Cation–Anion Interactions involving Hydrogen Bonds. Syntheses, Structures and Spectroscopic Studies of $[H_2dam][Bi^{III}Ph(O_2CCF_3)_4]$, $[Hpy]_2[Bi^{III}Ph(O_2CCF_3)_4]$ and $[H_2dam][Bi^{III}(O_2CCF_3)_5]$ (dam = diamine, py = pyridine)†

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New anionic bismuth(III) complexes $[H_2dam][BiPh(O_2CCF_3)_4]$ **1**, $[Hpy]_2[BiPh(O_2CCF_3)_4]$ **1g** and $[H_2dam][Bi(O_2CCF_3)_5]$ **2** (dam = diamine, py = pyridine) have been synthesised by the reaction of $BiPh_3$ with trifluoroacetic acid and diamines or pyridine. The crystal structures of $[H_2dam][BiPh(O_2CCF_3)_4]$ [dam = $Me_2N(CH_2)_3NMe_2$ **1a**, $Me_2NCH_2CH(OH)CH_2NMe_2$ **1b**, $Me_2N(CH_2)_4NMe_2$ **1c**, $Me_2N(CH_2)_2NMe_2$ **1d** or *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine **1f**], **1g**, and $[H_2teed][Bi(O_2CCF_3)_5]$ **2e** [teed = $Et_2N(CH_2)_2NEt_2$] have been determined by single-crystal X-ray diffraction analyses. The structure of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion in the solid state has been found to be dependent on the structure of the protonated diamine or pyridine. In **1a**–**1c** it has a cup-like structure with the Bi^{III} adopting a square-pyramidal geometry, while in **1d** it has an irregular shape with the Bi^{III} of approximate pentagonal-pyramidal geometry. The $[BiPh(O_2CCF_3)_4]^{2-}$ anion in **1f** and **1g** has intermediate structure between the 'cup' and the pentagonal pyramid. Compound **2e** has an irregular polyhedral geometry and the bismuth is surrounded by ten oxygen atoms. The structural variations observed in these compounds are attributed to hydrogen-bonding interactions between the anion and the cation, and the stacking of aromatic rings in the crystal lattice. The solution behaviour of $[BiPh(O_2CCF_3)_4]^{2-}$ has been examined by ^1H NMR spectroscopic analysis. In cases where the dam is an aliphatic diamine, compound **1** is in equilibrium with $[H_2dam][Bi(O_2CCF_3)_5]$ **2** and $[Hdam][BiPh_2(O_2CCF_3)_2]$ **3**, except for **1b** which undergoes irreversible decomposition in solution. When dam is an aromatic diamine or pyridine the $[BiPh(O_2CCF_3)_4]^{2-}$ anion is stable in solution. Solvent molecules such as tetrahydrofuran or acetone have been found to affect the equilibrium between compounds **1** and **2** and **3**.

Inorganic bismuth complexes have attracted much attention recently due to their potential applications in materials, medicine and catalysis.[1] Bismuth complexes with metal–oxygen bonds are especially interesting not only for their potential use as precursors for advanced ceramic materials,[1] but also because of the lack of chemical and structural data concerning this class of compounds. Most of the known bismuth complexes involving Bi–O bonds are limited to compounds such as $Bi(NO_3)_3{\cdot}xH_2O$ and $Bi(O_2CMe)_3$ which have poor solubilities in common organic solvents.[2] Recently, a few soluble bismuth complexes with alcohol or aminoalcohol ligands have been reported.[1a,3] We have been investigating the synthesis of homo- and hetero-nuclear bismuth complexes with aminoalcohol and trifluoroacetate as ligands.[4] Several new bismuth complexes were discovered which display interesting solution and solid-state behaviour. In a preliminary communication[5] we reported the crystal structures of $[H_2dam][BiPh(O_2CCF_3)_4]$ [dam = aliphatic diamine]. We have now found that the structure and the stability of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion is diamine dependent owing to the selective hydrogen-bonding interactions between the trifluoroacetate ligand of the complex and the diammonium cation. In view of the scarcity of information on cation–anion interactions involving hydrogen bonds and their influence on the structure and stability of metal complexes, we have extended our investigation by systematically examining the effect of protonated aliphatic and aromatic diamines on the structure and solution behaviour of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion. The details of this study are described herein.

Experimental

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled prior to use. Triphenylbismuth was obtained from Strem Chemicals, 1,3-bis(dimethylamino)propan-2-ol from Janssen Chimica. All other diamines were from Aldrich Chemical Company. Proton NMR spectra were recorded on a Brüker AC-300 spectrometer, IR spectra on a Bowman FTIR spectrometer. Elemental analyses were performed at Desert Analytics, Tucson, AZ.

Syntheses.—$[H_2tmpd][BiPh(O_2CCF_3)_4]$ **1a**. A sample of $BiPh_3$ (200 mg, 0.45 mmol) was dissolved in tetrahydrofuran (15 cm^3) and trifluoroacetic acid (0.14 cm^3, 1.87 mmol) was added. The solution was stirred for 1 h, and *N,N,N′,N′*-tetramethylpropane-1,3-diamine (78 mg, 0.45 mmol) was added. After 1 h the solution was concentrated to about 5 cm^3 and hexane was added to crystallize the product. Colourless crystals of complex **1a** were collected after about 24 h (250 mg, 0.26 mmol, 63% yield), m.p. 160 °C.

$[H_2bdmap][BiPh(O_2CCF_3)_4]$ **1b**. A solution of $BiPh_3$ and trifluoroacetic acid was prepared as above. It was stirred for 1 h at 23 °C, and 1,3-bis(dimethylamino)propan-2-ol (bdmap) (66 mg, 0.45 mmol) was added. After being stirred for an additional 1 h, the solution was concentrated to about 5 cm^3 and hexane was added to crystallize the product. On standing at room temperature for 24 h colourless crystals of complex **1b** were obtained (256 mg, 0.29 mmol, 64% yield), m.p. 151 °C.

The compounds $[H_2tmbd][BiPh(O_2CCF_3)_4]$ **1c** [tmbd = $Me_2N(CH_2)_4NMe_2$], $[H_2tmed][BiPh(O_2CCF_3)_4]$ **1d** [tmed = $Me_2N(CH_2)_2NMe_2$] and $[H_2teed][BiPh(O_2CCF_3)_4]$ **1e** [teed = $Et_2N(CH_2)_2NEt_2$] were obtained in good

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

yields by the procedure used for **1a** and **1b**: m.p. 138 (**1c**). 151 (**1d**) and 103–105 °C (**1e**).

$[H_2tmphd][BiPh(O_2CCF_3)_4]\cdot thf$ **1f**. A solution of $BiPh_3$ and trifluoroacetic acid was prepared as before. It was stirred for 1 h at 23 °C and *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (tmphd) (75 mg, 0.45 mmol) was added. The solution turned dark blue immediately. After 1 h its volume was reduced to about 5 cm^3. Addition of an excess of hexane resulted in a colourless clear layer and a blue oily layer. The oily layer was collected and kept at 0 °C for 1 week at which time colourless crystals of complex **1f** were isolated and washed with diethyl ether (135 mg, 0.15 mmol, 33% yield), m.p. 102 °C.

$[Hpy]_2[BiPh(O_2CCF_3)_4]$ **1g**. A solution of $BiPh_3$ and trifluoroacetic acid was prepared as before. It was stirred for 1 h at 23 °C and pyridine (py) (71 mg, 0.90 mmol) was added. After 1 h the solution was concentrated to about 5 cm^3 and hexane was added to crystallize the product. On standing at 23 °C for 24 h colourless crystals were obtained (275 mg, 0.31 mmol, 68% yield), m.p. 123 °C.

$[H_2teed][Bi(O_2CCF_3)_5]$ **2e**. Compound **2e** was obtained in good yield from the reaction of $BiPh_3$ with teed and an excess of CF_3CO_2H, m.p. 179 °C.

Infrared data and elemental analyses are listed in Table 1.

Table 1 Infrared and analytical data

Compound	Analysis (%)* C	H	N	IR (KBr) (cm^{-1})
1a	28.85 (28.95)	2.90 (2.85)	3.25 (3.20)	1688s, 1429m, 1384m, 1201s, 1133m
1b	28.45 (28.45)	2.80 (2.80)	3.10 (3.15)	1688s, 1475m, 1428m, 1205s, 1130s
1c	30.50 (29.85)	3.15 (3.05)	3.10 (3.15)	1678s, 1468m, 1428m, 1210s, 1130s
1d	27.25 (28.05)	2.60 (2.70)	3.05 (3.25)	1686s, 1473m, 1430m, 1198s, 1130s
1e	31.60 (31.60)	3.25 (3.40)	2.80 (3.05)	1678s, 1475m, 1421m, 1202s, 1131s
1f	34.05 (34.45)	2.95 (3.20)	3.50 (2.85)	1679s, 1468m, 1427m, 1201s, 1129m
1g	32.40 (32.10)	1.80 (1.90)	3.05 (3.10)	1692s, 1482m, 1378m, 1188s, 1130s
2e	26.20 (25.30)	2.90 (2.75)	3.05 (2.95)	1678s, 1440m, 1186s, 1132s

* Calculated values in parentheses.

X-Ray Diffraction Analysis.—Colourless single crystals of complexes **1a**–**1d**, **1f**, **1g** and **2e** were obtained from thf–hexane solutions by slow diffusion of solvents at 23 or 0 °C. They were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo-Kα radiation, operating at 50 kV and 35 mA. The orientation matrices for all crystals were obtained from 20 reflections located by the SEARCH routine. Three standard reflections were measured every 147. Data were processed on a Silicon Graphics computer using the TEXSAN[6] crystallographic software package and corrected for Lorentz polarization effects. Empirical absorption corrections were applied for all crystals. Neutral atom scattering factors were taken from Cromer and Waber.[7]

