Azamacrocyclic stabilisation of the halogenocations MX_3^+ where $M = Ge$ or Sn and $X = Cl$ or Br. Synthesis and molecular structures of $[GeCl_3(L^1)]^+{}_2[H_3O]^+Cl^-{}_3 \cdot MeCN$, $[SnCl_3(L^1)]^+{}_2[SnCl_6]^{2-} \cdot 4MeCN$, $[GeBr_3(L^2)]^+{}_2[MeNH_3]^+Br^-{}_3 \cdot MeCN$ and $[SnBr_3(L^2)]^+{}_2[SnBr_6]^{2-}$ where $L^1 = $ 1,4,7-trimethyl-1,4,7-triazacyclononane and $L^2 = $ 1,3,5-trimethyl-1,3,5-triazacyclohexane

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Treatment (1:1 in acetonitrile) of the reaction systems MCl_4–1,4,7-trimethyl-1,4,7-triazacyclononane (L^1) and MBr_4–1,3,5-trimethyl-1,3,5-triazacyclohexane (L^2), where $M^{IV} = Ge$ or Sn, provided ionic compounds featuring the trihalogenocationic species $[MX_3(L^n)]^+$ rather than direct adduct formation $[MX_4(L^n)]$. Crystal structure determinations (X-ray diffraction) confirmed an ionic formulation for each of the four products isolated, *viz.* $[GeCl_3(L^1)]^+{}_2[H_3O]^+Cl^-{}_3 \cdot MeCN$ **1**, $[SnCl_3(L^1)]^+{}_2[SnCl_6]^{2-} \cdot 4MeCN$ **2**, $[GeBr_3(L^2)]^+{}_2[MeNH_3]^+Br^-{}_3 \cdot MeCN$ **3**, and $[SnBr_3(L^2)]^+{}_2[SnBr_6]^{2-}$ **4**. Ligand attachment to M^{IV}, both for L^1 and L^2, is terdentate N-donor (η^3) throughout and the resulting six-co-ordinate cations $[MX_3(L^n)]^+$ show the anticipated *fac*-octahedral metal geometry. Individual M–N bond distances within each cation are the same, *viz.* mean values 2.113(2) **1**, 2.244(8) **2**, 2.142(7) **3**, 2.311(6) Å **4**, reflecting a uniform central location of the MX_3^+ unit over the ring cavity. The 'cone angle' N_{ring}–M–N_{ring} values (mean) for compounds **3** 64.3(3) and **4** 59.7(2)° involving L^2 are conspicuously smaller, *ca.* 20°, than those for compounds **1** 82.90(8) and **2** 79.1(3)° involving L^1 as a reflection of the insistent steric demands of the more compact six-membered triazacyclohexane ligand.

Beyond question Wieghardt and colleagues[1] have been instrumental in establishing the azamacrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (L^1) as a terdentate N-donor ligand *par excellence*. Their extensive compilation of structural (X-ray diffraction) data features a wide variety of transition metal (d-block) compounds and also embraces the heavier p-block metals, *e.g.* In^{III},[2] Tl^I,[3] Tl^{III}[3] and Pb^{II}.[4] More recently we have isolated the 1:1 adducts[5] with the Group 15 halides MCl_3 (M = As, Sb or Bi) and, in the case of M = Bi, identified the half-sandwich structure *fac*-$BiCl_3(L^1)$ incorporating a somewhat distorted octahedral metal geometry.[6] The cationic species $[MCl_2(L^1)]^+$, where M = As[5] or Sb,[7] have also been structurally characterised, with an incipient lone pair occupying one of the pseudo-octahedral sites.

