Halide-transfer Reactions involving Bismuth(III) Chloride: Synthesis and Identification of the Ternary Complexes $BiCl_3$·$SbCl_5$·4MeCN, $2MgCl_2$·$4BiCl_3$·12MeCN and $3MgCl_2$·$4BiCl_3$·18MeCN. Structural Characterisation of $2MgCl_2$·$4BiCl_3$·12MeCN as $[Mg(MeCN)_6]_2[Bi_4Cl_{16}]$ and its Structural Relationships with Other Complex Chlorobismuth(III) Anions *

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Reaction (1:1 stoichiometry) of $BiCl_3$ and $SbCl_5$ in acetonitrile provides the ternary complex $BiCl_3$·$SbCl_5$·4MeCN **1** which has been identified (microanalyses, conductivity, IR, ^{121}Sb NMR and UV–VIS data) as the ionic salt $[BiCl_2(MeCN)_4][SbCl_6]$. The product $2MgCl_2$·$4BiCl_3$·12MeCN **2** isolated from the reaction of $MgCl_2$ and $BiCl_3$ (1:2 stoichiometry) in acetonitrile has been characterised by X-ray diffraction studies as the ionic salt $[Mg(MeCN)_6]_2[Bi_4Cl_{16}]$. Crystals of **2** are monoclinic, space group $P2_1/a$ with a = 16.022(11), b = 21.513(22), c = 9.217(10) Å, β = 96.5(1)° and Z = 2. Structure refinement gave a final R value of 0.067 for 1635 independent reflections. The six-co-ordinate magnesium atoms of the $[Mg(MeCN)_6]^{2+}$ cations have a distorted octahedral geometry with Mg–N distances in the range 2.20(2)–2.25(3) Å. The $[Bi_4Cl_{16}]^{4-}$ anions are discrete and centrosymmetric; each tetranuclear Bi^{III} unit consists of two pairs of non-equivalent six-co-ordinate bismuth atoms involving terminal Bi–Cl bonds with lengths in the range 2.426(16)–2.552(16), bridging Bi–Cl bonds in the range 2.678(13)–2.976(13) and triply bridging Bi–Cl bonds of 2.930(14) and 3.009(16) Å. Each bismuth atom has distorted octahedral geometry. The ternary complex $3MgCl_2$·$4BiCl_3$·18MeCN **3** isolated from the reaction of $MgCl_2$ and $BiCl_3$ (3:4 stoichiometry) is formulated as the ionic salt $[Mg(MeCN)_6]_3[Bi_4Cl_{18}]$ (by microanalyses, conductivity and IR data). The structure of **2** and possible structures of **3** are discussed within the context of a short review of the structural chemistry of known tetranuclear bismuth(III) chloroanions.

Removal of a chloride ion from a covalent M–Cl bond (M = metal or metalloid) can be effected by $SbCl_3$ or $SbCl_5$ and results in the formation of antimonate(III) or antimonate(V) salts respectively, which incorporate discrete cationic M^{n+} species.[1] For example the reaction system $TiCl_4$–$SbCl_5$–MeCN[2,3] gives *fac*-$[TiCl_3(MeCN)_3][SbCl_6]$ and $MgCl_2$–$SbCl_3$–MeCN[4] gives $[Mg(MeCN)_6][Sb_2Cl_8]$ reflecting the powerful halide-acceptor characteristics of both Sb^{III} and Sb^{V}. Despite a similar reputation as a halide acceptor, $AsCl_3$ does not appear to follow this pattern; the reaction systems MCl_2–$AsCl_3$–MeCN (M = Mg or Zn) or $TiCl_4$–$AsCl_3$–MeCN[5] simply yield the bis(acetonitrile) adducts $[MCl_2(MeCN)_2]$ or $[TiCl_4(MeCN)_2]$ respectively.

To expand on this theme of halide abstraction with respect to the Group 15 series (As, Sb, Bi) we have been studying the behaviour of $BiCl_3$ in such systems. What is of particular interest here is that as well as acceptor behaviour, *e.g.* formation of complex anions of several types such as $[Bi_2Cl_8]^{2-}$,[6] $[BiCl_5]^{2-}$,[6] $[BiCl_6]^{3-}$,[7] $[Bi_2Cl_9]^{3-}$[8] and $[Bi_4Cl_{18}]^{6-}$,[9] bismuth(III) chloride can also act as a halide-ion donor with ensuing formation of cationic species, *e.g.* $[BiCl_2(18\text{-crown-6})]_2[Bi_2Cl_8]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane).[10] Bismuth clusters and even the 'naked' Bi^+ cation are also known.[11] Herein we report our studies of the reaction systems $MgCl_2$–$BiCl_3$–MeCN and $BiCl_3$–$SbCl_5$–MeCN.