Crystals of complexes **1a**–**1c** are isomorphous, crystallizing in the monoclinic system with similar unit-cell dimensions. The systematic absences (hkl, $h + k \neq 2n$, $h0l$, $l \neq 2n$) were consistent with two possible space groups, Cc and $C2/c$. Based on packing considerations, a statistical analysis of the intensity distribution, and the successful solution and refinement of the structures, the space group for these three structures was determined to be $C2/c$. The crystals of **1d** belong to the orthorhombic system. Systematic absences ($0kl$, $k + l \neq 2n$, $h0l$, $h \neq 2n$) were consistent with two possible space groups, $Pnma$ and $Pna2_1$. The centric $Pnma$ space group was chosen initially; however, the structure could not be completely solved. It is clear that this molecule does not possess any symmetry elements; therefore, the acentric space group $Pna2_1$ is more likely. Indeed, by use of it the complete structure was determined successfully. Compounds **1f** and **2e** crystallize in the triclinic space group $P\bar{1}$ while **1g** belongs to the monoclinic space group $P2_1/n$. The metal atoms in all structures were located either by direct methods or by heavy-atom methods. The positions of all non-hydrogen atoms were located by subsequent Fourier syntheses. The molecules of **1a**–**1c** possess a two-fold proper rotation axis on which the central carbon atom in **1a** and the CO group of the bdmap in **1b** are situated. The diammonium cations in all three structures display some degree of disorder which was successfully modelled in **1a** and **1b**. Two sets of CH_2 groups were located and refined with a 50% occupancy factor in both structures. One of the CH_3 groups bonded to the nitrogen atom in both structures is disordered over two positions related by the C_2 symmetry. The carbon atoms at both positions were refined with a 50% occupancy factor. Some degree of disorder of the CF_3 groups in **1a**–**1c** is present as indicated by the large thermal ellipsoids of some of the fluorine atoms. All four CF_3 groups in **1d** displayed significant disorder and could only be refined as rigid bodies with the fixed C–F bond length of 1.31 Å and F–C–F angle of 109°. Single crystals of compounds **1d** and **1e** are very difficult to grow, partly due to disproportionation in solution (see Discussion). While we have not been able to grow a suitable crystal of **1e** for X-ray diffraction analysis, very small crystals (approximate 0.10 × 0.10 × 0.05 mm) of **1d** displaying severe twinning were obtained. Owing to the lack of sufficient data, the disorder of the CF_3 groups in **1d** could not be modelled. Only the metal, fluorine, and oxygen atoms were refined anisotropically in **1a** and **1b** because of the limitation of data. In addition to the low data-to-variables ratio, the severe disorder of the CF_3 groups and the poor quality of the data for **1d** only allowed us to refine the bismuth and oxygen atoms anisotropically, but not the fluorine atoms. Two of the CF_3 groups in **1f** and **2e** and all the CF_3 groups in **1g** showed a C_2 disorder with two sets of fluorine atoms for each disordered CF_3 group refined successfully with a 50% occupancy factor. The bismuth atom, the undisordered fluorine atoms and some of the oxygen atoms in these molecules were refined anisotropically. The positions of all the hydrogen atoms in **1d**, **1f**, **1g** and **2e**, and those on the undisordered carbon and nitrogen atoms in **1a**–**1c**, were calculated and their contributions included in the calculation of structure factors. A disordered thf solvent molecule was found in the lattice of **1f**; however, we were unable to model the disorder. Only part of the thf molecule was refined successfully, and this could be partially responsible for the high *R* factor of the structure **1f**. The crystals of **1f** and **2e** also showed some degree of twinning. This factor together with the disorder of the CF_3 groups and the imperfect absorption corrections could account for the high *R* factors for the structures of **1d**, **1f** and **2e**. The data for the X-ray diffraction analyses are given in Table 2, final atomic coordinates in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The new anionic bismuth(III) complex $[BiPh(O_2CCF_3)_4]^{2-}$ **1** was obtained readily as the major product from the reaction of $BiPh_3$ with trifluoroacetic acid and a diamine or pyridine in a 1:4:1 or 1:4:2 ratio. Two bismuth(III) complexes involving phenyl and trifluoroacetate ligands, $[Bi^{III}Ph_2(O_2CCF_3)]$ and $[Bi^VPh_4][Bi^{III}Ph_2(O_2CCF_3)_2]$, have been reported previously.[1d]

Table 2 Crystallographic data

Compound	**1a**	**1b**	**1c**	**1d**	**1f**	**1g**	**2e**
Formula	$C_{21}H_{25}BiF_{12}N_2O_8$	$C_{21}H_{25}BiF_{12}N_2O_9$	$C_{22}H_{27}BiF_{12}N_2O_8$	$C_{20}H_{23}BiF_{12}N_2O_8$	$C_{28}H_{31}BiF_{12}N_2O_9$	$C_{24}H_{17}BiF_{12}N_2O_8$	$C_{20}H_{24}BiF_{15}N_2O_{10}$
M	870.42	886.42	884.32	856.41	976.52	898.37	946.20
Space group	$C2/c$	$C2/c$	$C2/c$	$Pna2_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	9.015(3)	9.242(6)	9.072(3)	26.117(9)	10.606(5)	10.740(2)	10.743(9)
b/Å	16.640(7)	16.53(1)	16.817(2)	13.176(4)	16.454(9)	15.760(3)	17.38(2)
c/Å	19.845(8)	19.840(6)	20.666(4)	8.644(2)	10.335(4)	18.837(1)	9.636(5)
α/°	90	90	90	90	91.09(4)	90	100.97(6)
β/°	95.03(3)	93.69(4)	92.48(2)	90	101.91(4)	104.48(1)	101.85(6)
γ/°	90	90	90	90	75.31(4)	90	105.64(6)
U/Å^3	2965(1)	3025(3)	3149(1)	2974(1)	1706(1)	3087.3(8)	1636(2)
Z	4	4	4	4	2	4	2
D_c/g cm^{-3}	1.95	1.95	1.86	1.91	1.90	1.93	1.93
μ(Mo-Kα)/cm^{-1}	60.55	59.30	57.00	60.20	52.77	58.20	55.20
2θ Range/°	3–50	2–48	2–50	2–48	2–51	2–50	2–46
Reflections							
measured	$+h, +k, \pm l$, 2466	$+h, +k, \pm l$, 2655	$+h, +k, \pm l$, 2875	$-h, -k, +l$, 3084	$+h, \pm k, \pm l$, 6009	$+h, +k, \pm l$, 5666	$+h, \pm k, \pm l$, 5007
observed [$F_o^2 \geqslant 3\sigma(F_o)^2$], N_o	1209	1069	1121	1217	2656	2051	2053
No. of parameters refined, N_p	150	152	166	162	373	372	298
Largest shift/e.s.d. in final cycle	0.46	0.01	0.00	0.13	0.33	0.11	0.26
Largest electron-density peak/e Å^{-3}	1.12	1.21	0.78	1.99	3.19	1.70	1.92
R[a]	0.056	0.060	0.051	0.074	0.086	0.063	0.079
R'[b]	0.055	0.038	0.046	0.081	0.090	0.056	0.081
Goodness of fit,[c] S	1.98	1.72	1.77	1.19	2.60	2.17	2.10

[a] $R = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, where $w = 1/\sigma^2(F_o)$. [c] $S = [\Sigma(|F_o| - |F_c|)/\sigma]/(N_o - N_p)$.

The monophenyl complex [BiPh(O$_2$CCF$_3$)$_2$] has also been found to be unstable and thus not isolable from solution.[1d] This is in sharp contrast to the high stability of the previously unknown anion [BiPh(O$_2$CCF$_3$)$_4$]$^{2-}$ in **1a**–**1g** where the diammonium cation appears to play an important role in the stability of these compounds. In order to understand the role of the cation in this system, we have examined the structure and stability of the [BiPh(O$_2$CCF$_3$)$_4$]$^{2-}$ anion with several protonated aliphatic or aromatic diamines, or with protonated pyridine as the counter ion. The new bismuth compounds were isolated as colourless crystalline materials and formulated as [H$_2$dam]-[BiPh(O$_2$CCF$_3$)$_4$] **1** and [HPy]$_2$[BiPh(O$_2$CCF$_3$)$_4$] **1g**, respectively, where the diamine (dam) = *N,N,N′,N′*-tetramethylpropane-1,3-diamine (tmpd) **1a**, 1,3-bis(dimethylamino)-propan-2-ol (bdmap) **1b**, *N,N,N′,N′*-tetramethylbutane-1,4-diamine (tmbd) **1c**, *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmed) **1d**, *N,N,N′,N′*-tetraethylethane-1,2-diamine (teed) **1e** or *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (tmphd) **1f**. They are soluble only in polar solvents such as thf and acetone and are air-stable in the solid state. Full characterization was attained *via* a combination of ^{1}H NMR and IR spectroscopic methods along with elemental and single-crystal X-ray diffraction analyses.

Solid-state Structure of the [BiPh(O$_2$CCF$_3$)$_4$]$^{2-}$ *Anion.*— Depending on the cations, three different types of structures **I**–**III** have been observed for the [BiPh(O$_2$CCF$_3$)$_4$]$^{2-}$ anion. In type **I** the four carboxylate groups form a ‘cup’ shape and the bismuth centre has a square-pyramidal geometry, in **II** one of the carboxylate ligands chelates to the bismuth ion which has an approximate pentagonal-pyramidal geometry and in **III** the bismuth centre is five-co-ordinate but the complex does not have a ‘cup’ shape. Type **III** could therefore be described as an intermediate structure between **I** and **II**. Selected bond lengths and angles for all structures are given in Table 3.

The crystals of complexes **1a**–**1c** are isomorphous and their structures belong to type **I**; ORTEP[8] drawings are given in Fig.

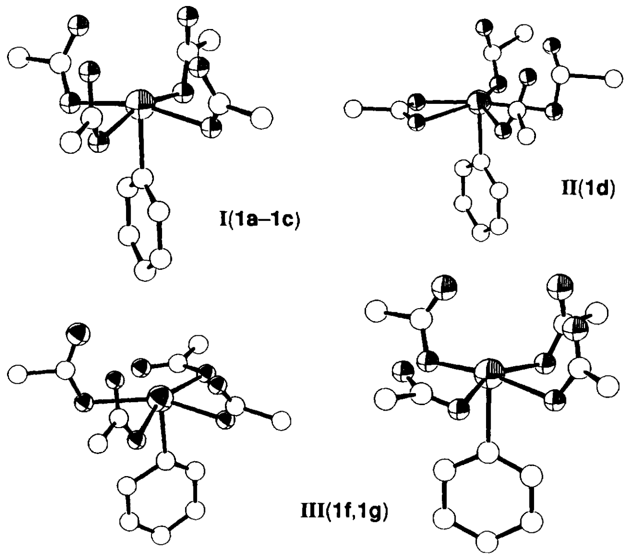
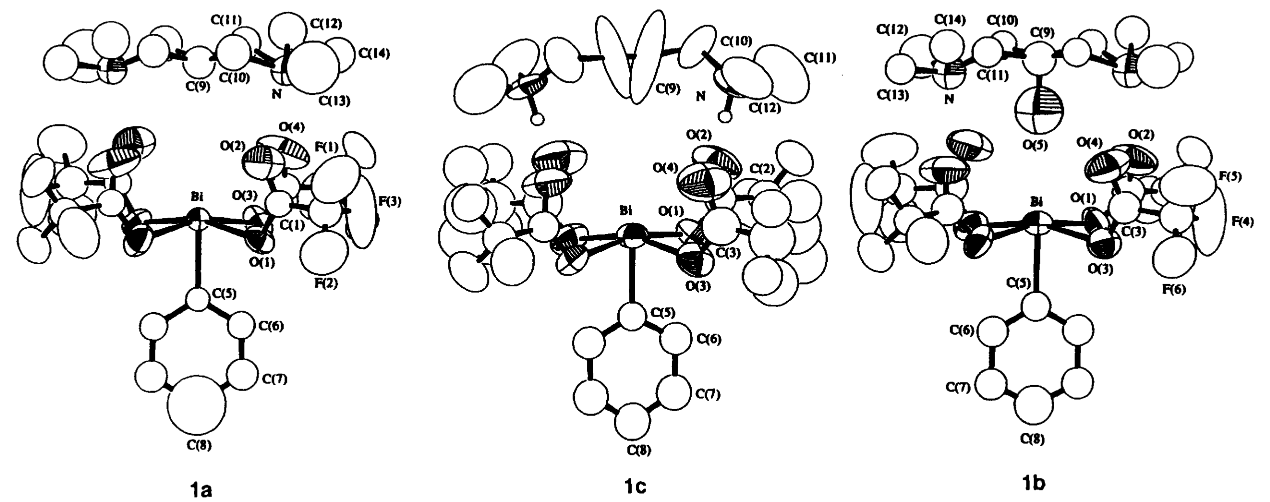