The six-membered ring analogue 1,3,5-trimethyl-1,3,5-triazacyclohexane (L^2) represents a much more compact terdentate N-donor system by virtue of the single methine linkages between the aza centres. The co-ordination chemistry of L^2 and other tris-N-alkylated $(RNCH_2)_3$ analogues is limited to just a handful of examples: with $InMe_3$, a 1:1 complex with R = Et, ¹H NMR only;[8] with $ZnMe_2$, a 1:2 complex with L^2 (η^1 co-ordination);[9] with $InMe_3$, a 1:1 complex with R = Pr^i (η^3 co-ordination);[10] substitution of CO groups on $Mo(CO)_6$ by L^1, spectroscopic/kinetic data;[11] with $(L^2)[Cu(NH_3)]_2Co(CO)_4$, a 1:1 complex with L^2 [η^2 with bridging across two copper(I) centres];[12] with AlH_3, a 1:2 complex with L^2 (η^1 co-ordination) and a 1:1 polymer with L^2 [η^2 with bridging across two aluminium(III) centres];[13] with $FeCl_3$, a 1:1 complex with L^2 (η^3 co-ordination) and with $CrCl(CH_2SiMe_3)_2$ a 1:1 complex with R = Pr^i (η^3 co-ordination);[14] with $Cr(CH_2Ph)_3$, a 1:1 complex with R = cyclo-C_6H_{11} (η^3 co-ordination);[15] with $Cr(CO)_3$, 1:1 complexes with L^2 and R = Bu^t (η^3 co-ordination);[16] with $CrCl_3$, a 1:1 complex with R = Bu^n (η^3 co-ordination).[17]

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In this report we describe the reactions (1:1) of L^1 with MCl_4 and L^2 with MBr_4 (M = Ge or Sn) as a probe of the relative binding characteristics of these triaza cyclic ligands with Group 14 tetrahalide acceptors.

Experimental

Preparation of the compounds

(a) $[GeCl_3(L^1)]^+{}_2[H_3O]^+Cl^-{}_3 \cdot MeCN$ 1. Dropwise addition of a solution of $GeCl_4$ (0.38 g, 1.75 mmol, 0.20 cm³) in acetonitrile (25 cm³) to a stirred, chilled (0 °C) solution of L^1 (0.30 g, 1.75 mmol) in acetonitrile (25 cm³) resulted in a cloudy light yellow solution. This solution was heated at 70 °C (3 h) and filtered while still warm. On standing at room temperature a yellow solid deposited from the filtrate. Recrystallisation from CH_3CN–CH_2Cl_2 (1:1) provided light yellow needles of the product **1**. Yield 0.47 g, 77% (Found: C, 27.50; H, 5.32; N, 11.17.

Calc. for $C_{20}H_{48}Cl_9Ge_2N_7O$: C, 27.71; H, 5.58; N, 11.31%). IR $\tilde{v}_{max}/cm^{-1}$ (Nujol): 3226vs (br) (H_2O), 2353m, 2254m, (MeCN), 1463s, 1329s, 1221s, 1149m, 1127m, 1095s, 983s, 908m, 864w, 775m, 686m, 659s, 546w, 432w, 420w (ligand), 372s, 324vs (br) [ν(GeCl)]. $\delta_H(CD_3CN)$ 3.61, 3.56 (12 H, multiplet based on AA′BB′ backbone CH_2) and 3.15 (9 H, s, N−CH_3). $\delta_C(CD_3CN)$ 49.60 (N−CH_3) and 52.56 (backbone CH_2).

(b) $[SnCl_3(L^1)]^+_2[SnCl_6]^{2-}\cdot4MeCN$ 2. A solution of $SnCl_4$ (1.03 g, 3.95 mmol, 0.46 cm³) in acetonitrile (40 cm³) was added dropwise to a stirred and chilled (0 °C) solution of L^1 (0.45 g, 2.63 mmol), in acetonitrile (30 cm³). The reaction mixture was heated at 70 °C (3 h) and then filtered whilst still warm. The filtrate was cooled to 0 °C, to provide a mass of colourless rectangular crystals which were collected and allowed to dry under a stream of argon. Yield 0.86 g, 51% (Found: C, 24.82; H, 4.14; N, 10.89. Calc. for $C_{26}H_{54}Cl_{12}N_{10}Sn_3$: C, 24.24; H, 4.22; N, 10.87%). IR $\tilde{v}_{max}/cm^{-1}$ (Nujol): 2360m, 2252m (MeCN), 1440s, 1322m, 1297s, 1196w, 1156w, 1123w, 1051vs, 997vs, 961vs, 885m, 780s, 739s, 563w, 451w, 425w, 416w (ligand), 325s (br) and 300s (br) [ν(SnCl)]. $\delta_H(CD_3CN)$ 3.40 (12 H, s, backbone CH_2) and 3.03 (9 H, s, N−CH_3).

