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Group 12 and heavier Group 13 alkali metal 'ate complexes

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Contents

Abstract 54
1. Introduction 54
2. Group 12 alkali metal 'ate complexes 54
  2.1 Solution and reactivity studies 54
  2.2 Solid-state and theoretical structural studies 57
    2.2.1 Lithium zincates 57
    2.2.2 Sodium, potassium and higher zincates 60
    2.2.3 Lithium cadmates and mercurates 61
    2.2.4 Sodium, potassium and higher cadmates and mercurates 64
3. Group 13 alkali metal 'ate complexes 69
  3.1 Solution and reactivity studies 69
  3.2 Solid-state and theoretical structural studies 72
    3.2.1 Lithium aluminates 72
      3.2.1.1 Hydride bridges 72
      3.2.1.2 Carbon bridges 73
      3.2.1.3 Oxygen and sulfur bridges 74
      3.2.1.4 Nitrogen bridges 76
      3.2.1.5 Phosphines and arsines 77
      3.2.1.6 Halide bridges 78
      3.2.1.7 Miscellaneous lithium aluminates 78
    3.2.2 Sodium, potassium and higher aluminates 81
    3.2.3 Lithium gallates, indates and thallates 87
    3.2.4 Sodium, potassium and higher gallates, indates and thallates 95
4. Overview 103
References 104

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Abstract

Heterobimetallic complexes in which a Group 1 metal centre counteracts the negative charge placed on a Group 12 or higher Group 13 metal have been known for some years. Their usefulness in chemical transformations is discussed in the context of the regiospecificity with which they effect reaction and the manner in which it differs to that resulting from the use of homometallic alkali metal reagents. Their structural properties are reported both in solution and in the solid state. Theoretical studies are presented where appropriate.

Keywords: Alkali metal; 'ate Complex; Group 12; Group 13; Solid-state structure

1. Introduction

Organometallic and metallo-organic reagents exhibit Lewis acidity by virtue of the metal centre possessing a vacant orbital, and so are capable of forming complexes with anionic fragments. This results in the formation of ''ate complexes' in which the Lewis acid is usually, though not invariably, coordinatively saturated. Species derived from reaction of the Lewis acid with a second metal-containing reagent are of particular interest because they contain at least two types of metal centre and consequently exhibit structures and reactivities differing from both of their homometallic precursors [1,2]. This review aims to cover the major aspects of alkali metal 'ate chemistry where a Group 12 or heavier Group 13 element constitutes the Lewis acidic centre. In order that the scope of the review is limited to compounds containing a Group 12/Group 13 *metal*, alkali metal borates have been excluded. By and large, the compounds considered will be heterobimetallic, though discussion will, on occasion, extend to higher-order polymetallic systems.

Complexes of Group 12 and heavier Group 13 elements are presented in Sections 2 and 3, respectively. Each section is subdivided into two subsections: the first dealing with attempts to elucidate the solution structures and dynamics of these compounds and also their potential as novel reagents — often exhibiting unusual and selective reactivity; the second discussing their extensively studied solid-state properties and, where appropriate, the use of theoretical techniques to predict or corroborate structural data. In each section the complexes will be discussed in ascending order of atomic mass, firstly by alkali metal and thereafter by Group 12/Group 13 element.

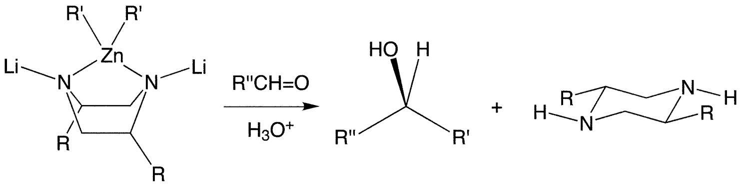
2. Group 12 alkali metal 'ate complexes

2.1. Solution and reactivity studies

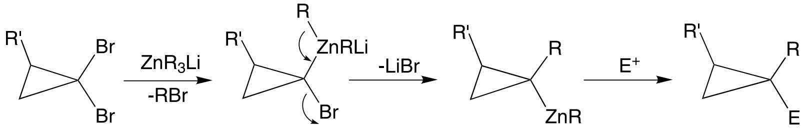
Lithium zincates can adopt two possible formulations — $LiZnR_3$ and Li_2ZnR_4 — and it is the former of these classes which will be considered first. NMR spectroscopy has been used to probe Li–Zn systems for some time. It has, for example, been determined that the exchange of ^{7}Li between LiMe and $LiZnMe_4$ is rapid relative to dissociation of the methyllithium tetramer to the more reactive dimer [3]. Recently, more complex NMR spectroscopic techniques have been applied to the little-understood solution structures of ligand–reagent complexes of a type which effect stereoselective alkylation of carbonyl groups [4–7], with ^{6}Li-NMR spectroscopy and ^{1}H,^{1}H-NOESY having been used to study one such complex. It has been noted that dilithium piperazide–dialkylzinc adducts [8] stereospecifically catalyse the asymmetric alkylation of simple aldehydes, with spectroscopic results pointing to an initial complex with a boat conformation reverting to the chair form on treatment with aldehyde (Scheme 1) [9]. Following on from much early work with mixed lithium–zinc systems [10–13], it was found that lithium [phenyl(dimethyl)silyl](dialkyl)zincates are more useful than their cuprate analogues [14] for performing conjugate additions on synthetically useful [15–19] α,β-unsaturated ketones [20]. Similar reactivity has also been reported for Li–Zn systems in the presence of a nickel catalyst [21].

Reduction of carbonyl groups has been observed by mixed alkali metal–zinc systems. Thus, treatment of MH (M = Li, Na) with dialkylzinc reagents affords the corresponding dialkylzinc hydride 'ate complex [22]. The preparation and study of zinc hydrides has been undertaken in the contexts of both neutral zincanes (ZnH_2) [23] and of charged zincates (ZnH_3^- and ZnH_4^{2-}) [24–27]. The application of these alkali metal dialkylzinc hydrides to stereoselective and catalytic carbonyl reduction chemistry has lately been investigated [22]. More recently, chiral zinc alkoxides have been employed to form complexes with lithium cyclopropylacetylide, facilitating the asymmetric alkynylation of a ketoaniline [28].

