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Cationic group 13 complexes

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Abstract

In order to provide a foundation for continued work on group 13 cations as a class of distinct compounds, this overview will provide a classification system based upon the reactions that are used in their formation. The literature on the formation of aluminum cations is broad so the classification system will be developed with a focus on this element. However, in most cases the reaction types are of sufficient generality such that they can be applied to gallium and indium as well. In some instances the formation of gallium and indium cations occur through unique routes. In these cases new reaction types will be defined in the gallium and indium chemistry. At this point in time the interest in group 13 cations has largely been fundamental in nature. However, there is a growing awareness that these types of complexes may be applicable to a wide range of Lewis acid mediated reactions and catalytic applications. Brief mention will be made of those that are currently known.

Keywords: Group 13 cations; Gallium; Indium; Aluminium

1. Introduction

Historically viewed as scientific curiosities, group 13 cations are now receiving increasing attention due to their potential as Lewis acid catalysts [1–3]. It is likely that most of the transformations conducted with neutral group 13 derivatives [4] could also be accomplished with those that are cationic. These would have enhanced Lewis acidity by comparison and could easily be air stable. This would remove one of the primary difficulties in handling neutral reagents; their often explosive air sensitivity. However, up till this point group 13 (Al, Ga, In) cations have yet to be treated as a general class of compounds. This is in contrast to charged boron [5,6] and thallium [7] systems which have a rich history of usage in organic synthesis.

In order to provide a foundation for continued work on group 13 cations as a class of distinct compounds, this overview will provide a classification system based upon the reactions that are used in their formation. The literature on the formation of aluminum cations is broad so the classification system will be developed with a focus on this element. However, the reaction types are of sufficient generality to be applied to gallium and indium as well. Where applicable new reaction types will be defined in the gallium and indium chemistry. The aqueous chemistry of the group 13 elements has been reviewed recently and so will not be covered to an appreciable extent in the present work [8]. Other useful reviews of the group 13 elements include some that are general [9–12], and focused (fluorides of Al, Ga, In, Tl) [13].

2. Formation of trivalent derivatives

The formation reactions fall into seven different categories based upon the types of starting materials that are used to generate the cation. Six of these have been demonstrated for aluminum and account for the majority of work done in this area. There are substantially fewer gallium and indium cations although their formation reactions are the same as aluminum. The only exception is the autoionization reaction that has only been observed for indium. Table 1 contains selected information on the majority of known group 13 cations. They are grouped by element and listed in the order in which each formation reaction is described in text.

2.1. *Asymmetric cleavage*

2.1.1. *Aluminum*

This reaction was involved in the formation of the well-known boron salt $[BH_2(NH_3)_2]^+$ $[BH_4]^-$ [14,15]. For aluminum compounds this generally involves the cleavage of a halide-bridged dimeric compound. Like the boron diammoniate it also involves the action of a Lewis base. Thus $[AlCl_2(NH_3)_4]^+$ $[AlCl_4]^-$ forms from the asymmetric cleavage of $[AlCl_3]_2$ in the presence of NH_3 [16]. Other early examples of products derived from this reaction are $[AlCl_2(Py)_4]^+$ $[AlCl_4]^-$ and $[AlCl_2(thf)_4]^+[AlCl_4]^-$ [17,18].

$$[R_2Al(\mu - Cl)]_2 + n\text{Base} \rightarrow [R_2Al(\text{base})_n]^+ [R_2AlCl_2]^- \ (R = \text{halide, alkyl, aryl}) \quad (1)$$

The halides on the cation can be replaced by other groups through salt elimination reaction as demonstrated in the formation of $[L_2Al]^+$ $[AlCl_4]^-$ $\{L = \eta^3\text{-HB(3-Phpz)}_2\text{(5-Phpz)}\}$ [19]. The formation of this compound might be aided by the relative stability of six- and four-coordinate aluminum atoms rather than two that are five-coordinate ($LAlCl_2$).

Table 1
A listing of formation reactions for Al, Ga, and In.

Compound	Structural Parameters (Å or deg)	Reference
	Aluminum	
Asymmetric cleavage		
$[Cl_2Al(NH_3)_4]^+ [AlCl_4]$	Al–Cl 2.318(2); Al–N 2.004(4) (*trans*-Cl)	[16]
$[Cl_2Al(py)_4]^+ [AlCl_4]^-$	Al–Cl 2.279(3); Al–N 2.070(4) (*trans*-Cl)	[17]
$[Cl_2Al(thf)_4]^+ [AlCl_4]^-$	Al–Cl 2.230(9); Al–O 1.94(1) (*trans*-Cl)	[18]
$[Cl_2Al(NH_3)_4]^+ [AlCl_4(NH_3)_2]^-$	Al–Cl 2.324(2); Al–N 2.019(2) (*trans*-Cl)	[93]
$[Cl_2Al(12\text{-crown-}4)]^+ [AlCl_4]^-$		[94]
$[Cl_2Al(18\text{-crown-}6)]^+ [AlMe_2Cl_2]^-$	(*cis*-Cl)	[97]
$[Cl_2Al(15\text{-crown-}5)]^+ [AlMe_2Cl_2]^-$	(*trans*-Cl)	
$[Me_2Al(18\text{-crown-}6)]^+ [AlMe_2Cl_2]^-$	Al–C 1.915(6), 1.939(7); Al–O 1.929(5) (*trans*-Me)	[23]
$[Me_2Al(15\text{-crown-}5)]^+ [AlMe_2Cl_2]^-$	Al–C 2.00(2); Al–O 2.13(1), 2.26(1) (*trans*-Me)	[23]
$[(AlEt)_2(aza\text{-crown}]^{2+}\ 2[AlEtCl_3]^-$	Al–C 1.944(5); Al–O 1.950(5), 1.959(5) Al–N 1.972(3), 1.963(4)	[21,22]
$[H_2Al(thf)_4]^+ [(Cp_3Yb)_2Na]^-$	Al–O 2.01(1), Al–H 1.48 (*trans*-H)	[95]
$[{}^tBu_2Al(tmeda)]^+ [Al({}^tBu)_2X_2]^-$ (tmeda = tetramethylethylenediamine; X = Cl, Br)	For X = Cl: Al–C 2.006(6); Al–N 2.043(6)	[25]
$[Me_2Al(pmedta)]^+ [AlMe_2Cl_2]^-$ (pmedta = pentamethylethylenetriamine)	Al–C 1.96(1); Al–N 2.067(3)-2.286(4)	[26]
$[Al(pz)_2]^+ [AlCl_4]^-$ (pz = η^3-HB(3-phenylpyrazolyl)$_2$(5-phenylpyrazolyl))	Al–N 1.949(8)-2.066(8)	[19]
Halide displacement		
$[{}^tBu_2Al(tmeda)]^+ X^-$	(X = Cl, Br)	[25]
$[R_2Al(NH_2{}^tBu)_2]^+ X$	X = Br; R = Me, Al–N 1.995(8), Al–C 1.953(3) C–Al–C 116.6(3), N–Al–N 97.5(2)	[32,33]
	X = I; R = Me, Al–N 1.992(6), Al–C 1.95(2) C–Al–C 117.9(4), N–Al–N 98.2(3)	[32,33]
	X = Br; R = Et, X = Br; R = ^{i}Bu	[32,33]
$[Me_2Al(base)_n]^+ Br^-$ (base, n = H_2N^tBu, 2; $OPPh_3$, 2; pmedta, 1)		[26]
$[X_2Al(base)_2]^+ X^-$	base = bipyridine, X = Cl: Al–Cl 2.256(6), Al-N 2.032(6) Cl–Al–Cl 96.4(1) base = phenanthroline	[96]

