O(1)—C(17) and O(2)—C(27) are shorter than those of the corresponding distances of (I) and (II). This may be attributed to the large electronegativity of the CF_3 groups.

It is revealed by the structure refinement that crystals of (III) contain water molecules as a crystal solvent. These water molecules bridge two molecules of (III) to form a dimer structure through the hydrogen bonding, as shown in Fig. 4. Selected lengths and angles related to the hydrogen bonding are listed in Table 5. The O···O lengths are 2.946 (9) and 2.866 (9) Å and the O···O···O angles are 109.1 (3)°. These values and the similarity between observed and calculated density prove the existence of water

Table 4. *Torsion angles (°) of spiro five-membered rings*

	C—Bi—O—C	Bi—O—C—C	O—C—C—C	C—C—C—Bi	O—Bi—C—C
(I)	−13.9 (5)	18.5 (9)	−13.1 (11)	2.2 (10)	5.8 (6)
	−16.9 (5)	21.5 (9)	−16.3 (10)	2.2 (11)	7.1 (5)
(II*A*)	−3.9 (10)	6.1 (16)	−6 (2)	3 (2)	0.4 (10)
(II*B*)	−4.6 (11)	7.9 (18)	−9 (2)	5 (2)	−0.5 (11)
	1.3 (10)	−0.7 (17)	−1 (2)	2 (2)	−1.8 (10)
(III)	−7.6 (4)	11.2 (7)	−9.6 (8)	3.1 (8)	1.9 (4)
	−11.9 (4)	13.6 (7)	−6.6 (8)	−3.5 (8)	7.7 (4)

molecules in the crystals. There are no special contacts less than the sum of the van der Waals radii between cations and anions.

To summarize, in these three compounds Bi—O bond lengths, 2.57 for (I) and 2.3 Å for (II) and (III), are longer than a normal single bond and Bi—C bond lengths. The O—Bi—O angles are 157–160°. The structures of these three bismuth compounds are of a σ-sulfurane type, with a distorted trigonal bipyramid and apical O—Bi—O hypervalent bonds. Most of the bismuth compounds with trigonal bipyramidal structures reported so far have been five-

