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Organobismuth(v) complexes containing bifunctional ligands: hydrogen-bonded extended structures and stereoselectivity

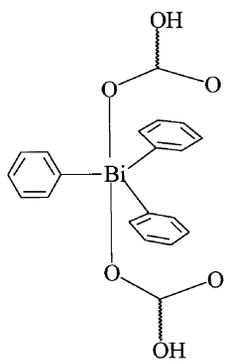
Abdi Hassan and Suning Wang*

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada

New bismuth(v) complexes with the general formula of $Bi^{V}R_3(O_2CR')_2$ have been synthesized by the reaction of BiR_3Cl_2 with $Ag(O_2CR')$, where R is an aromatic ligand and R′ a substituent containing a hydroxyl group. The role of these new bismuth(v) complexes as building blocks to form hydrogen-bonded extended structures in the solid has been examined by single-crystal X-ray diffraction analyses. The bismuth atoms in these compounds adopt distorted trigonal-bipyramidal geometries. The hydrogen-bonding pattern and the extended structure displayed have been found to be highly dependent on the R and the R′ groups. Unusual hydrogen-bonded extended structures such as double strands and double layers have been observed. In an attempt to obtain chiral helical extended structures, the reactions of BiR_3Cl_2 with several silver salts, $Ag(O_2CR^*)$, where R* contains one chiral centre and a hydroxyl group, were examined. The bismuth(v) centre shows an unusual stereoselectivity towards the chiral ligand $R^*CO_2^-$. When a racemic mixture of $Ag(O_2CR^*)$ was used only the enantiomers (*R*,*R*)- and (*S*,*S*)-$BiR_3(O_2CR^*)_2$ were obtained.

The assembly of extended molecular arrays has been a considerably active and attractive research area because molecules with long-range structural ordering often display interesting anisotropic physical properties which are useful in various applications of material science.[1] Extensive and systematic research efforts have been taken on the assembly of organic and bioorganic molecules *via* hydrogen bonds, which produced many interesting examples of supramolecular structures.[2] Incorporation of metal ions into the supramolecular structures adds a new dimension to the development of supramolecular chemistry because metal ions have unique electronic structures and can perturb the electronic structures of organic molecules by co-ordination, hence modifying the physical properties of the supramolecular arrays.[3] In addition, many metal ions display versatile but often predictable co-ordination geometries, giving new avenues for the manipulation of the extended structures.[1] Hydrogen-bonded extended structures involving inorganic molecules are abundant, but many of them were obtained by serendipity.[4] The systematic assembly of inorganic molecules through hydrogen bonds did not occur until recently.[1,5] Organometallic molecules which form extended hydrogen-bonded arrays are still rare due to their relative poor stability towards acidic protons.

We have been interested in the assembly of organobismuth complexes with extended structures, promoted by the various applications of bismuth compounds in ceramic materials, catalysis and medicine.[6,7] Bismuth(v) compounds with the general formula $BiR_3(O_2CR')_2$, where R′ is a substituent containing an OH group, were chosen for our investigation for the following considerations: (*a*) the hydroxyl group can function as both proton donor and acceptor to promote the formation of intermolecular hydrogen bonds; (*b*) one of the oxygen atoms of the acetate ligand is only weakly associated with the bismuth(v) centre, hence it could act as a proton acceptor and participate in the formation of hydrogen bonds; (*c*) the bismuth(v) centre has an approximately trigonal-bipyramidal geometry with the acetate ligands occupying the axial positions, making it possible to extend the structure along the axial direction. We have examined the effect of the R′ group and the aryl group R on the extended hydrogen-bonded structures of the bismuth complexes. We have also explored the assembly of extended helical structures by introducing chiral centres in the R′ group of the $BiR_3(O_2CR')_2$ complexes. Unusual hydrogen-bonded extended structures such as double strands and double layers have been obtained. An unusual stereoselectivity of the bismuth(v) centre towards chiral ligands (±)-$R'CO_2^-$, have been observed. The details are reported herein.



Experimental

All reactions were performed under a dry nitrogen atmosphere. The compounds $Bi^{V}(C_6H_4NMe_2\text{-}p)_3Cl_2$ and $BiPh_3Cl_2$ were synthesized by a modified procedure reported in the literature,[8] $Ag(O_2CCH_2CH_2CH_2OH)$, $Ag(O_2CCH_2CH_2C_6H_4OH\text{-}p)$, $Ag[O_2CCH(CH_2OH)Ph]$, $Ag[O_2CH(OH)CH_2CH_3]$, $Ag[O_2CH_2CH(OH)CH_3]$ and $Ag[O_2CCH(Ph)(C_5H_9)]$ were obtained by reaction of $AgNO_3$ with the corresponding sodium salt. The sodium salts were either obtained directly from Aldrich or prepared by the reaction of NaOH with the corresponding acid. Proton and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer. Elemental analyses were performed at Canadian Microanalytical Service Ltd., Delta, British Columbia. The TGA experiments were conducted on a Perkin-Elmer TGA-7 analyser.

Preparations

$Bi(C_6H_4NMe_2\text{-}p)_3(O_2CCH_2CH_2CH_2OH)_2$ 1. The compound $Ag(O_2CCH_2CH_2CH_2OH)$ (132 mg, 0.625 mmol) was added to $Bi^{V}(C_6H_4NMe_2\text{-}p)_3Cl_2$ (200 mg, 0.31 mmol) in tetrahydrofuran (thf) (10 cm^3). The mixture was stirred for 17 h at 23 °C. After filtration a yellow solution was obtained. The volume of the solution was reduced to about 3 cm^3 *in vacuo*. After the solution was kept at 0 °C for a few days yellow crystals of **1** were

obtained. Yield 75%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.63 (qnt, 4 H, CH_2), 2.19 (t, 4 H, CH_2), 2.98 (s, 18 H, CH_3), 3.41 (t, 4 H, CH_2), 6.78 (d, 6 H, Ph) and 7.93 (d, 6 H, Ph) (Found: C, 49.25; H, 5.75; N, 5.2. Calc. for $C_{32}H_{44}BiN_3O_6$: C, 49.55; H, 5.7; N, 5.4%).

$BiPh_3(O_2CCH_2CH_2CH_2OH)_2$ 2. The compound $Ag(O_2CCH_2CH_2CH_2OH)$ (166 mg, 0.787 mmol) was added to $Bi^VPh_3Cl_2$ (200 mg, 0.39 mmol) in tetrahydrofuran (10 cm^3). The mixture was stirred for 17 h at 23 °C. After filtration a colourless solution was obtained. The volume of this solution was reduced to about 3 cm^3 *in vacuo*. After the addition of hexane (1 cm^3) and a few days standing at 0 °C, colourless crystals of **2** were obtained. Yield: 84%. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.63 (qnt, 4 H, CH_2), 2.19 (t, 4 H, CH_2), 3.33 (t, 4 H, CH_2), 7.53 (t, 3 H, Ph), 7.62 (m, 6 H, Ph) and 8.10 (d, 6 H, Ph) (Found for the solvent-free sample: C, 48.1; H, 4.4. Calc. for $C_{26}H_{29}BiO_6$: C, 48.3; H, 4.5%).

$BiPh_3(O_2CCH_2CH_2C_6H_4OH$-*p*)$_2$ 3. Compound **3** was obtained by the same procedure as described for **2** in 70% yield. ^{1}H NMR ([$^2H_8$]thf, 25 °C): **3**, δ 2.24 (t, 4 H, CH_2), 2.58 (t, 4 H, CH_2), 6.48 (d, 4 H, C_6H_4), 6.78 (d, 4 H, C_6H_4), 7.45 (m, 3 H, Ph), 7.54 (m, 6 H, Ph), 8.10 (d, 6 H, Ph); $BiPh_3$(*p*-$O_2CC_6H_4OH)_2$, δ 6.82 (d, 4 H, C_6H_4), 7.60 (m, 3 H, Ph), 7.72 (m, 6 H, Ph), 7.99 (d, 4 H, C_6H_4) and 8.50 (d, 6 H, Ph) (Found for the solvent-free sample: C, 55.75; H, 4.4. Calc. for $C_{36}H_{33}BiO_6$ **3**: C, 56.1; H, 4.3%). The compound $BiPh_3$(*p*-$O_2CC_6H_4OH)_2$ was obtained by the same procedure [Found: C, 54.55; H, 4.15. Calc. for $BiPh_3$(*p*-$O_2CC_6H_4OH)_2$·thf: C, 54.95; H, 4.2%].