Table 1 (*Continued*)

		Al-O(base)	Al-O	Al-N	
$[LAl(base)_2]^+\ Cl^-$ (L = Salen, Salen(Cl), Acen; base = H_2O, MeOH)	L = Salen, base = H_2O,	1.95(2)	1.82(2)	1.980(5)	[1,2]
$[LAl(hmpa)_2]^+\ X^-$	L = 2-aminophenol; X = Cl	1.905(2)	1.841(9)	2.037(3)	[35]
	L = Salen; X = Cl	1.92(1)	1.828(4)	2.007(5)	
	L = Salen; X = CF_3SO_3	1.905(4)	1.815(8)	2.00(1)	
	L = Salen; X = I	1.924(6)	1.815(1)	2.023(2)	
Halide or alkyl abstraction					
$[R_2Al]^+\ [AlCl_4]^-$ (R = $2\text{-}C(SiMe_3)_2C_5H_4N$)	Al–C 2.00(2), Al–N 1.92(1)				[40]
$[SalenAl(thf)_2]^+\ [AlCl_4]^-$	Al–O(thf) 2.001(7), Al–O 1.795(4), Al–N 1.997(8) (*trans*-thf)				[35]
$[Cp_2Al]^+\ [MeB(C_6F_5)_3]^-$					[42]
$[{}^tBu(CNR)_2AlMe]^+\ [MeB(C_6F_5)_3]^-$					[3]
Halide elimination					
$[Al(tpp)(thf)(H_2O)]^+\ \{[Fe(tpp)(thf)][Cu(mnt)_2]\}\cdot 2thf$ (tpp = 5,10,15,20-tetraphenylporphyrinate, mnt = *cis*-1,2-dicyanoethylenedithiolate)	Al–O(thf) 2.069(7), Al–N 2.006(9) Al–O(H_2O) 1.912(8)				[97]
$[LAl(MeOH)_2]^+\ [BPh_4]^-$	L = Salen(Cl), Salen; Al–O(MeOH) 1.99(2), Al–O 1.803(8) Al–N 1.982(1) L = Acen; Al–O(MeOH) 1.96(2), Al–O 1.80(2) Al–N 1.98(1)				[2]
$[Me\{CN({}^iPr)\}_2AlMe(base)]^+\ [B(C_6F_5)_4]^-$ (base = NMe_2Ph, PMe_3)					[3]
Redistribution					
$[Cl_2Al(benzo\text{-}15\text{-}crown\text{-}5)]^+[AlCl_3Et]^-$	Al–Cl 2.2; Al–O 2.0-2.3 (*trans*-Cl)				[20]
$[R_2Al(crown)]^+\ [R_2AlX_2]^-$ (X = Br, I; R = Me, Et)					[21]
$[RAlX(crown)]^+\ [R_3AlX]^-$ (X = Br, I; R = Me, Et)					
$[Al_2Cl_2(acac)_3]^+$ (acac = acetylacetonate)	$[AlCl_4]^-$ Al–Cl 2.104(18), 2.108(2) Al–O 1.767(34)-1.933(29)				[53]
$[(acac)_2Al(base)]^+\ [AlCl_4]^-$ (base = thf, dme, dmf, Et_2O, dmp, py)					[54–56]
$[Al(C_5Me_5)]^+\ [Li(C_5Bz_5)_2]^-$					[58]
$[\eta^5\text{-}Cp^*{}_2Al]^+\ [\eta^1\text{-}CpAlCl_3]^-$	Al–Cen 2.16(3), Cen–Al–Cen (linear)				[57]
$[H_2Al(L)]^+\ [AlH_4]^-$ L = pmedta	Al–N 2.01(1)-2.158(7), Al–H 1.62				[59]
L = Me_4cyclam	Al–N 2.13(2), Al–H 1.60, 1.64				

Table 1 (*Continued*)

Ligand conversion		
$[(pmedtaH)AlCl]^+ X^-$ (X = Cl and $AlCl_4$)	Al–Cl 2.103(2), Al–NH 1.947(3) Al–N 1.947(3), 1.963(3)	[62]
	Gallium	
Reaction 1. Asymmetric cleavage		
$[GaCl_2(py)_2]^+ [GaCl_4]^-$	Ga–Cl 2.3, Ga–N 2.2, (*trans*-Cl)	[98]
$[GaCl_2(monoglyme)_2]^+ [GaCl_4]^-$		[99]
$[GaCl_2(4\text{-}Mepy)_4]^+ [GaCl_4]^-$	Ga–Cl 2.32(2), Ga–N 2.106(3)	[30]
$[GaCl_2(bipy)_2]^+ [GaCl_4]^-$	Ga–Cl 2.265(1), Ga–N 2.095(4), 2.111(4) Cl–Ga–Cl 97.3(1)	[27]
$[L_2Ga]^+ [GaCl_4]^-$ L = pz	Ga–N 2.064(5)	[28]
L = BnN	Ga–C 1.95(1), 2.09(1)	[29]
L = dab	Ga–N 1.981(2)	[29]
Reaction 2. Halide displacement		
$[Me_2Ga(NH_3)_2]^+ Cl^-$		[36,37]
$[Me_2Ga(NH_2{}^tBu)_2]^+ Br^-$	Ga–C 1.99(2), Ga–N 2.040(8)	[39]
Reaction 3. Halide (or alkyl) abstraction		
$[I_2Ga(L)]^+ [GaI_4]^-$ L = 18-Crown-6		[43]
$[R_2Ga]^+ GaCl_4{}^-$ ($R = 2\text{-}C(SiMe_3)_2C_5H_4N$)		[44]
Reaction 4. Halide elimination		
$[Me_2Ga(base)_2]^+ X^-$ (base = NH_3, $X = BH_4$; base = H_2O, $X = ClO_4, NO_3$)		[48]
$([R_2Ga(H_2O)_2]^+)_2 [SO_4]_2{}^-$ (R = Me, Et)		[49]
$[Ga(tpp)(thf)_2]^+ \{[Fe(tpp)(thf)][Cu(mnt)_2]\}$ (tpp = 5,10,15,20-tetraphenylporphyrinate, mnt = *cis*-1,2-dicyanoethylenedithiolate)	Ga–O 2.13(3), Ga–N 2.02(2)	[50]
Reaction 6. Ligand conversion		
None reported		
	Indium	
Reaction 1. Asymmetric cleavage		
$[InX_2(Ph_3P=O)_4]^+ [InX_4]^-$ (X = Br and Cl)	In–Cl 2.428(6), In–O 2.15 (*trans*-Cl)	[31]
$[InBr_2(Ph_2MeP=O)_4]^+ [InBr_4]^-$		

Table 1 (*Continued*)

