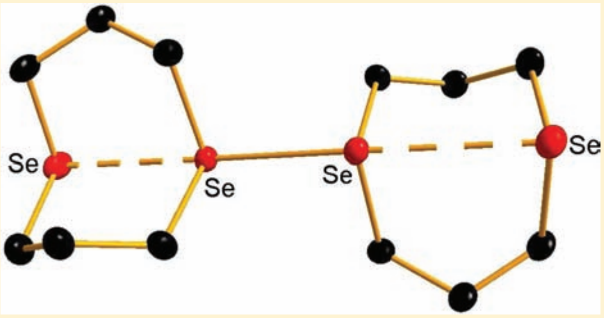
Inorganic Chemistry
Article
pubs.acs.org/IC

Unexpected Reactivity and Coordination in Gallium(III) and Indium(III) Chloride Complexes With Geometrically Constrained Thio- and Selenoether Ligands

Kathryn George,[†] Marek Jura,[‡] William Levason,[†] Mark E. Light,[†] Luke P. Ollivere,[†] and Gillian Reid*[,†]

[†]School of Chemistry, University of Southampton, Southampton, United Kingdom SO17 1BJ
[‡]ISIS, STFC, Harwell Innovation Campus, Didcot, Oxfordshire, United Kingdom OX11 0QX

Supporting Information



ABSTRACT: Reaction of $GaCl_3$ with 1 mol equiv of $[14]\text{aneS}_4$ in anhydrous CH_2Cl_2 gives the exocyclic chain polymer $[GaCl_3([14]\text{aneS}_4)]$ (**1**) whose structure confirms trigonal bipyramidal coordination at Ga with a planar $GaCl_3$ unit. In contrast, using $[16]\text{aneS}_4$ and $GaCl_3$ or $[16]\text{aneSe}_4$ and MCl_3 (M = Ga or In) in either a 1:1 or a 1:2 molar ratio produces the anion−cation complexes $[GaCl_2([16]\text{aneS}_4)][GaCl_4]$ (**2**) and $[MCl_2([16]\text{aneSe}_4)][MCl_4]$ (M = Ga, **3** and M = In, **4**) containing *trans*-octahedral cations with endocyclic macrocycle coordination. The ligand-bridged dimer $[(GaCl_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$ (**5**) is formed from a 2:1 mol ratio of the constituents and contains distorted tetrahedral Ga(III). This complex is unusually reactive toward CH_2Cl_2, which is activated toward nucleophilic attack by polarization with $GaCl_3$, producing the bis-sulfonium species $[o\text{-}C_6H_4(SMeCH_2Cl)_2][GaCl_4]_2$ (**6**), confirmed from a crystal structure. In contrast, the xylyl-based dithioether gives the stable $[(GaCl_3)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ (**8**). However, replacing $GaCl_3$ with $InCl_3$ with $o\text{-}C_6H_4(CH_2SEt)_2$ preferentially forms the 4:3 In:L complex $[(InCl_3)_4\{o\text{-}C_6H_4(CH_2SEt)_2\}_3]$ (**9**) containing discrete tetranuclear moieties in which the central In atom is octahedrally coordinated to six bridging Cl's, while the three In atoms on the edges have two bridging Cl's, two terminal Cl's, and two mutually trans S-donor atoms from different dithioether ligands. $GaCl_3$ also reacts with the cyclic bidentate $[8]\text{aneSe}_2$ to form a colorless, extremely air-sensitive adduct formulated as $[(GaCl_3)_2([8]\text{aneSe}_2)]$ (**10**), while $InCl_3$ gives $[InCl_3([8]\text{aneSe}_2)]$ (**14**). Very surprisingly, **10** reacts rapidly with O_2 gas to give initially the red $[\{[8]\text{aneSe}_2\}_2][GaCl_4]_2$ (**11**) and subsequently the yellow $[\{[8]\text{aneSe}_2\}Cl][GaCl_4]$ (**12**). The crystal structure of the former confirms a dimeric $[\{[8]\text{aneSe}_2\}_2]^{2+}$ dication, derived from coupling of two mono-oxidized $\{[8]\text{aneE}_2\}^{+\bullet}$ cation radicals to form an Se−Se bond linking the rings and weaker transannular 1,5-Se···Se interactions across both rings. The latter (yellow) product corresponds to discrete doubly oxidized $\{[8]\text{aneSe}_2\}^{2+}$ cations (with a primary Se−Se bond across the 1,5-positions of the ring) with a Cl^- bonded to one Se. Tetrahedral $[GaCl_4]^-$ anions provide charge balance in each case. These oxidation reactions are clearly promoted by the Ga(III) since $[8]\text{aneSe}_2$ itself does not oxidize in air. The new complexes have been characterized in the solid state by IR and Raman spectroscopy, microanalysis, and X-ray crystallography where possible. Where solubility permits, the solution characteristics have been probed by ^1H, $^{77}Se\{^1H\}$, and ^{71}Ga NMR spectroscopic studies.

■ INTRODUCTION

Renewed interest in the coordination chemistry of p-block elements[1] can be attributed to several influences. First, the increased use and availability of certain isotopes of these elements for radiopharmaceutical applications in imaging and therapy (e.g., ^{68}Ga, ^{111}In, ^{113m}In, ^{117m}Sn, ^{123}I)[1,2] and as molecular carriers for ^{18}F in PET applications, e.g., in Al−F complexes based upon carboxylate derivatives of 1,4,7-triazacyclononane which are attracting interest at present,[3] demands a much more thorough understanding of their coordination chemistry. Second, the importance of many of the p-block elements in III−V and III−VI semiconductors and other electronic materials together with the increased focus on controlling deposition of the materials as thin films or into confined spaces such as narrow pores or trenches has prompted development of their coordination chemistry and organometallic chemistry to provide molecular reagents for these purposes.[4] Third, the trivalent ions in Group 13 (Al, Ga, and In) are important Lewis acids in organic/organometallic transformations and catalysis.[5] Finally, the need for a more thorough understanding of their fundamental chemistry so that the key differences between the coordination behavior of p-block ions and d-block ions may be better understood. Within this context, factors such as ligand denticity, donor type(s), and architecture combined with the lability inherent to closed-shell

Received: October 17, 2011
Published: January 27, 2012

systems and variations in ionic radii are key considerations within the p-block, although how they combine to produce the observed chemistry is often unclear.

The increasing ionic radii of the elements and trivalent ions down Group 13 results in four coordination being prevalent for Al(III) and Ga(III) with most common ligands, except for those based upon hard anionic mixed N/O-donor systems, where five- and six-coordinate species can occur.[2a] In contrast, five and more commonly six coordination dominates with the larger In(III) ion. In an earlier paper we reported the first systematic series of Ga(III) halide complexes involving neutral (soft) thio- and selenoether ligands, specifically mono-, bi-, and tripodal tridentate ligands incorporating various linking backbone architectures and terminal substituents (Me, Ph, ^{n}Bu). A combination of solution NMR spectroscopic data and single-crystal X-ray structural studies on these and related species reported subsequently showed that neutral complexes based upon distorted tetrahedral Ga(III) (X_3E donor set; E = S or Se) were the only species observed, irrespective of ligand denticity, and that displacement of coordinated halide did not occur.[6] We noted then that these observations contrasted with those for Ga(III) complexes with diphosphines and diarsines where neutral pseudo-tetrahedral X_3P/As coordination, cationic pseudo-tetrahedral X_2P_2/As_2 coordination, and pseudo-octahedral X_2P_4 coordination have been observed depending upon the steric and electronic properties of the phosphine/arsine employed.[7] On the other hand, InX_3 show much wider coordination chemistry with similar chalcogenoether ligands, forming both distorted tetrahedral and octahedral species as well as incorporating higher chalcogen:M ratios cf. Ga.[8] In an effort to gain further insights into the factors that influence the coordination chemistry of Ga(III) and In(III) and to explore this chemistry in more detail, we have undertaken a study of MCl_3 (M = Ga and In) with a series of macrocyclic thio- and selenoethers and with the (semi)rigid dithioethers o-$C_6H_4(SMe)_2$ and o-$C_6H_4(CH_2SEt)_2$. This work has established that a much wider range of complexes with differing coordination numbers and geometries exists as well as unprecedented reaction chemistry. These results are described herein.

■ EXPERIMENTAL SECTION

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum100 spectrometer over the range 4000−200 cm^{-1}. Raman spectra were obtained using a Perkin-Elmer FT2000R with a Nd:YAG laser. Significant bands in the range 400−200 cm^{-1} are listed below. ^1H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 unless otherwise stated using a Bruker AV300 spectrometer. ^{71}Ga, $^{77}Se\{^1H\}$, and ^{115}In NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to aqueous $[Ga(H_2O)_6]^{3+}$ (^{71}Ga), neat Me_2Se (^{77}Se), and aqueous $[In(H_2O)_6]^{3+}$ at pH = 1 (^{115}In). Electrospray (ES) MS data were obtained from solutions in MeCN using a VG Biotech Platform. Microanalyses were undertaken by Medac Ltd. Solvents were dried by distillation prior to use: CH_2Cl_2 from CaH_2, hexane from sodium benzophenone ketyl. $GaCl_3$, $InCl_3$, [14]aneS_4 (1,4,8,11-tetrathiacyclotetradecane), and [16]aneS_4 (1,5,9,13-tetrathiacyclohexadecane) (Aldrich) were used as received. Ligands [8]aneSe_2 (1,5-diselenocyclooctane), [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane),[9] o-$C_6H_4(SMe)_2$,[10] o-$C_6H_4(CH_2SEt)_2$,[11] $C(CH_2SMe)_4$, $C(CH_2SeMe)_4$, and 1,2,4,5-$C_6H_2(CH_2SMe)_4$[12] were prepared via literature methods or minor modifications thereof. All preparations were performed under an atmosphere of dry N_2 using Schlenk techniques, and spectroscopic samples were prepared in a dry N_2-purged glovebox.