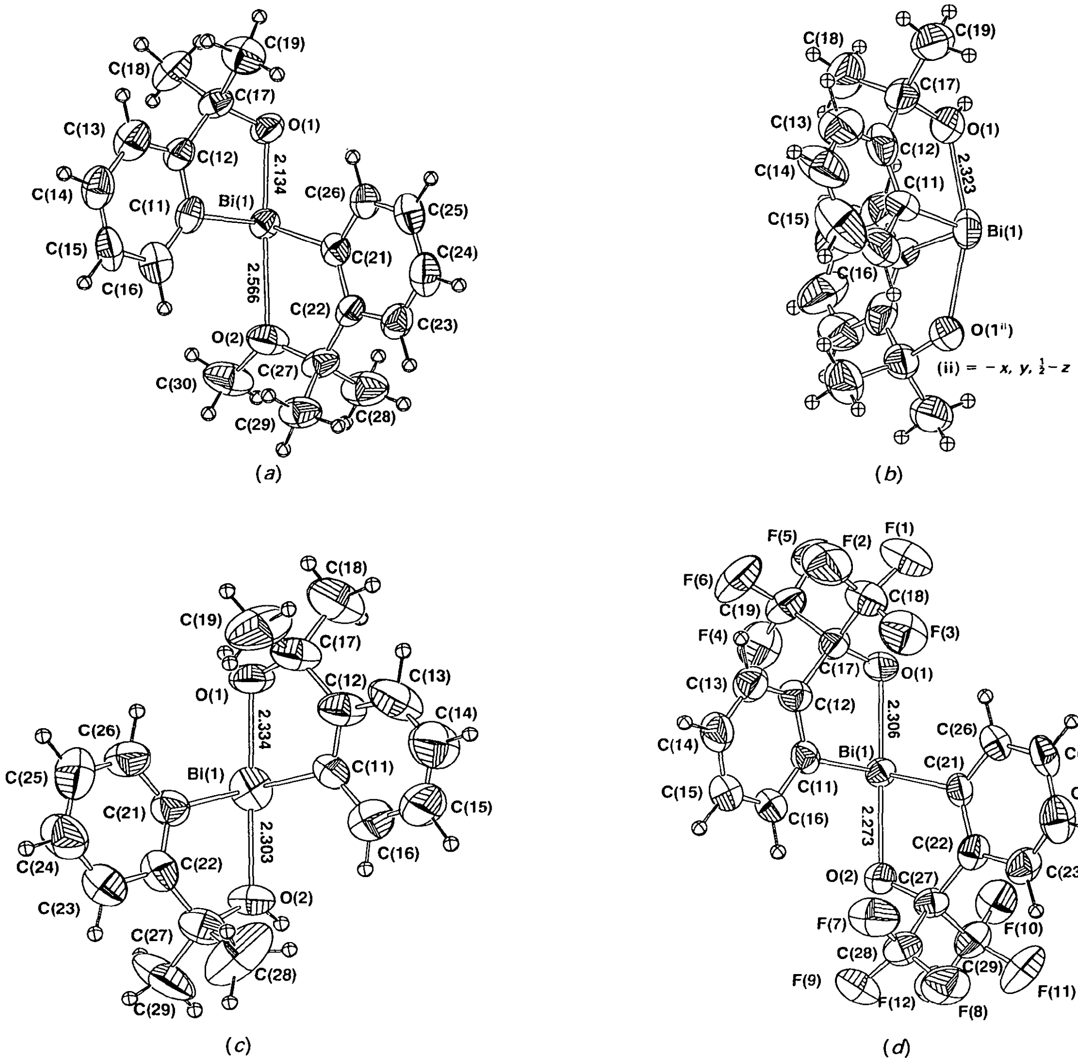


Fig. 1. Molecular structures with the atom-numbering schemes. The thermal ellipsoids for the non-H atoms are drawn at 50% probability. Distances are given in Å. (*a*) (I), (*b*) (II*A*), (*c*) (II*B*) and (*d*) (III).

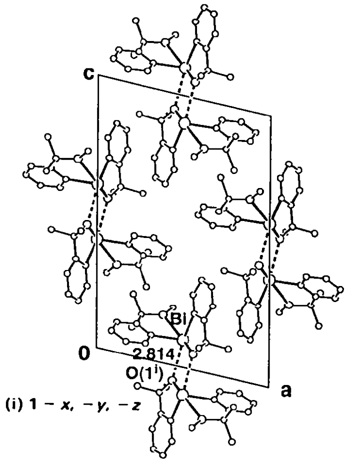


Fig. 2. Projection of the crystal structure of (I) viewed along the b axis. Broken lines show the Bi···O intermolecular interactions. Distances are given in Å.

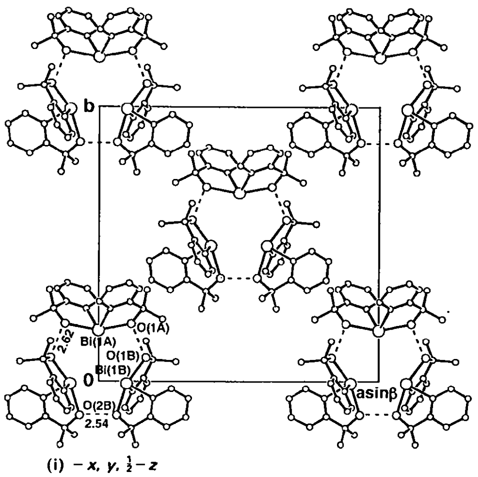


Fig. 3. Projection of the crystal structure of (II) viewed along the c axis within the range x = 0.0–0.5. Broken lines shown the O···O hydrogen bonding. Distances are given in Å.

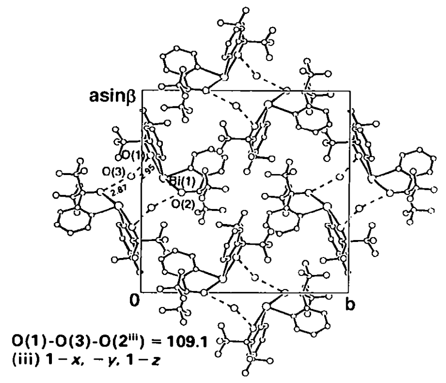


Fig. 4. Projection of the crystal structure of (III) showing the dimer structure through the water molecules. Broken lines show the O···O hydrogen bonding. Cations are omitted for clarity. Distances are given in Å, angles in °.