Reaction 2. Halide displacement		
None reported		
Reaction 3. Halide (or alkyl) abstraction		
$[I_2In(L)]^+ [InI_4]^-$ L = dibenzo-18-crown-6 and 18-crown-6:	In–I 2.618, In–O 2.43-2.96 I–In–I 170.14(4)	[43]
Reaction 4. Halide elimination		
$([R_2In(H_2O)_2]^+)_2 [SO_4]^{2-}$ (R = Me, Et)		[49]
Reaction 5. Redistribution		
$[^{i}Pr_2In(thf)_2]^+ [BF_4]^-$	In–C 2.128(6), In–O 2.36(8), In ··· F 2.62(4) C–In–C 160.3(4)	[60]
$[^{i}Pr_2In]^+ [BF_4]^-$		[60]
$[R_2In]^+ BF_4^-$ (R = CH_2Ph; Mes)	In–C 2.13(1), In ··· F 2.713(7), C–In–C 174(1)	[61]
$[(dibenzo\text{-}18\text{-}crown\text{-}6)InX_2]^+ [InX_4]^-$ (X = Cl, Br, I)		[45]
Reaction 7. Ligand conversion		
None reported		
Reaction 8. Autoionization		
$[Me_2In]^+ Br^-$	In ··· Br 3.105, In–C 2.17, C–In–C 180	[64]
$[Me_2In]^+ [InI_4]^-$		[63]
$[Me_2In(H_2O)]^+ X^-$		[49]
Univalent Cations		
	Gallium	
$[(C_6H_6)_2Ga]^+ [GaX_4]^-$ (X = Br, Cl)	Ga ··· Cl 3.716, Ga–Cen 2.758 and 2.929 Cen–Ga–Cen, 124.4	[80]
$[(Me_3C_6H_3)_2Ga]^+ [GaCl_4]^-$		[82]
$[(C_6Et_6)(C_6H_5Me)Ga]^+ [GaCl_4]^-$	Ga ··· Cl, 2.15, 2.19; Ga–Cen 2.535, 3.145 Cen–Ga–Cen, 137.2(1)	[84]
$[(Me_4C_6H_2)(MeC_6H_5)Ga]^+ [GaCl_4]^-$	Ga ··· Cl, 2.14-2.17; Ga–Cen 2.642, 3.039(tol) Cen–Ga–Cen, 118.7	[81]
$[Me_6C_6]^+ [GaX_4]^-$ (X = Cl)	Ga ··· Cl 2.18, Ga–Cen 2.43, 2.51	[85]
(X = Br)	Ga ··· Br 3.347, Ga–Cen 2.552	[86]
$[LGa]^+ GaX_4^-$ (L = [2.2]paracyclophane; X = Cl, Br)	Ga ··· Br 2.3, Ga–Cen 2.733(8) Cen–Ga–Cen 131.1(8)	[88]

Table 1 (*Continued*)

	Indium	
$[(Me_3C_6H_3)_2In]^+ [InBr_4]^-$	In ··· Br ~ 3.5	[83]
$[LIn]^+ InBr_4^-$ (L = [2.2]paracyclophane)	In ··· Br ~ 2.5, In–Cen 2.95, Cen–In–Cen 124.4	[89]
$[LIn]^+ [InX_4]^-$ (X = Cl, Br, I; L = dibenzo 18-crown-6 and cyclam)		[45]

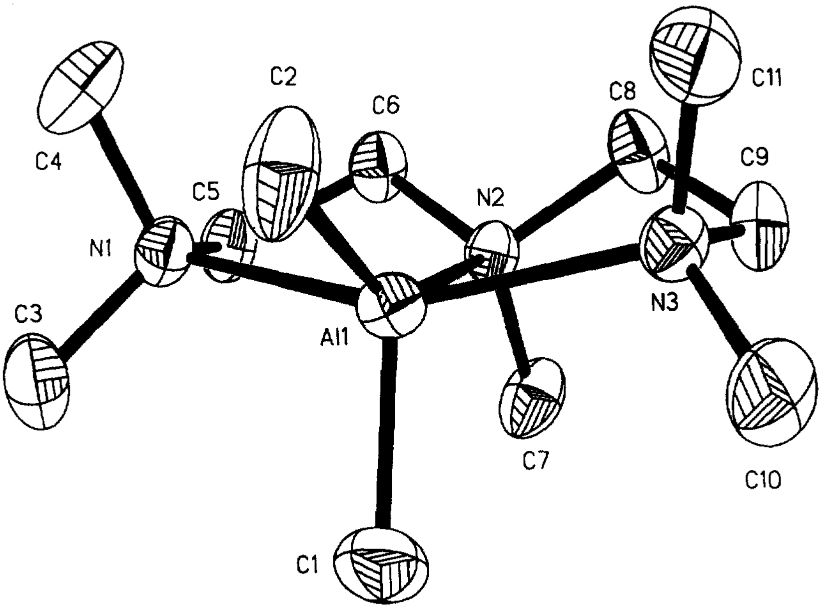


Fig. 1. The cation of $[Me_2Al(pmedta)]^+$ $[Me_2AlCl_2]^-$

A wide range of cationic complexes can be prepared in conjunction with crown ethers [20] and aza-crowns [21,22]. A representative example is the formation of $[Me_2Al(18\text{-crown-}6)]^+$ $[Me_2AlCl_2]^-$ [23]. (There is some evidence that a redistribution process is occurring in these systems leading also to the formation of the $[R(X)Al\text{-crown ether}]^+$cations) [24]. The use of one equivalent of tmeda with $[^tBu_2Al(\mu\text{-}X)]_2$ leads to $[^tBu_2Al(tmeda)]^+$ $[^tBu_2AlX_2]^-$ (X = Cl, Br) although the halide-displaced products $[^tBu_2Al(tmeda)]^+$ X^- can also be isolated by changing the solvent or by using two equivalents of tmeda [25].

A five-coordinate cationic species (with $Me_2AlCl_2^-$ as the counter anion) is obtained from pmedta (pentamethyldiethylenetriamine) and $[Me_2Al(\mu\text{-}X)]_2$ with X = Cl (the cation is shown in Fig. 1), but not with X = Br [26]. It would appear that the asymmetric cleavage reaction predominates for the chlorinated derivatives (which exist as chloride-bridged dimers) and that the presence of a base to promote this cleavage is a necessity.

2.1.2. Gallium

Four-coordinate cations can be formed by the action of a bidentate chelate. This has been demonstrated with bipy in the formation of $[GaCl_2(bipy)_2]^+$ $[GaCl_4]^-$ [27]. Other compounds are the result of an asymmetric cleavage of the $[GaCl_3]_2$ dimer followed by a salt elimination reaction. This was used to form the six-coordinate complexes $[L_2Ga]^+$ $[GaCl_4]^-$ (L = tris(3,5-dimethyl-1-pyrazolyl)hydridoborate [28], L = 2-(dimethylamino)benzyl [29], and L_2 = 1,4-diazabutadiene) [29]. The product, $[GaCl_2(4\text{-methylpyridine})_4]^+$ $GaCl_4^-$ may be viewed as forming after disproportionation of a Ga(II) starting material and asymmetric cleavage of the dimeric Ga(III) intermediate [30]. It is also six-coordinate and structurally similar to the $[AlCl_2(\text{base})_4]^+$ cations.