Preparations. *[GaCl$_3$([14]aneS$_4$)] (**1**).* [14]aneS_4 (0.053 g, 0.20 mmol) was dissolved in CH_2Cl_2 (5 mL) and added to a solution of $GaCl_3$ (0.035 g, 0.20 mmol) dissolved in CH_2Cl_2 (5 mL) with constant stirring. After 45 min the volume of the solvent was reduced in vacuo to 5 mL. Colorless crystals suitable for X-ray diffraction studies were obtained from the solution which was kept in a freezer for several days. Yield: 0.073 g, 83%. Anal. Calcd for $C_{10}H_{20}Cl_3GaS_4\cdot 1/2CH_2Cl_2$: C, 25.9; H, 4.3. Found: C, 26.0; H, 4.0. ^1H NMR (CD_2Cl_2, 295 K): 2.07 (quin, [4H], $CH_2CH_2CH_2$), 2.90 (t, [8H], SCH_2CH_2), 3.01 (s, [8H], SCH_2CH_2S), 5.3 (s, CH_2Cl_2). IR (cm^{-1}, Nujol): 381 (s,br). Raman (cm^{-1}): 386 (w), 331 (s).

*[GaCl$_2$([16]aneS$_4$)][GaCl$_4$] (**2**).* [16]aneS_4 (0.025 g, 0.08 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) and added to a solution of $GaCl_3$ (0.030 g, 0.17 mmol) in anhydrous MeCN (5 mL) with constant stirring. After 30 min the volume of the solvent was reduced in vacuo to 7 mL. A white precipitate was obtained from the solution, which was kept in the freezer overnight. Colorless crystals suitable for X-ray diffraction studies were also obtained from the solution. Yield: 0.037 g, 68% (combined). The bulk solid and crystals are spectroscopically identical. Microanalytical measurements showed variable %C and %H values but always lower than predicted, and data on the crystals gave values which decreased steadily during analysis, suggesting decomposition. ^1H NMR (CD_2Cl_2, 295 K): 2.14 (quin, [8H], SCH_2CH_2), 2.95 (t, [16H], SCH_2CH_2). IR (cm^{-1}, Nujol): 368 (br), 301 (br). Raman (cm^{-1}): 370 (w), 346 (s). ^{71}Ga NMR: CD_2Cl_2, no resonance observed; MeCN, 251 ppm ($[GaCl_4]^-$).

*[GaCl$_2$([16]aneSe$_4$)][GaCl$_4$] (**3**).* [16]aneSe_4 (0.07 g, 0.14 mmol) was dissolved in CH_2Cl_2 (10 mL) and added to a solution of $GaCl_3$ (0.05 g, 0.28 mmol) in CH_2Cl_2 (5 mL) with constant stirring. After 45 min the volume of the solvent was reduced in vacuo to 7 mL. Colorless crystals suitable for X-ray diffraction studies were obtained from the solution which was kept in a freezer for several days. Yield: 0.059 g, 50%. Anal. Calcd for $C_{12}H_{24}Cl_6Ga_2Se_4$: C, 17.2; H, 2.9. Found: C, 16.9; H, 2.6. ^1H NMR ($CDCl_3$, 295 K): 2.15 (quin, [8H], $CH_2CH_2CH_2$), 2.85 (t, [16H], $SeCH_2$). $^{77}Se\{^1H\}$ NMR (CD_2Cl_2, 295 K) 138. IR (cm^{-1}, Nujol): 371 (s). Raman (cm^{-1}): 373 (w), 346 (s).

*[InCl$_2$([16]aneSe$_4$)][InCl$_4$] (**4**).* [16]aneSe_4 (0.22 g, 0.45 mmol) was dissolved in CH_2Cl_2 (5 mL) and added to a suspension of $InCl_3$ (0.10 g, 0.45 mmol) in CH_2Cl_2 (5 mL) with constant stirring. After 30 min the white solid was collected by filtration. The volume of the filtrate was reduced in vacuo to 5 mL. Colorless crystals suitable for X-ray diffraction studies were obtained from the filtrate which was kept in a freezer for several days. Yield: 0.127 g, 40% (combined). The bulk solid and crystals are spectroscopically identical. Anal. Calcd for $C_{12}H_{24}Cl_6In_2Se_4$: C, 15.5; H, 2.6. Found: C, 15.3; H, 2.4. ^1H NMR ($CDCl_3$, 295 K): 2.07 (quin, [8H], $CH_2CH_2CH_2$), 2.71 (t, [16H], $SeCH_2$). $^{77}Se\{^1H\}$ NMR (CD_2Cl_2, 295 K): 158. ^{115}In NMR (CD_2Cl_2, 298 K): 446 ($[InCl_4]^-$). IR (cm^{-1}, Nujol): 338 (s), 323 (m), 275 (m). Raman (cm^{-1}) 346 (w), 336 (w), 320 (s), 281 (s), 242 (s).

*[(GaCl$_3$)$_2${o-C$_6$H$_4$(SMe)$_2$}] (**5**).* $GaCl_3$ (0.22 g, 1.24 mmol) was dissolved in CH_2Cl_2 (5 mL), and o-$C_6H_4(SMe)_2$ (0.11 g, 0.62 mmol) was added dropwise with constant stirring. The solution was stirred for a further 10 min and then concentrated in vacuo, yielding a pale orange precipitate. The product was filtered off, washed with hexane (3 mL), and dried in vacuo. Yield: 0.22 g, 68%. Anal. Calcd for $C_8H_{10}Cl_6Ga_2S_2$: C, 18.4; H, 1.9. Found: C, 19.0; H, 2.4. IR (cm^{-1}, Nujol): 395(br), 366(sh). ^1H NMR ($CDCl_3$, 295 K): 2.92 (s, [6H], Me), 7.6−7.7 (m, [4H], aromatic CH). ^{71}Ga NMR: (CH_2Cl_2, 295 K): 250 ($w_{1/2}$ = 1100 Hz).

*[o-C$_6$H$_4$(SMeCH$_2$Cl)$_2$][GaCl$_4$]$_2$ (**6**).* A solution of $[(GaCl_3)_2\{o$-$C_6H_4(SMe)_2\}]$ in anhydrous CH_2Cl_2 was left to stand at −20 °C under an inert atmosphere for ca. 1 week, furnishing a small number of pale yellow crystals shown by X-ray crystallographic analysis to be $[o$-$C_6H_4(SMeCH_2Cl)_2\}][GaCl_4]_2$. Positive-ion ESMS (MeCN) on the crystals: found m/z = 219 $[o$-$C_6H_4(SMe)(SMeCH_2Cl)]^+$. Negative-ion ESMS (MeCN): found m/z = 211 $[GaCl_4]^-$. IR (cm^{-1}, Nujol): 381 (s).

*[InCl$_3${o-C$_6$H$_4$(SMe)$_2$}] (**7**).* $InCl_3$ (0.22 g, 1.0 mmol) was suspended in CH_2Cl_2 (7 mL), and o-$C_6H_4(SMe)_2$ (0.17 g, 1.0 mmol) was added dropwise with constant stirring. The solution was stirred for a further 1

Table 1. Crystal Data and Structure Refinement Details[a]

	1	2	3	4
formula	$C_{10}H_{20}Cl_3GaS_4$	$C_{12}H_{24}Cl_6Ga_2S_4$	$C_{12}H_{24}Cl_6Ga_2Se_4$	$C_{12}H_{24}Cl_6In_2Se_4$
M	444.57	648.69	836.29	926.49
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$Pbca$ (no. 61)	$P2_1/m$ (no. 11)
a [Å]	21.781(4)	14.503(4)	9.9535(10)	6.9436(15)
b [Å]	6.5370(10)	21.168(5)	21.461(4)	22.508(5)
c [Å]	12.307(2)	15.591(3)	23.331(4)	8.4877(15)
α [deg]	90	90	90	90
β [deg]	108.560(10)	100.711(10)	90	100.735(10)
γ [deg]	90	90	90	90
U [Å^3]	1661.2(5)	4703.1(18)	4983.7(14)	1303.3(4)
Z	4	8	8	2
μ(Mo Kα) [mm^{-1}]	2.622	3.325	8.646	7.967
total reflns	10 950	31 853	31 334	14 834
unique reflns	1897	8246	5697	3064
R_{int}	0.0264	0.123	0.055	0.082
no. of params, restraints	83, 0	439, 0	217, 0	115, 0
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.019	0.098	0.037	0.065
R_1 [all data]	0.021	0.189	0.056	0.118
$wR_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.041	0.210	0.075	0.101
wR_2 [all data]	0.042	0.267	0.085	0.120

	6	8	9·2CH$_2$Cl$_2$	11	12·CH$_2$Cl$_2$
formula	$C_{10}H_{14}Cl_{10}Ga_2S_2$	$C_{12}H_{18}Cl_6Ga_2S_2$	$C_{38}H_{58}Cl_{16}In_4S_6$	$C_{12}H_{24}Cl_8Ga_2Se_4$	$C_7H_{14}Cl_7GaSe_2$
M	692.27	578.52	1733.68	907.19	573.97
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	9.4813(15)	18.561(4)	24.016(5)	9.0156(15)	7.3566(10)
b [Å]	14.009(3)	10.809(3)	18.726(5)	14.148(3)	12.521(2)
c [Å]	18.403(3)	13.495(3)	14.995(4)	10.4855(15)	18.670(3)
α [deg]	90	90	90	90	90
β [deg]	104.377(10)	126.201(5)	114.76(2)	99.204(10)	93.107(10)
γ [deg]	90	90	90	90	90
U [Å^3]	2367.9(6)	3.384	6123(3)	1320.2(4)	1717.2(4)
Z	4	4	4	2	4
μ(Mo Kα) [mm^{-1}]	3.576	3.384	2.419	8.365	6.908
total no. reflns	27 701	11 619	69 930	16 831	17 301
unique reflns	5415	2500	7092	3030	3907
R_{int}	0.066	0.0425	0.1492	0.042	0.0349
no. of params, restraints	217, 0	100, 0	290, 0	118, 0	154, 0
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.073	0.074	0.083	0.027	0.020
R_1 [all data]	0.099	0.103	0.123	0.0355	0.024
$wR_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.181	0.126	0.146	0.0527	0.0486
wR_2 [all data]	0.199	0.140	0.160	0.056	0.051

[a] Common items: temperature = 120 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$.