(*R*,*R*)/(*S*,*S*)-Bi($C_6H_4NMe_2$-*p*)$_3$[$O_2CCH(CH_2OH)Ph$]$_2$ 4. Compound **4** was obtained by the same procedure as described for **1** in 89% yield. NMR (25 °C); ^{1}H ($CDCl_3$): δ 2.98 (s, 18 H, CH_3), 3.24 (m, 2 H, CH), 3.61 (m, 2 H, CH_2), 3.74 (m, 2 H, CH_2), 6.73 (m, aryl), 6.87 (m, aryl), 7.09 (m, aryl) and 7.80 (m, aryl); ^{13}C (CD_2Cl_2): δ 40.07 (CH_3), 54.79 (CH), 65.41 (CH_2), 113.57, 126.67, 128.35, 128.57, 135.11, 138.51, 145.18, 151.84 (aryl) and 178.27 (CO_2) (Found: C, 55.55; H, 4.3; N, 4.5. Calc. for $C_{42}H_{48}BiN_3O_6$: C, 56.05; H, 4.35, N, 4.65%).

(*R*,*R*)/(*S*,*S*)-Bi($C_6H_4NMe_2$-*p*)$_3$[$O_2CCH(OH)CH_2CH_3$]$_2$ 5, -Bi($C_6H_4NMe_2$-*p*)$_3$[$O_2CCH_2CH(OH)CH_3$]$_2$ 6 and -Bi($C_6H_4NMe_2$-*p*)$_3$[$O_2CCH(Ph)(C_5H_9)$]$_2$ 8. These compounds were prepared by the same procedure as described for **1** in about 70% isolated yield. NMR (25 °C) **5**, ^{1}H (CD_2Cl_2): δ 0.71 (m, 6 H, CH_3), 1.43 (m, 2 H, CH_2), 1.61 (m, 2 H, CH_2), 3.01 (s, 18 H, NCH_3), 3.81 (q, 2 H, CH), 6.83 (d, 6 H, aryl) and 7.87 (d, 6 H, aryl); ^{13}C (CD_2Cl_2): δ 8.99 (CH_3), 27.95 (CH_2), 40.05 (NCH_3),71.98 (CH), 113.61, 135.09, 144.15 and 151.91 (aryl); ^{1}H **6**, ($CDCl_3$): δ 0.99 (d, 6 H, CH_3), 2.10 (m, 2 H, CH_2), 2.25 (m, 2 H, CH_2), 2.97 (s, 18 H, NCH_3), 3.85 (m, 2 H, CH), 6.77 (d, 6 H, aryl) and 7.89 (d, 6 H, aryl); ^{13}C **6** (CD_2Cl_2): δ 22.26 (CH_3), 40.05 (NCH_3), 43.87 (CH_2), 64.58 (CH), 113.60, 134.96, 145.64 and 151.82 (aryl); ^{13}C **8**, (CD_2Cl_2): δ 26.90, 27.13, 32.57, 33.35, 45.60 (cyclopentyl), 41.85 (NCH_3), 61.65 (CH), 115.23, 127.91, 129.91, 130.37, 136.48, 143.01, 147.90, 153.36 (aryl) and 180.20 (CO_2).

(*R*,*R*)/(*S*,*S*)-$BiPh_3$[$O_2CCH(CH_2OH)Ph$]$_2$ 7. Compound **7** was obtained by the same procedure as employed for **3** in 95% yield. NMR ($CDCl_3$); ^{1}H (25 °C): δ 2.86 (m, 2 H, CH), 3.63 (m, 2 H, CH_2), 3.74 (m, 2 H, CH_2), 3.76 (m, 2 H, CH_2), 6.85 (m, aryl), 7.09 (m, aryl), 7.52 (m, aryl) and 7.98 (m, aryl); ^{13}C (−40 °C): δ 53.75 (CH), 65.38 (CH_2), 126.95, 128.01, 128.54, 131.28, 131.57, 134.04, 137.00, 158.80 (aryl) and 179.46 (CO_2) (Found: C, 56.1; H, 4.3. Calc. for $C_{36}H_{33}BiO_6$: C, 55.55; H, 4.4%).

X-Ray crystallography

Crystals of compounds **1**–**7** obtained from concentrated thf solutions were mounted on glass fibres. Data were collected at 23 °C over the range 2θ 3–50° for compounds **1**–**6** on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), operated at 50 kV and 35 mA while data for **7** were collected in the range 2θ 3–50° on a Siemens P4 diffractometer with graphite-monochromated Mo-Kα radiation, operated at 50 kV and 40 mA. Three standard reflections were measured every 147. No significant decay was observed for all samples. Data were processed on a Silicon Graphics computer using the TEXSAN crystallographic package[9a] for compounds **1**–**6** and SHELXTL for **7**.[9b] An empirical absorption correction based on azimuthal scans of several reflections was applied for all crystals. The data were also corrected for Lorentz-polarisation effects. Neutral atom scattering factors were taken from Cromer and Waber.[10] The crystals of **1** and **5** belong to the triclinic space group, $P\bar{1}$, while those of **2**, **4** and **6** belong to the monoclinic space group, $P2_1/c$, $P2_1/n$ and $P2/c$ (no. 13), respectively, uniquely determined by the systematic absences. The systematic absences of the crystals of **3** and **7** were in accord with *Cc* and *C*2/*c*. The structural solution and refinement confirmed that the *C*2/*c* space group is the correct choice for **3** and **7**. The structures of **1** and **5** were solved by heavy-atom methods while those of **2**–**4** and **6** were solved by direct methods. Full-matrix least-squares refinements minimising the function $\Sigma w(|F_o| - |F_c|)^2$ were applied for compounds **1**–**6**, while the function $\Sigma w(F_o^2 - F_c^2)^2$ was minimised for **7**. There are thf solvent molecules in the crystal lattice of compounds **2** and **3** (one per molecule). All non-hydrogen atoms in **1** and **3** except the thf solvent molecule were refined anisotropically while only the metal atom and some of the non-hydrogen atoms in **2**, **5** and **6** were refined anisotropically owing to the limitation of the data. All non-hydrogen atoms in compound **7** were refined anisotropically. The crystals of compound **4** displayed significant twinning, as shown by the peak profiles, and low diffraction intensity. The quality of the data was poor and the ratio of data/parameters low. As a consequence, only the bismuth atom was refined anisotropically. We attempted several data collections for **4** by using different crystals which consistently showed the twinning problems. Low-temperature data collection was not attempted because of the unavailability of a low-temperature device. The data presented were the best results from our repeated measurements. The positions of the acidic protons bonded to the oxygen atoms in **1**–**3** were located directly from the Fourier-difference maps. The approximate positions of the acidic protons in **4** were calculated. The positions of non-acidic hydrogen atoms in all compounds except those of the disordered thf solvent molecule were calculated and their contributions included in structure-factor calculations. The crystallographic data are given in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/514.