2.1.3. *Indium*

Asymmetric cleavage would appear to be responsible for the formation of the ionic derivatives $[X_2In(Ph_3P=O)_4]^+$ $[InX_4]^-$ (X = Cl, Br) if the presence of the halide bridged dimers, $[X_2In(\mu\text{-}X)]_2$, is assumed [31]. When the base $Ph_2MeP{=}O$ is used with X = Cl the adduct, $InCl_3(\text{base})_3$ forms, but the charged system, $[InBr_2(\text{base})_4]^+$ $[InBr_4]^-$ forms with X = Br.

2.2. *Halide displacement.*

2.2.1. *Aluminum*

This is related to reaction (2.1) since it involves a symmetric cleavage of a dimeric halide-bridged species. The result is a tetracoordinate species containing covalent bonds and one coordinate covalent bond from the incoming base. In forming the cation a second mole of base acts to displace the halide. This leads to a four-coordinate cation with the X group as the counter-anion. In studies of the adducts (Eq. (2)b) for combinations where R = Me, Et, ^{i}Bu, ^{t}Bu; X = F, Cl, Br and I, it was shown that cations form with X = Br and I and when the base = NH_2^iBu, NH_2^tBu and $Ph_3P{=}O$ (the cation of $[Me_2Al(NH_2^tBu)_2]^+$ Br^- is shown in Fig. 2 [32,33]. Other strong bases and primary amines are expected to work with bromide and iodide as well. For instance, the adduct, $^tBu_2AlBr(\text{tmeda})$ (tmeda = tetramethylethylenediamine)slowly converts to the ion pair $[^tBu_2Al(\text{tmeda})]^+$ Br^- in solution [25]. The complex, $[(\text{pmedta})AlMe_2]^+$ Br^-, forms from the combination of the ligand with $[Me_2Al(\mu\text{-}Br)]_2$ [26].

$$1/2\left[\underset{(a)}{R_2M(\mu - X)}\right]_2 \xrightarrow[\text{base}]{} \underset{(b)}{R_2MX(\text{base})} \xrightarrow[\text{base}]{} \left[R_2M\left(\underset{(c)}{\text{base}}\right)_2\right]^+ X^- \qquad (2)$$

$$X^-(R = \text{alkyl}, X = \text{halide})$$

Based upon the fact that $Ph_3P{=}O$ and non-protic bases are effective in inducing cation formation, it is likely that the mechanism involves a higher coordinate group 13 species rather than a hydrogen-bonded intermediate (with hydrogen bonding between the halide and incoming primary or secondary amine). The availability of a fifth coordination site in these types of complexes has been supported experimentally for some indium compounds [34].

Halide displacement also occurs in the tetradentate-chelate compounds, LAlX

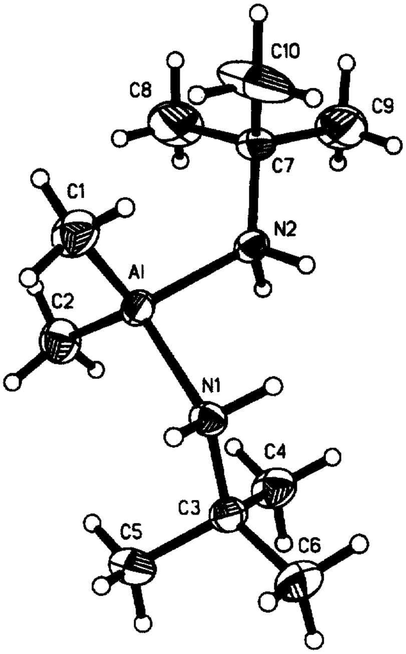


Fig. 2. The cation of $[Me_2Al(NH_2^tBu)_2]^+ Br^-$

(where L = Salen, SalenCl, Acen; and X = Cl, OTf, I) when the bases, MeOH [1,2], H_2O [1,2], HMPA [35], and thf [35] are added. This leads to the extensive class of six-coordinate cations of general formula, $[LAl(base)_2]^+ X^-$. (The cation of $[SalenAl(H_2O)_2]^+ Cl^-$ is shown in Fig. 3.) The utilization of a sixth coordination site and trans activation of the halide is likely in the cation formation. This would explain why chloride displacement occurs with these compounds and not with the four-coordinate analogues. Although the gallium and indium derivatives have not been reported it is clear that, at least for gallium, that such cations should be easily accessible.

2.2.2. Gallium

The first gallium cation, $[Me_2Ga(NH_3)_2]Cl$, was prepared in 1933 [36], although it was not accurately described as a cation until 1962 [37]. The formation of this compound contrasts with the related aluminum chloride complexes which form adducts. This difference may be explained in terms of the lessened strength of the Ga–Cl bond (~ 350 kJ mol^{-1}) [38] when compared to an Al–Cl bond (~ 420 kJ mol^{-1}). An example of bromide displacement is $[Me_2Ga(NH_2^tBu)_2]Br$ [39]. It is clear that a wide range of these could be made simply by combining a $[R_2GaX]_2$ reagent with an excess of just about any type of strong Lewis base. The ease of cation formation should increase with the size of the halide.

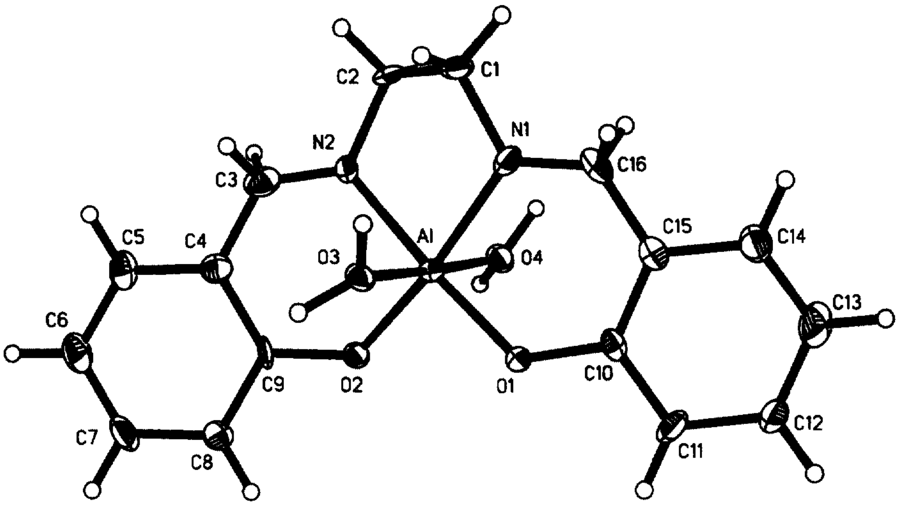


Fig. 3. The cation of $[SalenAl(H_2O)_2]^+ Cl^-$

2.3. Halide (or alkyl) abstraction

2.3.1. Aluminum

The halide can be removed from an alkyl aluminum compound by the action of a Lewis acid. Lewis basic groups must usually be present in order to stabilize the newly formed cationic aluminum center. When the added Lewis acid is an aluminum reagent the products bear a similarity to those derived from an asymmetric cleavage (reaction 2.1). This reaction was used to prepare $[\{2\text{-}C(SiMe_3)_2C_5H_4N\}_2Al]^+ [AlCl_4]^-$ from the R_2AlCl species and added $AlCl_3$ [40]. There are some inherent limitations to this reaction. For instance, combination of the tridentate ligated complex, $\{(^iPr_2PCH_2SiMe_2)_2N\}Al(Et)Cl$ with $AlCl_3$ leads to a neutral bimetallic complex [41].