Treatment of LiTMP (TMP = 2,2,6,6-tetramethyl-piperidide) with Zn^tBu_2 has recently afforded a lithium zincate, $LiZn^tBu_2TMP$, which has been found to act as a chemoselective base for directed *ortho*-metallation [29]. The reaction of triorganozincates with aryl halides [30–33] has been noted to effect halogen–zinc exchange (cf. halogen–copper exchange [34,35]). In a similar vein the treatment of 1,1-dihalocyclopropyls with various lithium trialkylzincates has been found to afford 1-halocyclopropylzincates (metal carbenoids) [36,37]. These species act as non-stereochemical alkylation precursors by undergoing invertive 1,2-alkyl migration (Scheme 2) [38]. While 1,1-dihaloalkenes can be sequentially reacted with a lithium trialkylzincate and an electrophile to furnish a host of polyfunctionalised products [39] it has also been noted that at 0 °C their 1-haloalkenylzincate



Scheme 1.



Scheme 2.

derivatives undergo a 1,2-alkyl migration similar to that shown by 1-halocyclopropylzincates [40,41].

Lately, some stereochemical understanding has also been gained of the reactions of these metal carbenoids [42]. At low temperature halogen–metal exchange occurs at the sterically more hindered halogen atom with retention of configuration at the carbenoid C-centre. While 1-haloalkenyl- and 1-halocyclopropylzincates have been shown to react readily with electrophiles to give polyfunctionalised products [39], an analogous migration for 1-haloalkylzincates has been effected [43]. However, in this last case it has been noted that for efficient conversion a palladium catalyst [44–46] must be present. Recent studies into the efficiency with which allylmetals react with vinylmetals to yield 1,1-dimetallated species [47] have led to the theoretical study of the allyl zincation of vinyllithium. Results suggest the importance of substrate pre-organisation via ZnBrLi coordination [48].

In the same way as for conjugate addition and halogen–metal exchange processes, triorganozincate salts have been found to exhibit comparable reactivity to their cuprate analogues in the synthesis of allenes from propargylic species [49]. Crucially, however, the triorganozincate route differs from the cuprate one by virtue of the significant reactivity of the intermediate allenic zinc species towards electrophiles. This offers a synthetic route not just to allenes, but also to α-, γ-disubstituted propargyles [50–55].

Unlike uncomplexed trialkylzincates, which have trigonal planar anions, tetraalkylzincates are essentially tetrahedral [56]. This latter class of zincate has been known for some years [57] but it is only much more recently that its synthetic potential has begun to be realised [58]. The efficiency with which epoxides undergo intermolecular ring-opening is notably greater if Li_2ZnMe_4 is used in place of $LiZnMe_3$, while halogen- and tellurium–zinc exchange — which fail to occur for the triorganozincate — are both significantly enabled [59]. Similarly, intramolecular processes (Michael addition, carbozincation and epoxide ring-opening) have all been shown to be enhanced by the use of Li_2ZnMe_3R ($R = Me$, CN, SCN), the structures and reactivities of which have been probed by ^{1}H-NMR and IR spectroscopies [59,60] and, more recently (for $R = Me$) by ^{13}C-NMR spectroscopy using fully ^{13}C-labelled material [61].

The solution structures of various solvates of lithium tris[bis(trimethylsilyl)amido]zincate have been probed by NMR spectroscopy [62]. Moreover, while several sodium [63–66] organozincates have been prepared by transmetallation chemistry, lithium bis(trimethylsilyl)methylzincates have been prepared by the metathesis reaction of $LiCH(SiMe_3)_2$ with $ZnMe_2$ [67]. More recently, amine adducts of lithium tris[bis(trimethylsilyl)methyl]zincate have been prepared by the addition of aliphatic amines to equimolar amounts of $LiCH(SiMe_3)_2$ and $Zn[CH(SiMe_3)_2]_2$ in ethereal solution [68]. ^1H- and $^{13}C\{^1H\}$-NMR spectroscopies have been used to characterise the homoleptic, metallocyclic 'ate complexes $(L)_n \cdot Li_2Zn[(CHR)_4]_2$ ($L = Et_2O$, DME, TMEDA; $R = H$, Me) and $(TMEDA \cdot Li)_2Zn[(CH_2)_5]_2$ in solution [69,70].

One synthetic route to functionalised organolithium species utilises the transmetallation capabilities of mercury [71,72]. ^7Li-NMR spectroscopy has successfully been used to monitor the titration of $(LiPh)_n$ ($n = 1,2$) with $HgPh_2$. This has allowed the detection of the triorganomercurate species $(THF)_4 \cdot Li^+$ $HgPh_3^-$ in situ [73]. While trisilylmercurates have been noted elsewhere [74,75] and both $LiHg^tBu_3$ [72] and $LiHgMe_3$ [76] have been postulated, this represents the first direct observation of a triorganomercurate complex. The employment of multinuclear NMR spectroscopy has also allowed the elucidation of dynamic processes in supramolecular mercuracarborand chemistry. The ability of carboranes to undergo double deprotonation followed by the formation of C–R interactions has facilitated the development of mercuracarborand hosts [77], with treatment of *closo*-1,2-$(Li)_2$-$C_2B_{10}H_{10}$ [78] with HgX_2 ($X = Cl$, [79–81], I [82]) resulting in the association of four *ortho*-carborane ligands via mercury bridges. The solid-state structure of this species reveals a 12-membered $(HgC_2)_4$ heterocycle capped by a halide anion and is discussed below. A similar 12-membered $(HgC_2)_4$ heterocycle has been observed to be bicapped by an I_2 fragment [80,82], affording an array of contiguous $Hg(\mu\text{-}I)_2Hg$ rings with gradual addition of AgOAc affording a convenient route to the neutral [12]mercuracarborand-4. Just as this titration can be monitored by ^{199}Hg-NMR spectroscopy (a signal at δ -667 converts to one at δ -1145, ref. $HgMe_2$) [82], so the reversibility of the process has been demonstrated by spectroscopic monitoring of the titration of [12]mercuracarborand-4 with $^nBu_4N^+I^-$ with a broad signal at δ -1212 [83] converting to a sharp resonance at δ -714 for the dianion via an observable monoanionic intermediate [84].