(c) $[GeBr_3(L^2)]^+_2[MeNH_3]^+Br^-_3\cdot MeCN$ 3. A solution of $GeBr_4$ (0.91 g, 2.32 mmol) in acetonitrile (30 cm³) was added slowly to a stirred and chilled (0 °C) solution of L^2 (0.30 g, 2.32 mmol) in acetonitrile (25 cm³). The resulting slight yellow solution was heated at 70 °C (5 h) and filtered while still warm. The clear yellow filtrate was stored in a refrigerator overnight when yellow platelets of the product 3 deposited. Yield 0.80 g, 78% (Found: C, 14.92; H, 3.18; N, 9.19. Calc. for $C_{15}H_{39}Br_9Ge_2N_8$: C, 15.07; H, 3.29; N, 9.37%). IR $\tilde{v}_{max}/cm^{-1}$ (Nujol): 2365m, 2254m (MeCN), 1689w, 1481s, 1341m, 1278m, 1258m, 1166w, 1104m, 1059w, 1031w, 990m, 948m, 924s, 826m, 793m, 583w, 511w, 420w (ligand), 305vs (br) and 240vs (br) [ν(GeBr)]. $\delta_H(CD_3CN)$ 4.25 (6 H, s, backbone CH_2) and 2.90 (9 H, s, N−CH_3). $\delta_C(CD_3CN)$ 34.87 (N−CH_3) and 70.56 (backbone CH_2).

(d) $[SnBr_3(L^2)]^+_2[SnBr_6]^{2-}$ 4. A solution of L^2 (0.30 g, 2.32 mmol) in acetonitrile (25 cm³) was added dropwise to a stirred and chilled (0 °C) solution of $SnBr_4$ (1.53 g, 3.48 mmol) in acetonitrile (30 cm³). The reaction mixture was heated at 70 °C (5 h) and then filtered while still warm. The filtrate was concentrated and allowed to stand at room temperature overnight when light yellow needle crystals separated. Yield 1.13 g, 62% (Found: C, 9.02; H, 1.79; N, 5.18. Calc. for $C_{12}H_{30}Br_{12}N_6Sn_3$: C, 9.16; H, 1.92; N, 5.34%). IR $\tilde{v}_{max}/cm^{-1}$ (Nujol): 1654w, 1559w, 1507w, 1460s, 1419m, 1375s, 1284w, 1255w, 1172w, 1100s, 1032w, 992m, 932w, 914s, 839w, 722w, 555m, 517w, 500m, 411w (ligand), 308 and 254s [ν(SnBr)]. $\delta_H(CD_3CN)$ 4.12 (6 H, s, backbone CH_2) and 2.77 (9 H, s, N−CH_3). $\delta_C(CD_3CN)$ 36.42 (N−CH_3) and 71.47 (backbone CH_2).