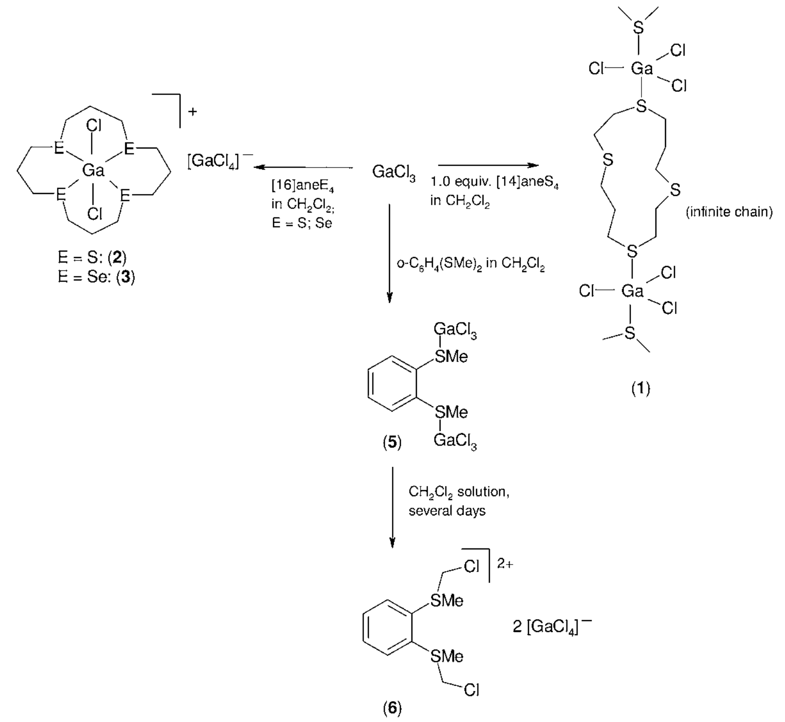
h and filtered, and the solid was washed with CH_2Cl_2 (5 mL). The product was then dried in vacuo to yield a white solid. Yield: 0.20 g, 51%. Anal. Calcd for $C_8H_{10}Cl_3InS_2$: C, 24.5; H, 2.6. Found: C, 24.3; H, 2.6. IR (cm^{-1}, Nujol): 302 (s), 257 (s). Raman (cm^{-1}): 307 (s), 280 (s). ^{1}H NMR ($CDCl_3$, 295 K): 2.50 (s, [6H], Me), 7.1−7.4 (m, [4H], aromatic CH).

*[(GaCl$_3$)$_2${o-C$_6$H$_4$(CH$_2$SEt)$_2$}] (**8**).* $GaCl_3$ (0.22 g, 1.24 mmol) was dissolved in CH_2Cl_2 (5 mL), and *o*-$C_6H_4(CH_2SEt)_2$ (0.14 g, 0.62 mmol) was added dropwise. The solution was stirred for a further 10 min and then concentrated in vacuo, yielding a pale yellow precipitate. The product was filtered off, washed with cold CH_2Cl_2 (3 mL), and dried in vacuo. Yield: 0.23 g, 64%. Crystals were grown from the filtrate stored at −20 °C for 2 days. Anal. Calcd for $C_{12}H_{18}Cl_6Ga_2S_2$: C, 24.9; H, 3.1. Found: C, 24.5; H, 2.5. IR (cm^{-1}, Nujol): 394 (s), 357 (m). ^{1}H NMR (d_6-acetone, 295 K): 1.23 (t, [6H], ^3J = 6 Hz, CH_2CH_3), 2.50 (q, [4H], CH_2CH_3), 3.94 (s, [4H], SCH_2Ar), 7.2−7.4 (m, [4H], aromatic CH). ^{71}Ga NMR: (CH_2Cl_2, 295 K): 233 ($w_{1/2}$ = 10 000 Hz).

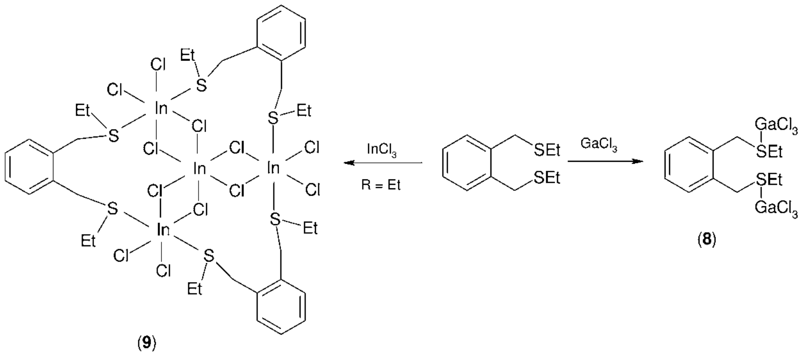
*[(InCl$_3$)$_4${o-C$_6$H$_4$(CH$_2$SEt)$_2$}$_3$] (**9**).* $InCl_3$ (0.22 g, 1.0 mmol) was suspended in CH_2Cl_2 (7 mL), and *o*-$C_6H_4(CH_2SEt)_2$ (0.23 g, 1.0 mmol) was added dropwise with constant stirring. After 1 h the solid was filtered to remove undissolved $InCl_3$, and the filtrate was placed in the freezer at −18 °C for 2 weeks to give colorless crystals. Yield: 0.043 g, 10%. Anal. Calcd for $C_{36}H_{54}Cl_{12}In_4S_6 \cdot 2CH_2Cl_2$: C, 26.3; H, 3.4. Found: C, 26.1; H, 3.8. IR (cm^{-1}, Nujol): 341(s), 330(s), 307(s). ^{1}H NMR (CD_2Cl_2, 295 K): 1.28 (t, [6H], ^3J = 6 Hz, CH_2CH_3), 2.54 (q, [4H], CH_2CH_3), 3.94 (s, [4H], SCH_2Ar), 7.2−7.4 (m, [4H], aromatic CH).

*[(GaCl$_3$)$_2$([8]aneSe$_2$)] (**10**).* [8]aneSe_2 (0.069 g, 0.28 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL) and added to a solution of $GaCl_3$ (0.100 g, 0.57 mmol) in anhydrous CH_2Cl_2 (5 mL) with constant stirring to give a pale yellow solution. After 30 min a white

Scheme 1



Scheme 2



precipitate had formed, which was collected by filtration and dried in vacuo. Yield: 0.082 g, 46%. ^{1}H NMR (CDCl$_3$, 295 K): 2.47 (quin, [4H], SeCH$_2$C*H*$_2$), 3.23 (t, [8H], SeC*H*$_2$CH$_2$). ^{71}Ga NMR (CDCl$_3$, 295 K): 237 ($w_{1/2}$ = 4500 Hz). ^{77}Se{^{1}H} NMR (CDCl$_3$, 203 K): 112.1. IR spectrum (cm^{-1}, Nujol): 386 (s), 360 (m). Satisfactory microanalyses were not obtained due to the extreme sensitivity of this complex, leading to severe difficulties in handling the solid.

[8]aneSe$_2$Cl$_4$ (13). [8]aneSe$_2$ (0.040 g) was added to a saturated solution of Cl$_2$ in CCl$_4$ (6 mL) with stirring. A pale yellow precipitate formed immediately. After 1 h the reaction mixture was filtered to yield a pale yellow solid, which was washed with CH$_2$Cl$_2$ (2 × 2 mL) and dried in vacuo. Yield: essentially quantitative. Anal. Calcd for C$_6$H$_{12}$Cl$_4$Se$_2$: C, 18.8; H, 3.2. Found: C, 19.5; H, 3.2. ^{13}C{^{1}H} NMR ((CD$_3$)$_2$SO, 295 K): 49.1 (SeCH$_2$), 44.2 (CH$_2$CH$_2$CH$_2$). ^{77}Se{^{1}H} NMR ((CD$_3$)$_2$SO, 295 K): 656.5 (s).