2.2. Solid-state and theoretical structural studies

2.2.1. Lithium zincates

It is surprising, given the synthetic utility of lithium zincates (see above), that the structural chemistry of these species is not better understood. It is, however, some years since the straightforward ion-separated bis(lithium)tetraalkylzincate, $(Li^+)_2$-$ZnMe_4^{2-}$ became the first such compound to be structurally characterised [63]. Complexes with this 2:1 Li/Zn stoichiometry will be discussed in more depth below. The extension of studies into the oxygen-scavenging properties of mixed Group 1/Group 2 metal systems [85–87] has recently led to the synthesis of $LiZnMe[N(SiMe_3)_2]$ [88]. Certain lithium triorganozincates have been shown by X-ray crystallography to be ion-separated — but only in the presence of coordinating Lewis bases. Mixed encapsulation of the Group 1 metal centre is observed in $(Et_2O) \cdot (TMEDA) \cdot Li^+Zn[CH(SiMe_3)_2]_3^-$ [68] whereas exclusively bis(TMEDA) chelation of the Li^+ ion is recorded for the heteroleptic zincate fragments

$ZnMe_2CHPhSiMe_3^-$ and $ZnMe[CHPhSiMe_3]_2^-$ [89], and two equivalents of 1,3,5-trimethyl-1,3,5-triazine envelop the lithium cation in the complex $[(CH_2)_3(NMe)_3]_2 \cdot Li^+ZnMe[CH(SiMe_2CH_2)_2SiMe_2]_2^-$ (Fig. 1) [90]. In this context it is interesting to note the effect of the inclusion of electron-rich heteroatoms in the organic residues bonded to the zinc centre; $[(CH)_3(NMe)_3] \cdot LiZn(CH_2SiMe_3)_2N(SiMe_3)_2$ is no longer ion-separated in the solid state but instead displays a Li(μ-N)Zn bridge [90]. Such monobridged motifs are also possible in the absence of a heteroatom, and in fact Li(μ-C)Zn and $Li(\mu\text{-}C)_2Zn$ motifs are predominant in ion-bonded lithium zincate chemistry. The first of these structural possibilities is demonstrated by monomeric $THF \cdot LiZn[(2\text{-}Me_2NCH_2)C_6H_4]_3$ wherein amine-group chelation and THF solvation otherwise support the mono-aryl intermetallic bridge [91]. The second of these motifs — the doubly bridged four-membered heterocycle — is the more common of the two models. However, rather than applying to compounds of the form $LiZnR_3$, it is associated with the formation of spirocyclic species of the type Li_2ZnR_4. Hence, $Li(\mu\text{-}C)_2Zn(\mu\text{-}C)_2Li$ arrangements define the structures of $(L \cdot Li)_2Zn[(CH_2)_n]_2$ ($n = 4$ [69], 5,[70]; Fig. 2a; see Section 2.1 for their solution characteristics), $(L \cdot Li)_2Zn(C{\equiv}CPh)_4$ [92] and $(L \cdot Li)_2Zn[(CH_2SiMe_2)_2]_2$ [93], (L = TMEDA; Fig. 2b) and also $Li_2Zn[(2\text{-}Me_2NCH_2)C_6H_4]_4$ [91]. A more complicated structure is observed for $LiZn[O_2C(CH)_2Me]_4$ wherein the ability of the *trans*-butenate anions to not only perform intramolecular coordination to zinc but to exhibit both intra- and intermolecular interactions to lithium affords a complex polymeric aggregate (Fig. 3) [94]. EXAFS spectroscopy [59,60] and also DFT theoretical studies have lately been applied to the study of intramolecular reactions known to be enhanced by the employment of Li_2ZnMe_3R (R = Me, CN, SCN). Notably, calculations point to an

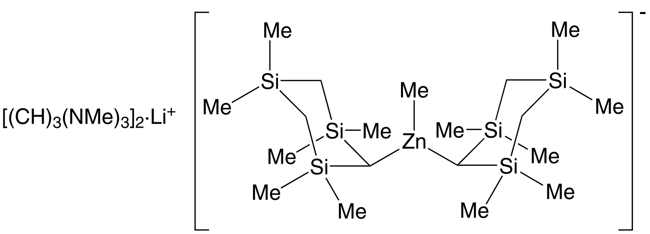
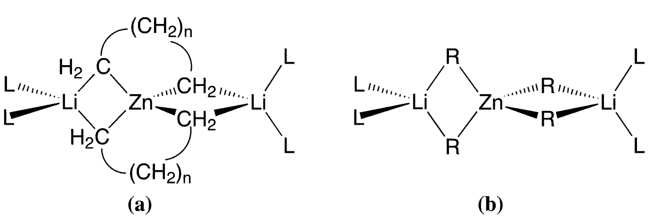


Fig. 1.



(a) (b)

Fig. 2. L = TMEDA; $n = 2$, 3 R = C≡CPh, CH_2SiMe_2 [69,70,92,93].

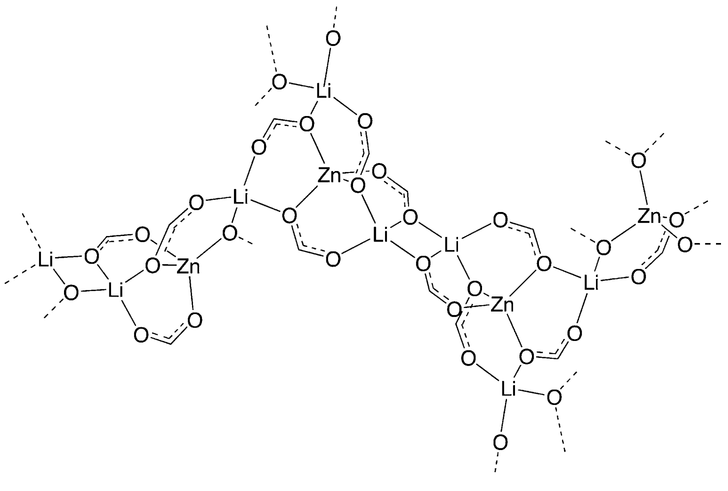


Fig. 3. The polymeric core of $LiZn[$*trans*$-O_2C(CH)_2Me]_4$ [94].

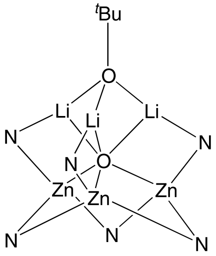


Fig. 4. Structure of $^tBu(\mu_3-O)Li_3(\mu_6-O)Zn_3[N(2-C_5H_4N)Me]_6$. N-centred pyridyl rings and methyl groups omitted [102,103].

energetic preference for triorganozincate monoanions over tetraorganozincate dianions [59].