Use of the Cp (cyclopentadienide) group on aluminum obviates the need for the added Lewis base. Abstraction of methyl from Cp_2AlMe with $B(C_6F_5)_3$ leads to the base-free complex, $[Cp_2Al]^+ [MeB(C_6F_5)_3]^-$ [42].

$$[R_2AX]_{1,2} + \text{Lewis base} + \text{Lewis acid} \rightarrow [R_2Al(\text{base})_2]^+ [\text{acid} - X]^- \qquad (3)$$

2.3.2. Gallium

Addition of 18-crown-6 to $Et_2O\text{–}GaI_3$ leads to $[I_2Ga(crown)]^+ GaI_4^-$ [43]. It may be envisioned to proceed through chelation of one of the GaI_3 molecules which is subsequently de-halogenated by the second GaI_3 molecule. The intramolecularly base-stabilized four-coordinate cation, $[R_2Ga]^+ GaCl_4^-$ ($R = 2\text{-}C(SiMe_3)_2C_5H_4N$) was prepared by the addition of $GaCl_3$ to the five-coordinate R_2GaCl derivative [44].

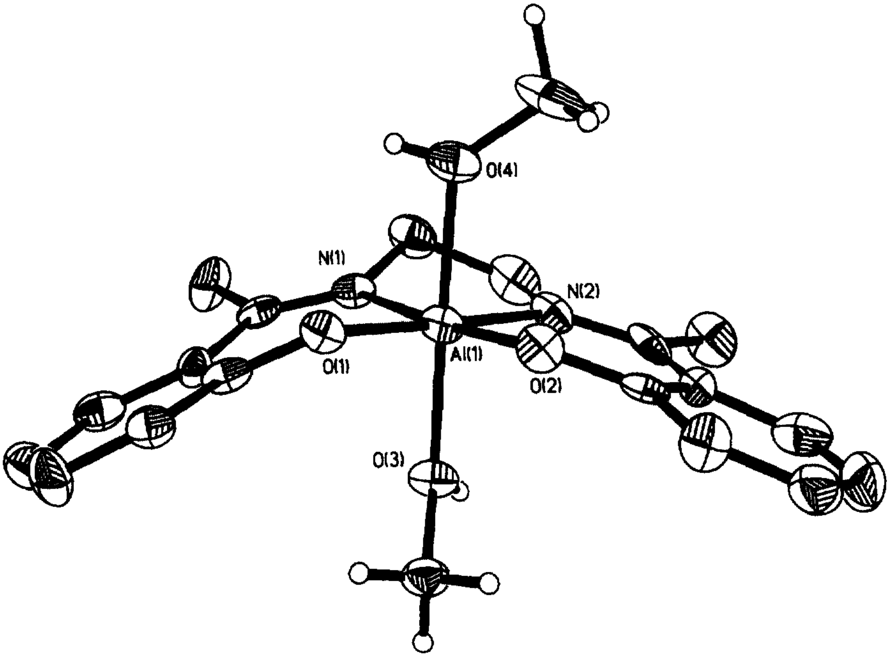


Fig. 4. The cation of $[\mathrm{AcenAl(MeOH)_2}]^+$ $[\mathrm{BPh_4}]^-$

2.3.3. Indium

The same reaction is used to prepare indium derivatives with a wider range of chelates and halogens (e.g. $[\mathrm{X_2In(L)}]^+$ $\mathrm{InX_4^-}$ (L = 18-crown-6; X = I; L = dibenzo-18-crown-6, X = Cl, Br, I [43]).

2.4. Halide elimination

2.4.1. Aluminum

The halide originally on the aluminum atom may be removed from the reaction and replaced by a non-coordinating anion. This is performed by a salt elimination reaction between an aluminum halide derivative and a metallated reagent. It has most commonly been observed for the formation of chelated derivatives having the form: $[\mathrm{LAl(base)_2}]^+$ $\mathrm{BPh_4^-}$ (where L = Salen, SalenCl, Acen) [1,2,35]. (The cation of $[\mathrm{AcenAl(MeOH)_2}]^+$ $[\mathrm{BPh_4}]^-$ is shown in Fig. 4.)

$$\mathrm{LAlX} + \mathrm{ME} + \mathrm{base} \xrightarrow[-\mathrm{MX}]{} [\mathrm{LAl(base)_2}]^+\ \mathrm{E}^- \qquad (4)$$

where: M = metal (I); E = anion; and X = halide.

Attempts to form the analogous six-coordinate gallium complexes have thus far been unsuccessful. The result is generally a mixture of uncharacterizable products except in one instance, were the unusual bimetallic cation,

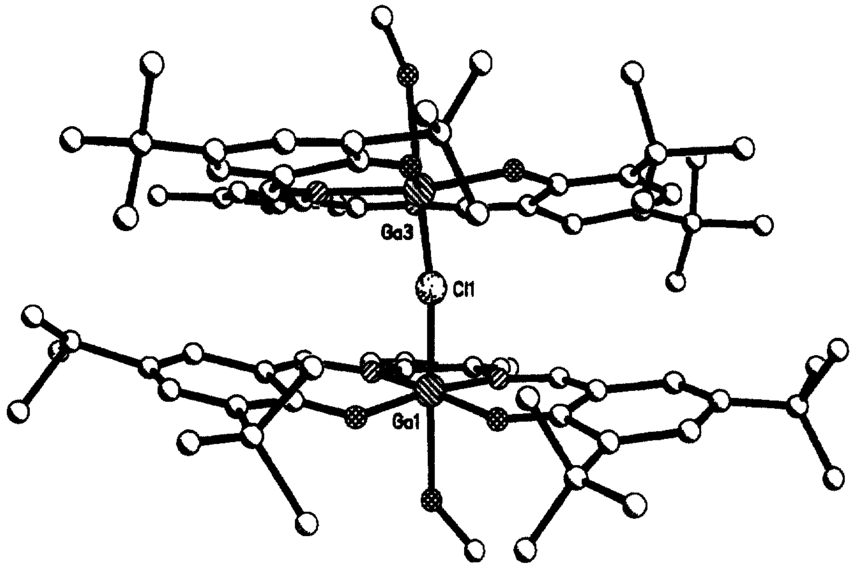


Fig. 5. The cation of $[\{\text{Salomphen(tBu)Ga(MeOH)}\}_2(\mu\text{-Cl})]^+$ $[BPh_4]^-$

$[\{\text{Salomphen(tBu)Ga(MeOH)}\}_2\,\mu\text{-Cl}]^+$ BPh_4^- (the cation is shown in Fig. 5) was isolated [46]. It is related to the cation, $[\{\text{MeC(NiPr)}_2\text{AlMe}\}_2\,\mu\text{-Me}]^+$ $[B(C_6F_5)_4]^-$ [3].