Table 3 Selected bond lengths (Å) and angles (°)

Compound	Bi–O and Bi–C		O–Bi–O and O–Bi–C				O···N	
1a [H$_2$tmpd][BiPh(O$_2$CCF$_3$)$_4$]	Bi–O(1)	2.38(1)	O(1)–Bi–O(1′)	164.2(6)	O(1)–Bi–O(3′)	88.5(5)	N···O(2)	2.77(2)
	Bi–O(3)	2.35(1)	O(3)–Bi–O(3′)	163.4(7)	O(1)–Bi–C(5)	82.1(3)	N···O(4)	3.02(3)
	Bi–C(5)	2.19(2)	O(1)–Bi–O(3)	89.2(5)	O(3)–Bi–C(5)	81.7(4)		
1b [H$_2$bdmap][BiPh(O$_2$CCF$_3$)$_4$]	Bi–O(1)	2.40(1)	O(1)–Bi–O(1′)	167.8(7)	O(1)–Bi–O(3′)	89.9(4)	N···O(2′)	2.77(2)
	Bi–O(3)	2.41(1)	O(3)–Bi–O(3′)	165.1(7)	O(1)–Bi–C(5)	83.9(3)	N···O(4′)	3.28(2)
	Bi–C(5)	2.25(3)	O(1)–Bi–O(3)	88.5(4)	O(3)–Bi–C(5)	82.6(3)		
1c [H$_2$tmbd][BiPh(O$_2$CCF$_3$)$_4$]	Bi–O(1)	2.38(1)	O(1)–Bi–O(1′)	165.1(5)	O(1)–Bi–O(3′)	89.7(4)	N···O(2)	2.81(2)
	Bi–O(3)	2.37(1)	O(3)–Bi–O(3′)	161.9(5)	O(1)–Bi–C(5)	82.5(2)	N···O(4)	3.15(2)
	Bi–C(5)	2.22(2)	O(1)–Bi–O(3)	88.0(4)	O(3)–Bi–C(5)	80.9(3)		
1d [H$_2$tmed][BiPh(O$_2$CCF$_3$)$_4$]	Bi–O(1)	2.62(4)	O(1)–Bi–O(4)	73(1)	O(8)–Bi–C(9)	83(2)	N(1)···O(2)	2.77(6)
	Bi–O(4)	2.50(4)	O(1)–Bi–O(8)	69(1)	O(6)–Bi–O(8)	86(2)	N(2)···O(3)	2.68(8)
	Bi–O(5)	2.59(4)	O(4)–Bi–O(5)	77(1)	O(5)–Bi–O(6)	52(2)		
	Bi–O(6)	2.35(4)	O(5)–Bi–C(9)	88(1)	O(1)–Bi–C(9)	83(1)		
	Bi–O(8)	2.40(4)	O(6)–Bi–C(9)	87(2)	O(4)–Bi–C(9)	86(1)		
	Bi–C(9)	2.22(4)						
1f [H$_2$tmphd][BiPh(O$_2$CCF$_3$)$_4$]	Bi–O(1)	2.37(2)	O(1)–Bi–O(3)	83.0(8)	O(1)–Bi–C(9)	86.3(8)	N···O(2)	2.77(2)
	Bi–O(3)	2.31(2)	O(1)–Bi–O(5)	159.8(8)	O(3)–Bi–C(9)	80.5(9)	N···O(4)	3.02(3)
	Bi–O(5)	2.53(2)	O(3)–Bi–O(7)	155.5(7)	O(5)–Bi–C(9)	80.7(9)	N(1)···O(8)	2.74(3)
	Bi–O(7)	2.46(2)	O(5)–Bi–O(7)	120.6(7)	O(7)–Bi–C(9)	89(1)	N(2)···O(6)	2.79(4)
	Bi–C(9)	2.29(3)	O(1)–Bi–O(7)	74.3(8)				
	Bi···O(6)	2.91(3)						
1g [Hpy]$_2$[BiPh(O$_2$CCF$_3$)$_4$]	Bi–O(1)	2.41(2)	O(1)–Bi–O(3)	89.7(7)	O(5)–Bi–O(7)	114.1(8)	N(1)···O(6)	2.78(4)
	Bi–O(3)	2.36(2)	O(1)–Bi–O(5)	168.4(6)	O(1)–Bi–C(1)	82(1)	N(2)···O(2)	2.66(3)
	Bi–O(5)	2.40(2)	O(1)–Bi–O(7)	64.4(9)	O(3)–Bi–C(1)	85.8(9)	N(2)···O(4)	2.79(3)
	Bi–O(7)	2.51(3)	O(3)–Bi–O(5)	85.2(7)	O(5)–Bi–C(1)	87(1)		
	Bi–C(1)	2.27(2)	O(3)–Bi–O(7)	155.6(8)	O(7)–Bi–C(1)	80.9(9)		
	Bi···O(8)	2.78(3)						
2e [H$_2$teed][Bi(O$_2$CCF$_3$)$_5$]	Bi–O(1)	2.55(3)	O(1)–Bi–O(3)	130.6(6)	O(2)–Bi–O(7)	142.4(8)	N(1)···O(8)	3.02(4)
	Bi–O(2)	2.62(2)	O(1)–Bi–O(4)	174.5(8)	O(2)–Bi–O(8)	119.5(8)	N(2)···O(2′)	3.16(5)
	Bi–O(3)	2.58(2)	O(2)–Bi–O(3)	145.2(7)	O(5)–Bi–O(7)	145.7(9)		
	Bi–O(4)	2.58(3)	O(2)–Bi–O(4)	126.8(7)	O(6)–Bi–O(7)	126.4(7)		
	Bi–O(5)	2.44(3)	O(5)–Bi–O(9)	90.2(8)	O(5)–Bi–O(8)	132.3(7)		
	Bi–O(6)	2.57(3)	O(5)–Bi–O(10)	136.7(7)	O(6)–Bi–O(8)	84.2(7)		
	Bi–O(7)	2.60(2)	O(6)–Bi–O(9)	136.6(8)	O(7)–Bi–O(9)	96.0(8)		
	Bi–O(8)	2.52(2)	O(6)–Bi–O(10)	144.8(9)	O(7)–Bi–O(10)	69.3(8)		
	Bi–O(9)	2.58(2)	O(1)–Bi–O(7)	107.6(8)	O(8)–Bi–O(9)	137.5(8)		
	Bi–O(10)	2.53(3)	O(1)–Bi–O(8)	70.6(7)	O(8)–Bi–O(10)	87.7(7)		



1a 1c 1b

Fig. 1 The ORTEP diagrams showing the structures of complexes **1a**–**1c** with 50% thermal ellipsoids

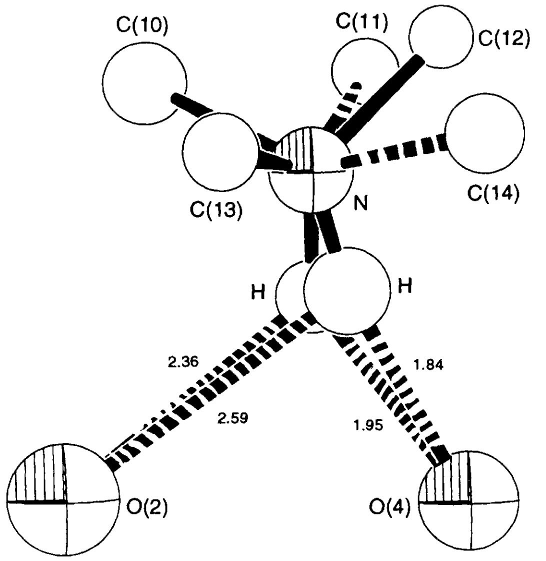
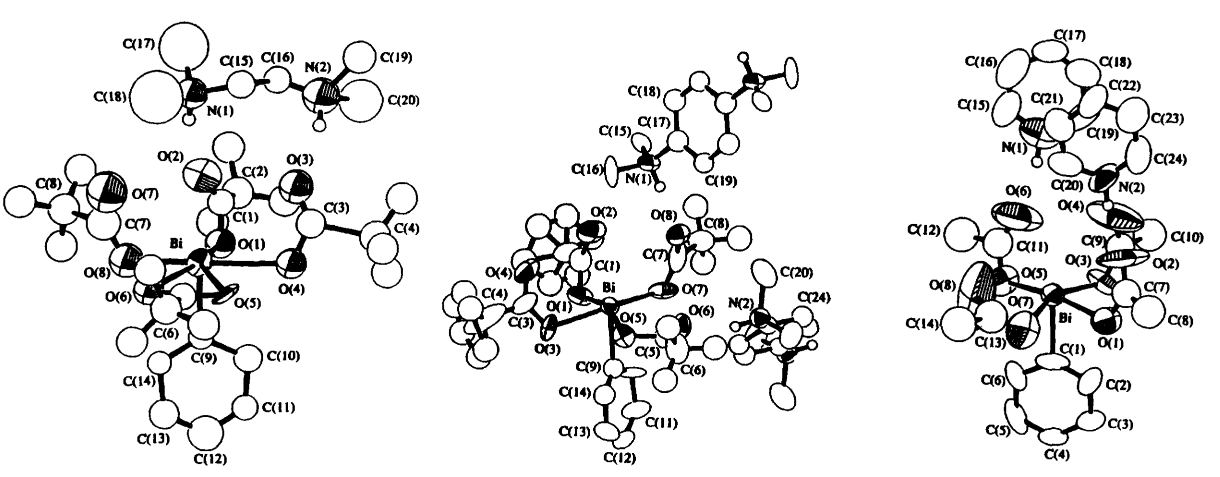