Recently, investigations have sought to study the behaviour of mixed Li–Zn systems on exposure to oxygen. The sequential treatment of $HN(2-C_5H_4N)R$ ($R = Ph$, $3,5-Me_2C_6H_3$) with $ZnMe_2$, ^tBuLi and dry air affords (among other products) $\{THF \cdot Li[(\mu-O)Me]ZnR_2\}_2$, both dimers featuring a core $(ZnO)_2$ ring with exocyclic lithium centres [95]. For $R = CH_2Ph$ the trigonal pyramidal compound $(\mu_4-O)Zn_4[N(2-C_5H_4N)CH_2Ph]_6$ results [96–100], adopting the beryllium acetate structure [101] in the solid state. Further structural modification is observed for $R = Me$, with formation of the octahedral *fac*-isomeric $M_3M'_3$ oxo-encapsulation complex $^tBu(\mu_3-O)Li_3(\mu_6-O)Zn_3[N(2-C_5H_4N)Me]_6$ (Fig. 4) [102,103], in which the Li_3 face is μ_3-capped by virtue of oxo-insertion into a Li–C(^{t}Bu) bond [104].

2.2.2. Sodium, potassium and higher zincates

It is now many years since the syntheses of the first sodium zincates [105–108]. However, even now very few crystallographically characterised examples exist and until recently, all of those that did pertained to the ion-separated, homoleptic formula $Na^+ZnR_3^-$. Recently, however, the sodium zincate 'inverse crown ether' $(\mu_4\text{-}O)Na_2Zn_2[N(SiMe_3)_2]_4$ has been isolated [88] and found to be a precise structural analogue of its Li–Mg relative [85]. Regarding, sodium triorganozincates, a naked lattice sodium ion counteracts the charge on $Zn(CH_2^tBu)_3^-$ [66] whereas 12-crown-4 has been used to encapsulate the sodium cations in 'ate species with the counterions $Zn[N(SiMe_3)_2]_3^-$ and $Zn(C{\equiv}CPh)_3^-$ [109]. Dimerisation of the anion has been recorded for $Na^+Zn(O^tBu)_3^-$, with bis(*tert*-butoxy)-bridging of two zinc centres affording a $(ZnO)_2$ ring (Fig. 5) [110]. Finally a polymetallic, ion-separated sodium zincate complex has been reported in which a simple $[(15\text{-crown-}5)\cdot Na^+]_2$ component counteracts the charge on the spirocyclic arrangement of two Zn-fused five-membered $ZnSe_4$ rings which comprise the dianion [Zn–Se = 2.465 Å] [111].

Like their sodium analogues, potassium zincates show a predilection for $M^+ ZnR_3^-$ type structures in the solid state. Naked potassium ions prevail for the simple monomers in which $R = CH_2SiMe_3$ and CH_2^tBu [66] while THF coordination of the Group 1 metal centre has been reported for R = 2,6-bis(*tert*-butyl)phenoxide [112]. As for the sodium complexes discussed above, anion dimerisation is also known; $K^+Zn(O^tBu)_3^-$ reveals a $Zn(\mu\text{-}O)_2Zn$ motif in the solid state [cf. $Na^+Zn(O^tBu)_3^-$, above] [110]. For heteroleptic $(K^+ZnRR_2'^-)$ species analogous monomers [66] and dimerised-anion [113] species exist. The behaviour of the $[^tBuN(CH)_2N^tBu]^{2-}$ ligand is noteworthy in the context of potassium zincate structural chemistry. A single zinc centre is tetrahedrally coordinated by the N-centres of two such dianions, one of which η^4-interacts with a THF-solvated potassium ion (mean K–N = 2.976 Å, mean K–C = 2.885 Å) in $(THF)_3\cdot KZn[MeN^tBu(CH)_2N^tBu]_2$ [114]. In the ion-bonded polymer $THF\cdot KZnMeN^tBu(CH)_2N^tBu$, the $[^tBuN(CH)_2N^tBu]^{2-}$ ion acts as a η^4-donor in both intra- and intermolecular fashion (mean K–N = 3.06 Å, mean K–C = 2.97 Å) (Fig. 6) [115,116]. A similar polymer is observed for $Et_2O\cdot KZn(CH_2Ph)N^tBu(CH)_2N^tBu$ (mean K–N = 3.12 Å, mean K–C = 2.95 Å) [116]. Akin to the Na–Zn oxo-capture inverse crown structure described above, $\{K_2Zn_2[N(SiMe_3)_2]_4(O_2)_x(O)_y\}$ ($x = 0.82$, $y = 0.18$) has recently been observed [88]. Its solid-state structure reveals that polymerisation has occurred via interaction of the alkali metal centre with one methyl group on an adjacent monomer. Lastly, an ion-separated potassium zincate in which the anion is based on a bimetallic $ZnTe_7^{2-}$ motif reveals a ZnTe edge-fused [Zn–Te = 2.518(3) Å] bicycle of five-membered $ZnTe_4$ rings [Zn–Te = 2.542(5) Å, Te–Te = 2.684(4)–3.253(3) Å] [117].

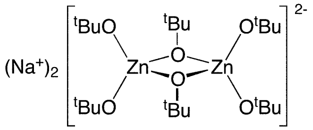


Fig. 5.

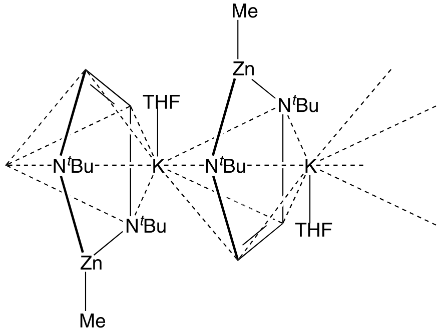


Fig. 6. Dimeric fragment of the infinite THF·KZnMeN^{t}Bu(CH)$_2$N^{t}Bu chain [115,116].