Experimental

All manipulations were conducted under an inert atmosphere of N_2 using a glove-box and/or a conventional Schlenk system. Anhydrous $SbCl_5$, $MgCl_2$ and $BiCl_3$ were used as obtained commercially. Acetonitrile was purified following the procedure of Walter and Ramaley[12] UV–VIS spectra were obtained from a Shimadzu UV 35 spectrophotometer using MeCN solutions sealed in 1 cm light-path quartz cells. Antimony-121 NMR spectra (95.72 MHz) were recorded on a Bruker WH400 spectrometer using MeCN solutions doped (10% by volume) with CD_3CN and with $[NEt_4]SbCl_6$ (δ = 0, $w_{\frac{1}{2}}$ 190 Hz) as external reference. Infrared spectra were recorded as mulls (CsI plates) using a Perkin-Elmer 580B spectrometer. Conductivity measurements were carried out using a Philips PW 9527 digital conductivity meter with MeCN solutions contained in a glass apparatus having a side-arm attachment incorporating the Pt electrodes. The sample, from a tared ampoule, was placed in the vessel under N_2 and dry solvent introduced directly from the distillation unit. Prior calibration of the cell was effected with aqueous potassium chloride solutions: all solutions were thermostatted at 298.0 ± 0.1 K.

* Bis[hexakis(acetonitrile)magnesium] [di-μ_3-chloro-1:1′:2κ*Cl*; 1:1′:2′κ*Cl*-tetra-μ-chloro-1:2κ*Cl*; 1:2′κ*Cl*; 1′:2κ*Cl*; 1′:2′κ*Cl*-decachloro-1κ²*Cl*; 1′κ²*Cl*; 2κ³*Cl*; 2′κ³*Cl*-tetrabismuthate(III)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for complex **2**

Atom	*x*	*y*	*z*
Bi(1)	4821(1)	6036(1)	5376(2)
Bi(2)	2680(1)	4750(1)	4532(3)
Cl(2)	4244(8)	4816(7)	6508(18)
Cl(1)	3699(8)	3922(7)	2840(18)
Cl(3)	2223(8)	3837(5)	5978(17)
Cl(4)	1940(10)	5447(8)	6013(19)
Cl(5)	1436(9)	4635(8)	2562(21)
Cl(6)	3504(7)	5852(6)	3359(16)
Cl(7)	5123(11)	7020(8)	4199(22)
Cl(8)	3992(11)	6534(10)	7227(21)
Mg	1205(9)	6752(7)	5(17)
N(11)	1802(21)	6899(17)	2274(33)
C(12)	2010(22)	7120(18)	3414(33)
C(13)	2237(17)	7193(16)	4989(30)
N(21)	2290(18)	7268(17)	−643(43)
C(22)	2727(21)	7645(17)	−1042(48)
C(23)	3279(31)	8104(25)	−1662(69)
N(31)	220(18)	6212(15)	975(10)
C(32)	−121(21)	5782(17)	1431(47)
C(33)	−803(28)	5325(23)	1564(63)
N(41)	648(24)	6504(21)	−2259(36)
C(42)	347(44)	6507(34)	−3464(44)
C(43)	34(19)	6303(17)	−4947(33)
N(51)	430(23)	7625(15)	55(49)
C(52)	320(29)	8139(17)	400(64)
C(53)	139(40)	8789(19)	791(85)
N(61)	2093(23)	5953(17)	−192(52)
C(62)	2563(22)	5564(16)	−215(49)
C(63)	3083(23)	5032(16)	−282(53)

Table 2 Dimensions (distances in Å, angles in °) in the anion co-ordination sphere for complex **2**