Results and Discussion

Syntheses and structures of $Bi^VR_3(O_3CR')_2$ where R′ has no chiral centres, Bi($C_6H_4NMe_2$-*p*)$_3$($O_2CCH_2CH_2CH_2OH$)$_2$ 1, $BiPh_3(O_2CCH_2CH_2CH_2OH)_2$ 2 and $BiPh_3(O_2CCH_2CH_2C_6H_4OH$-*p*)$_2$ 3

Earlier work on organobismuth(v) complexes[7a,b] focused mostly on the derivatives of $BiPh_3X_2$ due to the relatively easy accessibility of $BiPh_3$. Structural information on other bis-

Table 1 Crystallographic data for compounds **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{32}H_{44}BiN_3O_6$	$C_{26}H_{29}BiO_6 \cdot C_4H_8O$	$C_{36}H_{33}BiO_6 \cdot C_4H_8O$	$C_{42}H_{48}BiN_3O_6$	$C_{32}H_{44}BiN_3O_6$	$C_{32}H_{44}BiN_3O_6$	$C_{36}H_{33}BiO_6$
M	775.7	718.6	866.8	899.8	775.70	775.7	770.6
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2/c$	$C2/c$
a/Å	11.9893(7)	11.668(3)	14.44(1)	11.715(7)	12.342(4)	11.667(4)	17.245(3)
b/Å	12.736(2)	12.184(2)	22.542(6)	21.03(1)	13.059(3)	12.425(4)	9.920(2)
c/Å	11.348(2)	21.167(2)	13.254(8)	15.67(1)	11.823(3)	12.275(4)	19.144(4)
α/°	108.15(1)				90.10(2)		
β/°	98.515(8)	103.09(1)	122.13(4)	100.45(6)	118.34(2)	109.16(2)	106.98(3)
γ/°	92.535(8)				96.16(3)		
U/Å^3	1621.0(4)	2930.8(9)	3653(3)	3797(4)	1664.6(9)	1680.8(10)	3132.2(11)
Z	2	4	4	4	2	2	4
D_c/g cm^{-3}	1.59	1.63	1.58	1.57	1.55	1.53	1.63
μ(Mo-Kα)/cm^{-1}	54.7	60.5	48.7	46.9	53.3	52.8	56.7
Transmission coefficient	0.52–1.00	0.50–1.00	0.29–1.00	0.75–1.00	0.75–1.00	0.77–1.00	0.41–1.00
2θ Range/°	3–50	3–50	3–50	3–50	3–50	3–45	4–45
Measured reflections	$+h, \pm k, \pm l$; 5694	$+h, +k, \pm l$; 5395	$+h, +k, \pm l$; 3305	$+h, +k, \pm l$; 4025	$+h, \pm k, \pm l$; 4755	$+h, +k, \pm l$; 1704	$+h, +k, \pm l$; 2671
Observed reflections	3562, $I >$ 3.00σ(I)	2132, $I >$ 1.6σ(I)	1900, $I >$ 3.00σ(I)	1460, $I >$ 1.5σ(I)	1749, $I >$ 2.7σ(I)	708, $I >$ 2.0σ(I)	2056, all data
No. variables	385	252	212	214	219	103	196
Largest shift/e.s.d. in final cycle	0.00	0.09	0.00	0.00	0.02	0.00	0.00
Largest electron-density peak/e Å^{-3}	1.13	1.60	1.92	1.87	0.57	1.10	1.886
R^a	0.039	0.074	0.045	0.113	0.048	0.064	0.063
R'^b	0.033	0.049	0.033	0.075	0.040	0.069	0.115 ($wR2$)^c
Goodness of fit^d	1.24	1.34	1.78	1.48	1.34	1.59	1.176

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$. ^{c} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. ^{d} $S = \Sigma(|F_o| - |F_c|)/\sigma(N_o - N_v)$ except for compound **7** where the goodness of fit is on F^2 (N_o = number of observed reflections and N_v = number of variables or parameters).

muth(v) complexes, BiR_3X_2, where R is not a phenyl ligand, is still scarce. By using a modified literature procedure, we have been able to obtain several BiR_3 complexes in good yield, where the aryl ligand contains functional groups such as pyridyl or amino.[7c] These BiR_3 compounds can be oxidised readily by halogens to form the corresponding bismuth(v) complexes,[7c] BiR_3X_2, thus, enabling us to investigate the chemistry of BiR_3X_2. Compound **1** was synthesized by the reaction of $Bi^V(C_6H_4NMe_2\text{-}p)_3Cl_2$ with 2 equivalents of $Ag(O_2CCH_2CH_2CH_2OH)$ and fully characterised by ^{1}H NMR spectroscopy, elemental and X-ray diffraction analysis. Compound **1** is stable in anhydrous solvents such as thf and dichloromethane.

The structure of compound **1** resembles that of $BiPh_3(O_2CCF_3)_2$ reported earlier by Ferguson *et al.*[11a] As shown in Fig. 1, the co-ordination geometry of the bismuth centre is a distorted trigonal bipyramid with oxygen atoms occupying the axial positions and carbon atoms occupying the equatorial positions. Such a distorted trigonal-bipyramidal geometry has been observed previously for five-co-ordinate organobismuth(v) complexes.[11,13] Two of the aromatic rings are perpendicular to the Bi–O bond while the third is parallel to it. The nitrogen lone pair of the $N(CH_3)_2$ group conjugates with the aromatic ring, as indicated by its trigonal-planar geometry and the short bond length between the nitrogen and the aromatic carbon atom, 1.38(1) Å. The weakly co-ordinated oxygen atoms of the two carboxylate ligands located at 2.78 [O(4)] and 2.83 Å [O(2)] from the bismuth are *cis* to each other, which apparently causes the significant deviation of the C–Bi–C angles from 120° in the equatorial plane. The protons bonded to the oxygen atoms were located directly from the X-ray Fourier-difference map. One of the protons H(1) from the two OH groups is shared between the two alkoxo oxygen atoms O(5′) and O(6) of neighbouring molecules, linking the $Bi^V(C_6H_4NMe_2\text{-}p)_3(O_2CCH_2CH_2CH_2OH)_2$ units together as a hydrogen-bonded[14] one-dimensional chain [O(5′) · · · O(6) 2.80(1) Å]. Most interestingly, these two chains are further coupled together *via* the formation of interchain hydrogen bonds by sharing the remaining proton H(2) from the two OH groups between the weakly co-ordinated carboxylate oxygen atom O(2′) and the O(5) atom [O(2′) · · · O(5) 2.84(1) Å], resulting in the unusual *double-stranded* structure (Fig. 2). There are two types of cavities in the double strands, a small one consisting of eight carbon, four oxygen and two protons, and a large one consisting of ten carbon atoms, ten oxygen atoms, four protons and two bismuth

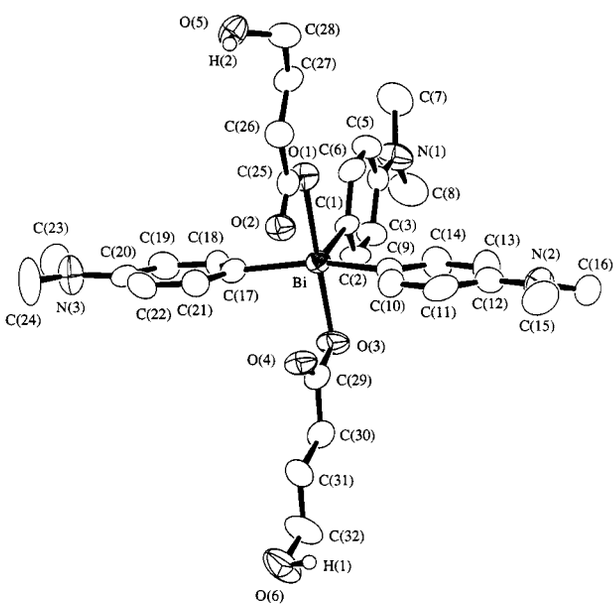


Fig. 1 An ORTEP[12] diagram showing the molecular structure of compound **1** with 50% thermal ellipsoids and labelling scheme. Important bond lengths (Å) and angles (°): Bi–O(1) 2.328(6), Bi–O(3) 2.287(6), Bi–C(1) 2.210(7), Bi–C(9) 2.181(10) and Bi–C(17) 2.179(9); O(1)–Bi–O(3) 175.7(2), C(9)–Bi–C(17) 152.9(3), C(1)–Bi–C(9) 103.8(3) and C(1)–Bi–C(17) 103.3(3)

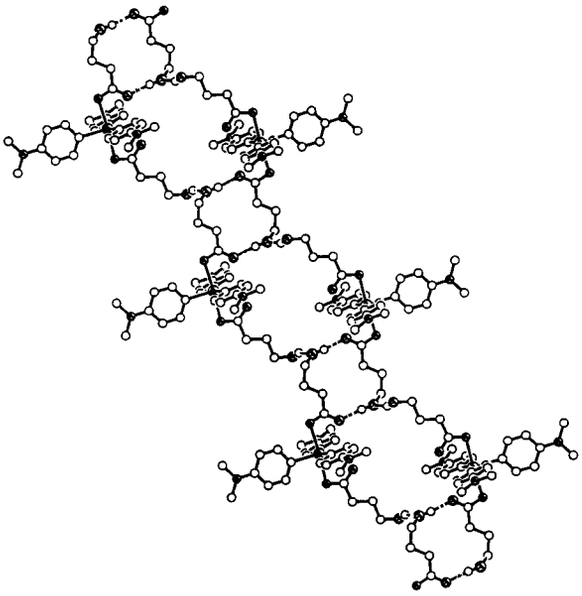


Fig. 2 The double-stranded structure of compound **1**. Hydrogen bonds are shown as dashed lines