Higher Group 1 metal zincate structures are few and far between. Ion-separated complexes incorporating both rubidium and caesium along with thiofulvalene ligands have been reported as part of a study into three-component organic conductors containing both neutral and monocationic bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) ligands [118,119]. Both the rubidium zincate and its caesium analogue incorporate unusual structures in which the alkali metal centres are tetra(NCS)$^-$-solvated [mean Rb–N = 1.97 Å, Cs–N = 1.95(4) Å] but with the inability of the soft sulfur centres to interact with the Group 12 metal ion affording naked Zn^{2+} centres in the crystal lattice [118]. A trimetallic, Se-based rubidium zincate analogue of [(15-crown-5)·Na$^+$]$_2$ Zn(Se$_4$)$_2^{2-}$ has been found in which an asymmetric dianion contains both 5- and 7-membered heterocycles. Hence, spirocyclic Se$_6$ZnSe$_4^{2-}$ features a mean Zn–Se bond length of 2.458 Å [120].

2.2.3. Lithium cadmates and mercurates

A single crystallographically characterised example exists in which two THF-encapsulated Li$^+$ ions are counterbalanced by a dianion in which four carbazole ligands bond to cadmium via their N-centres (Fig. 7) [121]. However, ion-bonded structures are much more common for Li–Cd systems. Bridging of a Li–Cd divide by oxygen and nitrogen atoms has been observed in Li$_2$(O$_2$CEt)$_4$Cd with its lithium-centred spirocyclic Li[(μ-O)CEtO]$_2$Li[(μ-O)CEtO]{[μ-OCEtO]}Cd arrangement [122], and in the Li(μ-N)$_2$Cd-based bis(lithium)triphenylguanidide derivative (Fig. 8), respectively [123]. While phosphorus has also been observed to participate in double bridging, the Group 15 centre has been found to be oxygen-bonded with the chalcogen centre also incorporated into the bridging motif and bonding to the hard alkali metal ion. Hence a straightforward six-membered ring is observed in the monomeric lithium diorganophosphinite complex (THF)$_2$·Li[OP(Mes)$_2$]$_2$CdN-(SiMe$_3$)$_2$ (Cd–P = 2.594 Å) which results from the sequential treatment of Mes$_2$P(H)=O [Mes = (2,4,6-Me$_3$)C$_6$H$_2$] with ^{n}BuLi and Cd[N(SiMe$_3$)$_2$]$_2$ [124].

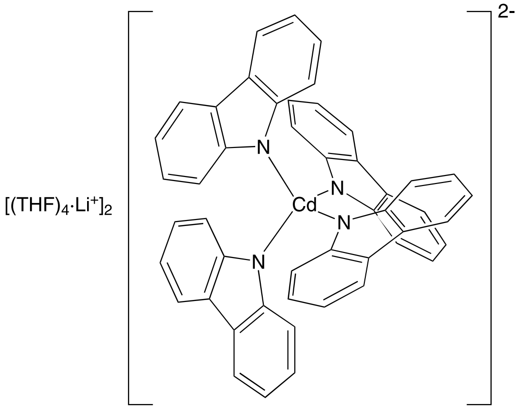


Fig. 7.

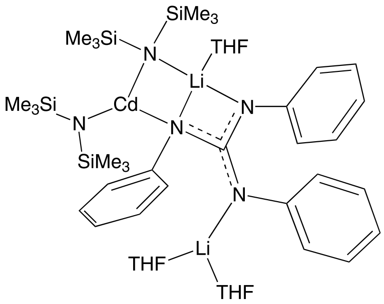


Fig. 8.

The propensity of heteroatoms for bridging bimetallic arrangements also extends to Group 17. The structure of $(THF)_4 \cdot Li^+(THF)_2 \cdot Li[(\mu\text{-Cl})CdC(SiMe_3)_3(\mu\text{-Cl})]_2^-$ reveals an anionic lithium bis(cadmate) fragment based on a contiguous array of bi- and trimetallic heterocycles in which metal centres are mono- and bis(bridged) by chloride ligands (Fig. 9) [125]. Bridging bromide ligands afford a cluster of $Cd(\mu\text{-Br})_2Cd$ heterocycles in the related structure of $(THF)_4 \cdot Li^+[CdC(SiMe_3)_3]_3Br_4^-$ wherein the anionic component adopts a pseudo-cubane structure with a single vertex missing (Fig. 10) [126].

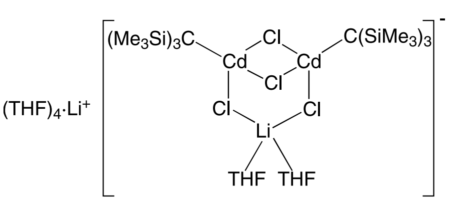


Fig. 9.

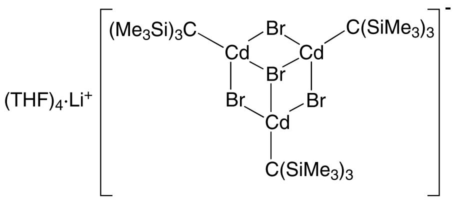


Fig. 10.

Studies into possible single source precursors to Cd/P phases have led to the report that in the ion-separated bis(lithium) complex $[(THF)_4\cdot Li^+]_2$-$[Cd(PPh_2)]_4(PPh_2)_6^{2-}$ the dianionic moiety adopts an adamantanoid structure akin to those reported elsewhere for cadmium sulfides [127–130]. The cluster contains two types of Cd–P interaction [mean = 2.63 Å to terminal P-centres and mean = 2.66 Å to bridging P-centres] (Fig. 11) [131]. Ion-separation and a hexanuclear tetraanion are observed in the solid-state structure of lithium cadmate $[(MeCN)_4\cdot Li^+]_4Cd_6I_{16}^{4-}$. The negatively charged moiety is based on a chain of Cd(μ-I)$_2$Cd units [mean Cd–(μ-I)Cd = 2.792 Å, mean Cd–(μ-I)$_2$Cd = 2.841 Å] with one terminal iodine centre on each of the four cadmium centres in the middle of the chain and two terminal iodine atoms on the cadmium centres at either end of the chain (mean Cd–I = 2.708 Å) [132]. Finally a chalcogenic, ion-separated lithium cadmate complex has been isolated and structurally characterised. The cationic fragment of the tris(lithium) octa(seleno)cadmate $[(12\text{-crown-}4)_3\cdot MeCO_2\cdot Li_3]^{2+}\cdot[Cd(Se_4)_2]^{2-}$ incorporates alkali metal ions in two distinct environments — two Li^+ centres being coordinated to a single acetate O-centre (mean Li–O = 1.836 Å), the third spanning both such O-centres (mean Li–O = 2.148 Å). The counter-ion is analogous to the arrangement noted for $Zn(Se_4)_2^{2-}$ [111] and thus features two Cd-fused five-membered $CdSe_4$ rings wherein mean Cd–Se = 2.635 Å [133].