Bi(1)–Cl(1)	3.009(16)	Bi(2)–Cl(1)	2.930(14)
Bi(1)–Cl(6)	2.678(13)	Bi(2)–Cl(2)	2.974(17)
Bi(1)–Cl(7)	2.453(18)	Bi(2)–Cl(3)	2.528(14)
Bi(1)–Cl(8)	2.516(20)	Bi(2)–Cl(4)	2.426(16)
Bi(1)–Cl(2*i*)	2.730(14)	Bi(2)–Cl(5)	2.552(16)
Bi(1)–Cl(1*i*)	3.034(16)	Bi(2)–Cl(6)	2.976(13)
Cl(1)–Bi(1)–Cl(6)	82.1(4)	Cl(2)–Bi(2)–Cl(3)	91.1(4)
Cl(1)–Bi(1)–Cl(7)	172.1(5)	Cl(1)–Bi(2)–Cl(4)	93.4(5)
Cl(6)–Bi(1)–Cl(7)	90.0(5)	Cl(2)–Bi(2)–Cl(4)	176.0(5)
Cl(1)–Bi(1)–Cl(8)	86.0(5)	Cl(3)–Bi(2)–Cl(4)	89.7(5)
Cl(6)–Bi(1)–Cl(8)	95.7(5)	Cl(1)–Bi(2)–Cl(5)	172.4(5)
Cl(7)–Bi(1)–Cl(8)	94.5(6)	Cl(2)–Bi(2)–Cl(5)	90.0(5)
Cl(1*i*)–Bi(1)–Cl(1)	82.1(4)	Cl(3)–Bi(2)–Cl(5)	92.9(5)
Cl(1*i*)–Bi(1)–Cl(6)	170.1(4)	Cl(4)–Bi(2)–Cl(5)	93.9(5)
Cl(2*i*)–Bi(1)–Cl(6)	170.1(4)	Cl(1)–Bi(2)–Cl(6)	78.7(4)
Cl(2*i*)–Bi(1)–Cl(7)	92.1(5)	Cl(2)–Bi(2)–Cl(6)	89.6(4)
Cl(2*i*)–Bi(1)–Cl(8)	93.8(5)	Cl(3)–Bi(2)–Cl(6)	167.8(4)
Cl(2*i*)–Bi(1)–Cl(1)	85.0(4)	Cl(4)–Bi(2)–Cl(6)	88.7(5)
Cl(7)–Bi(1)–Cl(1*i*)	97.7(5)	Cl(5)–Bi(2)–Cl(6)	99.3(5)
Cl(8)–Bi(1)–Cl(1*i*)	167.8(6)	Bi(1)–Cl(1)–Bi(2)	95.8(5)
Cl(1)–Bi(2)–Cl(2)	82.7(4)	Bi(1)–Cl(6)–Bi(2)	102.3(4)
Cl(1)–Bi(2)–Cl(3)	89.3(4)		

Preparation of the Complexes.—(*a*) $BiCl_3$·$SbCl_5$·4MeCN **1**. Antimony pentachloride (2.9 g, 9.6 mmol) in MeCN (20 cm^3) was added dropwise to an ice-cold solution of $BiCl_3$ (3.0 g, 9.6 mmol) in MeCN (50 cm^3) and the resulting pale yellow solution was stirred at room temperature for 12 h. Removal of solvent *in vacuo* provided a white solid which was washed with hexane (2 × 20 cm^3) and pumped dry for 1 h. The product **1** was recrystallised from MeCN–CH_2Cl_2 as colourless crystals of poor definition (yield: 6.11 g, 81.3%), m.p. (uncorrected) 75–76 °C (Found: C, 12.5; H, 1.5; N, 7.4. $C_8H_{12}BiCl_8N_4Sb$ requires C, 12.3; H, 1.5; N, 7.2%); IR: ν_{max}(Nujol) 2300s, 2260vs (MeCN); 348vs (SbCl), 280m and 255–250m(br) cm^{-1}; UV–VIS: ν_{max}(MeCN) 44 250, 37 037 and 31 545 cm^{-1}; ^{121}Sb NMR: $\delta(CD_3CN)$ 0.05 ppm, $w_{\frac{1}{2}}$ 182 Hz.

(*b*) $2MgCl_2$·$4BiCl_3$·12MeCN **2**. An intimate mixture of $BiCl_3$ (19.5 g, 61.7 mmol) and $MgCl_2$ (3.0 g, 31.7 mmol) was extracted with hot MeCN (150 cm^3) using a standard Soxhlet system. The resulting clear colourless solution was concentrated ($\frac{1}{2}$ volume) and placed in a refrigerator overnight when colourless needles of **2** separated; these were filtered off and washed with hexane (2 × 25 cm^3) (yield: 19.4 g, 64.8%), m.p. (uncorrected) 127–128 °C (Found: C, 14.7; H, 1.9; N, 8.6. $C_{24}H_{36}Bi_4Cl_{16}Mg_2N_{12}$ requires C, 14.8; H, 1.9; N, 8.6%); IR: ν_{max}(Nujol) 2322vs, 2290vs (MeCN); 405vs, 350–340vs (br), 276m and 255–250s (br) cm^{-1}; UV–VIS: ν_{max}(MeCN) 30 959 cm^{-1}.