2.4.2. Gallium

New cationic derivatives can be prepared by metathesizing the chloride of $[Me_2Ga(NH_3)_2]^+$ Cl^- with [37] $NaBH_4$ and by replacing the NH_3 groups with an ethylenediamine (en) ligand. This latter reaction is the only member of what could be called a ligand substitution reaction. Since it takes place on a pre-formed cation it is not a true cation forming reaction and is not numbered in the reactions listed herein.

The Me_2Ga^+ fragment is remarkably stable [47]. Thus, cations containing this fragment can be obtained from aqueous solution containing an appropriate HX reagent and $[Me_2GaOH]_4$. This version of the halide elimination reaction (taking the OH- group to be a pseudo-halide) can be used to prepare $[Me_2Ga(H_2O)_2]^+$ X^- (where X = ClO_4^- and NO_3^-) [48]. Alternatively, the trialkyl derivative (R = Me or Et) can be combined with anhydrous H_2SO_4 to form, $[R_2Ga]_2SO_4$. The aqueous cation is then formed by the addition of water [49]. Although this may be viewed as a halide displacement it is possible that the dialkylgallium sulfate exists as a salt in the solid state (as observed for some R_2In^+ derivatives, see below). Removal of X^- from TPPGaX (X = O_2CCF_3) leads to the formation of the cation $[TPPGa(thf)_2]^+$ with an Fe–Cu based anion [50].

2.4.3. Indium

As for gallium, the trialkyl derivative (R = Me or Et) can be combined with anhydrous H_2SO_4 to form, $[R_2In]_2SO_4$ [49]. Subsequent dissolution in water produces the hydrated cation. Under similar conditions $[R_2InOOCCH_3]$ does not ionize [51].

2.5. Redistribution

2.5.1. Aluminum

Group 13 compounds are well-known to undergo redistribution reactions in solution [52]. This also occurs in the formation of aluminum cations by exchange of ligands and/or halide between two or more aluminum centers. A good example of how this operates can be found in an acac derivative (Eq. (5)) (acac = acetylacetonate) [53]. A bimetallic cationic fragment forms as part of an equilibrium mixture. Addition of base to this mixture leads to a six-coordinate cation (c). Other acac derivatives include those of the formula $[(acac)_2Al(base)_n]^+$ $AlCl_4^-$ (base = thf [54], dme (dimethoxyethane), dmf (dimethylformamide) [55], Et_2O, dmp (2,6-dimethylpyridine), py [56]) prepared by adding the base to $(acac)AlCl_2$ (apparently a monomer).

In its most simple form the redistribution reaction can involve the transfer of one alkyl group. This is observed in the formation of $[Cp^*_2Al]^+$ $[\eta^1\text{-}Cp^*AlCl_3]^-$ from Cp^*_3Al and $AlCl_3$ [57]. A related reaction involves the disproportionation and redistribution of CpAl with LiC_5Bn_5 (Bn = $-CH_2Ph$) to yield, as a minor product, the salt $[Cp_2Al]^+$ $[Li(C_5Bn_5)_2]^-$ [58]. After loss of NMe_3 a single hydride transfer occurs in the combination of $AlH_3{-}NMe_3$ with PMEDTA to form $[(PMEDTA)AlH_2]^+$ $[AlH_4]^-$ [59].

$$\underset{(a)}{3Cl_2Al(acac)} \leftrightarrow \left[\underset{(b)_3}{Al_2Cl_2(acac)_3}\right]^+ [AlCl_4]^- \xrightarrow[\text{base}]{} \underset{\substack{(\text{base} = \text{thf, DMF, Et}_2\text{O, Py})\\(c)}}{[(acac)_2Al(base)_2]^+ [AlCl_4]^-} \tag{5}$$

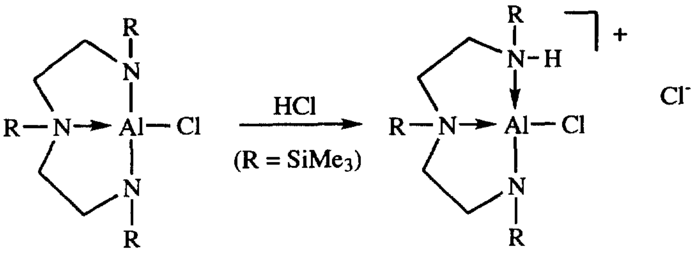
2.5.2. Indium

The combination of R_3In with $BF_3{-}Et_2O$ leads to the precipitation of the salt $[R_2In]^+$ BF_4^-. (R = ^iPr [60], CH_2Ph [61], Mes [60]). The ^iPr derivative can be recrystallized from thf to afford the tetracoordinate indium containing compound, $[^iPr_2In(thf)_2]^+$ BF_4^-. It was suggested that the same types of compounds could be prepared by halide abstraction from R_2InF with $BF_3^-Et_2O$ [60].

2.6. Ligand conversion

2.6.1. Aluminum

This rather inventive method of cation formation has not been widely used. It involves converting a covalent N–Al bond into one that is coordinate covalent,



(6)

N → Al, by protonation of the nitrogen (Eq. (6)) [62]. This transformation could easily be of utility in other systems provided the HCl elimination is conducted under relatively mild conditions.

2.7. Autoionization

2.7.1. Indium

This reaction is similar to halide displacement but it occurs without solvent instigation. It has only been observed for indium halide compounds. For instance the combination of MeI with InI leads to a compound formulated as $[InMe_2]^+$ InI_4^- in the solid state [63]. The linear arrangement of the Me–In–Me unit was confirmed crystallographically in the structure of $[InMe_2]^+$ Br^- [64]. In contrast, the structure of Et_2InBr consists of neutral units connected by intermolecular In–Br contacts (primary In–Br = 2.777(2) Å and secondary contacts ranging from 2.8 to 3.4 Å) albeit with an obtuse C–In–C angle (151.6(3) Å) [65].

3. Spectroscopic trends

3.1. Aluminum

There is little change in the ^1H NMR chemical shift of the alkyl groups on aluminum as a result of a change in the ligands. In general they are found around 0 ppm. Compare, for instance, $[Me_2Al(NH_2{}^iBu)_2]^+$ Br^- (δ 0.74 ppm), $[Me_2Al(O{=}PPh_3)_2]^+$ Br^- (δ 0.01 ppm) and $[Me_2Al(pmedta)]^+$ $[Me_2AlCl_2]^-$ (δ 0.95 ppm) [26]. Neutral trialkyl aluminum–amine adducts display similar values. However, there is usually a difference in values for cations when compared to the anions. For instance, $[{}^tBu_2Al(tmeda)]^+$ $[{}^tBu_2AlBr_2]^-$ has a ^{t}Bu–Al shift of δ 1.60 ppm while this group on the anion is much more shielded with a value of δ 0.78 ppm [24].

^{27}Al NMR gives clear information on the coordination number around the aluminum atom [66]. In general, six-coordinate species exhibit shifts around 0 ppm, those that are five-coordinate around 50 ppm and those that are four-coordinate around 100 ppm. As an example consider $[Pz_2Al]^+$ which has a shift of 4 ppm (br)

[19]. The most anomalous shift is found for the Cp-supported compound, $[Cp^*_2Al]^+$, δ 114.5 ppm ($w^{1/2} = 50$ Hz) [57].