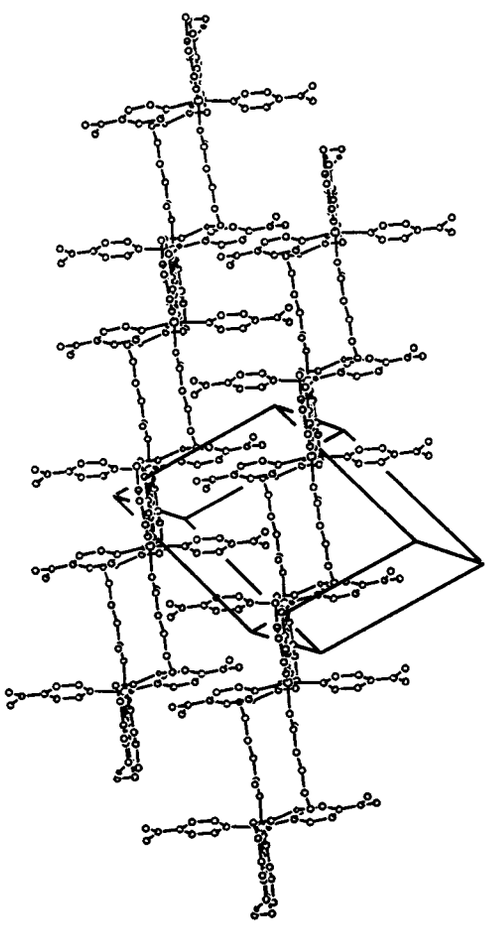


Fig. 3 The π–π stacking between two double strands in compound **1**

atoms. The $C_6H_4NMe_2$-*p* ligands perpendicular to the Bi–O bonds are situated at upper and lower positions inside the large cavity. Space-filling models show that there is essentially no space left in the small cavity while a large empty space is available in the large cavity. There are extensive π–π stacking interactions between the parallel $C_6H_4NMe_2$-*p* ligands from two neighbouring double strands (Fig. 3). The shortest atomic contact distance between them is 3.71 Å. The amino group is situated above the neighbouring phenyl ring, perhaps acting as an

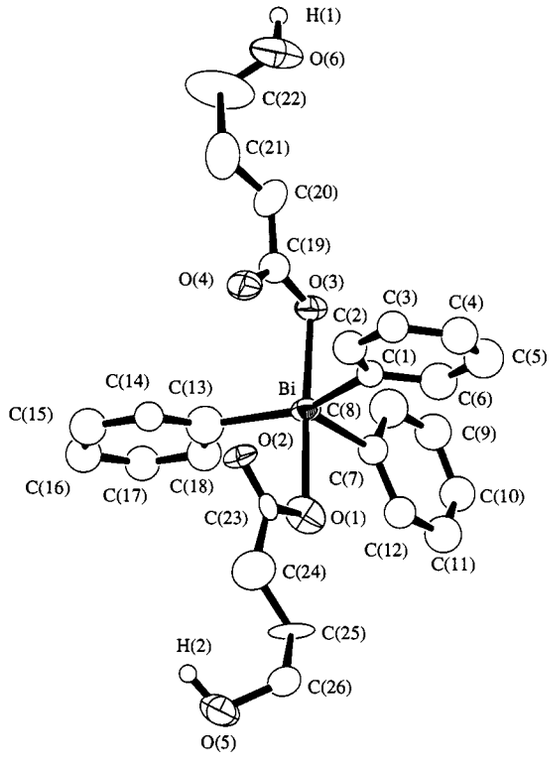


Fig. 4 An ORTEP diagram showing the molecular structure of compound **2** with 50% thermal ellipsoids and labelling scheme. Important bond lengths (Å) and angles (°): Bi–O(1) 2.28(2), Bi–O(3) 2.31(1), Bi–C(1) 2.21(2), Bi–C(7) 2.22(2) and Bi–C(13) 2.24(3); O(1)–Bi–O(3) 174.5(6), C(1)–Bi–C(13) 150(1), C(7)–Bi–C(1) 106.3(8) and C(7)–Bi–C(13) 103(1)

electron donor while the aromatic ring acts as an acceptor. The hydrogen bonds and π–π interactions between the $C_6H_4NMe_2$-*p* ligands are believed to be responsible for the formation of the double-stranded structure of **1**. Hydrogen-bonded double-stranded structures are common for biomolecules and are known to play important roles in their functions.[15] Such structures have also been observed in organic molecules,[1] but are previously unknown for organometallic molecules.

To determine the role of the dimethylamino group in the extended structure of compound **1**, we synthesized $Bi^{V}Ph_3(O_2CCH_2CH_2CH_2OH)_2$, **2** by the reaction of $BiPh_3Cl_2$ with $Ag(O_2CCH_2CH_2CH_2OH)_2$. Compound **2** was characterised by ^{1}H NMR spectroscopy, elemental and X-ray diffraction analysis. Its molecular structure resembles that of **1**, as shown in Fig. 4. Interestingly, however, instead of forming the extended double-stranded structure, **2** displays a *double-layered* structure. As observed in **1**, one of the protons H(1) from the two OH groups in **2** is shared between the two alkoxo oxygen atoms O(6) and O(5′), resulting in the formation of a hydrogen-bonded chain [O(5′) · · · O(6) 2.90(2) Å]. In the crystal lattice there are two types of such chains running approximately at right angles to each other. These two types of chains are interlinked through the formation of hydrogen bonds by sharing the second proton H(2) of the two OH groups between the O(5) atom and the non-co-ordinated oxygen atom O(4″) of the carboxylate [O(4″) · · · O(5) 2.84(2) Å], producing a hydrogen-bonded *double-layered* structure (Fig. 5). The phenyl rings are at the surface of the double layers while the OH groups and the non-co-ordinated oxygen atoms of the carboxylates are inside the double layers. In addition, there are channels of various sizes inside the double layers. The thf solvent molecule is intercalated in the cavity between two double layers. No π–π stacking with distances less then 4.0 Å is evident in **2**. Hydrogen-bonded two-dimensional networks are known for inorganic compounds,[4,5] but there are no precedents of inorganic or organometallic molecules displaying the double-layered struc-

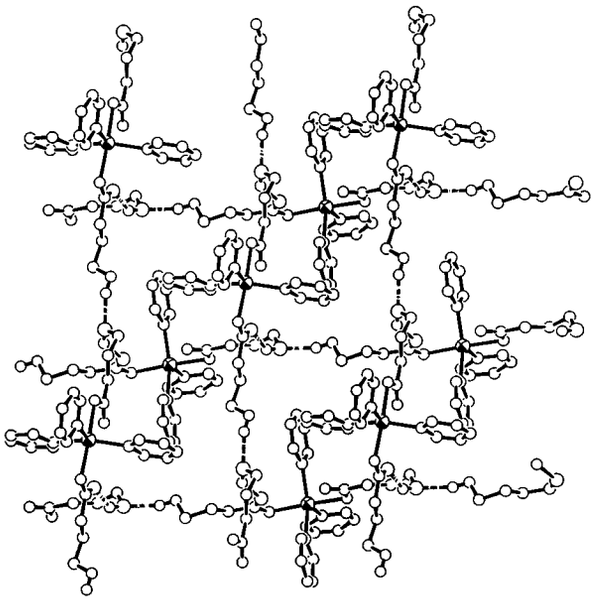


Fig. 5 The two layers of hydrogen-bonded chains in compound **2** running at approximately right angles. Hydrogen bonds are shown as dashed lines