Fig. 2 The disordered cation and hydrogen bonds in complex **1a**

1. The $[BiPh(O_2CCF_3)_4]^{2-}$ anion in all three compounds has a cup-like structure. The square-pyramidal bismuth centre is co-ordinated to four oxygen atoms of the trifluoroacetate ligands and the carbon atom of the phenyl ligand with normal bond lengths. The BiO_4 unit is essentially planar with the bismuth atom approximately 0.27 Å above the plane formed by the four oxygen atoms. The lone pair of electrons on bismuth may be situated at the missing vertex of the octahedron. The most unusual feature of these molecules, however, is the orientation of the four carboxylate ligands which all point up to form the 'cup' shape. Since these ligands are negatively charged, one would predict that they would prefer to orient away from each other and from the lone pair of electrons of the bismuth ion to minimize the repulsion energy. The examination of the structures of **1a**–**1c** revealed that the unusual 'cup' structure is stabilized by hydrogen-bonding interactions between the oxygen atoms of the carboxylate ligands and the diammonium cation. The N $\cdots$ O(2) and N $\cdots$ O(4) distances are 2.77(2) and 3.02(3) Å in **1a**, 2.77(2) and 3.28(2) Å in **1b**, and 2.81(2) and 3.15(2) Å in **1c**, respectively. These are comparable to the sum of the van der Waals radii (3.05 Å) of nitrogen and oxygen, indicative of weak hydrogen bonds.[9] The O(2) $\cdots$ O(4) distance of 3.17(4) in **1a**, 3.22(2) in **1b** and 3.13(2) Å in **1c** also indicates possible weak hydrogen bonds between these oxygen atoms. Although the positions of the protons could not be accurately determined by X-ray diffraction analysis, we believe that they are bonded to the nitrogen atoms of the diamine and hydrogen bonded to the O(2) and O(4) atoms, since the diamine is a much stronger Lewis base than is the trifluoroacetate ligand. Such three-centred hydrogen bonds have been observed frequently.[9] The idealized positions of the protons bonded to the nitrogen atoms in **1a** and **1c** were calculated and due to the disorder two possible positions were determined for **1a**. The two hydrogen atoms appear to form asymmetric hydrogen bonds with atoms O(2) and O(4) as shown in Fig. 2, and in the case of **1c** the hydrogen bonds also appear to be asymmetric, as indicated by the H(3) $\cdots$ O(2) and H(3) $\cdots$ O(4) distances of 2.03 and 2.42 Å. While the OH group of the bdmap ligand in **1b** is also believed to form hydrogen bonds with the carboxylate ligands as indicated by the O(5) $\cdots$ O(2) and O(5) $\cdots$ O(4) distances of 3.18(2) and 3.03(2) Å, it appears not to be essential for the formation of the 'cup' structures since **1a** and **1c** have similar structures without the presence of an OH group. This OH group in **1b** does, however, cause considerable variations in bond lengths and angles, in comparison with those in **1a** (see Table 3).

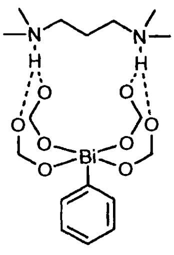
Although the 'cup' structure is new for bismuth carboxylate compounds, it has been observed previously in the bimetallic complex[10a] $[Ca(H_2O)_4][Cu^{II}(O_2CCH_2OC_6H_4Cl\text{-}2)_4(H_2O)]$, where the copper(II) ion has a square-pyramidal geometry and the calcium ion is co-ordinated by four oxygen atoms of the carboxylate ligands and four oxygen atoms of the water molecules. The 'cup' structure of the $[Cu^{II}(O_2CR)_4(H_2O)]^{2-}$ anion is apparently stabilized by strong ionic bonding interactions between the Ca^{2+} ion and the carboxylate ligands. A similar 'cup' structure has also been observed in the $[Cu^{II}\{NC_5H_4(OH)\text{-}2\}(O_2CCF_3)_4]^{2-}$ anion reported recently by our group,[10b] where the pyridin-2-ol ligand occupies the fifth position of the copper ion and the anion is stabilized by hydrogen-bonding interactions between the carboxylate ligand, the chlorine anion, and the pyridinol ligand of a $[Cu\{NC_5H_4(OH)\text{-}2\}_6]^{2+}$ cation.

The crystal structure of $[H_2tmed][BiPh(O_2CCF_3)_4]$ **1d** belongs to type **II** and the ORTEP diagram is shown in Fig. 3. In contrast to the structures of **1a**–**1c**, the $[BiPh(O_2CCF_3)_4]^{2-}$ anion in **1d** has an irregular shape. Instead of a square-pyramidal geometry the bismuth centre has an approximate pentagonal-pyramidal geometry. Three of the four carboxylate ligands still point up while the remaining one chelates the Bi^{3+} ion in the equatorial plane. Some of the Bi–O bond lengths in **1d** are considerably longer than those in **1a**–**1c**, but still within the range of normal Bi–O bond lengths.[2] We believe that the irregular geometry of the bismuth ion in **1d** is the consequence of selective hydrogen-bonding interactions between the

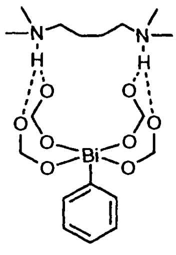


1d **1f** **1g**

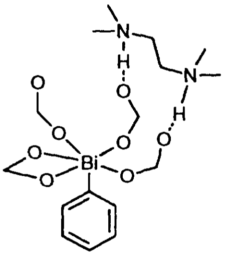
Fig. 3 The ORTEP diagrams showing the structures of complexes **1d**, **1f** and **1g** with 50% thermal ellipsoids. For clarity, the fluorine atoms in **1g** are omitted and those in **1d** and **1f** are shown as ideal spheres



1a



1c



1d

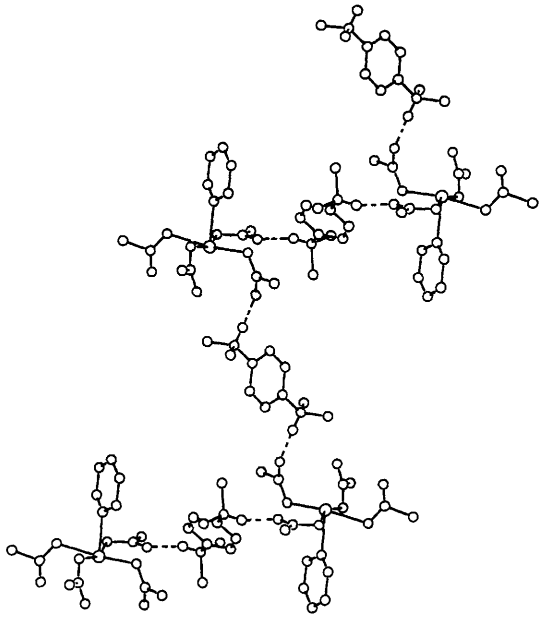


Fig. 4 The extended hydrogen-bonded zigzag chain structure of complex **1f**. Fluorine atoms are omitted for clarity

carboxylate groups of the anion and the ammonium group of the cation. Instead of forming hydrogen bonds to all four oxygen atoms, the two ammonium groups of the H_2tmed^{2+} cation in **1d** are hydrogen bonded to two oxygen atoms only, as indicated by the N(1)···O(2) and N(2)···O(3) distances of 2.77(6) and 2.68(8) Å. No single crystals suitable for X-ray diffraction analysis were obtained for **1e** (dam = teed). It is very likely that the structure of **1e** is similar to that of **1d**. The hydrogen bonds in **1a**–**1d** are illustrated in the sketches of **1a**, **1c** and **1d**.

The structures of complexes **1a**–**1d** demonstrate the selectivity and dependence of the hydrogen-bonding interactions on the diammonium cation. The prime factor effecting such selectivity appears to be the separation between the two nitrogen atoms of the diammonium cation. The distances between O(2) and O(2'), O(4) and O(4') of the carboxylate ligands are 5.22(3) and 5.08(3) Å in **1a**, 5.62(3) and 5.51(3) Å in **1b**, and 5.25(3) and 5.39(3) Å in **1c**, while the distance between O(2) and O(4') is 4.16(2) Å in **1a**, 4.55(2) Å in **1b** and 4.31(2) Å in **1c**. These values are comparable to the N···N separation in H_2tmpd^{2+} [4.77(3) Å] and in H_2bdmap^{2+} [4.92(3) Å], but much longer than that [3.67(7) Å] in H_2tmed^{2+} in **1d**. The N···N separation of H_2tmbd^{2+} in **1c** is 5.61(3) Å, significantly longer than the O(2)···O(4') distances. The two protons, however, are oriented toward the centre of the molecule giving a H···H separation of about 5.09 Å, comparable with the O···O separations. Conversely, the N···N separation in H_2tmed^{2+} is apparently too short for the two nitrogen atoms to form hydrogen bonds effectively to all four oxygen atoms. As a result, the $[BiPh(O_2CCF_3)_4]^{2-}$ anion has the 'cup' structure in **1a**–**1c**, but not in **1d**.

Further to understand the steric effects of the cation on the structure of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion, we replaced the aliphatic diamine with pyridine (py) and *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (tmphd). The distance between the two nitrogen centres in H_2tmphd^{2+} is 5.76 Å, but the two protons bonded to the nitrogen atoms are oriented away from the phenyl ring and may be too far away from each other to form intramolecular hydrogen bonds with all four oxygen atoms. However, the formation of intermolecular hydrogen bonds with this cation is very likely. Indeed, as shown in Figs. 3 and 4, there are two independent diammonium cations in the crystal lattice of **1f**, and each forms an intramolecular hydrogen bond [N(1)···O(8) 2.74(3), N(2)···O(6) 2.79(4) Å] and an intermolecular hydrogen bond with the oxygen atoms which are related by an inversion centre. As a consequence of the intra- and inter-molecular hydrogen bonds, compound **1f** forms an extended zigzag chain in the solid state (Fig. 4). Inorganic complexes with this type of hydrogen-bonded extended structure have been reported previously.[10b]

Since protonated pyridine is a monocation and should not have significant steric constraints in the formation of hydrogen bonds, we anticipated that the $[BiPh(O_2CCF_3)_4]^{2-}$ anion in complex **1g** would prefer the type **I** structure. However, as revealed by the crystal structure, it does not have the 'cup' shape. Instead of forming four hydrogen bonds, the two Hpy^+