[InCl$_3$([8]aneSe$_2$)$_2$] (14). [8]aneSe$_2$ (0.121 g, 0.50 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL) and added to a suspension of InCl$_3$ (0.111 g, 0.50 mmol) in CH$_2$Cl$_2$ (5 mL) with constant stirring. After 30 min the white solid was collected by filtration, washed with CH$_2$Cl$_2$, and dried in vacuo. Yield: 0.062 g, 35% (based on [8]aneSe$_2$). Anal. Calcd for C$_{12}$H$_{24}$Cl$_3$InSe$_4$: C, 20.4; H, 3.4. Found: C, 20.9; H, 3.8. ^{1}H NMR (CD$_3$CN, 295 K): 2.23 (quin, [4H], CH$_2$C*H*$_2$CH$_2$), 2.89 (t, [8H], SeC*H*$_2$). IR (cm^{-1}, Nujol): 298 (m), 283 (s). Raman (cm^{-1}): 278 (s), 252 (m).

X-ray Crystallography. Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals were obtained as described above. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated (confocal mirrors) Mo Kα X-radiation (λ = 0.71073 Å). Crystals were held at 120 K in a nitrogen gas stream. Structure solution and refinement were generally routine,[13,14] except as described below, with hydrogen atoms on C added to the model in calculated positions and using the default C−H distance. The data obtained for the crystal of **2** were weak; however, given the similarity of this structure to those of **3** and **4** it was not considered necessary to recollect the data. The data for **8** (Supporting Information) display characteristics indicative of a modulated structure. Indexing was possible using most reflections and a large cell (a = 13.4632 Å, b = 53.8898 Å, c = 15.1497 Å, β = 99.554° (P)) but this did not lead to a solution. Indexing was also possible using a smaller C-centered monoclinic cell and a modulation vector 0.0069, −0.6039, −0.0036 up to order 1. Using this cell and conventional data reduction, ignoring the modulation, leads to the solution presented here. The data for **9** were originally collected as triclinic (P) and later transformed to the monoclinic (C) cell presented here. The crystal quality for **9** was modest, and structure refinement revealed some disorder of the C atoms of the Et substituents associated with S3 (and S3a) (elongated thermal ellipsoids), possibly suggesting that the molecule is disordered across the crystallographic mirror plane.

CCDC reference numbers 847024−847032 contain the supplementary crystallographic data for the crystal structures reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ RESULTS AND DISCUSSION

The complex syntheses (Schemes 1 and 2) were typically undertaken in anhydrous CH_2Cl_2 solution to prevent competition from coordination of the solvent, although in some specific cases (see Experimental Section) a small amount of MeCN was added to aid solubility (especially of the $InCl_3$), promoting cleaner reactions and typically higher yields. IR and Raman spectroscopy readily identified the presence or absence of $[MCl_4]^-$ in the products[15,16] (or S/Se coordinated MCl_3 by comparison with literature data)[6,8] and, together with microanalyses, allowed initial identification of the products and their stoichiometries. Due to the known lability of Ga(III) and In(III) complexes in solution, NMR spectroscopic studies provide limited structural information, although where possible ^{77}Se, ^{71}Ga, and ^{115}In NMR spectroscopic studies[17] were performed to provide supporting evidence for the solution speciation. X-ray crystallographic studies have enabled unambiguous identification of the structures of key complexes.

Tetradentate Ligands. In order to probe the effect ligand architecture has on the complexes with MCl_3 (M = Ga and In) within the series of tetradentate ligands, the following chalcogenoethers were examined: the macrocycles $[14]aneS_4$, $[16]aneS_4$, and $[16]aneSe_4$, $C(CH_2EMe)_4$ (E = S or Se) and 1,2,4,5-$C_6H_2(CH_2SMe)_4$.[18] The only structurally characterized example of a tetrathia macrocyclic complex with Group 13 halides is $[InCl_2([14]aneS_4)][InCl_4]$,[8] although Atwood, Robinson, and co-workers reported several examples of $AlMe_3$ complexes with thia-macrocycles and Al(III) chloride complexes with crown ethers.[19]

Reaction of $GaCl_3$ with 1 mol equiv of the macrocycle $[14]aneS_4$ (1,4,8,11-tetrathiacyclotetradecane) led initially to a white precipitate which redissolved as the 1:1 Ga:macrocycle ratio was reached. Concentration of the solution in vacuo allowed isolation of a white solid formulated as the neutral $[GaCl_3([14]aneS_4)]$ (**1**) from IR/Raman and microanalyses. Upon the basis of our earlier work on Ga(III) halide thioether complexes, distorted tetrahedral Cl_3S coordination was considered most likely. However, the IR and Raman spectra support local D_{3h} symmetry (tbp Cl_3S_2 coordination at Ga), showing the e′ mode at 381 and the a_1′ mode at 331 cm^{-1} for the $GaCl_3$ unit. The crystal structure of this 1:1 complex provides confirmation of this, showing (Figure 1, Table 2) an infinite chain structure formed via Ga atoms coordinated to three Cl ligands occupying a trigonal plane and two further axial S atoms from bridging $[14]aneS_4$ molecules, giving a distorted trigonal bipyramidal (exocyclic) coordination geometry at Ga. Within the chains the macrocyclic rings are centrosymmetric, and there is a crystallographic 2-fold axis passing through the Ga atoms.

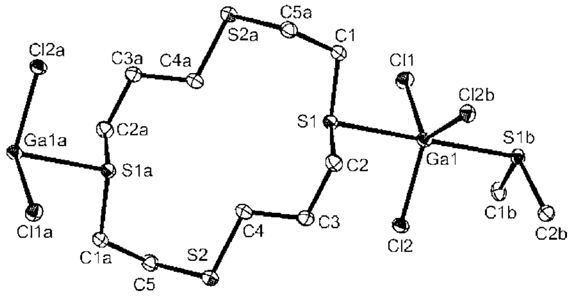


Figure 1. View of the structure of a section of the chain polymer of **1** with atom-numbering scheme. Ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Symmetry operators: a = 1/2 − *x*, 1/2 − *y*, − *z*; b = 1 − *x*, y, 1/2 − *z*.

Table 2. Selected Bond Lengths (Angstroms) and Angles (degrees) for 1[a]

Ga1−Cl1	2.1828(7)	Ga1−Cl2	2.1835(4)
Ga1−S1	2.5744(6)	Cl1−Ga1−Cl2	119.681(13)
Cl2−Ga1−Cl2b	120.64(3)	Cl1−Ga1−S1	89.653(10)
Cl2−Ga1−S1	88.54(2)	Cl1−Ga1−S1b	89.653(10)
Cl2−Ga1−S1b	91.81(2)	S1−Ga1−S1b	179.31(2)

[a] Symmetry operators: a = 1/2 − *x*, 1/2 − *y*, − *z*; b = 1 − *x*, *y*, 1/2 − *z*.

The Ga−S distances (2.5744(6) Å) are considerably longer than those in $[(GaCl_3)_2(L{-}L)]$ (L−L = $PhS(CH_2)_2SPh$ and *o*-$C_6H_4(CH_2SMe)_2$) (2.389(1) and 2.357(2) Å, respectively).[6] Although less pronounced, a similar trend is evident for *d*(Ga−Cl). This species presents the first example where the three Cl ligands adopt a trigonal planar geometry, the pyramidal $GaCl_3$ fragment being much more common. It was surprising to us that there appeared to be no tendency toward chelation (endocyclic coordination) in this system despite the presence of the four S donor atoms in the macrocyclic ring. The polymeric structure also contrasts with the product from the $InCl_3/[14]aneS_4$ reaction system reported previously, which forms the ionic complex *cis*-$[InCl_2([14]aneS_4)][InCl_4]$, in which the cation adopts a distorted octahedral geometry with S_4 coordination of the macrocycle.[8] The smaller ionic radius of Ga(III) vs In(III) would suggest there is no intrinsic reason why a similar coordination mode would not be possible; however, we have not been able to isolate a pure, single product when using higher Ga:macrocycle ratios.

Given the unexpected five-coordinate Cl_3S_2 environment in **1**, the reaction was repeated using the larger ring $[16]aneS_4$, leading to a white product, this time with a 2:1 Ga:macrocycle stoichiometry. The same species was obtained using either a 1:1 or a 2:1 ratio of reactants, and IR and Raman spectroscopy clearly show the presence of the $[GaCl_4]^-$ anion (in addition, a further band in the far-IR region is attributed to the b_1 Ga−Cl stretching mode from *trans*-$[GaCl_2([16]aneS_4)]^+$). Although data were obtained from a rather small, weakly diffracting crystal, structure determination (Figure 2, Table 3) confirmed the product as $[GaCl_2([16]aneS_4)][GaCl_4]$ (**2**). The asymmetric unit contains four independent cations (each with a center of symmetry), and two $[GaCl_4]^-$ anions in general positions. Within each cation the Ga(III) ion is octahedrally coordinated, occupying the ring and coordinated via the four S-donor atoms as well as two trans Cl ligands.

Investigation of the reaction of the tetraselenoether crown $[16]aneSe_4$ with $GaCl_3$ furnished the ionic product *trans*-$[GaCl_2([16]aneSe_4)][GaCl_4]$ (**3**) as a colorless solid with similar IR and Raman spectroscopic features. The crystal structure of this product confirms it is isostructural with the analogous thioether complex, comprising a distorted octahedral cation (Figure 3, Table 4) and a tetrahedral anion. In the

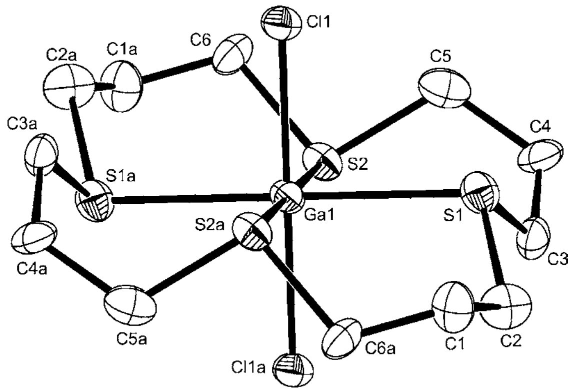


Figure 2. View of the cation in **2** with atom-numbering scheme. Ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: a = 2 − *x*, − *y*, 1 − *z*.