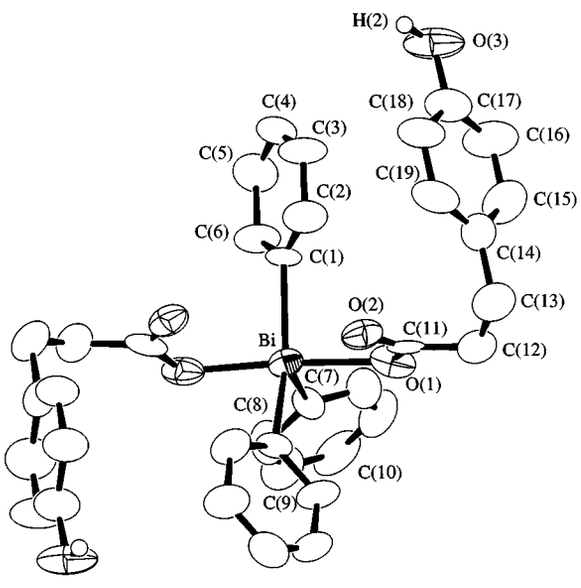


Fig. 6 An ORTEP diagram showing the molecular structure of compound **3** with 50% thermal ellipsoids and labelling scheme. Important bond lengths (Å) and angles (°): Bi–O(1) 2.253(7), Bi–C(1) 2.229(9) and Bi–C(7) 2.22(1); O(1)–Bi–O(1′) 170.1(3), C(1)–Bi–C(7) 107.2(3) and C(1)–Bi–C(1′) 145.7(5)

ture as observed in **2**. It is obvious that the dramatic structural difference between **1** and **2** is caused by the absence of the dimethylamino group in **2**. We believe that the dimethylamino group stabilises the double-stranded structure of **1** by acting as a π donor in the inter-double strand π–π interactions and providing the steric bulkiness as well.

To increase the possibility of π–π stacking interactions, we introduced an aryl group in the acetate ligand. Compound **3**, $Bi^{V}Ph_3(O_2CCH_2CH_2C_6H_4OH\text{-}p)_2$, was synthesized by the reaction of $BiPh_3Cl_2$ with $Ag(O_2CCH_2CH_2C_6H_4OH\text{-}p)$. As shown in Fig. 6, **3** has a two-fold rotation axis on which the Bi, C(7) and C(10) atoms lie. The O(2) atom is 2.88 Å away from the bismuth. The two phenol groups are oriented *trans* to each other. The H(2) proton of the hydroxyl group forms a hydrogen bond with the O(2′) atom of the carboxylate from the neighbouring molecule in a head-to-tail fashion, as evidenced by the O(2′)···O(3) distance of 2.77(1) Å, leading to the formation of a one-dimensional hydrogen-bonded chain (Fig. 7). The phenyl rings are all located between two bismuth centres, but there is no evidence for significant π–π interactions between these rings. The thf solvent molecule is situated in the cavity between two chains. The head-to-tail formation of hydrogen bonds and the lack of hydrogen bonds between two OH groups in **3** can be attributed to the geometry of the 3-(4-hydroxyphenyl)propionate ligand; the ethylene linkage provides the flexibility for the ligand to bend over and the phenol portion provides the required spacing for the OH group to reach the oxygen atom of the acetate ligand from the neighbouring molecule.

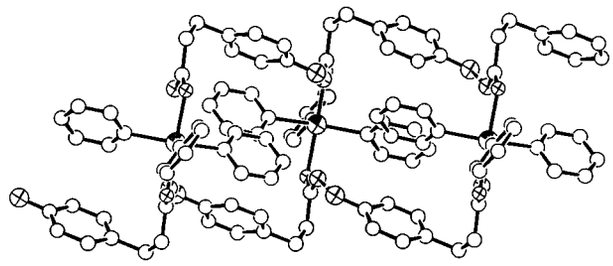


Fig. 7 The hydrogen-bonded chains in compound **3**. Hydrogen bonds are shown as dashed lines

Syntheses and structures of $BiR_3(O_2CR')_2$ where R′ contains a chiral centre, (*R*,*R*)/(*S*,*S*)-$Bi(C_6H_4NMe_2\text{-}p)_3[O_2CCH(CH_2OH)Ph]_2$ 4, -$Bi(C_6H_4NMe_2\text{-}p)_3[O_2CCH(OH)CH_2CH_3]_2$ 5, -$Bi(C_6H_4NMe_2\text{-}p)_3[O_2CCH_2CH(OH)CH_3]_2$ 6 and -$Bi^{V}Ph_3[O_2CCH(CH_2OH)Ph]_2$ 7

Stereoselectivity. The most interesting extended array is perhaps the chiral helical structure due to its many unique roles in biological systems and materials.[16] Molecules with chiral centres have been known often to promote the long-range chiral structural ordering such as a helical array and have been widely used in the design of cholesteric mesophases of liquid crystals.[17] It is therefore conceivable that, by introducing the appropriate chiral centres in the carboxylate ligands of the bismuth(V) complexes, a hydrogen-bonded helical structure of organobismuth(V) compounds may be achieved. The other interesting point to examine is the selectivity of the bismuth(V) centre toward the chiral ligands. When a racemic chiral ligand, (±)-$R^*CO_2^-$, is used in the reaction of $Bi^{V}(C_6H_4NMe_2\text{-}p)_3Cl_2$ with $Ag(O_2CR^*)$ two possible diastereomers, (*R*,*R*)- or (*S*,*S*)-$Bi^{V}(C_6H_4NMe_2\text{-}p)_3(O_2CR^*)_2$ and (*R*,*S*)-$Bi^{V}(C_6H_4NMe_2\text{-}p)_3(O_2CR^*)_2$, could be obtained. One would therefore ask 'does the bismuth(V) complex have any preference for any of the diastereomers?'. For these reasons we investigated the syntheses and structures of compounds **4**–**7**.

By using the same procedure described for compound **1**, **4**–**6** were obtained readily from the reaction of $Bi^{V}(C_6H_4NMe_2\text{-}p)_3Cl_2$ with the corresponding racemic silver salt, Ag[(±)-O_2CR^*]. The crystal structures of these compounds were determined by single-crystal X-ray diffraction analyses. They all crystallise in centric space groups with equal portions of (*R*,*R*) and (*S*,*S*) isomers. The ORTEP diagrams showing the molecular structures of compounds **4**–**6** along with important bond lengths and angles are given in Figs. 8–10, respectively. Compound **6** has a crystallographically imposed C_2 axis. The co-ordination environment surrounding the bismuth centre in all three compounds is similar with the exception of **4** where only one of the $C_6H_4NMe_2\text{-}p$ groups is perpendicular to the Bi–O bonds. One very important feature for these three structures, as established by the X-ray analysis, is that the chirality of the two carboxylate ligands attached to the Bi^{V} is identical in all three compounds, *i.e.* *R* and *R* or *S* and *S*, but not *R* and *S*. several crystals from compounds **4**–**6** have been examined by X-ray diffraction, which consistently show the presence

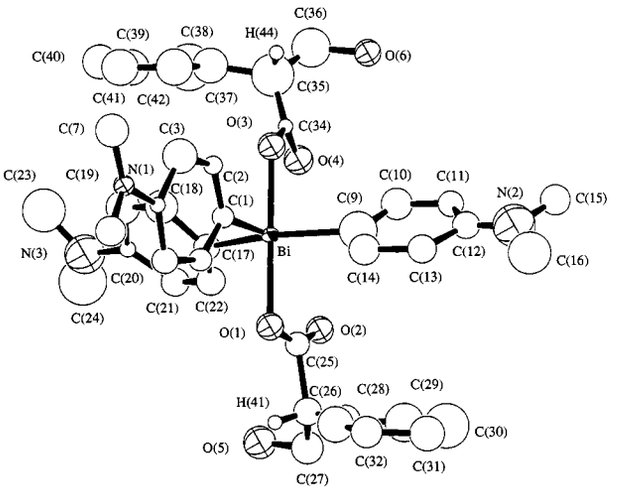


Fig. 8 An ORTEP diagram showing the molecular structure of compound **4** with 50% thermal ellipsoids and labelling scheme. Important bond lengths (Å) and angles (°): Bi–O(1) 2.30(3), Bi–O(3) 2.19(4), Bi–C(1) 2.15(5), Bi–C(9) 2.21(6) and Bi–C(17) 2.29(5); O(1)–Bi–O(3) 177(1), C(1)–Bi–C(9) 108(2), C(1)–Bi–C(17) 105(2) and C(9)–Bi–C(17) 147(2)