Table 4 Proton NMR data (δ, J in Hz) in $(CD_3)_2CO$ at 23 °C

Compound	Aromatic region	Aliphatic region
$[H_2dam][BiPh(O_2CCF_3)_4]$		
1a dam = tmpd	7.37 (m, 1 H), 7.91 (m, 2 H), 8.90 (m, 2 H)	2.52 (qnt, CH_2, 2 H), 3.07 (s, CH_3, 12 H), 3.47 (t, CH_2, 4 H)
1b dam = bdmap	7.39 (m, 1 H), 7.90 (m, 2 H), 8.86 (m, 2 H)	3.14 (s, CH_3, 12 H), 3.42 [q, CH_a, 2 H, $J(H_aH_b)$ = 12, $J(H_aH_x)$ = 10], 3.53 [q, CH_b, 2 H, $J(H_aH_b)$ = 12, $J(H_bH_x)$ = 3], 4.88 (m, CH_x, 1 H)
1c dam = tmbd	7.35 (m, 1 H), 7.90 (m, 2 H), 8.88 (m, 2 H)	2.05 (t, CH_2, 4 H), 3.02 (s, CH_3, 12 H), 3.39 (t, CH_2, 4 H)
1d dam = tmed	7.38 (m, 1 H), 7.92 (m, 2 H), 8.86 (m, 2 H)	3.16 (s, CH_3, 12 H), 3.98 (s, CH_2, 4 H)
1e dam = teed	7.38 (m, 1 H), 7.92 (m, 2 H), 8.85 (m, 2 H)	1.40 (t, CH_3, 12 H), 3.50 (q, CH_2, 8 H), 3.96 (s, CH_2, 4 H)
1f dam = tmphd	7.24 (s, 4 H), 7.38 (m, 1 H), 7.93 (m, 2 H), 8.85 (m, 2 H)	3.21 (s, CH_3, 12 H)
1g H_2dam = 2Hpy	7.36 (m, 1 H), 7.90 (m, 2 H), 8.14 (m, 4 H), 8.65 (m, 2 H), 8.85 (m, 2 H), 9.02 (m, 2 H)	
$[Hdam][BiPh_2(O_2CCF_3)_2]$		
3a dam = tmpd	7.32 (m, 2 H), 7.55 (m, 4 H), 8.37 (m, 4 H)	2.00 (qnt, CH_2, 2 H), 2.64 (s, CH_3, 12 H), 2.99 (t, CH_2, 4 H)
3d dam = tmed	7.30 (m, 2 H), 7.58 (m, 4 H), 8.34 (m, 4 H)	2.60 (s, CH_3, 12 H), 2.97 (s, CH_2, 4 H)
$[BiPh_2(O_2CCF_3)]$	7.42 (m, 2 H), 7.70 (m, 4 H), 8.32 (m, 4 H)	
$[H_2tmed][O_2CCF_3]_2$		2.96 (s, CH_3, 12 H), 3.68 (s, CH_2, 4 H)
$[Htmed][O_2CCF_3]$		2.50 (s, CH_3, 12 H), 2.85 (s, CH_2, 4 H)

cations form three hydrogen bonds with three of the uncoordinated oxygen atoms, as evidenced by the N(1)···O(6), N(2)···O(2) and N(2)···O(4) distances of 2.78(4), 2.66(3) and 2.79(3) Å. The structures of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion in **1f** and **1g** are thus between those of types **I** and **II**. As found in **1d**, three carboxylate ligands point up, but the remaining carboxylate is bonded to the bismuth centre through one oxygen atom only. The other oxygen atom [O(6) in **1f**, O(8) in **1g**] of this carboxylate ligand is 2.91(3) (**1f**) and 2.78(3) Å (**1g**) away from the Bi atom. These distances are significantly longer than those found in **1d**; hence, this carboxylate group could, at most, be described as a semi-chelating ligand. The long Bi–O(6) distance in **1f** can be attributed to the formation of the hydrogen bond. The fact that the $[BiPh(O_2CCF_3)_4]^{2-}$ anion in **1g** does not have the anticipated 'cup' structure could be attributed to the stacking effect of the aromatic rings in the crystal lattice. As shown in Fig. 5, the phenyl ring in **1g** is sandwiched between the N(1) and N(2) rings with an approximately eclipsed configuration. The shortest and longest atomic distances between the N(1) ring and the phenyl ring are 3.54 and 4.37 Å, while between the N(2) ring and the phenyl ring these distances are 3.64 and 4.17 Å. The shortest and longest atomic distances between the two pyridine rings are 4.16 and 4.37 Å.

The structures of complexes **1f** and **1g** further demonstrate that hydrogen-bonding interactions and the geometry of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion can be affected not only by the separations of the two ammonium centres, but also by lattice packing forces such as the stacking of aromatic rings.

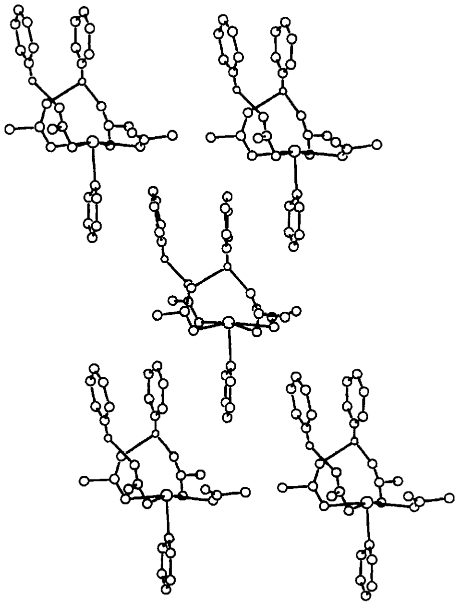


Fig. 5 The stacking of aromatic rings in complex **1g**. Fluorine atoms are omitted for clarity

Solution Behaviour of Compounds **1a**–**1g**.—The behaviour of compounds **1a**–**1g** in solution was studied by ^1H NMR spectroscopic analysis and the data at 23 °C are summarized in Table 4. The chemical shift assignments for the aliphatic region are straightforward for all compounds except for the bdmap diammonium. Owing to the presence of the CH(OH) group the two protons on the CH_2 groups are not equivalent. As a result the $CH_2CH(O)CH_2$ portion of bdmap is a A_2B_2X system. For the neutral bdmap molecule the CH_2 groups and the CH_3 groups have similar chemical shifts and can therefore not be distinguished by ^1H NMR spectroscopy. In contrast, the chemical shifts of these two groups in **1b** are well separated and the CH_2 group displays a well resolved A_2B_2X pattern.

All aliphatic proton signals of the diamines in complexes **1a**–**1f** are shifted significantly downfield in comparison with those of the neutral diamine molecules, consistent with protonation of the diamines. If the structure of the diammonium in **1** is the same as that in the solid state only one acidic proton signal would be present since the diammonium is symmetric. Unexpectedly, however, variable-temperature ^1H NMR spectra unequivocably show the presence of two distinct acidic proton signals in the spectra of **1a**–**1d**, where the diammonium is aliphatic. Both signals are very broad with one located at δ 10–11, typical of a CO_2H group, and the other at about δ 5–6, consistent with an NH group.[11] These two signals are also temperature dependent, moving toward each other with a decrease in temperature, as shown by the variable-temperature ^1H NMR spectra of **1a** (Fig. 6). Since these two chemical shifts were observed at 23 °C, the exchange between these two acidic protons must be quite slow. These NMR data thus imply that the structures of compounds **1a**–**1e** in solution are different from those observed in the solid state. We believe that the formation of these two different proton sites is due to the different acidities of the two protons on the aliphatic diammonium.[12] For example, the pK_{a1} and pK_{a2} values[13] for H_2tmed^{2+} are 2.20 and 6.35, respectively. The acidity of the first proton is comparable to that of CF_3CO_2H (pK_a = 0.5), while that of the second is significantly less than that of CF_3CO_2H. As a result one of the protons could undergo a relatively rapid site exchange between

Table 5 Atomic coordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **1a**							
N	0.406(2)	0.332(1)	0.633 9(9)	C(2)	0.633(4)	0.116(2)	0.538(1)
Bi	0.5000	0.078 05(8)	0.7500	C(3)	0.228(3)	0.119(1)	0.663(1)
F(1)	0.694(3)	0.175(1)	0.512 7(8)	C(4)	0.079(3)	0.110(1)	0.618(1)
F(2)	0.714(3)	0.053(1)	0.525 9(8)	C(5)	0.5000	−0.053(1)	0.7500
F(3)	0.519(2)	0.109(2)	0.502 6(9)	C(6)	0.431(2)	−0.098(1)	0.694 9(9)
F(4)	0.090(2)	0.052 3(8)	0.570 7(7)	C(7)	0.426(3)	−0.181(1)	0.693(1)
F(5)	0.026(2)	0.171 9(10)	0.586 6(7)	C(8)	0.5000	−0.230(4)	0.7500
F(6)	−0.023(1)	0.087(1)	0.655 2(8)	C(9)	0.5000	0.345(2)	0.7500
O(1)	0.591(2)	0.058 4(7)	0.642 4(6)	C(10)	0.545(6)	0.368(3)	0.691(2)
O(2)	0.614(2)	0.190(1)	0.633 5(9)	C(11)	0.365(6)	0.370(3)	0.703(2)
O(3)	0.258(2)	0.057 6(9)	0.699 1(7)	C(12)	0.299(6)	0.388(3)	0.650(3)
O(4)	0.286(2)	0.183(1)	0.657 8(10)	C(13)	0.476(5)	0.345(3)	0.583(2)
C(1)	0.610(3)	0.122(1)	0.611(1)	C(14)	0.260(6)	0.350(3)	0.582(2)
Complex **1b**							
Bi	0.5000	0.079 65(9)	0.7500	C(2)	0.073(2)	0.109(1)	0.621(1)
F(1)	0.029(1)	0.173 2(8)	0.587 8(5)	C(3)	0.620(3)	0.123(2)	0.611(1)
F(2)	−0.021(1)	0.085(1)	0.658 1(5)	C(4)	0.632(3)	0.113(2)	0.535(1)
F(3)	0.089(1)	0.052 0(8)	0.571 7(5)	C(5)	0.5000	−0.056(2)	0.7500
F(4)	0.527(2)	0.103(2)	0.502 2(7)	C(6)	0.561(2)	−0.097(1)	0.803 6(7)
F(5)	0.704(2)	0.172 8(9)	0.511 3(8)	C(7)	0.562(2)	−0.185(1)	0.804 5(9)
F(6)	0.726(2)	0.054 7(9)	0.525 4(6)	C(8)	0.5000	−0.220(2)	0.7500
O(1)	0.262(1)	0.064 2(8)	0.695 6(5)	C(9)	0.5000	0.356(2)	0.7500
O(2)	0.294(2)	0.178 2(10)	0.641 4(8)	C(10)	0.464(4)	0.373(2)	0.808(2)
O(3)	0.599(1)	0.060 8(8)	0.641 8(6)	C(11)	0.625(4)	0.373(2)	0.809(2)
O(4)	0.643(2)	0.194 1(10)	0.632 9(7)	C(12)	0.518(3)	0.352(2)	0.917(1)
O(5)	0.5000	0.271(2)	0.7500	C(13)	0.755(4)	0.349(2)	0.916(2)
N	0.605(2)	0.336(1)	0.866 0(8)	C(14)	0.727(4)	0.388(3)	0.854(2)
C(1)	0.226(3)	0.118(2)	0.655(1)				
Complex **1c**							
Bi	0.5000	0.092 62(6)	0.2500	N	0.391(2)	0.344 5(9)	0.120 7(10)
F(1)	0.033(1)	0.185 2(7)	0.091 3(6)	C(1)	0.223(2)	0.131(1)	0.165 5(9)
F(2)	0.096(2)	0.063 8(7)	0.079 9(6)	C(2)	0.080(2)	0.123(1)	0.125(1)
F(3)	−0.032(1)	0.098 6(9)	0.158 4(6)	C(3)	0.607(3)	0.128(2)	0.110(1)
F(4)	0.515(6)	0.122(3)	0.023(2)	C(4)	0.650(4)	0.117(2)	0.035(2)
F(5)	0.614(4)	0.179(2)	0.003(1)	C(5)	0.5000	−0.039(1)	0.2500
F(6)	0.732(3)	0.177(1)	0.024(1)	C(6)	0.435(2)	−0.080(1)	0.197 9(8)
F(7)	0.757(3)	0.068(2)	0.033(1)	C(7)	0.434(2)	−0.167(1)	0.200 7(10)
F(8)	0.688(5)	0.050(2)	0.027(2)	C(8)	0.5000	−0.210(2)	0.2500
F(9)	0.523(5)	0.073(2)	0.012(2)	C(9)	0.486(5)	0.389(3)	0.228(1)
O(1)	0.262(1)	0.074 2(6)	0.199 6(5)	C(10)	0.353(3)	0.395(1)	0.177(1)
O(2)	0.282(1)	0.197 6(7)	0.162 2(8)	C(11)	0.269(3)	0.349(2)	0.074(2)
O(3)	0.600(1)	0.070 4(7)	0.147 3(6)	C(12)	0.516(4)	0.367(2)	0.086(1)
O(4)	0.617(2)	0.201 8(9)	0.132 2(8)				
Complex **1d**							
Bi	−0.622 29(8)	0.2251	0.2500	N(2)	−0.672(3)	0.668(7)	0.557(5)
F(1)	−0.582(2)	0.047(5)	0.615(4)	C(1)	−0.601(3)	0.246(7)	0.483(5)
F(2)	−0.648(1)	0.190(5)	0.634(5)	C(2)	−0.601(2)	0.187(4)	0.603(3)
F(3)	−0.573(2)	0.285(5)	0.656(5)	C(3)	−0.714(2)	0.373(7)	0.378(5)
F(4)	−0.417(2)	0.196(6)	0.281(4)	C(4)	−0.783(1)	0.385(4)	0.397(3)
F(5)	−0.451(3)	0.012(5)	0.366(5)	C(5)	−0.639(2)	0.273(7)	0.048(5)
F(6)	−0.448(2)	0.240(6)	0.429(4)	C(6)	−0.640(1)	0.325(4)	−0.077(2)
F(7)	−0.800(2)	0.247(4)	0.422(4)	C(7)	−0.507(2)	0.221(8)	0.279(5)
F(8)	−0.785(2)	0.476(5)	0.476(3)	C(8)	−0.454(1)	0.160(5)	0.345(4)
F(9)	−0.812(2)	0.442(6)	0.325(3)	C(9)	−0.644(2)	−0.020(5)	0.227(4)
F(10)	−0.689(1)	0.334(5)	−0.101(4)	C(10)	−0.693(2)	−0.078(5)	0.268(6)
F(11)	−0.618(2)	0.216(4)	−0.131(4)	C(11)	−0.705(2)	−0.230(5)	0.237(4)
F(12)	−0.618(2)	0.457(4)	−0.095(4)	C(12)	−0.676(3)	−0.324(9)	0.188(5)
O(1)	−0.615(2)	0.140(4)	0.441(3)	C(13)	−0.634(2)	−0.261(7)	0.139(4)
O(2)	−0.578(2)	0.338(4)	0.460(3)	C(14)	−0.615(2)	−0.099(5)	0.156(3)
O(3)	−0.686(2)	0.454(5)	0.413(4)	C(15)	−0.599(2)	0.717(6)	0.451(4)
O(4)	−0.710(1)	0.259(4)	0.325(3)	C(16)	−0.623(2)	0.681(5)	0.551(4)
O(5)	−0.678(1)	0.291(5)	0.093(3)	C(17)	−0.522(5)	0.73(1)	0.509(10)
O(6)	−0.597(2)	0.226(6)	0.079(3)	C(18)	−0.528(6)	0.68(2)	0.33(1)
O(7)	−0.506(2)	0.349(6)	0.262(7)	C(19)	−0.702(3)	0.842(8)	0.567(5)
O(8)	−0.540(2)	0.114(5)	0.284(3)	C(20)	−0.701(4)	0.60(1)	0.665(8)
N(1)	−0.552(2)	0.646(6)	0.428(4)				