Crystallography

Data were collected using a Siemans SMART CCD area-detector diffractometer. A full hemisphere of reciprocal space was scanned by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal to detector distance was 5.01 cm. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate refraction; for compounds 1–4 the decay was negligible. A multi-scan absorption correction was applied using SADABS.[21]

Each structure was solved by direct methods using SHELXTL-PC[22] and refined by full matrix least squares on F^2 for all data using SHELXL 97.[23] Hydrogen atoms were generally added at calculated positions and refined using a riding model; the H atoms associated with the H_3O^+ cation in com-
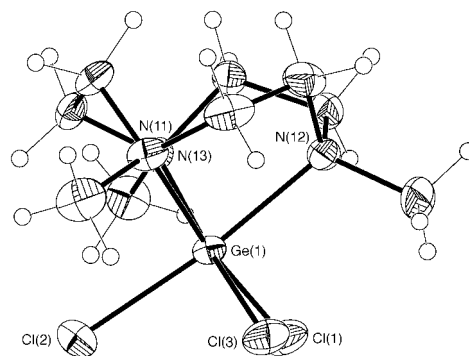

Fig. 1 Perspective view of the structure of the $[GeCl_3(L^1)]^+$ cation of compound 1. Atoms are represented by thermal vibration ellipsoids at the 50% level
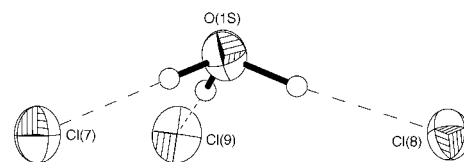

Fig. 2 Sideways view of the $H_3O^+\cdot3Cl^-$ unit of compound 1. Details as in Fig. 1

pound 1 were located from the electron density map and allowed to refine freely. Anisotropic thermal parameters were used for all non-H atoms; H atoms were given isotropic thermal parameters equal to 1.2 (or 1.5 for methyl hydrogens) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached.

Specific parameters are collected in Table 1.

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Results and Discussion

The reactions (1:1 in MeCN solution) of L^1 with MCl_4 (M = Ge or Sn) and L^2 with MBr_4 (M = Ge or Sn) were studied in the expectation of neutral [$MX_4(L)$] adduct formation featuring ligand η^3 attachment to seven-co-ordinate metal species (which are still somewhat of a rarity for M^{IV}). In each case, however, ionic compounds featuring MX_3^+ cations were isolated, *viz.* $[GeCl_3(L^1)]^+_2[H_3O]^+Cl^-_3\cdot MeCN$ 1, $[SnCl_3(L^1)]^+_2[SnCl_6]^{2-}\cdot4MeCN$ 2, $[GeBr_3(L^2)]^+_2[MeNH_3]^+Br^-_3\cdot$ MeCN 3 and $[SnBr_3(L^2)]^+_2[SnBr_6]^{2-}$ 4 as determined by single crystal X-ray diffraction studies. Compounds 1–3 contain acetonitrile trapped in the lattice as solvate molecules.

The structure of the germanium cation of compound 1, illustrative for ligand L^1, is depicted in Fig. 1 with atom notation; two independent cations were observed with almost identical dimensions. The structure of the accompanying $H_3O^+\cdot3Cl^-$ unit is shown in Fig. 2 with atom notation. The structure of the germanium cation of 3, illustrative for ligand L^2, is depicted in Fig. 3 with atom notation; again two independent cations were observed with almost identical dimensions. The principal bond lengths and angles of the cations of compounds 1–4 are listed in Table 2.

Several patterns of co-ordination behaviour emerge and these can be conveniently summarised as follows. (i) Ligand binding of both L^1 and L^2 to M^{IV} (M = Ge or Sn) is terdentate N-donor (η^3) in all cases.

(ii) The resulting MX_3^+ cations are effectively stabilised by (η^3) azamacrocyclic chelation to give six-co-ordinate species that show the anticipated *fac*-octahedral metal geometry.