Table 3. Selected Bond Lengths (Angstroms) and Angles (degrees) for 2

Ga1−Cl1	2.276(3)	Ga1−S1	2.518(4)
Ga1−S2	2.492(4)	Ga2−Cl2	2.293(3)
Ga2−S3	2.515(4)	Ga2−S4	2.464(4)
Ga3−Cl3	2.296(3)	Ga3−S5	2.486(4)
Ga3−S6	2.499(4)	Ga4−Cl4	2.292(3)
Ga4−S7	2.496(4)	Ga4−S8	2.482(4)
Cl1−Ga1−S1	88.28(12)	Cl1−Ga1−S2	92.27(12)
S1−Ga1−S2	90.60(12)	Cl2−Ga2−S3	88.35(12)
Cl2−Ga2−S4	91.81(13)	S3−Ga2−S4	89.57(12)
Cl3−Ga3−S5	91.83(12)	Cl3−Ga3−S6	91.24(12)
S5−Ga3−S6	90.40(13)	Cl4−Ga4−S7	91.19(12)
Cl4−Ga4−S8	92.01(14)	S7−Ga4−S8	90.02(13)

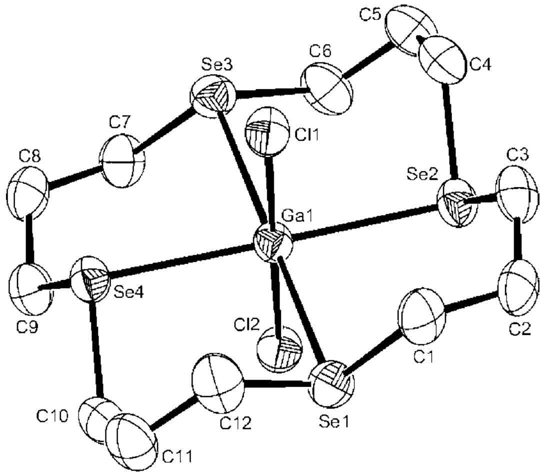


Figure 3. View of the structure of the cation in **3** with atom-numbering scheme. Ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Angstroms) and Angles (degrees) for 3

Ga1−Cl1	2.3220(12)	Ga1−Cl2	2.3058(11)
Ga1−Se1	2.6106(8)	Ga1−Se2	2.6031(7)
Ga1−Se3	2.6098(8)	Ga1−Se4	2.5906(7)
Cl1−Ga1−Cl2	178.96(5)	Cl1−Ga1−Se1	91.85(4)
Cl1−Ga1−Se2	92.20(3)	Cl1−Ga1−Se3	85.86(4)
Cl1−Ga1−Se4	87.13(3)	Cl2−Ga1−Se1	89.11(4)
Cl2−Ga1−Se2	87.41(3)	Cl2−Ga1−Se3	93.19(4)
Cl2−Ga1−Se4	93.26(3)	Se1−Ga1−Se2	88.56(2)
Se1−Ga1−Se3	177.60(3)	Se1−Ga1−Se4	91.71(2)
Se2−Ga1−Se3	92.23(2)	Se2−Ga1−Se4	179.28(3)
Se3−Ga1−Se4	87.47(2)	Cl3−Ga2−Cl4	108.69(6)
Cl3−Ga2−Cl5	109.18(7)	Cl3−Ga2−Cl6	110.22(7)
Cl4−Ga2−Cl5	109.99(7)	Cl4−Ga2−Cl6	108.93(8)
Cl5−Ga2−Cl6	109.83(8)		

former the Ga occupies the center of the macrocyclic ring and is coordinated equatorially to the four Se atoms (2.5906(7)−2.6106(8) Å) with two mutually trans Cl atoms completing the coordination. The four Se atoms are almost coplanar, and the Ga atom is only ca. 0.03 Å out of this plane, suggesting a very good size match between Ga(III) and the macrocyclic binding cavity; this may be important in promoting formation of this endocyclic cation. The Ga−Se bond distances in the six-coordinate cation are significantly longer than in the previously reported tetrahedral complexes [$GaCl_3(SeMe_2)$] (2.4637(7) Å) and [$(GaCl_3)_2\{^nBuSe(CH_2)_2Se^nBu\}$] (2.4683(11) Å).[6] The same trend occurs for the Ga−Cl distances within the cation (2.306(1), 2.322(1) Å) compared to those in the tetrahedral $[GaCl_4]^-$ anion (2.163(2)−2.175(2) Å).

The corresponding In(III) complex (**4**) obtained similarly (Figure 4) also contains a *trans*-octahedral cation with the In atom in the Se_4 plane. In this case the cation is centrosymmetric, with *d*= (In−Se) = 2.719(1) and 2.739(1) Å, similar to those in *trans*-[$InBr_2\{MeSe(CH_2)_2SeMe\}_2]^+$.[8]

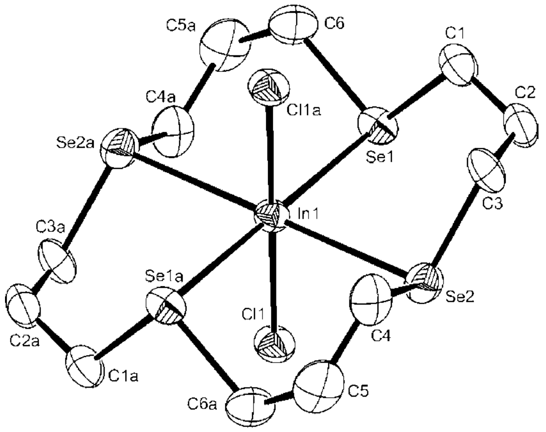


Figure 4. View of the structure of the centrosymmetric cation in **4** with atom-numbering scheme. Ellipsoids are shown at the 40% probability level, and H atoms are omitted for clarity. Symmetry operation: a = −*x*, 1 − *y*, 2 − *z*. Selected bond lengths (Angstroms) and angles (degrees): In1−Cl1 = 2.475(2), In1−Se1 = 2.7189(10), In1−Se2 = 2.7394(11); Cl1−In1−Se1 = 88.04(6), Cl1−In1−Se2 = 88.10(6).

Solution ^1H NMR spectroscopic studies in CH_2Cl_2 on **2**, **3**, and **4** show small high-frequency shifts, while ^{71}Ga and ^{115}In NMR spectra each show a resonance corresponding to the $[MCl_4]^-$ anion, but resonances from the six-coordinate cations are not observed. This is as expected for complexes involving the quadrupolar ^{71}Ga and ^{115}In nuclei for which small distortions from regular O_h (or T_d) geometry give rise to nonzero electric field gradients and significant line broadening. No ^{71}Ga (or ^{115}In) resonances were observed for the distorted octahedral *trans*-[$MX_2\{o\text{-}C_6H_4(E'Me_2)_2\}_2$] (E′ = P or As) or distorted tetrahedral [$MX_2\{o\text{-}C_6H_4(PMe_2)_2\}$].[7] Selenium-77

NMR spectroscopic data for **3** (in CH_2Cl_2) shows a singlet at 134 ppm to low frequency of the parent [16]aneSe_4 ligand (158 ppm), while in MeCN solution the resonance is a very sharp singlet at 158 ppm, suggesting the ligand is extensively dissociated in the more competitive MeCN solvent. As observed previously for InX_3 complexes with mono- and bidentate selenoethers **4** also appears to be extensively dissociated (or shows a negligible coordination shift), exhibiting a singlet at 158 ppm even in noncoordinating CH_2Cl_2.

The acyclic tetrathioethers $C(CH_2SMe)_4$ and 1,2,4,5-$C_6H_2(CH_2SMe)_4$ (L) react with 4 mol equiv of $GaCl_3$ to form complexes of stoichiometry $[(GaCl_3)_4(L)]$ and with $InCl_3$ to form the 2:1 complex $[(InCl_3)_2\{C(CH_2SMe)_4\}]$ (Supporting Information). Reaction of $GaCl_3$ with the tetraselenoether $C(CH_2SeMe)_4$ in anhydrous CH_2Cl_2 leads to fragmentation at C−Se, forming a yellow oil containing a complex mixture of species including the selenonium cation $[(CH_2)_2C(CH_2)_2SeMe]^+$ identified by positive-ion ESMS (m/z = 163) and $[GaCl_4]^-$ (IR, Raman and ESMS data) as well as other unidentified species.

Bidentate Ligands. As described in the Introduction, a range of GaX_3 and InX_3 complexes with simple mono- and flexible bidentate thio- and selenoethers was the basis of our earlier work. In this study we studied the effects of introducing geometric or steric constraints in the bidentate ligand architectures using the rigid *o*-$C_6H_4(SMe)_2$, the semirigid *o*-$C_6H_4(CH_2ER)_2$ (E = S; R = Me or Et; E = Se, R = Me), as well as the cyclic [8]aneSe_2 (Schemes 1 and 2).

Reaction of MCl_3 with *o*-$C_6H_4(SMe)_2$ gives $[(GaCl_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$ (**5**) and $[InCl_3\{o\text{-}C_6H_4(SMe)_2\}]$ (**7**), respectively. On the basis of the spectroscopic data both in solution and in the solid state these are assigned as adopting distorted tetrahedral Cl_3S coordination for M = Ga, whereas for M = In a chloro-bridged dimer with a distorted octahedral Cl_4S_2 donor set is likely; there is no evidence for $[MCl_4]^-$ in either case.