Table 5 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **1f**							
Bi	0.028 6(1)	0.219 70(8)	0.385 3(1)	N(2)	−0.068(2)	0.352(1)	−0.100(2)
F(1)	0.456(5)	0.298(2)	0.656(4)	C(1)	0.286(4)	0.226(2)	0.584(3)
F(2)	0.500(4)	0.224(3)	0.703(5)	C(2)	0.376(4)	0.259(3)	0.693(4)
F(3)	0.454(4)	0.190(2)	0.768(4)	C(3)	0.024(4)	0.103(2)	0.608(4)
F(4)	0.354(5)	0.225(3)	0.818(4)	C(4)	−0.038(5)	0.067(2)	0.704(6)
F(5)	0.313(4)	0.308(2)	0.778(5)	C(5)	−0.177(3)	0.220(2)	0.124(3)
F(6)	0.347(5)	0.336(2)	0.709(5)	C(6)	−0.278(5)	0.199(3)	0.019(4)
F(7)	0.021(5)	−0.010(3)	0.733(6)	C(7)	0.232(4)	0.279(2)	0.247(3)
F(8)	0.053(5)	0.059(4)	0.835(6)	C(8)	0.330(4)	0.329(2)	0.230(4)
F(9)	−0.026(6)	0.108(3)	0.828(5)	C(9)	−0.136(3)	0.333(2)	0.418(3)
F(10)	−0.147(5)	0.119(3)	0.737(6)	C(10)	−0.090(3)	0.412(2)	0.434(3)
F(11)	−0.169(4)	0.077(3)	0.669(5)	C(11)	−0.190(3)	0.484(2)	0.447(3)
F(12)	−0.054(6)	−0.006(3)	0.688(5)	C(12)	−0.312(3)	0.484(2)	0.455(3)
F(13)	−0.256(3)	0.121(2)	−0.009(2)	C(13)	−0.340(3)	0.406(3)	0.443(3)
F(14)	−0.281(3)	0.235(2)	−0.094(2)	C(14)	−0.248(3)	0.335(2)	0.419(3)
F(15)	−0.395(3)	0.213(2)	0.041(3)	C(15)	0.584(3)	0.090(2)	0.331(3)
F(16)	0.312(3)	0.401(2)	0.279(4)	C(16)	0.404(4)	0.013(2)	0.320(3)
F(17)	0.452(2)	0.293(2)	0.259(3)	C(17)	0.485(3)	0.036(2)	0.117(3)
F(18)	0.319(3)	0.353(2)	0.103(4)	C(18)	0.607(3)	−0.023(2)	0.116(3)
O(1)	0.163(2)	0.261(1)	0.575(2)	C(19)	0.381(3)	0.061(2)	0.006(3)
O(2)	0.337(2)	0.171(2)	0.512(2)	C(20)	0.053(3)	0.286(2)	−0.134(3)
O(3)	−0.053(2)	0.161(1)	0.542(2)	C(21)	−0.166(4)	0.369(2)	−0.230(3)
O(4)	0.133(3)	0.072(2)	0.607(3)	C(22)	−0.051(3)	0.453(2)	0.073(3)
O(5)	−0.169(2)	0.182(1)	0.239(2)	C(23)	−0.026(3)	0.427(2)	−0.051(3)
O(6)	−0.105(2)	0.263(1)	0.111(2)	C(24)	0.022(3)	0.473(2)	−0.124(3)
O(7)	0.140(2)	0.316(1)	0.303(2)	C(25)	0.628(8)	0.444(5)	−0.016(10)
O(8)	0.252(2)	0.210(1)	0.192(2)	C(26)	0.583(9)	0.492(5)	0.073(8)
N(1)	0.464(2)	0.073(1)	0.251(3)	C(28)	0.509(9)	0.467(5)	−0.111(8)
Complex **1g**							
Bi	0.537 66(10)	0.238 04(6)	0.343 20(5)	O(6)	0.393(4)	0.132(2)	0.439(2)
F(1)	0.875(4)	0.460(2)	0.351(2)	O(7)	0.765(3)	0.216(2)	0.335(1)
F(2)	0.886(4)	0.463(3)	0.433(2)	O(8)	0.719(3)	0.108(2)	0.377(3)
F(3)	0.812(5)	0.523(3)	0.445(2)	N(1)	0.295(3)	0.160(3)	0.560(2)
F(4)	0.738(5)	0.554(3)	0.414(3)	N(2)	0.582(3)	0.346(2)	0.561(1)
F(5)	0.698(4)	0.548(3)	0.332(3)	C(1)	0.504(2)	0.236(3)	0.219(1)
F(6)	0.783(5)	0.507(3)	0.325(3)	C(2)	0.472(3)	0.310(2)	0.181(2)
F(7)	0.144(4)	0.413(3)	0.417(3)	C(3)	0.442(3)	0.309(2)	0.106(1)
F(8)	0.176(3)	0.457(2)	0.377(2)	C(4)	0.434(3)	0.229(2)	0.071(1)
F(9)	0.145(4)	0.436(3)	0.311(3)	C(5)	0.456(3)	0.154(2)	0.108(2)
F(10)	0.095(4)	0.358(3)	0.300(2)	C(6)	0.484(3)	0.156(2)	0.186(2)
F(11)	0.087(4)	0.312(3)	0.336(3)	C(7)	0.662(3)	0.414(2)	0.385(2)
F(12)	0.113(3)	0.347(2)	0.422(2)	C(8)	0.774(4)	0.479(2)	0.383(2)
F(13)	0.232(4)	0.007(2)	0.430(2)	C(9)	0.307(3)	0.338(2)	0.376(2)
F(14)	0.201(3)	0.004(2)	0.343(2)	C(10)	0.161(4)	0.373(3)	0.365(2)
F(15)	0.265(6)	−0.032(4)	0.322(3)	C(11)	0.382(3)	0.092(2)	0.388(2)
F(16)	0.382(5)	−0.057(3)	0.355(3)	C(12)	0.318(4)	0.004(3)	0.383(2)
F(17)	0.407(4)	−0.056(3)	0.415(3)	C(13)	0.778(4)	0.150(3)	0.358(2)
F(18)	0.314(6)	−0.028(3)	0.446(3)	C(14)	0.917(4)	0.105(3)	0.375(2)
F(19)	0.928(3)	0.039(3)	0.325(2)	C(15)	0.322(5)	0.092(3)	0.605(3)
F(20)	0.917(4)	0.022(3)	0.391(3)	C(16)	0.319(4)	0.103(3)	0.674(3)
F(21)	0.959(5)	0.066(4)	0.438(3)	C(17)	0.301(3)	0.178(3)	0.704(2)
F(22)	0.997(4)	0.135(3)	0.430(2)	C(18)	0.279(3)	0.245(3)	0.664(2)
F(23)	1.016(4)	0.155(3)	0.375(3)	C(19)	0.279(3)	0.248(4)	0.592(3)
F(24)	0.969(4)	0.117(3)	0.314(2)	C(20)	0.614(3)	0.270(3)	0.588(2)
O(1)	0.641(2)	0.370(1)	0.330(1)	C(21)	0.642(3)	0.259(2)	0.661(2)
O(2)	0.644(3)	0.401(2)	0.440(1)	C(22)	0.642(3)	0.329(2)	0.706(2)
O(3)	0.338(2)	0.309(1)	0.321 5(9)	C(23)	0.603(4)	0.406(2)	0.676(2)
O(4)	0.366(2)	0.335(2)	0.443(1)	C(24)	0.580(4)	0.417(2)	0.603(2)
O(5)	0.412(2)	0.110(1)	0.331(1)				
Complex **2e**							
Bi	0.365 6(1)	0.247 91(8)	0.145 1(2)	N(1)	0.157(3)	−0.021(2)	0.091(3)
F(1)	0.560(2)	0.085(1)	0.471(3)	N(2)	0.577(5)	0.438(3)	0.609(4)
F(2)	0.716(3)	0.172(2)	0.449(4)	C(1)	0.518(4)	0.190(2)	0.366(4)
F(3)	0.632(3)	0.202(2)	0.605(3)	C(2)	0.605(4)	0.165(3)	0.479(5)
F(4)	0.111(5)	0.372(3)	−0.188(4)	C(3)	0.168(4)	0.309(2)	−0.007(4)
F(5)	−0.038(3)	0.302(2)	−0.141(5)	C(4)	0.078(5)	0.351(3)	−0.079(5)
F(6)	0.065(3)	0.417(2)	−0.014(3)	C(5)	0.192(4)	0.250(3)	0.339(4)
F(13)	0.388(6)	0.069(4)	−0.307(6)	C(6)	0.076(7)	0.235(4)	0.441(8)
F(14)	0.343(7)	0.023(4)	−0.280(6)	C(7)	0.315(3)	0.144(2)	−0.146(4)
F(15)	0.184(5)	0.005(3)	−0.309(5)	C(8)	0.277(7)	0.075(4)	−0.309(6)
F(16)	0.148(5)	0.054(3)	−0.354(5)	C(9)	0.032(4)	0.152(2)	0.418(5)