(iii) Interestingly for the germanium compounds 1 and 3 simple halide ions constitute the counter anion in salt formation. In contrast the hexahalogenostannate ion $[SnX_6]^{2-}$ is the counter anion for the tin compounds 2 and 4. This behaviour was noted previously in the $SnCl_4$–[9]aneS$_3$–MeCN reaction

Table 1 Crystal data and structure refinement for compounds **1–4**

	1	2	3	4
Formula	$C_{20}H_{48}Cl_9Ge_2N_7O$	$C_{26}H_{54}Cl_{12}N_{10}Sn_3$	$C_{15}H_{39}Br_9Ge_2N_8$	$C_{12}H_{30}Br_{12}N_6Sn_3$
M	866.88	1288.26	1195.91	1573.41
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	$Pbcn$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
$a/\text{Å}$	21.8349(12)	11.0359(9)	15.5406(6)	7.6350(9)
$b/\text{Å}$	13.2111(9)	14.7108(9)	11.4543(9)	8.9082(10)
$c/\text{Å}$	24.447(2)	16.4441(12)	19.8405(12)	13.907(2)
$\alpha/°$		77.285(3)		76.604(3)
$\beta/°$		75.811(2)	92.041(3)	79.553(3)
$\gamma/°$		89.697(3)		80.440(3)
$U/\text{Å}^3$	7051.9(9)	2521.4(3)	3529.5(4)	897.3(2)
T/K	180(2)	180(2)	180(2)	180(2)
Z	8	2	4	1
$\lambda/\text{Å}$	0.710 73	0.710 73	0.710 73	0.710 73
$D_c/\text{Mg m}^{-3}$	1.633	1.697	2.251	2.912
μ/mm^{-1}	2.415	2.141	11.913	15.448
hkl Ranges	−28, 22; −17, 17; −32, 21	−11, 14; −17, 19; −21, 22	−11, 20; −13, 15; −24, 26	−10, 10; −9, 11; −17, 16
Number of data collected	40 180	11 770	17 330	4917
Independent reflections (R_{int})	8495 (0.057)	8547 (0.036)	6181 (0.085)	3421 (0.026)
Transmission coefficients	0.803, 0.495	0.807, 0.425	0.218, 0.189	0.356, 0.144
$R(F)$ $[I > 2\sigma(I)]$	0.036	0.057	0.053	0.043
$wR(F^2)$ (all data)	0.072	0.152	0.093	0.103
Goodness of fit on F^2	1.009	0.969	1.022	0.967
Peak difference and hole/e Å^{-3}	0.384, −0.524	1.623, −1.781	0.762, −0.937	1.401, −2.288
Data, restraints, parameters	8495, 0, 371	8547, 51, 466	6181, 0, 316	3421, 0, 151
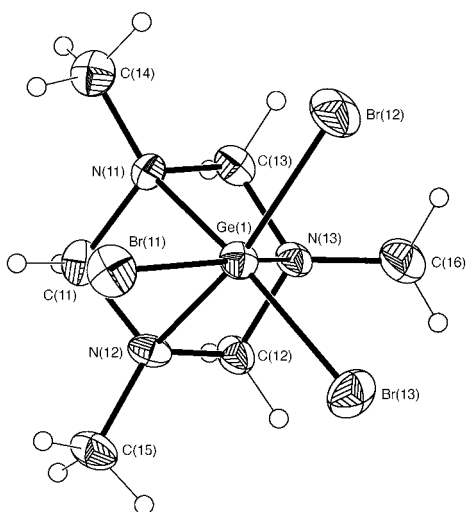
Fig. 3 Perspective view of the structure of the $[\text{GeBr}_3(\text{L}^2)]^+$ cation of compound **3**. Details as in Fig. 1

system [24] where the product was identified as the six-co-ordinate ionic species $[\text{SnCl}_3([9]\text{aneS}_3)]^+{}_2[\text{SnCl}_6]^{2-}$. Presumably Sn^{IV}, as a strong Lewis acid, readily 'mops up' available halide ion(s) to form $[\text{SnCl}_6]^{2-}$ in preference to $[\text{SnCl}_5(\text{MeCN})]^-$. Yet another comparison is provided by the lanthanide(III) reaction system LnCl_3–SnCl_4–thf (Ln = Ce, Gd or Yb) [25] where direct halide abstraction by Sn^{IV} provides the solvated $[\text{LnCl}_2(\text{thf})_5]^+$ cations and a common $[\text{SnCl}_5(\text{thf})]^-$ anion; formation of the latter reflects the preferential binding order O > Cl for Sn^{IV}. Again it is interesting that the germanium compounds **1** and **3** feature an accompanying cation, *e.g.* an oxonium ion in the case of **1** and a methylammonium ion in the case of **2**. For the former we can only surmise that limited hydrolysis of Ge–Cl bonds brought about by water contamination provides the proton source. The complex anion observed in **1** (see Fig. 2) results from a novel association of a pyramidal oxonium ion linked symmetrically to three separate chloride ions *via* strong O–H · · · Cl hydrogen bonding interactions with crystallographically imposed C_{3v} symmetry, *viz.* O · · · Cl 2.888(2), 2.861(2) and 2.852(2) Å, Cl–O–Cl 111.9, 112.5 and 107.1°. We can find no previous