Only a few lithium mercurates have been characterised in the solid state. Ion-association has been revealed by the polymeric structure of $NEt_4^+Li(NC)_4Hg^-$ with each cyanate ligand being C-bonded to the Hg-centre and N-bonded to the Group 1 metal ion [134,135]. Hg–Si interactions are recorded in the

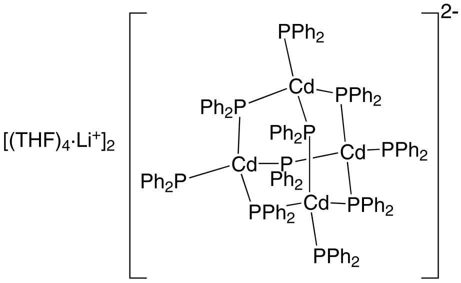


Fig. 11.

$Li_2Hg(SiMe_2Ph)_4$ and $Li_2Hg(SiMe_3)_4$ monomers, in both of which the two Li^+ ions are each stabilised by donation from two Si–C σ-bonds [136,137]. Lastly, steric hindrance resulting from the presence of four *ortho*-carborane ligands results in ion-separation in the lithium mercurate $(Li^+)_n(HgC_2B_{10}R_9)_4(X^-)_n$ {R = H, alkyl, aryl etc.; $n = 1$, X = Cl (Fig. 12); [77,80,81] $n = 2$, X = I [82]}, the solid-state structure of which reveals a 12-membered $(HgC_2)_4$ heterocycle capped by halide anions.

2.2.4. Sodium, potassium and higher cadmates and mercurates

The aggregation of two tripodal $Cd[SC({=}O)Ph]_3^-$ cadmate anions about a central Na^+ centre (a separate NMe_4^+ ion yielding electrical neutrality) affords a pseudo-octahedral coordination environment for the Group 1 metal ion [Na–O in the range 2.303(4)–2.470(5) Å] [138]. While ion-separated sodium cadmates incorporating mononuclear anions have been noted [139], it is more common for the Cd-based negatively charged moieties to associate. Hence, naked sodium ions counteract the charge on the $Cd(O_2CH)_3^-$ anion with two forms of oxo-bridging affording a negatively charged polymeric chain. Thus, either a single oxo-centre in each of two formate ligands links monomeric units to give a Cd_2O_2-based $Cd[(\mu\text{-}O)C({=}O)H]_2Cd$ fragment or else bridging of the whole formate ligand yields a Cd···O=C(H)–O–Cd motif [140,141]. The $(12\text{-crown-4})_2 \cdot Na^+$-spaced chains of anionic fragments arranged in antiparallel fashion, noted in the tris(thiocyanate) cadmate of sodium $(12\text{-crown-4})_2 \cdot Na^+$ $\{[Cd_2(NCS)_3(SCN)_3]^{2-}\}_{\frac{1}{2}}$, contain Group 12 metal centres which are symmetrically bridged such that each Cd centre participates in three Cd–N (mean = 2.312 Å) and three Cd–S (mean = 2.750 Å) interactions (Fig. 13) [142]. Instead of thiocyanate ligands, cyanates are used in sodium mercurate analogues of the polymeric lithium mercurate $NEt_4^+Li(CN)_4Hg^-$ [134,135] which incorporate lattice NEt_4^+ and $N^nPr_4^+$ ions [134,135]. The trimetallic chalcogen-incorporating 'ate complexes $[(15\text{-crown-5}) \cdot Na^+]_2\text{–}Cd(Se_4)^{2-}$ [111] and $[(15\text{-crown-5}) \cdot Me_2NCHO \cdot Na^+]_2Cd_4Te_{12}^{2-}$ [143] have both been reported. Whereas the former

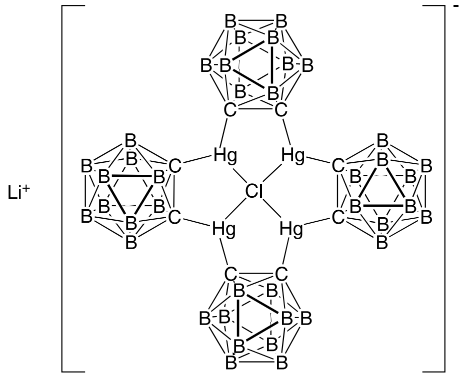


Fig. 12. H and R groups on *ortho*-carborane icosahedra omitted for clarity [77,80,81].

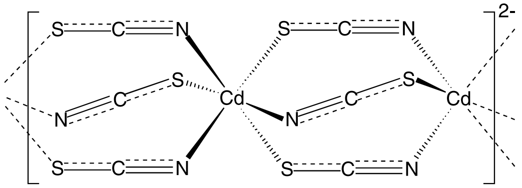


Fig. 13. Dimeric fragment of the anionic polymer in $(12\text{-crown-4})_2\cdot Na^+$ $\{[Cd_2(NCS)_3(SCN)_3]^{2-}\}_{1/2}$ [142].

complex is the precise structural analogue of $[(15\text{-crown-5})\cdot Na^+]_2\cdot Zn(Se_4)_2^{2-}$ [111] (Cd–Se = 2.642 Å), the latter species reveals a more complicated anion in the solid state. The $Cd_4Te_{10}^{2-}$ ion adopts a five-tier motif in which two relatively eclipsed $(CdTe)_2$ rings (within which mean Cd–Te = 2.913 Å) are bonded together via their Te centres (mean Te–Te = 2.757 Å) and also bridged by a further two Te centres [mean Cd–(μ-Te) = 2.782 Å] and terminally coordinated by a Te_3-chain (Cd–Te = 2.827 Å, Te–Te = 2.719 Å) (Fig. 14) [143]. Lastly, the only single crystallographically characterised sodium mercurate complex is the structural analogue of $[(15\text{-crown-5})\cdot Na^+]_2M(Se_4)_2^{2-}$ M = Zn, Cd (mean Hg–Se = 2.646 Å) [111].