Table 5 (*continued*)

Atom	*x*	*y*	*z*
F(17)	0.240(8)	0.116(4)	−0.404(7)
F(18)	0.329(5)	0.114(3)	−0.396(5)
F(19)	0.796(5)	0.400(4)	0.069(6)
F(20)	0.83(1)	0.308(6)	0.13(1)
F(21)	0.869(6)	0.351(5)	0.228(8)
F(22)	0.854(7)	0.415(5)	0.337(8)
F(23)	0.808(4)	0.470(3)	0.303(5)
F(24)	0.794(6)	0.440(4)	0.147(9)
O(1)	0.445(2)	0.140(1)	0.252(2)
O(2)	0.511(2)	0.259(2)	0.406(2)
O(3)	0.132(2)	0.240(1)	−0.007(2)
O(4)	0.282(2)	0.363(1)	0.062(3)
O(5)	0.270(2)	0.309(1)	0.330(3)
O(6)	0.180(2)	0.178(1)	0.255(3)
O(7)	0.362(3)	0.216(1)	−0.130(2)
O(8)	0.281(2)	0.111(1)	−0.048(2)
O(9)	0.574(2)	0.379(2)	0.230(3)
O(10)	0.599(2)	0.259(2)	0.117(3)
C(10)	0.818(7)	0.396(5)	0.21(1)
C(11)	0.190(4)	−0.083(3)	−0.001(4)
C(12)	0.334(5)	−0.084(3)	0.034(5)
C(14)	0.195(3)	−0.012(2)	0.259(4)
C(15)	0.123(4)	−0.082(3)	0.298(5)
C(16)	0.003(4)	−0.022(2)	0.046(4)
C(17)	0.722(7)	0.473(4)	0.664(6)
C(18)	0.803(6)	0.431(4)	0.667(6)
C(19)	0.502(5)	0.388(3)	0.700(6)
C(20)	0.505(6)	0.426(4)	0.834(7)
C(21)	0.493(6)	0.491(4)	0.563(5)
F(7)	0.150(5)	0.239(3)	0.558(5)
F(9)	0.077(4)	0.326(2)	0.462(5)
F(11)	−0.018(7)	0.195(3)	0.368(7)
F(8)	0.128(8)	0.279(3)	0.543(7)
F(10)	−0.024(5)	0.249(3)	0.341(6)
F(12)	0.032(4)	0.152(2)	0.418(5)

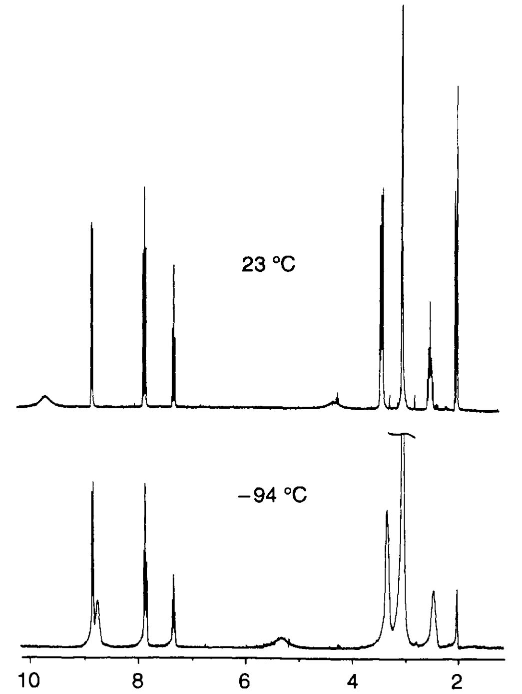
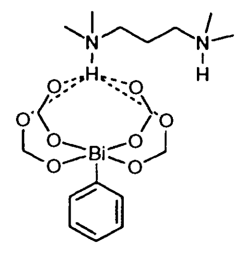


Fig. 6 Variable-temperature ^1H NMR spectra of complex **1a** in $(CD_3)_2CO$

the nitrogen centre and the oxygen centre of the trifluoroacetate ligands, while the other remains on the nitrogen centre. It is probable that the presence of the bismuth complex sufficiently hinders or slows down the proton exchange, allowing the detection of both protons in the ^1H NMR spectrum. For the purpose of comparison we also examined the ^1H NMR spectra of $[H_2tmpd][O_2CCF_3]_2$, where no bismuth is involved. No acidic proton signal was seen at 297 K, while at 245 K a broad signal was observed at δ 12.72. At 197 K two broad proton signals at δ 12.58 and 3.83 were observed, which presumably are due to the two acidic protons. The fact that these signals were not observed at higher temperature implies that the exchange between these two protons was much faster than that in the bismuth complex. No acidic proton signal was observed in the ^1H NMR spectra of **1f** and **1g** at 297 K and only one broad acidic proton signal was observed for both compounds at lower temperature (δ 9.62 for **1f** at 197 K and 16.58 for **1g** at 223 K). For **1g** (Hpy^+, $pK_a = 5.17$) this is expected since there is only one type of acidic proton in this compound. For **1f** this can be explained by the small difference in the pK_a values of the two acidic protons on the H_2tmphd^{2+} cation which could lead to a rapid exchange between these two protons. One of the possible structures of $[H_2dam][BiPh(O_2CCF_3)_4]$ in solution is shown in **A**.



A

The chemical shifts of the phenyl ligand in the ^1H NMR spectra of complexes **1a**–**1g** are nearly identical and did not show any appreciable changes with temperature. This implies that in solution the co-ordination environment around the bismuth centre in these compounds is similar, at least in the temperature range studied (188–313 K). We have found, however, that the stability of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion is highly dependent on the cation. For example, the ^1H NMR study indicated that compounds **1a**–**1e**, in which the cation is an aliphatic diammonium, undergo disproportionation reactions in solution while **1f** and **1g**, in which the cation is a aromatic diammonium or Hpy^+, are stable in solution. A new set of chemical shifts in the aromatic region were observed after $[H_2dam][BiPh(O_2CCF_3)_4]$ (dam = aliphatic diamine) was dissolved in solution for about 24 h (Fig. 7). Since these chemical shifts are close to those of $[BiPh_2(O_2CCF_3)]$ (see Table 4) we believe that they may belong to the $[BiPh_2(O_2CCF_3)_2]^-$ anion with a structure similar to that in the $[Bi^VPh_4][Bi^{III}Ph_2(O_2CCF_3)_2]$ compound.[1d] In fact this proposed $[BiPh_2(O_2CCF_3)_2]^-$ anion can be produced *in situ* by the reaction of $BiPh_3$ with 2 equivalents of CF_3CO_2H in the presence of 1 equivalent of diamine. The aromatic resonances in the ^1H NMR spectrum of the reaction mixture are identical with those of the proposed $[BiPh_2(O_2CCF_3)_2]^-$ anion, while the chemical shifts of the tmpd or tmed in this mixture are further upfield than those in $[H_2dam][O_2CCF_3]_2$. They are, however, similar to those in $[Hdam][O_2CCF_3]$, which is prepared *in situ* by mixing the diamine and CF_3CO_2H in a 1 : 1 ratio. This suggests that the diamine in this mixture is a monocation and probably hydrogen bonded to the carboxylate ligands in the $[BiPh_2(O_2CCF_3)_2]^-$ anion. We therefore have formulated this compound as [Hdam][$BiPh_2(O_2CCF_3)_2$] **3**. Attempts to isolate **3** or the [Hdam][O_2CCF_3] salt from the solution were unsuccessful; instead, the [H_2dam][O_2CCF_3]$_2$ salt was always obtained as the major solid product. This may be caused by the presence of equilibria (1) and (2) in solution. The crystallization

$$2[\text{Hdam}][\text{BiPh}_2(\text{O}_2\text{CCF}_3)_2] \rightleftharpoons 2[\text{BiPh}_2(\text{O}_2\text{CCF}_3)] + [\text{H}_2\text{dam}][\text{O}_2\text{CCF}_3]_2 + \text{dam} \quad (1)$$

$$2[\text{Hdam}][\text{O}_2\text{CCF}_3] \rightleftharpoons [\text{H}_2\text{dam}][\text{O}_2\text{CCF}_3]_2 + \text{dam} \quad (2)$$

process may drive the equilibrium to the right, perhaps owing to the favorable cation–anion interaction of the [H_2dam][O_2CCF_3]$_2$ compound in the crystal lattice.[14]

The other disproportionation product has been identified as the anion $[Bi(O_2CCF_3)_5]^{2-}$ **2** which can be isolated in good yield when an excess of CF_3CO_2H is used in the reaction. The solid-state structure of [H_2teed][$Bi(O_2CCF_3)_5$] **2e** has been determined by X-ray diffraction analysis and the ORTEP drawing is given in Fig. 8. The Bi^{3+} ion is co-ordinated by ten oxygen atoms from the five carboxylate ligands, with the Bi–O distances ranging from 2.44(3) to 2.62(2) Å. High co-ordination numbers for the Bi^{3+} ion have been reported previously, however significant variations in bong lengths (2.30–2.90 Å) were common and quite often very long Bi–O distances were involved.[2,15] In contrast, the Bi–O bond lengths in **2e** are similar, and the co-ordination sphere of the Bi^{3+} is rather symmetric. If each pair of oxygen atoms from the carboxylate ligands is assigned to one vertex of the polyhedron the geometry of the bismuth complex can be described as a distorted trigonal bipyramid. If each oxygen atom is considered separately the geometry can be regarded as a distorted pentagonal prism. The H_2teed^{2+} cation and the $[Bi(O_2CCF_3)_5]^{2-}$ anion are packed in such a way that they alternate in the crystal lattice to form a one-dimensional structure (Fig. 9). They are linked through weak inter- and intra-molecular hydrogen bonds, as indicated by the N(1) ••• O(8) and N(2) ••• O(2′) distances of 3.02(4) and 3.16(5) Å.