example of such an interaction involving halide ions but there are similarities with the 'secondary' bonding O–H$_{oxonium}$ · · · O$_{crown}$ observed in the crown ether compounds $[(18\text{-crown-6)}\text{-}(\text{H}_3\text{O})]^+\text{Y}^-$ involving an oxonium ion and long-range symmetrical interactions with three alternate oxygen atoms of the crown ether *viz.* O$_{oxonium}$ · · · O$_{crown}$, Y = HCl$_2^-$, 2.70–2.85 Å and Y = HBr$_2^-$, 2.69–2.84;[26a] Y = Mo$_6$O$_{19}^{2-}$ 2.705(28)–2.817(32);[26b] Y = ZnCl$_4^{2-}$, 2.603(9)–2.710(11) and Y = MnCl$_4^{2-}$, 2.66(3)–2.99(5) Å.[26c] The presence of the methylammonium cation in compound **3** can be traced to the original synthesis of the ligand L^2. Instead of the free amine MeNH$_2$ we used the hydrochloride salt (with an excess of base) in the condensation reaction with formaldehyde to release L^2. Clearly in the distillation of this batch of ligand residual quaternary salt was present.

(iv) A half-sandwich topology for the cation is common to the series. Within each compound **1–4** the three metal–nitrogen bond distances are equivalent as a reflection of a uniform central location of the MX$_3^+$ unit over the ring cavity, *e.g.* mean M–N, for L^1, M = Ge, 2.113(2); M = Sn, 2.244(8) and for L^2, M = Ge, 2.142(7), M = Sn, 2.311(6) Å. Likewise the three metal–halogen bond lengths show little variation, *viz.* mean M–Cl, for L^1, M = Ge, 2.237(1), M = Sn, 2.368(3) and mean M–Br, for L^2, M = Ge, 2.341(1) and M = Sn, 2.477(1) Å. A comparison of the separation distance of the metal from the plane containing the three N atoms of an individual ligand, *viz.*, 1.363(1) **1**, 1.525(4) **2**, 1.702(4) **3** and 1.891(4) Å **4**, clearly shows the greater extent by which the individual MX$_3^+$ fragments are sucked towards the larger ring cavity of L^1 as opposed to L^2. Interestingly the planes containing the three ring N atoms and the three halogen atoms respectively are parallel.

(v) Whereas the torsion angle sequence patterns for compounds **1–4** are normal for such macrocyclic derivatives,[27] the compactness of the ring, especially in the case of L^2, does impose a severe steric constriction at the metal centre. In the case of uncomplexed L^1 the preferred endodentate conformation identifies it as an (almost) ideal ligand for occupation of three metal co-ordination sites (*fac*-octahedral).[1] For free L^2 there are four chair conformers possible of which the aee arrangement with two methyl groups in equatorial positions and the remaining one in an axial location is preferred.[28] Formation of an η^3 complex is associated with rearrangement of all three methyl groups to equatorial sites thereby facilitating

Table 2 Principal bond lengths (Å) and bond angles (°) for cations of compounds **1**–**4**