3.2. Gallium and indium

The ^1H alkyl shifts for Ga and In are similar to that observed for Al. The alkyl shifts generally appear in the range of δ -0.5–1 ppm. There is little difference between the shifts of related Ga and In compounds despite the substantial increase in size between the two elements. Compare, for example, $[Me_2Ga(NH_2{}^tBu)_2]^+$ Cl^- (δ 0.19 ppm) [39], and $Me_2InI(NH_2{}^tBu)$ (δ 0.22 ppm); (there are no Me_2In^+ ^1H chemical shifts reported in the literature).

The ^{71}Ga nucleus is spin 3/2 with a natural abundance of 39.6%. Its quadrupole (0.112×10^{-24} cm^2) requires that the compound to be examined be highly symmetric. That is why there are relatively few ^{71}Ga NMR spectra reported [67]. Shifts for the $GaCl_4^-$ anion occurs around δ 239 ppm ($w_{1/2} = 60$ Hz). By comparison the cation, $[\{HB(pz^*)_3\}_2Ga]^+$ exhibits a peak at δ 2.8 pm ($w_{1/2} = 60$ Hz) [28].

4. Structural trends

4.1. Aluminum

The majority of the aluminum cations adopt a four-coordinate, tetrahedral geometry. Deviations from this geometry occur in the angles formed between the most electronegative atoms; these angles are narrowed due to a relative increase in the p-orbital character of the bonds. Despite the cationic nature of the aluminum atom, the Al–C, –N, –O bonds do not shorten by comparison to the neutral derivatives. This can be observed by comparing $Me_2AlCl(NH_2{}^tBu)$ and $[Me_2Al(NH_2{}^tBu)_2]^+$ [32,33]. Likewise, anionic $[Me_2Al(NHR)_2]^-$. The same effect is observed for gallium. There is less data available for this type of bonding in the indium derivatives so a definite conclusion cannot be drawn.

The C–Al–C angles are consistently widened by comparison to the corresponding heteroatom–Al–heteroatom angles. This is a consequence of the increased p-character in the Al–heteroatom bonds. In $[^tBu_2Al(tmeda)]^+$ $[^tBu_2AlBr_2]^-$ the cation features a C–Al–C angle of 117.8(2)° with an N–Al–N angle of 87.2(2)° [24] This can also be attributed to the more narrowed angles favored by bidentate chelates (like tmeda) and the fact that the ^tBu groups require more space between them. However, consideration of the angles in $[Me_2Al(NH_2{}^tBu)_2]$ (C–Al–C 116.6(3)°, N–Al–N 97.5(3)°) [32,33] establishes the trend.

The six-coordinate complexes $X_2Al(base)_4$ form when the X groups are electronegative (chloride for instance) and when the base molecules are sterically un-encumbered (thf, NH_3, etc.). Alternatively, tetradentate 2^- ligands can enforce this geometry (as in the Salen [1,2,35] systems). For both the four- and six-coordinate compounds the bond distances to the constituent atoms remain fairly consistent. This is observed in the distances of the aluminum atom to Cl (2.1–2.3 Å), O (1.8–2.0 Å), N (1.9–2.0 Å) and C (1.9–2.0 Å).

4.2. Gallium

One of the first structurally characterized examples of a gallium cation, $[Me_2Ga(NH_2^tBu)_2]^+$ Br^- is fairly representative of the entire class [39]. In it the Ga–C distances are approx. 1.99 Å and the Ga–N 2.0 Å. They are not all that different from the same types of distances in $Cy_2GaBr(NH_2Ph)$ [68] (Ga–C, 1.98 Å and Ga–N 2.1 Å) despite the difference in charge and the disparity in the groups around each of the gallium atoms. In each, the angle between the more electronegative constituents are more narrowed (96° for the N–Ga–N and Br–Ga–N angles). Within chelates the Ga–N distances shorten slightly. For instance, these distances in $[(1,4\text{-diazabutadiene})GaCl_2]^+$ are ~ 1.9 Å [29]. The Ga–Cl distances in this complex are as expected longer, ~ 2.1 Å.

4.3. Indium

Dialkyl indium cations (and the Tl analogues as well [69–71]) are unique in that they can exist as base-free linear species. This was originally proposed on the basis of spectroscopic data for the ion pair, $[Me_2In]^+$ InI_4^- [63]. It was later confirmed in the structure of $[Me_2In]^+$ Br^- [64]. The In–C distances in this compound are 2.1–2.2 Å and there are four secondary contacts to bromides at 3.1 Å making the indium atom six-coordinate with an octahedral geometry. A similar arrangement is observed for $[Mes_2In]^+$ BF_4^- which has In–C distances of 2.131(1) Å, a C–In–C angle of 174(1)°, and In–F contacts of 2.713(7) Å [61]. The four-coordinate cation, $[^iPr_2In(thf)_2]^+$ BF_4^- has essentially the same In–C distances as the two-coordinate cations [60]. Moreover, the C–In–C angle (160°) is still approaching linear. The In–O distances (2.3–2.4 Å) are similar to that observed in other compounds, such as the neutral $Et_2In(O_2CEt)$ (2.46, 2.64 Å) [72] and cationic $[InCl_2(R_3P{=}O)_4]^+$ $InCl_4^-$ (R = Me, Ph) [31]. The O–In–O angles are more narrowed (79.6(2)°) than is observed in the related Al and Ga cations. For comparison, neutral $Me_2InI(NH_2^tBu)$ [73] features In–C distances of 2.1 Å and a C–In–C angle of 134°. The I–In–N angle is 90°. For indium cations, then, there appears to be little difference in the bond distances when compared to neutral derivatives. In the $R_2In(base)_n$ derivatives the alkyl groups adopt the most linear angle possible. This is dependent upon the steric requirements of the donor groups. The In–C bond distances do not change substantially with increasing coordination number.

5. Univalent derivatives

Proceeding down the periodic chart the group 13 elements become progressively more stable in the (+1) oxidation state. Thus, cationic derivatives of gallium and indium (I) are known while those for aluminum are not. The widest class of compounds are those incorporating arene ligands for which an earlier review has been written [74]. This allows the metals to maintain a higher coordination number and remain in the low oxidation state.

5.1. Gallium and indium

It is known that $X_2Ga-GaX_2$ (X = Cl, Br) exists as the salt Ga^+ GaX_4^- in solution and in the melt [75–79]. This reagent serves as a convenient starting material to a wide range of Ga(I) cations, often by simply dissolving the material in an arene solvent. Crystallization of the compounds from dilute solutions generally leads to the bis-arene derivatives. Structurally characterized examples include the dimeric $[(C_6H_6)_2Ga]^+$ $GaCl_4^-$ [80] and $[(1,2,4,5\text{-}Me_4C_6H_2)(MeC_6H_5)Ga]^+$ $GaCl_4^-$ [81], the mesitylene derivatives, $[(1,3,5\text{-}Me_3C_6H_3)_2M]^+$ MX_4^- (M = Ga, X = Cl [82], Br; M = In, X = Br [83], and $[(C_6Et_6)(MeC_6H_5)Ga]^+$ $GaCl_4^-$ [84]. When the compounds are crystallized from concentrated solutions the mono-arene derivatives result. These typically contain intermolecular metal-arene interactions. Some structurally characterized examples include the hexamethylbenzene derivatives, $[(C_6Me_6)Ga]^+$, that are tetrameric (with $GaCl_4^-$) [85] and polymeric (with $GaBr_4^-$) [86]. Compounds having metal-ligand stoichiometries of 1:1 can also be obtained by combining the group 13 reagent with [2.2]paracyclophane. These are of the formula, $[LM]^+$ MX_4^- (M = Ga, X = Cl [87], Br [87]; M = In, X = Br [88]).