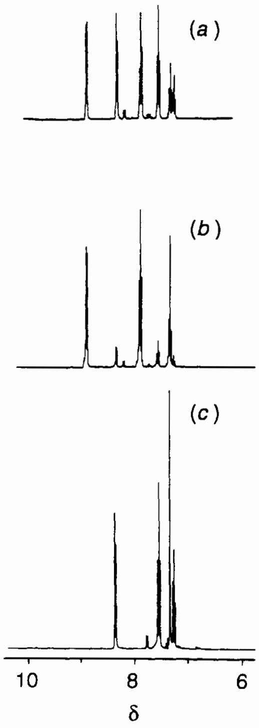


Fig. 7 The aromatic region of the ^1H NMR spectrum of (*a*) complex **1a** in $(CD_3)_2CO$ after **1a** was dissolved in thf for 2 d, (*b*) the same solution taken 2 d later and (*c*) a reaction mixture of $BiPh_3$ with CF_3CO_2H and tmpd in a 1:2:1 ratio in $(CD_3)_2CO$

The equilibrium between $[BiPh(O_2CCF_3)_4]^{2-}$, $[BiPh_2(O_2CCF_3)_2]^-$ and $[Bi(O_2CCF_3)_5]^{2-}$ for compounds **1a** and **1c**–**1e** was achieved in acetone at 23 °C over a few days, with the resulting $[BiPh(O_2CCF_3)_4]^{2-}:[BiPh_2(O_2CCF_3)_2]^-$ ratio being about 8–11:1, depending on the diamine involved. No benzene formation was observed. Based upon these observations a disproportionation reaction scheme is proposed (Scheme 1). Upon the addition of an excess of CF_3CO_2H, the $[BiPh_2(O_2CCF_3)_2]^-$ signals disappeared and a resonance due to benzene was observed. After some time, the integrals of the

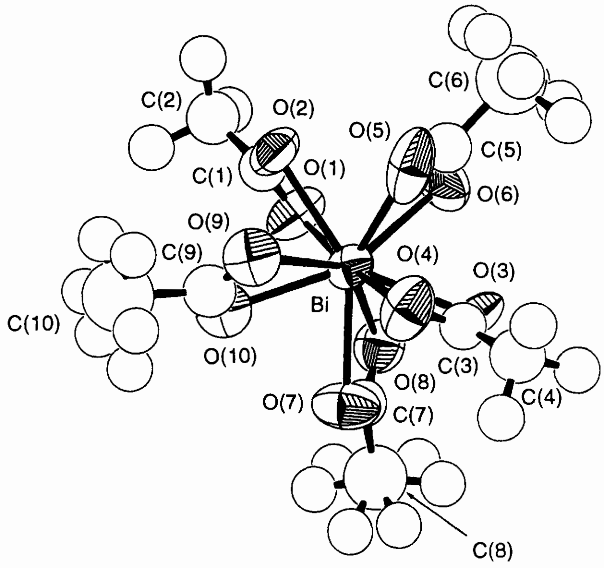


Fig. 8 The structure of the $[Bi(O_2CCF_3)_5]^{2-}$ anion in complex **2e** with 50% thermal ellipsoids. For clarity the fluorine atoms are shown as ideal spheres

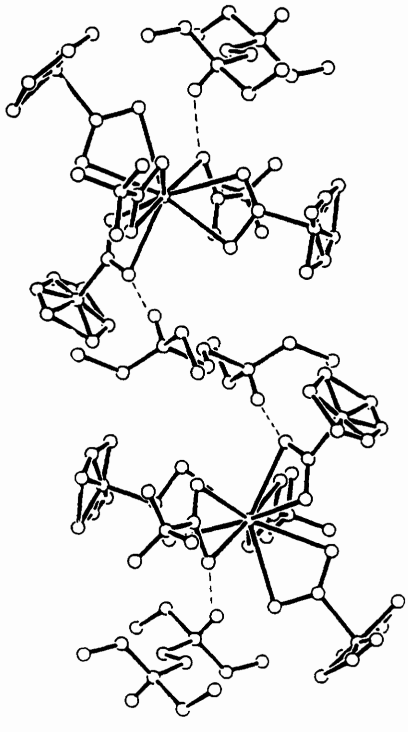
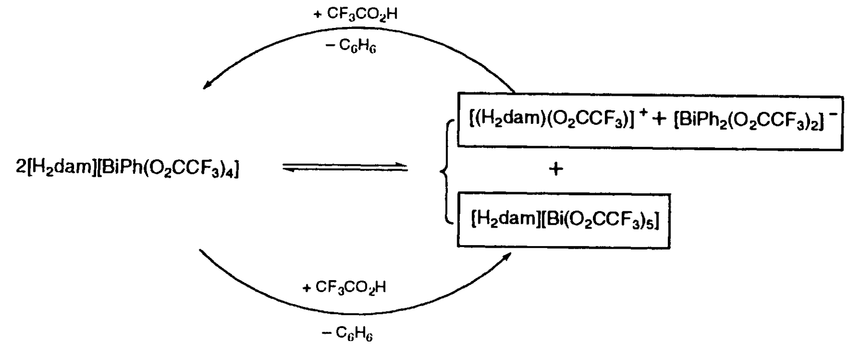


Fig. 9 The intra- and inter-molecular hydrogen bonds in complex **2e**



Scheme 1

chemical shifts due to the $[BiPh(O_2CCF_3)_4]^{2-}$ anion decreased gradually with further increase in the integral of the benzene signal. We believe that in the presence of an excess of CF_3CO_2H the $[BiPh_2(O_2CCF_3)_2]^-$ anion is initially converted into $[BiPh(O_2CCF_3)_4]^{2-}$ with elimination of benzene. The $[BiPh(O_2CCF_3)_4]^{2-}$ anion is subsequently converted into $[Bi(O_2CCF_3)_5]^{2-}$ with elimination of an additional equivalent of benzene, as illustrated by the curved arrows in Scheme 1. It has been previously reported that the neutral complex $[BiPh(O_2CCF_3)_2]$ is unstable in solution which could be caused by a similar disproportionation reaction (3). While several organobismuth halide compounds are known to disproportionate in solution,[16] no such reactions have been observed previously for organobismuth carboxylates.

$$2[BiPh(O_2CCF_3)_2] \rightleftharpoons [BiPh_2(O_2CCF_3)] + [Bi(O_2CCF_3)_3] \quad (3)$$

Compound **1b** undergoes irreversible decomposition with the formation of benzene in solution. Resonances due to the $[BiPh_2(O_2CCF_3)_2]^-$ anion were observed at the early stages of the decomposition, as monitored by ^1H NMR spectroscopy. Attempts to identify the final decomposition products have been unsuccessful. The irreversible decomposition may be caused by the OH group of the bdmap. In contrast to the behaviour of compounds **1a**–**1e**, **1f** and **1g** are stable in solution for days and exhibit no significant disproportionation. Again, we believe that the difference in stability of these compounds in solution is due to the difference in acidities of the cations. The high acidity of the first proton on the aliphatic diammonium would favour the formation of the $Hdam^+$ monocation,[12] which is in equilibrium with $[(H_2dam)(O_2CCF_3)]^+$ $\{[(H_2dam)(O_2CCF_3)]^+ \rightleftharpoons Hdam^+ + CF_3CO_2H\}$; this prompts the disproportionation of $[BiPh(O_2CCF_3)_4]^{2-}$. In contrast, the Hpy^+ and the $tmphd^{2+}$ cations are much weaker acids; thus, the $[BiPh(O_2CCF_3)_4]^{2-}$ anion in **1f** and **1g** is stable. Further investigation into the stability of compounds of formula $[Y]_2[BiPh(O_2CCF_3)_4]$ where Y is a cation without acidic protons would provide more information; unfortunately, we have not been able to synthesise such compounds.

Compounds **1a**–**1g** are not soluble in CH_2Cl_2 or $CHCl_3$, but are moderately soluble in the polar solvents thf and acetone. The thf and acetone solvent molecules also appear to play a role in the stability of these compounds in solution. For example, after **1a** was dissolved in thf for 2 d the ^1H NMR spectrum of the dried sample immediately taken in $(CD_3)_2CO$ showed the $[BiPh(O_2CCF_3)_4]^{2-}:[BiPh_2(O_2CCF_3)_2]^-$ ratio to be about 2:1. When the same solution was re-examined 2 d later this ratio had changed to about 11:1 (Fig. 7). This is similar to the equilibrium ratio observed by dissolving a solid sample of **1a** directly in acetone. The nature of such solvent effects is not yet understood.

Hydrogen-bonding interactions in organic molecules and their role in the construction and function of supramolecules and biomolecules have been extensively studied.[17] In contrast, only limited studies have been done on the influence of such interactions on the structures and stability of metal complexes. The structural variations observed in compounds **1a**–**1g** are unprecedented and may also exist in other unexplored inorganic systems. Bismuth(III) complexes have been known to display versatile structural features. The lone pair of electrons on the bismuth centre may also play an important role in the observed structural variations of this system. Examination of cation–anion interactions involving hydrogen bonds in other inorganic complexes where the metal centre has a relatively more rigid structure than that of bismuth(III) may provide useful information. Theoretical investigations on such systems, however, are necessary further to understand the phenomena observed here.

Conclusion

The structure of the $[Bi^{III}Ph(O_2CCF_3)_4]^{2-}$ anion in the solid state is dependent on the structure of the cation, owing to the hydrogen-bonding interactions between the ammonium group and the trifluoroacetate ligand. The hydrogen-bonding interaction of this system in solution is different from that in the solid state. When the cation is an aliphatic diammonium two distinct acidic proton sites are present in $[H_2dam][BiPh(O_2CCF_3)_4]$, and the $[BiPh(O_2CCF_3)_4]^{2-}$ anion undergoes disproportionation in solution. When the cation is an aromatic diammonium or Hpy^+ the $[BiPh(O_2CCF_3)_4]^{2-}$ anion is stable in solution. Solvents such as thf or acetone appear to affect the stability of the $[BiPh(O_2CCF_3)_4]^{2-}$ anion in solution.

Acknowledgements

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