Redissolving **5** in CH_2Cl_2 and leaving this solution to stand at −20 °C over several days leads to further reaction with the CH_2Cl_2 solvent and produced yellow crystals. Examination of these revealed the product to be $[o\text{-}C_6H_4(SMeCH_2Cl)_2][GaCl_4]_2$ (**6**) containing discrete bis-sulfonium dications (Figure 5) and tetrahedral $[GaCl_4]^-$ anions. IR spectroscopic data on this material shows $[GaCl_4]^-$, which was also the only significant anion evident in the negative-ion electrospray MS (MeCN). Positive-ion MS shows $[o\text{-}C_6H_4(SMe)(SMeCH_2Cl)]^+$ to be the major species present, although there is a weaker feature consistent with $[o\text{-}C_6H_4(SMe)(SMe_2)]^+$ also clearly evident. This reaction is readily reproducible, and mechanistically the sulfonium dication is likely to be formed via nucleophilic attack of the thioether sulfur on the CH_2Cl_2. Bis-sulfonium formation in this reaction is very unusual and is clearly promoted by the $GaCl_3$ polarizing the CH_2Cl_2. The thioether itself is stable in CH_2Cl_2 solution.

The semirigid *o*-xylyl ligands *o*-$C_6H_4(CH_2SEt)_2$ also exhibit unexpected chemistry with MCl_3 (Scheme 2). Reaction of *o*-$C_6H_4(CH_2SEt)_2$ with 2 mol equiv of $GaCl_3$ gives the simple dinuclear $[(GaCl_3)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ (**8**) from the spectroscopic data and a crystal structure determination (Supporting Information) with tetrahedral Cl_3S coordination at Ga and the S substituents anti. Maintaining the same conditions but replacing $GaCl_3$ with $InCl_3$ in the reaction with *o*-$C_6H_4(CH_2SEt)_2$ produces a colorless crystalline complex containing a 4:3 In:dithioether ratio (from microanalytical data) and without any tetrachloroindate in the IR spectrum.

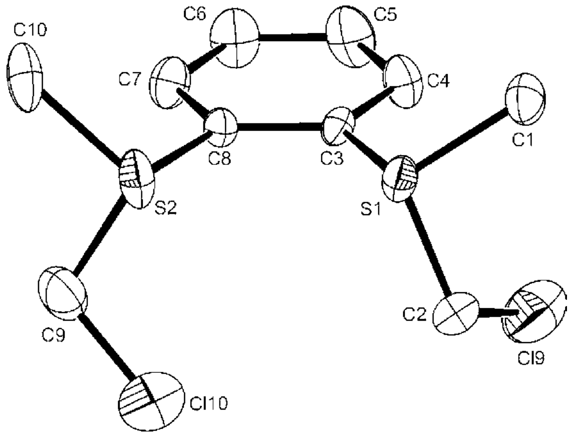


Figure 5. View of the structure of the dication in **6** with atom-numbering scheme. Ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): S1−C1 = 1.786(8), S1−C2 = 1.820(8), S1−C3 = 1.779(7), S2−C8 = 1.790(7), S2−C9 = 1.821(9), S2−C10 = 1.812(9); C1−S1−C2 = 101.3(4), C1−S1−C3 = 104.9(4), C2−S1−C3 = 103.5(4), C8−S2−C9 = 101.1(4), C8−S2−C10 = 104.0(4), C9−S2−C10 = 100.7(4).

The complex is formulated as $[(InCl_3)_4\{o\text{-}C_6H_4(CH_2SEt)_2\}_3]$ (**9**) also on the basis of crystal structure determination (Figure 6, Table 5), which shows a discrete tetranuclear moiety with mirror symmetry. The central In atom (In3) is octahedrally coordinated through six bridging Cl's, whereas the three In atoms on the edges (In1, In2, and In2a) have two bridging Cl's, two terminal Cl's, and two mutually trans S-donor atoms from different dithioether ligands. The structure is very unexpected; there is only one precedent, $[(BiCl_3)_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$, in which the thioether also incorporates the large *o*-xylyl linkage.[20] This suggests that this particular linkage leads to

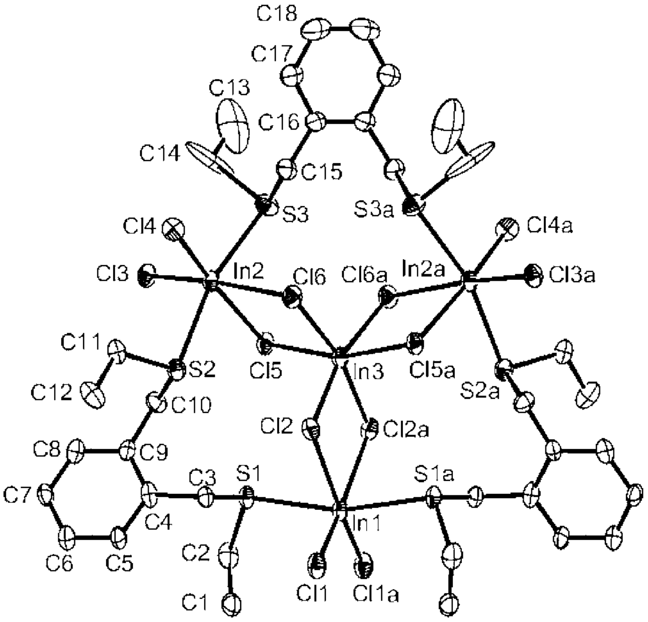


Figure 6. View of the structure of $[(InCl_3)_4\{o\text{-}C_6H_4(CH_2SEt)_2\}_3]$, **9**, with atom-numbering scheme. Ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: a = −*x*, *y*, 1/2 − *z*.

Table 5. Selected Bond Lengths (Angstroms) and Angles (degrees) for $9\cdot2CH_2Cl_2$[a]

In1–Cl1	2.396(3)	In1–Cl2	2.693(3)
In1–S1	2.646(2)	In2–Cl3	2.408(2)
In2–Cl4	2.407(3)	In2–Cl5	2.658(3)
In2–Cl6	2.639(2)	In2–S2	2.655(3)
In2–S3	2.657(3)	In3–Cl2	2.509(3)
In3–Cl5	2.496(2)	In3–Cl6	2.546(3)
Cl1a–In1–Cl1	105.25(14)	Cl1a–In1–S1	92.87(8)
Cl1–In1–S1	96.10(8)	S1–In1–S1a	165.20(12)
Cl1–In1–Cl2a	164.03(9)	S1–In1–Cl2a	88.38(8)
Cl1–In1–Cl2	89.77(9)	S1–In1–Cl2	79.93(8)
Cl2a–In1–Cl2	75.89(11)	Cl4–In2–Cl3	100.67(9)
Cl4–In2–Cl6	90.76(9)	Cl3–In2–Cl6	168.49(9)
Cl4–In2–S2	96.18(9)	Cl3–In2–S2	93.17(8)
Cl6–In2–S2	86.87(8)	Cl4–In2–S3	93.83(9)
Cl3–In2–S3	94.47(9)	Cl6–In2–S3	83.33(9)
S2–In2–S3	166.07(9)	Cl4–In2–Cl5	168.99(8)
Cl3–In2–Cl5	90.14(8)	Cl6–In2–Cl5	78.49(8)
S2–In2–Cl5	80.97(8)	S3–In2–Cl5	87.37(9)
Cl5a–In3–Cl5	163.13(13)	Cl5a–In3–Cl2	90.01(8)
Cl5–In3–Cl2	102.72(8)	Cl2a–In3–Cl2	82.63(12)
Cl5a–In3–Cl6	86.17(8)	Cl2a–In3–Cl6	167.02(8)
Cl5–In3–Cl6	83.30(8)	Cl5a–In3–Cl6	86.17(8)
Cl2a–In3–Cl6	167.02(8)	Cl2–In3–Cl6	87.99(9)
Cl6a–In3–Cl6	102.58(13)	In1–Cl2–In3	100.74(9)
In2–Cl5–In3	99.49(8)	In2–Cl6–In3	98.71(8)

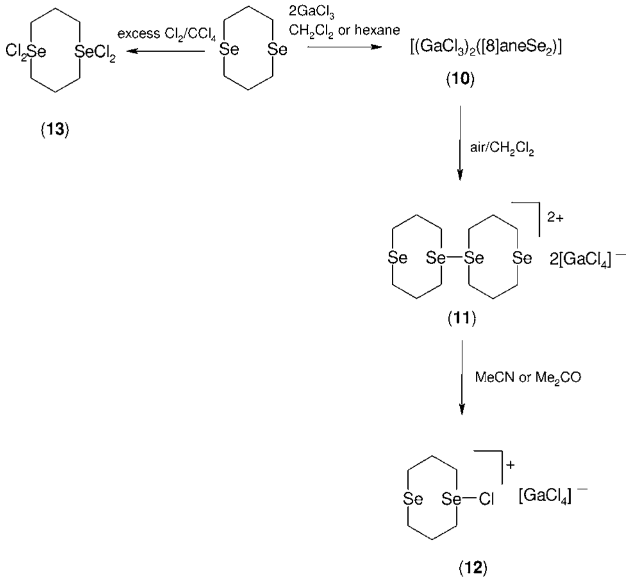
[a] Symmetry operation: a = $-x, y, 1/2 - z$.

more stable species with the ligand bridging two metals in this arrangement rather than chelating to form a seven-membered ring. It also contrasts with the majority of transition metal complexes incorporating this ligand architecture where bidentate chelation occurs, albeit with E–M–E angles significantly greater than 90°, suggesting a mismatch between the metal and the ligand.[11,21] While this will lead to a relatively less stable arrangement, the inherently stronger M–S bonds where M is a d-block ion compared to a p-block ion (likely to be much more kinetically labile) presumably allows the chelate structure to be retained in the former but not in the latter.