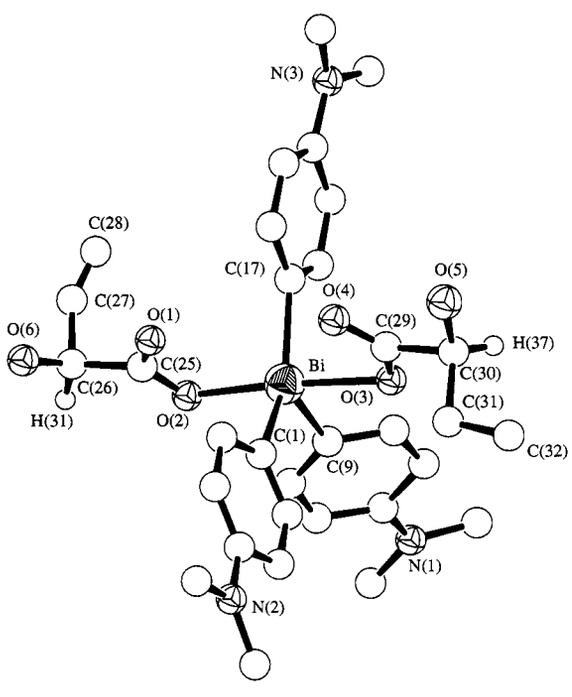


Fig. 9 An ORTEP diagram showing the molecular structure of compound **5** with 50% thermal ellipsoids and labelling scheme. Important bond lengths (Å) and angles (°): Bi–O(2) 2.27(1), Bi–O(3) 2.32(1), Bi–C(1) 2.14(2), Bi–C(9) 2.20(2) and Bi–C(17) 2.16(2); O(2)–Bi–O(3) 172.3(5), C(1)–Bi–C(9) 107.5(7), C(1)–Bi–C(17) 144.8(8) and C(9)–Bi–C(17) 107.4(7)

of (*R*,*R*) and (*S*,*S*) isomers only. It is possible that both diastereomers, (*R*,*R*) or (*S*,*S*) and (*R*,*S*), are present in the solution, but only the (*R*,*R*) and (*S*,*S*) isomers crystallise perhaps due to some favourable crystal-lattice packing forces. The high isolated yields (about 70%) of compounds **4**–**6** imply that even if the (*R*,*S*) isomers exist they must be minor products. Since the (*R*,*R*) or (*S*,*S*) isomer and (*R*,*S*) isomer are diastereomers in relationship, one could distinguish them by NMR spectroscopic methods in principle.[18] The two chiral centres in **4**–**6** are several atoms away from each other, which makes it difficult to distinguish the diastereomers by ^{1}H NMR spectroscopy. Carbon-13 NMR spectra have been known, however, to be more sensitive than the ^{1}H NMR in differentiating diastereomers.[18] We therefore examined the solution behaviour of compounds **4**–**6**

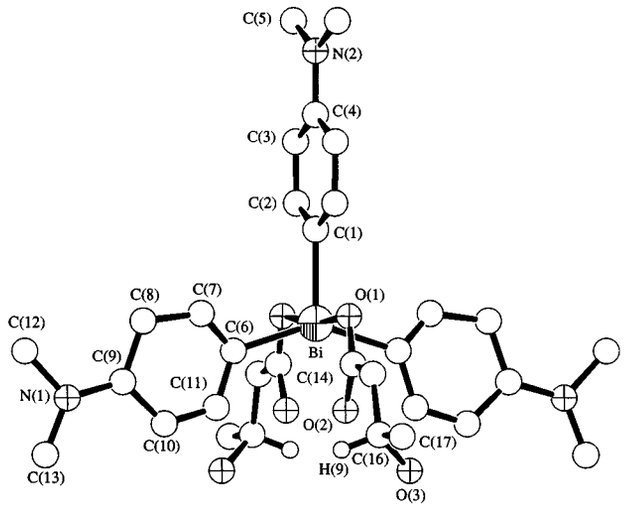


Fig. 10 An ORTEP diagram showing the molecular structure of compound **6** with 50% thermal ellipsoids and labelling scheme. Important bond lengths (Å) and angles (°): Bi–O(1) 2.31(2), Bi–C(1) 2.20(6), Bi–C(6) 2.11(4) and Bi–C(17) 2.16(2); O(1)–Bi–O(1′) 171(1), C(1)–Bi–C(6) 107(1) and C(6)–Bi–C(6′) 144(2)

by recording their ^{13}C NMR spectra. The spectra for all three compounds show only one set of chemical shifts for all carbon atoms in the temperature range 200–293 K, suggesting that the (*R*,*S*) diastereomer is likely not present in solution.

The preferential co-ordination of the bismuth(V) centre to two identical optical isomers is intriguing. To our knowledge, such a phenomenon has not been observed previously in organometallic compounds. The formation mechanism of compounds **4**–**6**, however, is still a mystery. If the reaction of $Bi(C_6H_4NMe_2\text{-}p)_3Cl_2$ with $Ag(O_2CR^*)$ proceeds in a stepwise fashion, an intermediate, $Bi(C_6H_4NMe_2\text{-}p)_3(O_2CR^*)Cl$, must be involved, which may play a critical role in the selective formation of (*R*,*R*) and (*S*,*S*) products. We attempted to synthesize and isolate this intermediate compound. However, unfortunately, it appears to be highly unstable and undergoes a rapid metathesis in solution to form $Bi(C_6H_4NMe_2\text{-}p)_3Cl_2$ and $Bi(C_6H_4NMe_2\text{-}p)_3(O_2CR^*)_2$, as evidenced by NMR spectroscopic studies.

One could argue that it is the bulkiness of the *p*-dimethylaminophenyl ligand in compounds **4**–**6** that promotes the chiral selectivity. We therefore synthesized compound **7**, $Bi^{V}Ph_3[O_2CCH(CH_2OH)Ph]_2$ by treating $BiPh_3Cl_2$ with 2 equivalents of $Ag[(\pm)\text{-}O_2CCH(CH_2OH)Ph]$. It was isolated as colourless block crystals in nearly quantitative yield (>90%). The crystals were examined by X-ray diffraction analyses which revealed that the enantiomers of (*R*,*R*) and (*S*,*S*) cocrystallize in the centric space group *C*2/*c* and there is no (*R*,*S*) isomer. The molecular structure resembles that of compound **4** (Fig. 11). We therefore conclude that there is no difference in chiral selectivity between the phenyl and *p*-dimethylaminophenyl ligands of the bismuth(V) complexes.

Since all the chiral compounds in **4**–**6** contain a hydroxyl group, it is conceivable that the chiral selectivity may be promoted by some hydrogen-bonded intermediate involving this group. To test this hypothesis we synthesized compound **8**, $Bi^{V}(C_6H_4NMe_2\text{-}p)_3[O_2CCH(Ph)(C_5H_9)]_2$, by using the racemic and non-hydroxyl-containing chiral silver cyclopentyl(phenyl)acetate. We have not been able to grow single crystals of **8**. However, the ^{13}C NMR spectrum of this compound shows only one set of chemical shifts for all carbon atoms, as observed for **4**–**7**. We therefore believe that the structure of **8** is likely to be similar to those of **4**–**6**, where two identical chiral ligands, *R* and *R* or *S* and *S*, are co-ordinated to the bismuth, and it is likely that the hydroxyl group in compounds **4**–**6** did not play any major role in the chiral selectivity.