(*c*) $3MgCl_2$·$4BiCl_3$·18MeCN **3**. The reaction of $BiCl_3$ (3.6 g, 11.6 mmol) and $MgCl_2$ (0.8 g 8.7 mmol) carried out as in (*b*) above provided a matte of colourless fibrous crystals of complex **3**. These were filtered off, washed with hexane (2 × 25 cm^3) and dried by pumping *in vacuo* at room temperature for *ca.* 2 h (yield: 4.1 g, 62.2%), m.p. (uncorrected) >208 °C with decomposition (Found: C, 19.1; H, 2.8; N, 10.6. $C_{36}H_{54}Bi_4Cl_{18}Mg_3N_{18}$ requires C, 18.9; H, 2.4; N, 11.0%); IR: ν_{max}(Nujol) 2320vs, 2289vs (MeCN); 401vs, 345–335s (br), 273(sh) and 240–230 cm^{-1}; UV–VIS: ν_{max}(MeCN) 48 500(sh), 43 600(sh) and 31 055 cm^{-1}.

X-Ray Crystallography.—*Crystal data.* $[Mg(MeCN)_6]_2[Bi_4Cl_{16}]$, $C_{24}H_{36}Bi_4Cl_{16}Mg_2N_{12}$, M = 972.0, space group $P2_1/a$, a = 16.022(11), b = 21.513(22), c = 9.217(10) Å, β = 96.5(1)°, U = 3156.6 $Å^3$, $F(000)$ = 1784, D_m = 2.10 g cm^{-3}, Z = 2, D_c = 2.04 g cm^{-3}, λ = 0.7107 Å, μ = 112.9 cm^{-1}.

A crystal of approximate size 0.35 × 0.25 × 0.20 mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected *via* variable width ω scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of (1.5 + sin μ/tan θ). 5200 Independent reflections were measured of which 1635 with $I > 3\sigma(I)$ were used in subsequent refinement. No deterioration in the crystal was observed during the data collection. An empirical absorption correction was made.[13] The structure was determined by direct methods. Hydrogen atoms on the methyl groups of several of the MeCN ligands could not be located either from a difference Fourier map or *via* refinement as a rigid group and were therefore not included in the refinement. The Bi, Cl and Mg atoms were refined anisotropically and the N and C atoms isotropically. Data were given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.067 (R' = 0.065). Calculations were carried out using SHELX 76[14] and some of our own programs on the Amdahl 5870 at the University of Reading. In the final cycles of refinement, no shift/error ratio was greater than 0.1σ. In the final difference Fourier maps, the maximum and minimum peaks were 1.65 e $Å^{-3}$ (located close to bismuth atoms), and −1.35 e $Å^{-3}$ respectively. Positional parameters are given in Table 1 and molecular dimensions for the metal co-ordination spheres in Table 2.

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

Results and Discussion

A 1:1 stoichiometric addition of $SbCl_5$ to $BiCl_3$ in acetonitrile provides colourless crystals of poor definition which analyse as $BiCl_3$·$SbCl_5$·4MeCN **1**. Of the several formulations possible the ionic structure $[BiCl_2(MeCN)_4][SbCl_6]$ is proposed. The ^{121}Sb NMR spectrum consists of a singlet at δ 0.05 ppm, $w_{\frac{1}{2}}$ 182 Hz, and the UV spectrum shows an intense charge-transfer band at ν_{max} 37 037 cm^{-1}, both features being diagnostic of $[SbCl_6]^-$ ions in solution.[3] Other charge-transfer bands at 44 250 and 31 545 cm^{-1} in the UV spectrum are assigned[15] to the cationic