Table 5. *Distances* (Å) *and angles* (°) *related to intermolecular interactions*

(I)			
Bi(1)···O(1^i)	2.814 (7)	C(21)—Bi(1)···O(1^i)	84.2 (3)
O(1)—Bi(1)···O(1^i)	67.0 (2)	Bi(1)—O(1)···Bi(1^i)	113.0 (3)
O(2)—Bi(1)···O(1^i)	122.1 (2)	C(17)—O(1)···Bi(1^i)	128.6 (6)
C(11)—Bi(1)···O(1^i)	143.7 (3)		
(II)			
O(1*A*)···O(1*B*)	2.622 (18)	Bi(1*B*)—O(1*B*)···O(1*A*)	107.3 (6)
O(2*B*)···O(2*B*^{i})	2.54 (2)	Bi(1*B*)—O(2*B*)···O(2*B*^{ii})	107.7 (6)
Bi(1*A*)—O(1*A*)···O(1*B*)	107.0 (6)		
(III)			
O(1)···O(3)	2.946 (8)	Bi(1)—O(1)···O(3)	99.5 (2)
O(2^{iii})···O(3)	2.866 (9)	Bi(1^{iii})—O(2^{iii})···O(3)	87.4 (2)
O(1)···O(3)···O(2^{iii})	109.1 (3)		

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, y, \frac{1}{2}-z$; (iii) $1-x, -y, 1-z$.

coordinate compounds. Examples of four-coordinate bismuth compounds have been limited to cations with tetrahedral geometry or an anion with a trigonal bipyramidal structure. This is the first case that four-coordinate neutral compounds, (I) and (II), exhibit trigonal bipyramidal structures like the spiro-σ-sulfurances. (III) is also the first case of four-coordinate anions with a trigonal bipyramid of a spiro type. It is very interesting that the apical O atoms of these three compounds play active roles in intermolecular interactions.

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Structure and Preliminary Electron Distribution of Copper Heptanoate from Room-Temperature X-ray Data

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Abstract

Tetrakis(μ-heptanoato-κO:$\kappa O'$)dicopper $[Cu_2(C_7H_{13}O_2)_4]$, $M_r = 643.4$, triclinic, $P\bar{1}$, $a = 5.170$ (1), $b = 8.518$, $c = 19.217$ (2) Å, $\alpha = 86.65$ (1), $\beta = 83.60$ (1), $\gamma = 75.46$ (1)°, $V = 813.78$ Å^3. The unit cell contains one dicopper dimer ($Z = 1$), $D_x = 1.314$ g cm^{-3}, $\mu = 1.350$ mm^{-1} for Mo $K\alpha$ radiation ($\lambda = 0.70928$ Å), $R(F) = 0.038$ for 4861 reflections. The copper–copper distance in the dimer is 2.578 Å and each copper is surrounded by five O atoms and one Cu atom in a pseudo-octahedral coordination polyhedron. The copper–copper distance between two dimers is 3.232 Å. The hydrocarbon chains are approximately along the c axis, explaining the high value of this parameter. A comparison is made with similar structures of copper alkanoates. Preliminary results of a charge-density study are also given.

Introduction

The crystal structure of copper heptanoate is of interest because thin coatings of this compound preserve copper metal or copper alloys from atmospheric corrosion (Rapin, Steinmetz, Steinmetz & Malaman, 1992). Crystal structures of similar compounds have been obtained: anhydrous copper butyrate, $Cu[CH_3(CH_2)_2COO]_2$ (Bird & Lomer, 1972), anhydrous copper(II) decanoate, $Cu[CH_3\text{-}(CH_2)_8COO]_2$, and copper octanoate, $Cu[CH_3\text{-}(CH_2)_6COO]_2$ (Lomer & Perera, 1974*a*,*b*). These authors reported the same space group ($P\bar{1}$), same stacking and same copper environment but the precision of the structural parameters was very low. Thus, we report the accurate crystal structure of copper heptanoate.

Experimental

The samples used in this study were obtained by the reaction of copper sulfate, $CuSO_4.5H_2O$, on sodium heptanoate. The blue–green precipitate obtained was filtered and washed with water to eliminate the excess sodium sulfate, then dried in vacuum. The crystallization was performed in xylene solution heated to 323 K. The crystals appeared after about 2 months of slow cooling from 323 K to room temperature.

These blue crystals have platelet or needle aggregate shapes which can be separated in xylene under the microscope. They are very brittle and show easy cleavage. The single crystal used for the X-ray investigation was a very thin platelet with the dimensions 0.57 × 0.28 × 0.03 mm. The X-ray diffraction experiment was carried out on an Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.70928$ Å)

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