Compound		M–N	M–X	X–M–X	N–M–N
1 [GeCl$_3$(L^1)]$^+$$_2$[H$_3$O]$^+$3Cl$^-$·MeCN *	Ge(1)	2.106(2)	2.2483(7)	92.46(3)	83.17(8)
		2.112(2)	2.2298(7)	92.72(3)	83.07(8)
		2.111(2)	2.2487(7)	92.67(3)	82.69(8)
	Ge(2)	2.114(2)	2.2309(7)	93.65(3)	82.59(8)
		2.110(2)	2.2123(7)	93.03(3)	83.15(8)
		2.125(2	2.2492(7)	93.64(3)	82.70(8)
2 [SnCl$_3$(L^1)]$^+$$_2$[SnCl$_6$]$^{2-}$·4MeCN *	Sn(1)	2.236(8)	2.362(3)	93.81(10)	79.2(3)
		2.251(7)	2.355(3)	94.72(10)	78.6(3)
		2.246(6)	2.374(2)	94.80(11)	78.7(3)
	Sn(2)	2.230(7)	2.375(2)	93.91(10)	79.7(3)
		2.255(7)	2.361(3)	94.29(10)	78.9(3)
		2.243(7)	2.379(3)	95.79(11)	79.7(3)
3 [GeBr$_3$(L^2)]$^+$$_2$[MeNH$_3$]$^+$3Br$^-$·MeCN *	Ge(1)	2.123(7)	2.3412(13)	99.51(5)	64.6(2)
		2.137(6)	2.3405(14)	100.14(5)	64.9(3)
		2.131(7)	2.3592(13)	100.72(5)	64.0(3)
	Ge(2)	2.156(6)	2.3391(13)	100.95(5)	63.9(3)
		2.150(7)	2.3247(13)	101.80(5)	64.2(3)
		2.154(7)	2.3432(13)	101.46(5)	64.1(3)
4 [SnBr$_3$(L^2)]$^+$$_2$[SnBr$_6$]$^{2-}$		2.304(6)	2.4771(10)	103.24(4)	59.8(2)
		2.323(6)	2.4709(10)	105.28(4)	59.5(2)
		2.305(6)	2.4822(10)	103.70(4)	59.8(2)

* Two independent cations.

maximal lone pair interactions with a metal ion acceptor. A measure of these steric restrictions, L^1 versus L^2, is provided by a comparison of the resulting interligand angles, viz. for L^1, N–M–N, M = Ge, 82.90(8) **1** and M = Sn, 79.1(3) **2**; for L^2, N–M–N, M = Ge, 64.3(3) **3** and M = Sn, 59.7(2)° **4**. Clearly there is a conspicuous decrease of N–M–N ca. 20°, on changing from L^1 to L^2 signifying, as expected, a much more compact N–M–N 'cone' angle for the six-membered triazacyclohexane derivatives. These constrictions are offset to some extent by an angular dilation between the corresponding set of fac-halogen atoms, viz. Cl–M–Cl, M = Ge, 93.03(3) **1**, M = Sn, 94.55(11) **2**; Br–M–Br, M = Ge, 100.76(5) **3**, M = Sn, 104.07(4)° **4**. For direct comparisons (mean values): for L^1, fac-BiCl$_3$(L^1)[6] shows N–Bi–N 71.3(7), Cl–Bi–Cl 103.7(6); [SbCl$_2$(L^1)][SbCl$_6$],[7] N–Sb–N 74.2(3), Cl–Sb–Cl 95.45(14); [AsCl$_2$(L^1)][As$_2$OCl$_5$][5] N–As–N 80.6(7), Cl–As–Cl 92.6(3)°. For L^2, [FeCl$_3$(L^2)],[14] N–Fe–N 60.98(9), Cl–Fe–Cl 103.37(4); [Cr(CO)$_3$(L^2)],[6] N–Cr–N 63.3(3), C–Cr–C 87(2); [Cr(CH$_2$Ph)$_3${(cyclo-C$_6$H$_{11}$NCH$_2$)$_3$}],[15] N–Cr–N 61.5(2), C–Cr–C 94(3)°.

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