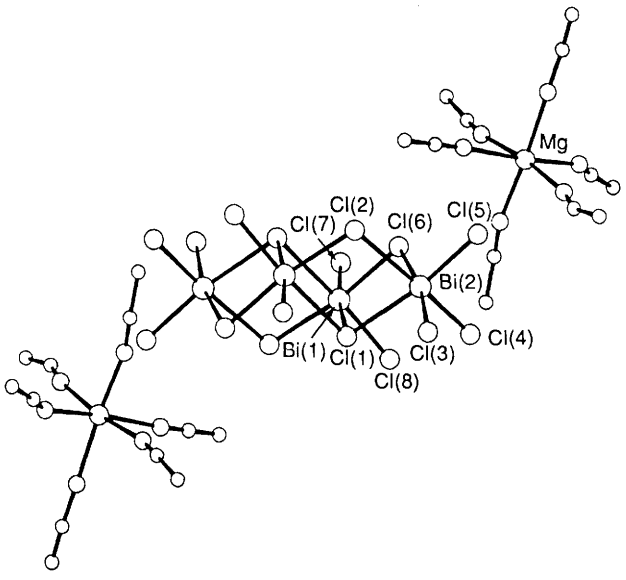


Fig. 1

complex $[BiCl_2(MeCN)_4]^+$. The IR spectrum includes a sharp doublet, ν(CN) at 2300 and 2260 cm^{-1} typical for co-ordinated MeCN and a broad intense band at 348 cm^{-1} assigned to ν(SbCl), *cf.* K[$SbCl_6$] [ν_3(Sb–Cl) at 346 cm^{-1}].[16] The medium intensity broad bands at 280 and 250–255 cm^{-1} are assigned tentatively to ν(Mg–N) stretching and ν(Mg–NCC) wagging modes.[17] Further confirmation of the ionic nature of **1** comes from conductivity measurements for a 1×10^{-3} mol dm^3 solution in acetonitrile at 25 °C for which Λ_m = 115.75 mS cm^2 mol^{-1}; 1:1 electrolytes typically have equivalent conductances in the range $\Lambda_m \approx$ 120–140 mS cm^2 mol^{-1} in this solvent under similar conditions.[18]

The ionic formulation of **1** is in accord with chloride-ion transfer from electropositive Bi^{III} to the powerful (Lewis acid) acceptor Sb^V. The polar solvent assists ionic formation *via* occupancy of co-ordinatively unsaturated metal sites arising from halide expulsion. In addition to choice of solvent, the stoichiometry of reactants used is evidently another influential factor in this particular system; preliminary studies indicate that with 1:3 stoichiometry the ternary complex $BiCl_3 \cdot 3SbCl_5 \cdot 8MeCN$ is produced.[19]

Treatment of $MgCl_2$ (1 mol) and $BiCl_3$ (2 mol) in acetonitrile provides the white ternary complex $2MgCl_2 \cdot 4BiCl_3 \cdot 12MeCN$ **2** identified as the ionic salt $[Mg(MeCN)_6]_2[Bi_4Cl_{16}]$. In this instance Bi^{III} acts as the chloride abstracting agent towards the electropositive Mg^{II} with formation of the tetranuclear anion. The structure of the magnesium complex cation has been described previously:[4] structures of other members of the octahedral series $[ML_6]^{2+}$ include those for L = C_2H_5OH,[20] tetrahydrofuran[21] and H_2O.[22] In the IR spectrum of **2** the characteristic sharp doublet, ν(CN) at 2322 and 2290 cm^{-1}, *cf.* 2287 and 2251 cm^{-1} for the free ligand, confirms strong ligand attachment to the Mg^{2+} ion. Bands at 405, 340–350 and 276, 250–255 cm^{-1} are assigned tentatively to ν(Bi–Cl) and Mg–N stretching/Mg–NCC wagging modes respectively. The intense charge-transfer band in the UV–VIS spectrum at ν_{max} 30 959 cm^{-1} is associated with the $[Bi_4Cl_{16}]^{4-}$ anion.[15] The equivalent conductivity, Λ_m 172.3 mS cm^2 mol^{-1} in dimethylformamide solution is within the range 130–170 mS cm^2 mol^{-1} found for 1:2 electrolytes.[18]

Discussion of the Structure of $[Mg(MeCN)_6]_2[Bi_4Cl_{16}]$.—The unit cell contains four discrete $[Mg(MeCN)_6]^{2+}$ cations and two discrete centrosymmetric $[Bi_4Cl_{16}]^{4-}$ anions. A view of the anion with two cations is shown in Fig. 1 together with the atomic numbering scheme. The cation has distorted octahedral geometry with Mg–N distances ranging from 2.20(2) to 2.25(3) Å. These distances are slightly longer than those found previously (2.14–2.18 Å).[4]