The In–S and In–Cl bond distances are comparable with those in the only other indium thioether complexes,[8] and we note that while S and Cl are neighboring elements in the periodic table, the In–S bond distances (ca. 2.65 Å) are approximately 0.25 Å longer than the terminal In–Cl bonds. This suggests weak, secondary In···S coordination.

Reactions with [8]aneSe$_2$. The chemistry of [8]aneSe$_2$ with $GaCl_3$ is illustrated in Scheme 3. Two mole equivalents of $GaCl_3$ reacted with the cyclic diselenoether, [8]aneSe$_2$, in anhydrous CH_2Cl_2 to give a colorless solution, from which an extremely air-sensitive white solid was isolated. On the basis of spectroscopic data this product is assigned as [$(GaCl_3)_2$([8]aneSe$_2$)] (**10**), most likely based upon tetrahedral coordination at each Ga(III). Its ^1H NMR spectrum shows the expected resonances with significant high-frequency coordination shifts relative to the diselenoether itself, while at 298 K the $^{77}Se\{^1H\}$ NMR spectrum of a freshly prepared (colorless) solution of the complex shows a singlet at 118.8 ppm, which shifts slightly to low frequency (112.1 ppm) at 203 K, ca. 25 ppm to low frequency of [8]aneSe$_2$ (137 ppm). The ^{71}Ga NMR spectrum shows no $[GaCl_4]^-$, but a broad resonance is observed at 237 ppm ($w_{1/2}$ = 4500 Hz), consistent with the Cl_3Se environment at Ga(III). The same product is formed from reaction of a suspension of $GaCl_3$ in hexane solution with [8]aneSe$_2$.

Scheme 3



Bubbling O_2 gas through a solution of **10** in CH_2Cl_2 led to rapid appearance of a red/orange-colored solution which precipitated a red solid within a few minutes, leaving the supernatant colorless. Selenium-77 and ^{71}Ga NMR experiments on this supernatant solution showed complete loss of the original resonances (and no new peak). Addition of Me_2CO to the red precipitate caused dissolution with formation of a bright yellow solution initially which lightened to pale yellow after a few minutes, suggesting that further reaction (oxidation) had occurred. The ^{71}Ga NMR spectrum of this solution showed a strong sharp singlet at 249.8 ppm indicative of $[GaCl_4]^-$; however, no ^{77}Se NMR signal was evident (out as far as +1000 ppm) either at 298 or 183 K, even after long data acquisitions, suggesting a dynamic process was occurring. Electrospray mass spectrometry (MeCN) on this product shows {[8]aneSe$_2$}$^+$ and $[GaCl_4]^-$ as the only significant species in the positive-ion and negative-ion modes, respectively. In order to probe this reaction further, a solution of $GaCl_3$ and [8]aneSe$_2$ in CH_2Cl_2 was exposed to air briefly and then placed in a freezer (−18 °C) for several days, leading to formation of both red and yellow crystals. Crystal structure determinations were undertaken on both crystal types.

The red crystals were shown to be [([8]aneSe$_2$)$_2$]$[GaCl_4]_2$ (**11**) containing a dimeric [([8]aneSe$_2$)$_2$]$^{2+}$ dication (Figure 7). The structure of this cation shows the Se–Se distance linking the two rings together is 2.6667(7) Å, while the intraring d(Se···Se) is 2.891(1) Å, consistent with a transannular hypervalent Se(II)···Se(III) 1,5-interaction. This dication appears likely to be formed via coupling two {[8]aneSe$_2$}$^{+\bullet}$ monocation radicals produced via oxidation of [8]aneSe$_2$ by O_2 in the presence of $GaCl_3$. Consistent with this description, the Se–C distances also fall into two groups; those connected to the Se–Se bond (Se1) are slightly longer (1.980(3) and 1.981(3) Å) than those connected to Se2 (1.957(3) and 1.962(3) Å). Note that [8]aneSe$_2$ itself is not air sensitive even over periods of several months.

The yellow crystals obtained from the same reaction mixture correspond to [{[8]aneSe$_2$}Cl]$[GaCl_4]\cdot CH_2Cl_2$ (**12**)$\cdot CH_2Cl_2$

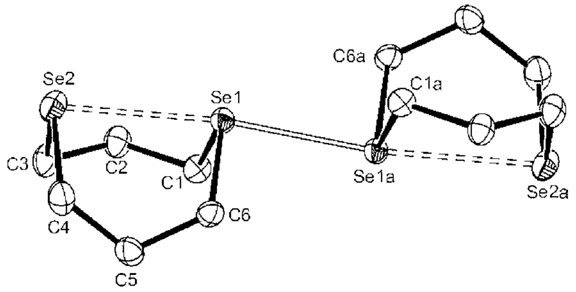


Figure 7. View of the structure of the dimeric cation in **11** with atom-numbering scheme. Ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: a = −*x*, −*y*, −*z*. Selected bond lengths (Angstroms) and angles (degrees): Se1−C1 = 1.980(3), Se1−C6 = 1.981(3), Se1−Se1a = 2.6662(7), Se1···Se2 = 2.891(1), Se2−C3 = 1.957(3), Se2−C4 = 1.962(3); C1−Se1−C6 = 99.69(13), C3−Se2−C4 = 99.71(15).

in which the cation (Figure 8) may be considered as a doubly oxidized $\{[8]\text{aneSe}_2\}^{2+}$ unit with a Cl^- associated with one of the Se atoms (Se−Cl = 2.5346(6) Å). The Se−Se distance of 2.5229(4) Å is consistent with this description, formed through coupling of the two radical cations across the ring. In both of these species tetrahedral $[GaCl_4]^-$ ions provide charge balance.

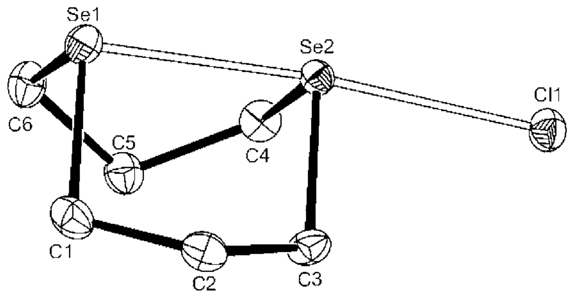


Figure 8. View of the structure of the cation in $\mathbf{12}\cdot CH_2Cl_2$ with atom-numbering scheme. Ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): Se2−Cl1 = 2.5346(6), Se1−C1 = 1.970(2), Se1−C6 = 1.967(2), Se1−Se2 = 2.5229(4), Se2−C3 = 1.981(2), Se2−C4 = 1.978(2); C1−Se1−C6 = 99.66(9), C3−Se2−C4 = 101.93(9), C4−Se2−Cl1 = 89.39(6), C3−Se2−Cl1 = 88.09(6), Se1−Se2−Cl1 = 175.23(2).

Oxidation of cyclic selenoethers has been investigated previously.[22,23] Of particular relevance, electrochemical studies on $[8]\text{aneE}_2$ (E = S, Se, or Te) in MeCN solution show that the mono-oxidized $\{[8]\text{aneSe}_2\}^{+\bullet}$ radical cation ($E^\circ_1 = 0.102$ V vs ferrocene/ferrocenium in MeCN) is thermodynamically very unstable; thus, oxidation of the second E atom occurs at a lower potential ($E^\circ_2 = 0.058$ V) than that of the first E atom (inverted potential). This causes spontaneous conversion of $\{[8]\text{aneSe}_2\}^{+\bullet}$ to $\{[8]\text{aneSe}_2\}^{2+}$. Our experiments show that both the mono- and the doubly oxidized species are formed and that oxidation by O_2 is promoted by Ga(III). Furthermore, the $\{[8]\text{aneSe}_2\}^{+\bullet}$ cation radical formed initially undergoes rapid coupling to form the dimeric **11** (red), which is isolated probably by virtue of the low solubility of its tetrachlorogallate salt in CH_2Cl_2 solution, allowing its crystallographic authentication. Consistent with the electrochemical studies, we found that immediately upon dissolving this solid in either MeCN or acetone rapid decoloration occurs, which we attribute to the intrinsic thermodynamic instability of the red dimer, which undergoes further oxidation to form $\{[8]\text{aneSe}_2\}^{2+}$. In the yellow crystal formed from CH_2Cl_2 solution a Cl^- anion is associated with one Se atom giving **12** determined by X-ray diffraction. The crystal structure of $\{[8]\text{aneSe}_2\}(BF_4)_2\cdot MeCN$ gives *d*(Se−Se) = 2.382(2) Å,[22d] somewhat shorter than observed in the present work for $\mathbf{12}\cdot CH_2Cl_2$ (2.5229(4) Å). The $\{[16]\text{aneSe}_4\}^{2+}$ dication, derived from Cu(II) oxidation of $[16]\text{aneSe}_4$, has also been structurally characterized, and the Se···Se distances within the ring are 2.592(2), 2.669(1), and 3.394(1) Å.[23]

In a separate experiment $NOBF_4$ was added to a solution of **10** in degassed CH_2Cl_2, also leading to a rapid red coloration, which dissipated over ca. 1 min to a pale yellow solution, indicating a similar process occurs. However, oxidation of a CH_2Cl_2 solution of $[8]\text{aneSe}_2$ by addition of a few drops (excess) of Cl_2-saturated CCl_4 caused a bright yellow precipitate to form. NMR spectroscopic studies (^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$) on this product were consistent with formation of the tetrachloride derivative, $[8]\text{aneSe}_2Cl_4$ (**13**).