Hydrogen bonds. Although there is no evidence for the involvement of the hydroxyl group in promoting chiral selectivity in compounds **4**–**7**, it does participate in hydrogen-bond formation and the hydrogen-bonding patterns in these compounds are quite different. In **5** the hydroxyl group forms an intramolecular hydrogen bond with the non-co-ordinating acetate oxygen atom, as indicated by the bond lengths of O(1)···O(6) 2.71(2) and O(4)···O(5) 2.67(2) Å. In addition, there are two intermolecular hydrogen bonds between O(4) and

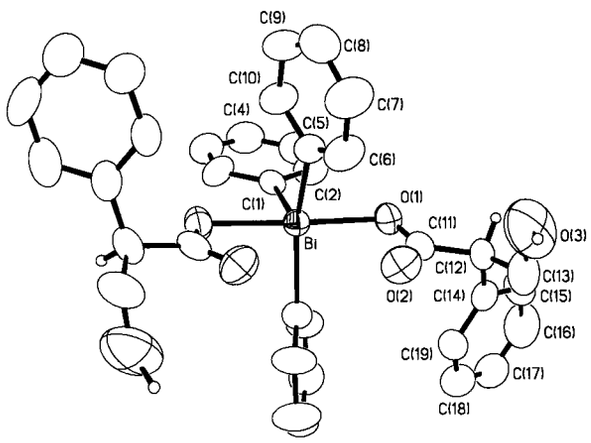


Fig. 11 An ORTEP diagram showing the molecular structure of compound **7** with 50% thermal ellipsoids and labelling scheme. Important bond lengths (Å) and angles (°): Bi–O(1) 2.307(7), Bi–C(1) 2.21(2) and Bi–C(5) 2.221(11); O(1)–Bi–O(1′) 175.8(4), C(1)–Bi–C(5) 105.0(3) and C(5)–Bi–C(5′) 149.9(7)

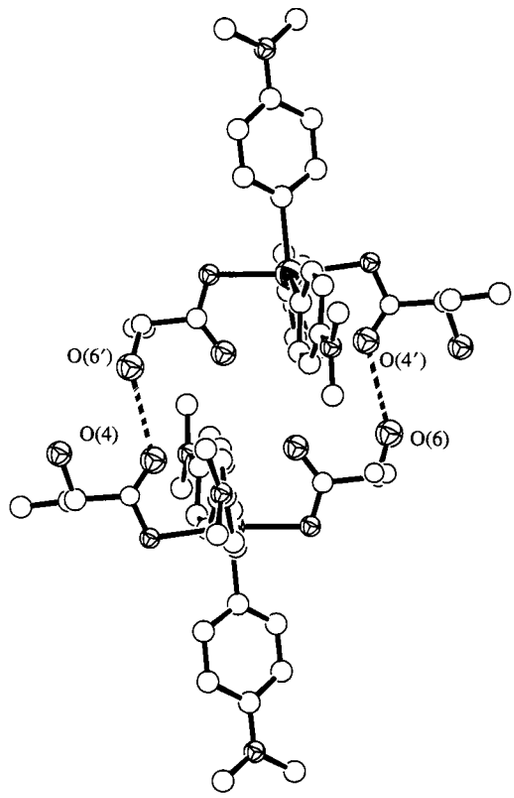


Fig. 12 The hydrogen-bonded dimer of compound **5**. The intermolecular hydrogen bonds are shown as dashed lines

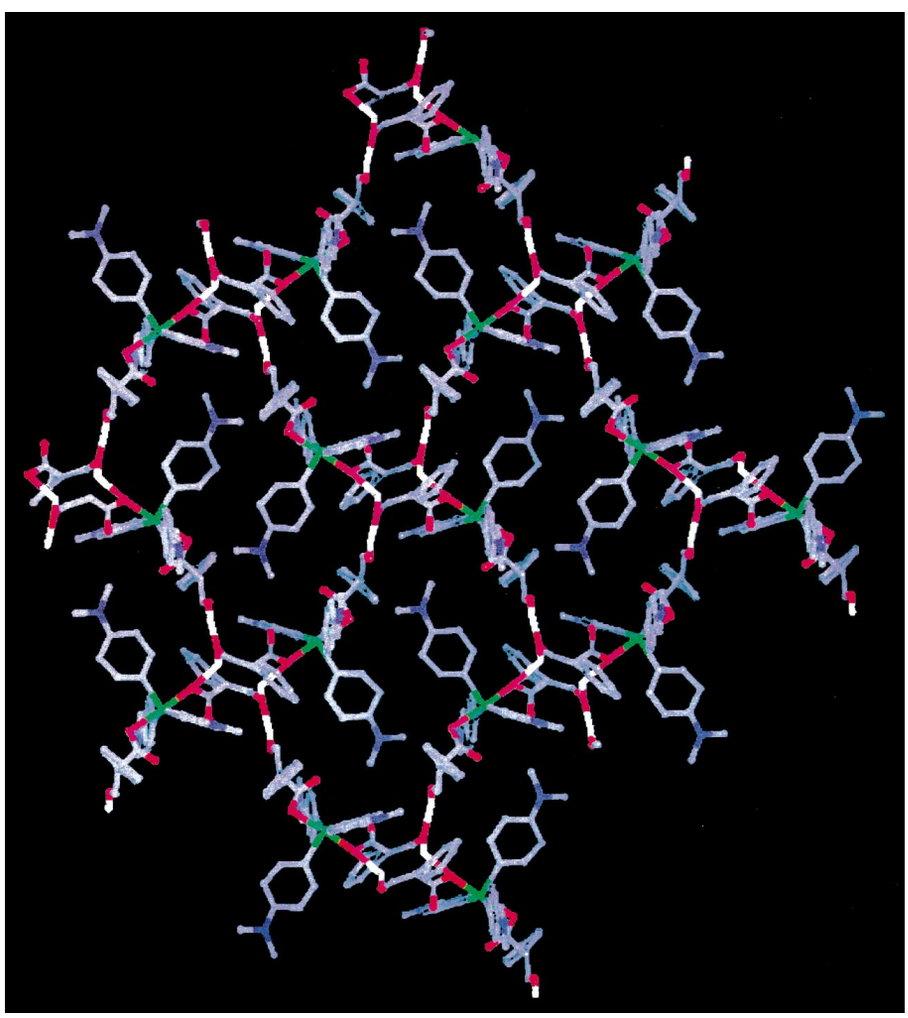


Fig. 13 The two-dimensional hydrogen-bonded network in compound **4**. Blue, nitrogen; red, oxygen; white, hydrogen; green, bismuth

O(6′), O(4′) and O(6), as indicated by their separation, 2.78(2) Å. There are also weak hydrogen bonds between O(5) and O(6′) or O(5′) and O(6) as suggested by the 3.21(2) Å separation between the two oxygen atoms. As a result of the intermolecular hydrogen bonds, the (*R*,*R*) enantiomer of compound **5** is linked to the (*S*,*S*) enantiomer to form a hydrogen-bonded dimer (Fig. 12). In contrast, compound **6** forms intramolecular hydrogen bonds only between the acetate O(2) atom and the hydroxyl O(3) atom with the oxygen–oxygen separation being 2.67(5) Å. The different hydrogen-bonding patterns in **5** and **6** can be attributed to steric factors.

The hydrogen-bonding pattern in compound **4** is complex. The two hydroxyl groups form two intermolecular hydrogen bonds with the hydroxyl groups of the neighbouring molecules as shown by the O(5) · · · O(6′) distance of 2.82(4) Å, leading to the formation of a worm-like chain. The mononuclear enantiomers, (*R*,*R*) and (*S*,*S*), alternate in the worm chain. In the crystal lattice these chains are stacked along one of the axes in such a fashion that the two neighbouring chains are out of phase by 180°. There are no significant π–π interactions between these two chains. Along the other two dimensions each worm chain is coupled to its two neighbouring chains through the formation of two intermolecular hydrogen bonds between the hydroxyl O(6) atom and the co-ordinated acetate O(3″) atom [O(6) · · · O(3″) 2.93(4) Å], resulting in the formation of a two-dimensional hydrogen-bonded network (Fig. 13). The interchain hydrogen-bond linkages in **4** resemble those in the double-stranded structure of **1** except that in **1** the interchain hydrogen bonds are between the non-co-ordinated oxygen atom of the acetate ligand and the OH group while in **4** they are between the co-ordinated oxygen atom of the acetate ligand and the OH group. The hydrogen-bonded cavity (*ca*. 10 × 20 Å^2) in **4** is also much larger than those in **1**. In **1** the large cavity is made of two hydrogen-bonded mononuclear units while in **4** the cavity consists of four mononuclear units. The cavity in **4** is so large that two of the $C_6H_4NMe_2$-*p* ligands lie flat inside the cavity. The (*R*,*R*) and (*S*,*S*) isomers in **7** are linked together through hydrogen bonds in the same manner as the worm chains of **4**, as evident from the distance of 3.32(3) Å between two neighbouring OH groups (Fig. 14). However, in contrast to compound **4**, the hydrogen-bonded chains in **7** are all parallel to each other and there are no interchain hydrogen bonds between the OH and the carboxylate oxygen atom.