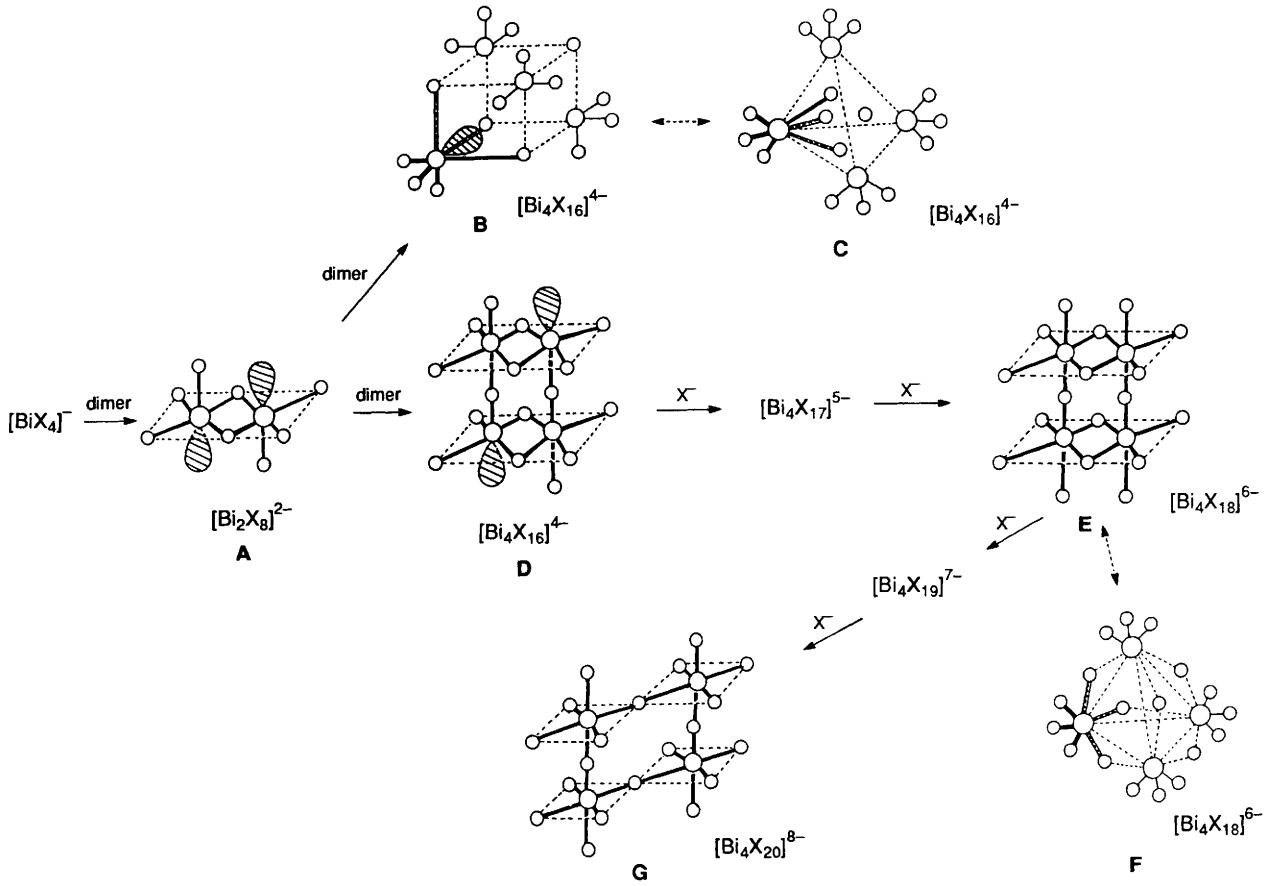
The $[Bi_4Cl_{16}]^{4-}$ anion contains a crystallographic centre of symmetry. Of the eight independent chlorine atoms, five are terminal while two [Cl(2) and Cl(6)] bridge two bismuth atoms and one [Cl(1)] bridges three. Atom Bi(1) is bonded to two terminal chlorine atoms [mutually *cis* at 2.453(18) and 2.516(20) Å], two bridging chlorine atoms [2.678(13), 2.730(14) Å] and two triply bridging chlorine atoms [3.009(16), 3.034(16) Å]. On the other hand Bi(2) is bonded to three terminal chlorine atoms in the *fac* configuration [2.426(16), 2.528(14), 2.552(16) Å] as well as two bridging chlorine atoms [2.974(17), 2.976(13) Å] and one triply bridging chlorine atom at 2.930(14) Å. It is interesting that the Bi–Cl–Bi bridges are asymmetrical, distances to Bi(1) being significantly shorter than those to Bi(2). This may reflect the fact that Bi(2) is bonded to three terminally bound chlorine atoms while Bi(1) has only two such bonds. As is expected with this wide variation in the bond lengths around the two metal atoms, the angles deviate considerably from 90° with several deviations of *ca.* 10°.