Unlike their sodium analogues, ion-separated potassium cadmates show little tendency for anion-aggregation. Hence the combined effect of 18-crown-6 and THF solvation of the Group 1 metal centre is to incur ion-separation — the solid-state structures of $(THF)_2\cdot(18\text{-crown-6})\cdot K^+Cd(C_6F_5)(SCPh_3)_2^-$ [144] and $(THF)_2\cdot(18\text{-crown-6})\cdot K^+Cd(SCPh_3)_3^-$ [145] revealing unsupported, monomeric, trigonal cadmium-based anions (mean Cd–S = 2.467 Å and 2.487 Å, respectively). The failure of the bulky cadmate moiety in $[(18\text{-crown-6})\cdot K^+]_2Cd(B_9H_{13})_2^{2-}$ (the product of the 2:1 metathesis reaction of $K_2(B_9H_{13})$ [146] with $CdCl_2$) to undergo aggregation results in the observation a monomeric anion containing six Cd–B interactions in the solid state [147]. The Group 12 metal centre caps one B_3-face of each borane cluster, residing approximately equidistant from two boron atoms (mean Cd–B = 2.581 Å) but closer to the third (mean Cd–B = 2.287 Å) (Fig. 15). Also sterically congested is the cadmium centred component of $KCd\{O{=}C[NH^nPr]NS({=}O)_2Ar\}_3$ (Ar = 4-chlorophenyl) — the first complex to incorporate a sulfonylurea ligand.

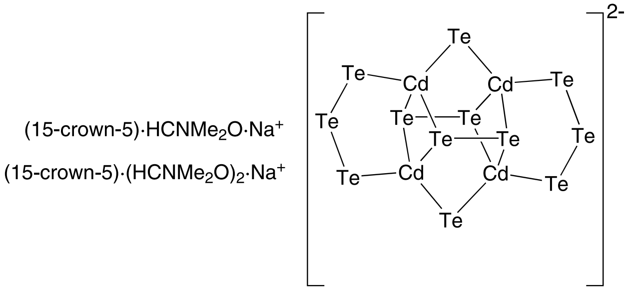


Fig. 14.

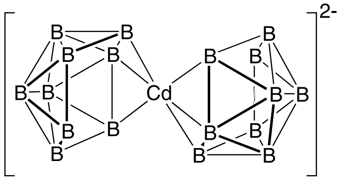


Fig. 15. Dianionic component of $[(18\text{-crown-6})\cdot K^+]_2\ Cd(B_9H_{13})_2^{2-}$. Boron-attached hydrogen atoms omitted for clarity [147].

The N and O centres of each sulfonamide ligand chelate the cadmium centre and render it octahedral (mean Cd–N = 2.212 Å, mean Cd–O = 1.255 Å) while the alkali metal centre is weakly bonded to one oxygen centre in each of two ligands (Fig. 16) [148].

Just as thiocyanate ligands have been noted in the solid-state structures of sodium cadmates [142], so too are they pertinent in the structural chemistry of potassium cadmates. Hence, the linear association of cadmate anions via the formation of three thiocyanate bridges between each metal centre is known [149,150] (cf. $(12\text{-crown-4})_2\cdot Na^+\{[Cd_2(NCS)_3(SCN)_3]^{2-}\}_{\frac{1}{2}}$). The replacement of thiocyanate ligands with straightforward cyanate ones leads, however, to the observation of more subtle, multi-dimensional polymerisation processes. Homoleptic $(K^+)_2Cd(CN)_4^{2-}$ reveals a three-dimensional array in the solid state [151] wherein each K^+ ion is rendered hexacoordinate by bonding to six cyanate N-centres. Of these interactions, two (relatively *trans*) are the result of K(NC)Cd bridges while four are the consequence of establishing $K(NC)_2Cd$ motifs [151]. The heteroleptic complex $(EtCN)_4\cdot K^+Cd(CN)_9^-$ reveals a remarkable structure in which the $Cd_4(CN)_9^-$ anion has polymerised to yield a mineralomimetic framework wherein cadmium centres exhibit tetrahedral $[Cd(CN)_4]$ and octahedral $[Cd(NC)_6]$ dispositions in the ratio 3:1 [152]. ^{113}Cd-CP MAS NMR spectroscopy has been employed to show the disordering of certain of the cyanate ligands in the solid state. A single potassium cadmate in which the anionic moiety contains multiple cadmium centres has been reported. In $(18\text{-crown-6})\cdot(THF)_2\cdot K^+H(\mu_3\text{-}O)[Cd(C_6F_5)SCPh_3]_3^-$ ion-separation is accompanied by the formation of a trigonal

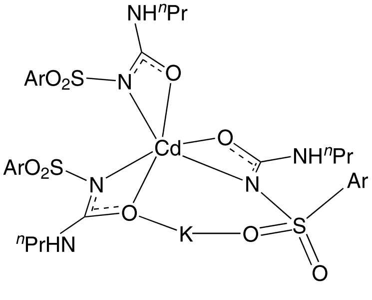


Fig. 16. Ar = 4-chlorophenyl [148].

pyramidal anion in which a six-membered $(CdS)_3$ ring (mean Cd–S = 2.565 Å) is hydroxy-capped (mean Cd–O = 2.390 Å) [144]. Just as a complex $Cd_4Te_{12}^{2-}$ anionic moiety has been observed in sodium cadmate chemistry [143], so the solid-state structure of the potassium cadmate $[(18\text{-crown-6})\cdot K]_2Cd_4Te_{12}$ reveals the expected bonding parameters [143,153] in a cadmium–tellurium moiety (Fig. 17) [154]. The potassium centres interact not only with 18-crown-6 but also with chalcogen centres which are members of Cd–Te–Cd bridges in the Cd–Te cluster.

Simple potassium mercurates are more common than their sodium analogues [155]. They feature in the series of BEDT-TTF ligand-based organic conductors referred to in Section 2.2.2 [118,119]. These mixed-cation systems reveal both ion-separated [156,157] and ion-bonded [via K(NCS)Hg bridges] [158] heterobimetallic fragments in the solid state. Mercurate analogues of $(12\text{-crown-4})_2\cdot K^+$ $\{[Cd_2(NCS)_3(SCN)_3]^{2-}\}_{\frac{1}{2}}$ with its polymerised anion have been observed both in molecular and polymeric contexts. Thus, $[(\text{dibenzo-18-crown-6})\cdot K^+]_2$-$\{[Hg(NCS)_4]^{2-}$ shows both a terminal thiocyanate group and $K(SCN)_nHg$ ($n = 1$, 2) motifs [159]. However, polymeric $[(\text{benzo-12-crown-6})\cdot K]_2Hg(SCN)_4$ reveals a dichotomy in the fashion of thiocyanate N-coordination to the K^+ ions, with both K(NCS)Hg and eight-membered heterocyclic $K(NCS)_2Hg$ motifs resulting (Fig. 18) [149]. Polymerisation has been noted for the compounds $N^nPr_4^+K(NC)_4Hg^-$ [134,135].