It has been observed by Suzuki *et al.*[16a] that the extended structure involving chiral ligands can be affected drastically by the optical purity of the starting material. For instance, they observed that the structure of the product from a reaction using an enantiomerically pure compound is very different from that obtained from one using a racemic mixture. We examined the reaction of $Bi(C_6H_4NMe_2$-*p*$)_3Cl_2$ with the enantiomerically pure Ag[(*S*)-$O_2CCH_2CH(OH)CH_3$]. The NMR spectra of the product from the reaction are the same as those of the corresponding racemic mixture of compound **6**, suggesting that they have the same molecular structure. The hydrogen-bonding pattern of this enantiomerically pure compound is anticipated to be the same as that of **6** since no intermolecular hydrogen bond is present in **6**. However, we have not been able to confirm this by X-ray diffraction due to the lack of suitable crystals of the enantiomerically pure compound **6**. The hydrogen-bonding patterns of enantiomerically pure compounds corresponding to **4**, **5** and **7**, however, would be quite different from those observed in the racemic mixture since there are hydrogen bonds between the (*R*,*R*) and (*S*,*S*) enantiomers in **4**, **5** and **7**. However, we have not been able to synthesize the enantiomerically pure compounds **4**, **5** and **7** because of the lack of enantiomerically pure ligands.

The extended hydrogen-bonded structures in compounds **1**, **2** and **4** can be considered as the extension of one-dimensional hydrogen-bonded chains as illustrated in Fig. 15. The interesting variations of these structures demonstrate that a small variation of the ligand can lead to a dramatic change in the extended structure. Steric factors, ligand geometry, and lattice packing forces could all play some role.

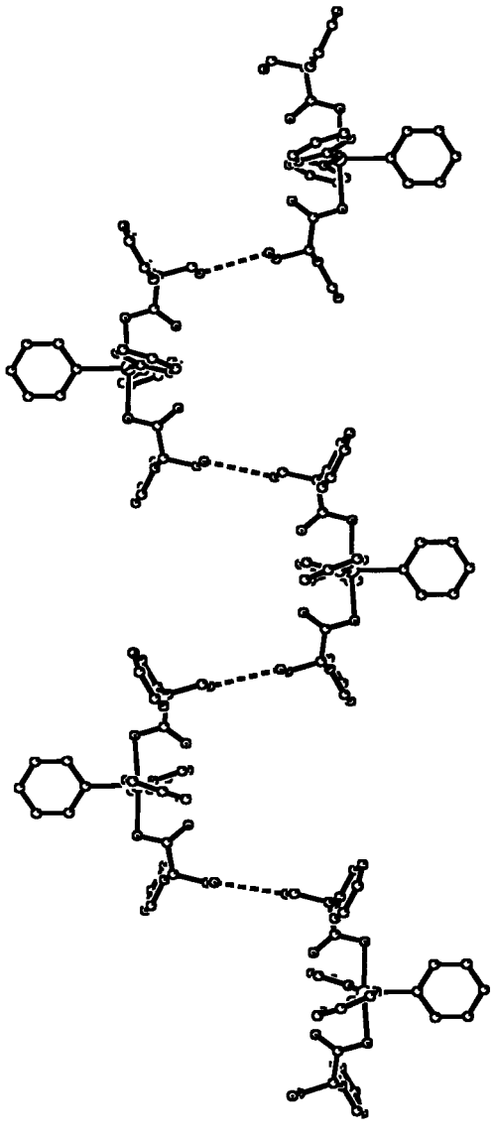


Fig. 14 The hydrogen-bonded chains in compound **7**

From the structures of compounds **1**–**7** one can see that when the hydroxyl group is at the terminal position of the acetate ligand such as in 4-hydroxybutyrate, 3-(4-hydroxyphenyl)propionate and tropic acetate, the mononuclear bismuth complex aggregates and forms extended hydrogen-bonded arrays, and when the hydroxyl group is not at the terminal position such as in 2-hydroxy- and 3-hydroxy-butyrate extended hydrogen-bonded structures do not form. Clearly, steric factors play a very important role here. In solution, we believe that the hydrogen-bonded structures dissociate to mononuclear units or oligomers. The poor solubility of these compounds in solvents which do not form hydrogen bonds prevents us from investigating their hydrogen-bonding behaviour in solution.

Thermal stability. Compounds **1**–**7** are thermally unstable and undergo decomposition upon heating. The thermal decomposition patterns and products appear to be dependent on the ligands surrounding the bismuth(v). Upon heating, the $Bi(C_6H_4NMe_2$-*p*$)_3(O_2CR')_2$ compounds became dark yellow, then dark brown and eventually formed Bi_2O_3, as shown by TGA experiments. The behaviour of the $BiPh_3(O_2CR')_2$ compounds is quite different. Upon heating no colour change was observed. One of the major thermal decomposition products

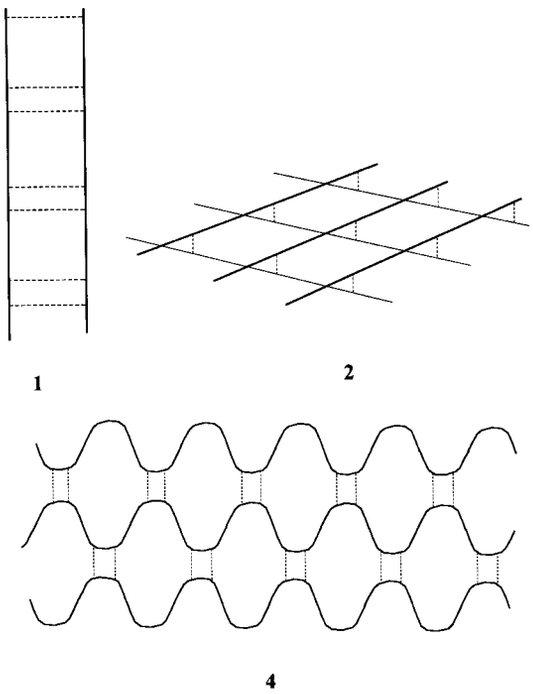


Fig. 15 Schematic representation of the extended hydrogen-bonded structures observed in compounds **1**, **2** and **4**

at about 100 °C from compound **2** was identified as $BiPh_3$, possibly the consequence of the reductive elimination of the carboxylate ligands. At about 140 °C the thf-free sample of compound **3** loses about 15% weight and becomes a colourless insoluble glassy material the composition and structure of which remain a mystery. There is, however, no evidence for the formation of $BiPh_3$ from the thermal decomposition of **3**.

Conclusion

The $Bi^{V}R_3(O_2CR')_2$ compounds, where R is an aromatic ligand and R′ a substituent containing a hydroxyl group, can be used as building blocks for the assembly of extended structures involving hydrogen bonds. The pattern of hydrogen bonds and the extended structures are highly dependent on the aryl ligand, the R′ substituent, and the position of the hydroxyl group in R′. The reactions of BiR_3Cl_2 ($R = C_6H_4NMe_2$-*p* or Ph) with racemic silver salts, $Ag(O_2CR^*)$, where R* is a chiral group, appear to be stereoselective and produce only (*R*,*R*) and (*S*,*S*) enantiomers, which may find applications in chiral discrimination. Further investigation is needed to establish the reaction mechanism and the stereoselectivity observed in $BiR_3(O_2CR^*)_2$.

Acknowledgements

We thank the Natural Science and Engineering Research Council of Canada for financial support, Mr. Mike Fuerth at the University of Windsor for his assistance in NMR spectroscopic study, and Dr. James R. Green for helpful discussions on the chiral bismuth(v) complexes.

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Received 21*st January* 1997; *Paper* 7/00477J