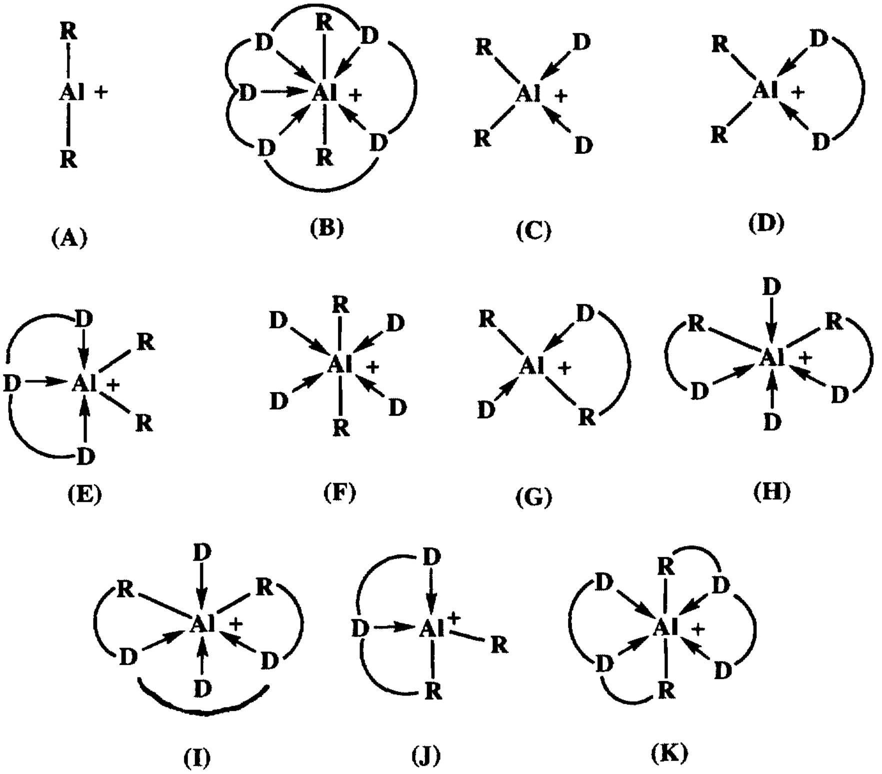
Using a chelate in the place of the arenes leads to the salts, $[In(chelate)]^+$ InX_4^- where chelate = dibenzo-18-crown-6, cyclam and X = Cl, Br, I [45]. If the group 13 starting material is $In[AlCl_4]$ [89] then the counter anion for these complexes is the aluminate.

5.2. Spectroscopic and structural trends

The arene derivatives of gallium (L_2Ga) provide well-defined peaks in the ^{71}Ga NMR. Those with $GaBr_4^-$ anions display shifts in the range δ 650–624 ppm while those with $GaCl_4^-$ display shifts from δ 650–675 ppm. By comparison, the $GaBr_4^-$ and $GaCl_4^-$ anions themselves have shifts of δ +62 and +247, respectively [75–79].

The structures display a range of oligomerization from dimer to polymer. In general the mono-arene derivatives form higher oligomers through secondary metal–arene contacts. This is best exemplified in the cyclophane derivatives which form chains of alternating ligands and metals that are bent at the metal centers. The compound, $[(C_6Me_6)Ga]^+$, $GaCl_4^-$ is tetrameric [86]. The bis-arene derivatives are not as highly aggregated as demonstrated by monomeric $[(C_6Et_6)(MeC_6H_5)Ga]^+$ $GaCl_4^-$ [85] and dimeric $[(C_6H_6)_2Ga]^+$ $GaCl_4^-$ [80], and $[(1,2,4,5\text{-}Me_4C_6H_2)(MeC_6H_5)Ga]^+$ $GaCl_4^-$ [82].

The arene-centroid to gallium distances fall in the range of 2.5–2.7Å whether the compound is a mono- or bis-arene. These distances are probably a function of how well the ligands pack in the structures they take. However, the longer



(R = 1- ligand and D = Lewis basic atom)

Fig. 6. General classification of group 13 cations.

distances are observed for the toluene ligands in $[(C_6Et_6)(MeC_6H_5)Ga]^+$ $GaCl_4^-$ (3.145 Å) [85] and $[(Me_4C_6H_2)(MeC_6H_5)Ga]^+$ $GaCl_4^-$ (3.039 Å) [82].

The metal halogen contacts depend on the coordination environment of the gallium atom and the aggregation of the molecular units. There are metal–halide contacts in all of the structures reported thus far. There is no correlation between the metal–halide distances and either the number of arene units present (either one or two) or the steric influence of the arene.

6. Applications

In coming years group 13 cations will clearly grow in importance in catalysis and organic synthesis. These three coordinate cationic species presumably function in a manner similar to group 4 catalysts of the general form $[Cp_2MR]^+$. In recent years two important applications have emerged. The first involves the use of the

$[SalenAl]^+$ as a catalyst for the polymerization of oxiranes [1,2]. The unique six-coordinate nature of these cations appears to be responsible for this activity. The second application is the polymerization of ethylene using low-coordinate derivatives [3].

7. Summary

As demonstrated by reactions 2.1–2.7 there is a diverse range of synthetic routes for the formation of aluminum, gallium, and indium cations. Autoionization (reaction 2.8) is a unique method for the formation of indium cations. These reactions can be generalized into two different groups by considering the nature of the Lewis basic ligands. One group is made up of Lewis base donors with varying numbers of coordinate covalent bonds (Fig. 6b–f). (Those having no supporting bases (Fig. 6a) may be thought of as the lower extreme of this group.) The upper extreme is defined by crown-ether complexes imparting a coordination number of seven on the cationic aluminum fragment (B) [21–23,97,98]. There are varying coordination numbers between these two extremes; four (C and D), five (E) and six (F). The bases typically contain either nitrogen or oxygen as the electron donating atom. The number of these groups that arrange around the cation is based upon steric considerations as well as the nature of the R group. When the R group is halide, or halide-like, higher coordination numbers usually result. This is observed in the compounds $[AlCl_2(base)_4]^+$ (base = py [17] and thf [18]) for instance, as well as in the neutral derivative, $Al(N_3)_3(py)_3$ [90,91].

The second set of cations incorporates those with ligands capable of both coordinate covalent and covalent bonding. It represents the area where the most new contributions may occur. The known compounds include those utilizing bidentate ligands with one coordinate covalent and one covalent bond (G and H) and a related derivative (I) which may be viewed as a Type H with a connection between the ligands. The type I complexes include those incorporating the Salen ligands and porphyrins [1,2,35]. Tridentate ligands with two coordinate covalent and one covalent bond are fairly well-known (Types J and K). The tris-pyrazolylborates are a good example of this type with most of the group 13 work involving gallium and indium [92].

Noted added in proof

Some unusual indium cations including one that is seven coordinate have recently been reported [100].

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