■ CONCLUSIONS

This work has clearly demonstrated a much wider chemistry of MCl_3 (M = Ga or In) with thio- and selenoethers exists than previously thought. In particular, the work established that the highly Lewis-acidic $GaCl_3$ promotes unprecedented chemistry, on one hand, promoting sulfonium cation formation from *o*-$C_6H_4(SMe)_2$ and CH_2Cl_2 and, on the other, promoting oxidation of selenoether groups in the case of $[8]\text{aneSe}_2$ with O_2. Neither of these reactions occur in the absence of $GaCl_3$. Crystallographic evidence unequivocally authenticates the products.

The work has also produced the first series of five- and six-coordinate gallium halide complexes with thio- and selenoether ligation, specifically forming distorted tbp-coordinated Ga in the polymeric (**1**) and distorted octahedral Ga(III) in the cations present in **2**, **3**, and **4**. The latter also provide the first evidence for halide substitution by a neutral chalcogenoether ligand; undoubtedly, the macrocyclic framework and ring size available play important roles in dictating this chemistry. We note that only the sterically rigid, very strong σ-donor phosphine and arsine ligands *o*-$C_6H_4(E'Me_2)_2$ (E′ = P or As) have been shown to produce six-coordinate *trans*-$[GaX_2\{o\text{-}C_6H_4(E'Me_2)_2\}_2]^+$.[7] The importance of the ligand architecture within p-block chemistry in particular is also clearly evident, no more so than in the tetranuclear **9**, a structural motif that has not been replicated in d-block chalcogenoether chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparative details for $GaCl_3$ and $InCl_3$ complexes with acyclic tetrathio- and tetraselenoethers and crystallographic details for $[(GaCl_3)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$; cif files for all crystal structures described. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gr@soton.ac.uk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the EPSRC and CMSD at STFC for funding (K.G.). We also thank Dr. M. Webster for assistance with the crystallographic studies.

■ REFERENCES

(1) (a) See : In *The Chemistry of Aluminium, Gallium, Indium and Thallium*, 1st ed.; Downs, A. J., Ed.; Blackie: London, 1993. (b) Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2953. (c) Levason, W.; Reid, G.; Zhang, W. *Dalton Trans.* **2011**, *40*, 8491.

(2) (a) Bandoli, G.; Dolmella, A.; Tisato, F.; Porchia, M.; Refosco, F. *Coord. Chem. Rev.* **2009**, *253*, 56. (b) Reichert, D. E.; Lewis, J. S.; Anderson, C. J. *Coord. Chem. Rev.* **1999**, *184*, 3. (c) Anderson, C. J.; Webb, M. J. *Chem. Rev.* **1999**, *99*, 2219.

(3) (a) Laverman, P.; McBride, W.; Sharkey, R.; Eek, A.; Joosten, L.; Oyen, W.; Goldenberg, D.; Boerman, O. *J. Nucl. Med.* **2010**, *51*, 454. (b) McBride, W.; D'Souza, C.; Sharkey, R.; Karacay, H.; Rossi, E.; Chang, C.; Goldenberg, D. *Bioconjugate Chem* **2010**, *21*, 1331. (c) McBride, W.; Sharkey, R.; Karacay, H.; D'Souza, C.; Rosso, E.; Laverman, P.; Chang, C.; Boerman, O.; Goldenberg, D. *J. Nucl. Med. Chem.* **2009**, *50*, 991. (d) Shetty, D.; Choi, S. Y.; Jeong, J. M.; Lee, J. Y.; Hoigebazar, L.; Lee, Y.-S.; Lee, D. S.; Chung, J. K.; Lee, M. C.; Chung, Y. K. *Chem. Commun.* **2011**, *47*, 9732.

(4) (a) Malik, M. A.; O'Brien, P. In *Group 13 Metals Aluminium, Gallium, Indium and Thallium*, 2nd ed.; Aldridge, S., Downs, A. J., Eds.; Blackie: London, 2011; Chapter 10, p 612. (b) Malik, M. A.; Afzaal, M.; O'Brien, P. *Chem. Rev.* **2010**, *110*, 4417. (c) Jones, A. C.; O'Brien, P. In *CVD of Compound Semiconductors: Precursor Synthesis, Development and Applications*; Wiley-VCH: Weinheim, 1997.

(5) Dagorne, S.; Bellmin-Laponnaz, S. In *Group 13 Metals Aluminium, Gallium, Indium and Thallium*, 2nd ed.; Aldridge, S.; Downs, A. J., Eds.; Blackie: London, 2011; Chapter 11, p 654.

(6) (a) Gurnani, C.; Levason, W.; Ratnani, R.; Reid, G.; Webster, M. *Dalton Trans.* **2008**, 6274. (b) Mishra, S.; Jeanneau, E.; Daniele, S. *Polyhedron* **2010**, *29*, 500.

(7) (a) Cheng, F.; Davis, M. F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Inorg. Chem.* **2007**, *46*, 7215. (b) F. Cheng, F.; Friend, S. I.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Inorg. Chem.* **2008**, *47*, 9691.

(8) Gurnani, C.; Jura, M.; Levason, W.; Ratnani, R.; Reid, G.; Webster, M. *Dalton Trans.* **2009**, 1611.

(9) Batchelor, R. J.; Einstein, F. W. B.; Gay, I. D.; Gu, J.-H.; Johnston, B. D.; Pinto, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 6582.

(10) Kemmitt, T.; Levason, W. *Organometallics* **1989**, *8*, 1303.

(11) Levason, W.; Nirwan, M.; Ratnani, R.; Reid, G.; Tsoureas, N.; Webster, M. *Dalton Trans.* **2007**, 439.

(12) Levason, W.; Ollivere, L. P.; Reid, G.; Tsoureas, N.; Webster, M. *J. Organomet. Chem.* **2009**, *694*, 2299.

(13) Sheldrick, G. M. *SHELXS-97, Program for crystal structure solution*; University of Göttingen: Göttingen, Germany, 1997.

(14) Sheldrick, G. M. *SHELXL-97, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

(15) Tetrahedral $[MCl_4]^-$ show two Raman-active stretches (a_1 + t_2) and one IR-active stretch (t_2). M = Ga: a_1 = 346, t_2 = 386 cm^{-1}. M = In: a_1 = 321, t_2 = 337 cm^{-1}.

(16) Nakamoto, K. *IR Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1970.

(17) ^{71}Ga has $I = 3/2$, a natural abundance of 39.6%, $\Xi = 30.495$ MHz, and a quadrupole moment (Q) of 0.112×10^{-28} m^2. The ^{115}In nucleus, while inherently very sensitive, has a moderately large quadrupole moment [^{115}In, 95.7%, $I = 9/2$, $\Xi = 21.914$ MHz, $Q = 1.16 \times 10^{-28}$ m^2, $D_c = 1890$].

(18) The tetraselenoether 1,2,4,5-$C_6H_2(CH_2SeMe)_4$ was not included due to the observation that even *o*-$C_6H_4(CH_2SeMe)_2$ is fragmented by MCl_3 (M = Ga or In).

(19) For examples, see: (a) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796. (b) Atwood, J. L.; Hrncir, D. C.; Shakir, R.; Dalton, M. S.; Priester, R. D.; Rogers, R. D. *Organometallics* **1982**, *1*, 1081. (c) Self, M. F.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1991**, *10*, 36. (d) Robinson, G. H.; Zhang, H.; Atwood, J. L. *Organometallics* **1987**, *6*, 887.

(20) Levason, W.; Maheshwari, S.; Ratnani, R.; Reid, G.; Webster, M.; Zhang, W. *Inorg. Chem.* **2010**, *49*, 9036.

(21) (a) Evans, J.; Levason, W.; Manning, J. M.; Reid, G.; Tsoureas, N.; Webster, M. *Dalton Trans.* **2007**, 1986. (b) Levason, W.; Manning, J. M.; Pawelzyk, P.; Reid, G. *Eur. J. Inorg. Chem.* **2006**, 4380.

(22) (a) Evans, D. H.; Gruhn, N. E.; Jin, J.; Li, B.; Lorance, E.; Okumura, N.; Macias-Ruvalcaba, N. A.; Zakai, U. I.; Zhang, S.-Z.; Block, E.; Glass, R. S. *J. Org. Chem.* **2010**, *75*, 1997. (b) Fujihara, H.; Akaishi, R.; Furukawa, N. *Tetrahedron* **1993**, *49*, 1605. (c) Fujihara, H.; Akaishi, R.; Nakamura, A.; Furukawa, N. *Tet. Lett.* **1990**, *31*, 6375. (d) Iwasaki, F.; Morimoto, M.; Yasui, M.; Akaishi, R.; Fujihara, H.; Furukawa, N. *Acta Crystallogr., Sect. C* **1991**, *47*, 1463.

(23) (a) Batchelor, R. J.; Einstein, F. W. B.; Gay, I. M.; Gu, J.-H.; Pinto, B. M.; Zhou, X.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3706. (b) Nakahodo, T.; Takahashi, O.; Horn, E.; Furakawa, N. *Chem. Commun.* **1997**, 1767.