General Comments.—In order to place the structure of **2** in context with other known (and idealised) structures of tetranuclear halogenobismuth(III) anions a brief overview is presented (Scheme 1). For such species, all Bi^{III} centres are invariably six-co-ordinate, with or without a formal lone pair of electrons showing stereochemical activity, and it is possible to rationalise some, at least, of the structures as aggregates of the dinuclear $[Bi_2Cl_8]^{2-}$ unit[6,10] viewed as a basic building block. The latter can be regarded as edge-edge dimers of formal ψ-square-based pyramidal $[BiCl_4]^-$ units with retention of lone-pair activity (× 2) (structure **A**).

Transverse dimerisation of two such units leads to the $[Bi_4Cl_{16}]^{4-}$ structure **B** which, curiously, is unknown. The one example from Group 15 is provided by $[NEt_4]_4[Sb_4Cl_{16}]$;[23] other examples include $[\{TeCl_4\}_4]$,[24] $[\{SeBr_4\}_4]$[25] and $[\{PtEt_3Cl\}_4]$.[26] In this cubic structure each MX_6 octahedron shares three edges and the formal lone pairs associated with the M^{III} centres can be accommodated in the tetrahedral 'hole' in the centre of the cubic array. An alternative structural arrangement for $[Bi_4Cl_{16}]^{4-}$ is based on a tetrahedral Bi_4 array in which each metal centre has three terminal Bi–Cl bonds with the four remaining halogen atoms located as triply bridging in the centres of the four faces (structure **C**). This structural type is unknown.

Direct superpositioning (apex–apex, eclipsed) of two $[Bi_2Cl_8]^{2-}$ units would provide the hypothetical $[Bi_4Cl_{16}]^{4-}$ (structure **D**) featuring a rectangular Bi_4 array incorporating both single and double halogen bridges but with retention of two lone pairs. Removal of these lone pairs of electrons (formal) by the addition of first one and then another halide ion gives the hypothetical $[Bi_4Cl_{17}]^{5-}$ and symmetrical $[Bi_4Cl_{18}]^{6-}$ species (structure **E**) respectively. An example of the latter is provided by $[C_5H_5NH]_6[Bi_4Cl_{18}]$[9] in which two pairs of edge–edge octahedra are joined symmetrically by apex–apex fusion of their axial chlorines. Again there is an alternative structure for $[Bi_4Cl_{18}]^{6-}$ based on a tetrahedral Bi_4 array (structure **F**). In addition to three terminal Bi–Cl bonds per metal centre there are single halogen bridge bonds along the six edges of the tetrahedron as depicted. Structural type **F** is unknown. Yet further halide addition would lead to the idealised tetranuclear array for $[Bi_4Cl_{20}]^{8-}$ (structure **G**) in which the four MX_6 octahedra are fused apex-to-apex with a full complement of four single halogen bridge bonds and four terminal halogens for each Bi centre *cf.* the tetrameric pentafluorides $[\{MF_5\}_4]$ (M = Mo, Nb or Ta).[27]

Turning to the present structure, **H**, this can be regarded as resulting from the superpositioning of two $[Bi_2Cl_8]^{2-}$ units but with a lateral displacement such that Bi centres do not sit directly over one another (see Fig. 2). In this assemblage of four



Scheme 1

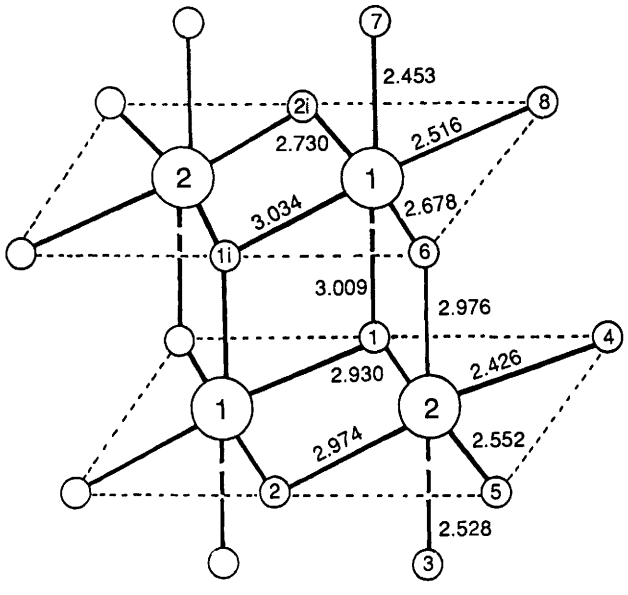


Fig. 2 Schematic representation of $[Bi_4Cl_{16}]^{4-}$, structure **H**

$BiCl_6$ octahedra there are two pairs of non-equivalent Bi atoms (1 and 2) resulting from fused octahedra which share two (atoms 2) or three common edges (atoms 1). There are three types of halogen environment: those bonded to only one Bi centre (10 atoms), those bonded to two Bi centres (4 atoms) and those bonded to three Bi centres (2 atoms). The compound $[\{Ti(OCH_3)_4\}_4]$[28] adopts this discrete centrosymmetric structure as do $[HL]_4[Sb_4Br_{16}]$[29] (L = 2-amino-1,3,4-thiadiazole) amd $[Fe(\eta\text{-}C_5H_5)_2]_4[Bi_4Br_{16}]$[30] but this is the first report of the $[Bi_4Cl_{16}]^{4-}$ anion structure.

There is a general concensus that the manner in which $[MX_4]^-$ units (M = As, Sb or Bi) condense (dimer, trimer, tetramer, oligomer or polymer, with lone pair activity or otherwise) is dependent upon or even influenced by the nature of the cation present. Bismuth(III) complex anions can be regarded as archetypal in this respect, *viz.* large cations would seem to promote the formation of large anions.[31] In all previous cases, however, the cations involved have been alkylammonium or related species for which $N\text{–}H_{cation}\cdots X_{anion}$ hydrogen bonding is invariably present. To what extent, if any, such auxiliary H-bonding is an influencing factor in the resulting structure is an open question. Clearly there is no question of H-bonding or direct ion–ion interactions in the present instance insofar as the bulky 'metallo' cation $[Mg(MeCN)_6]^{2+}$ is concerned.

A more relevant factor is stoichiometry. Formation of the hexakis (solvated) Mg^{II} cation in this present study and in previous studies, *viz.* $MgCl_2$–$SbCl_3$–MeCN ⟶ $[Mg(MeCN)_6][Sb_2Cl_8]$ and $MgCl_2$–$SbCl_5$–MeCN ⟶ $[Mg(MeCN)_6][SbCl_6]_2$, establishes $MgCl_2$ as a suitable double-chloride ion source in Group 15 halide exchange systems. Thus there is the distinct possibility that other complex anions may be isolated from the $MgCl_2$–$BiCl_3$–MeCN system following careful control of stoichiometry as represented simplistically in equation (1).

$$m MgCl_2 + 4BiCl_3 \xrightarrow{MeCN} [Mg(MeCN)_6]_m[Bi_4Cl_{12+2m}]^{2m-} \quad (1)$$

Taken in turn: $m = 1$ gives $[Bi_4Cl_{14}]^{2-}$ which is clearly outlawed on the grounds of halide deficiency if six-co-ordinate Bi^{III} centres are to be maintained; $m = 2$ gives $[Bi_4Cl_{16}]^{4-}$ as described above (structure **H**); $m = 3$ leads to the $[Bi_4Cl_{18}]^{6-}$ anion which has been reported in the literature.[9] The product isolated from our studies using 3:4 Mg:Bi stoichiometry was the ternary complex $3MgCl_2{\cdot}4BiCl_3{\cdot}18MeCN$ **3** which is formulated as the ionic salt $[Mg(MeCN)_6]_3[Bi_4Cl_{18}]$. The IR

spectrum contains two sharp ν(MeCN) bands at 2320 and 2289 cm^{-1} characteristic of the Mg^{II} complex cation, two broad bands at 230–240 and 273 cm^{-1} assigned to ν(Mg–N) stretching/ν(Mg–NCC) wagging modes and strong bands at 401 and 340 cm^{-1} assigned to ν(Bi–Cl) modes. The intense charge-transfer band in the UV–VIS spectrum at ν_{max} 31 055 cm^{-1} is associated with the $[Bi_4Cl_{18}]^{6-}$ anion. The equivalent conductivity in dimethylformamide, Λ_M = 251.8 mS cm^2 mol^{-1}, is within the range observed ($\Lambda_M \approx$ 200–250 mS cm^2 mol^{-1}) for 1:3 electrolytes. In the absence of X-ray data [19] a structure of type **C**, as determined for $[C_5H_5NH]_6[Bi_4Cl_{18}]$,[9] is thought to be the most likely. Our search for the $[Bi_4Cl_{20}]^{8-}$ anion continues optimistically.

Acknowledgements

We thank the SERC for a studentship award (to H. C.) and for funds for the diffractometer, the Cookson Group plc, Research Group for financial support and Mr. A. W. Johans for his assistance with the crystallographic investigations.

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Received 18*th October* 1990; *Paper* 0/04693K