A polymercury-containing anion for which potassium is the counter-ion has been reported [82] which incorporates four *ortho*-carborane groups arranged analogously to those in the lithium(carborano)mercurate complexes discussed above [77,80–82]. However, in this case a longer reaction time has favoured bicapping of the 12-membered $(HgC_2)_4$ heterocycle by an I_2^- fragment, affording an array of fused $Hg(\mu\text{-}I)_2Hg$ rings. A single related potassium(carborano)mercurate has been characterised in which two (18-crown-6)-bonded potassium ions are each bonded to the two O-centres of two separate nitrate ligands. These residues are found on either side of the 12-membered $(HgC_2)_4$ heterocycle that results from the aggregation of four $Hg(C_2B_{10}H_{10})$ units such that the free O-centre of one nitrate group interacts with all four mercury centres (mean Hg–O = 2.92 Å) while the free oxygen of the other nitrate group coordinates to only two (mean Hg–O = 2.68 Å) by virtue of the inhibitory presence of one molecule of water [160].

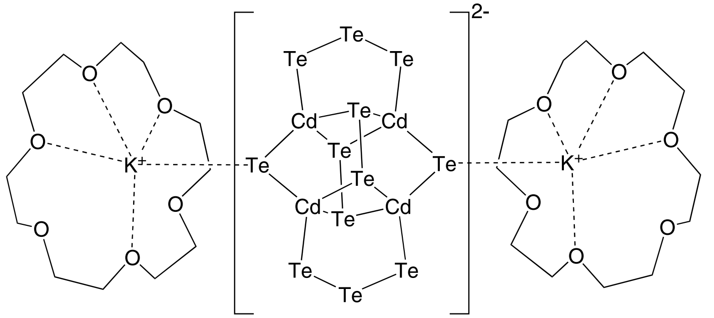


Fig. 17.

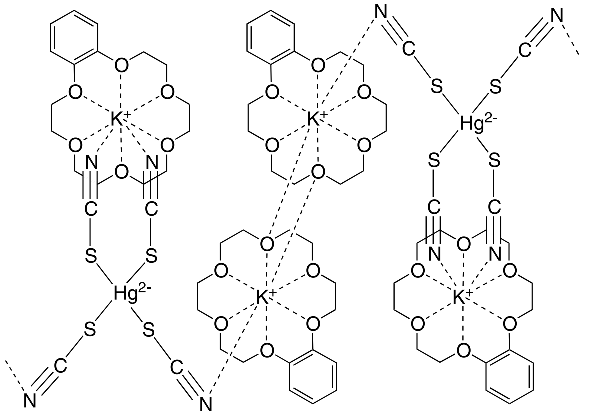


Fig. 18.

Lastly, anion-aggregation has been reported for several potassium mercurate complexes. Polydentate Lewis bases encapsulate the two potassium ions which counteract the charge on each of the $(HgO)_2$- and $(HgI)_2$-based heterocyclic dianions $[Hg(CN)_2OC(=O)Ph]_2^{2-}$ [161] and $(HgI_3)_2^{2-}$ [162]. Ion-separated potassium mercurates which incorporate a Group 16-based intermetallic-anion are known not only in the mixed Hg–Se spirocyclic context of $Hg(Se_4)_2^{2-}$ (mean Hg–Se = 2.658 Å) [133,163], but also for that of the simple linear arrangement $HgSe_2^{2-}$ (mean Hg–Se = 2.388 Å) [163]. The reaction of 2,2,2-cryptand with 'KHgTe' — a species afforded by the treatment of KHg [164] with Te(0) — affords the tellurium analogue of $HgSe_2^{2-}$ in which Hg–Te = 2.589(1) Å [165]. The more complicated $HgTe_7^{2-}$ ion is based on an HgTe-edge fused (Hg–Te = 2.709 Å) bicycle of $HgTe_4$ rings (in which the remaining mean Hg–Te = 2.682 Å), making it a precise structural analogue of $(K^+)_2ZnTe_7^{2-}$ [117].

Rubidium and caesium cadmates and mercurates have been noted only rarely and several of those which have been observed have been analogues of the $(BEDT\text{-}TTF)_2KHg(SCN)_4$ mixed-cation complexes noted above [156–158]. The caesium cadmate complex reveals the same unusual ion-separated motif as its zincate relative [118] with the Group 1 metal centre being tetra$(NCS)^-$ coordinated [Cs–N = 1.92(1) Å] and with the soft sulfur centres failing to interact with the Group 12 ion. Unlike their completely ion-separated zincate relatives [118,119], both rubidium and caesium mercurates have been observed as Group 1 metal tetra$(NCS)^-$ solvates in $M[Hg(SCN)_4]^-(BEDT\text{-}TTF)^+(BEDT\text{-}TTF)$ wherein bridging between the Group 1 and Group 12 metal ions affords a polymeric arrangement [158]. However, the caesium mercurate has been shown to be viable as an ion-separated species [166]. Straightforward caesium mercurates have been noted elsewhere: in the presence of DMSO caesium tetra(iodo)mercurate crystallises as an ion-separated species {cf. $(K^+)_2HgI_4^{2-}$ [155]} [167]. Treatment with 18-crown-6 affords a polymeric compound wherein pairs of Cs^+ ions bond both to crown molecules and to $(\mu\text{-I})_2(\mu_3\text{-I})\text{HgI}^{2-}$ anions [mean Cs–(μ-I) = 3.821 Å, mean Cs–(μ_3-I) = 3.954 Å] (Fig. 19) [168]. Finally, a selenium-containing caesium mercurate has been noted which features an unusual anionic moiety that is based on an asymmetric $(\text{HgSe})_2$ heterocycle peripheral to which are three HgSe_4 rings. While one of these rings incorporates only one of the core mercury centres, the other two are edge-fused to the core via the second Hg centre and its adjoined Se atoms (Fig. 20) [169].

3. Group 13 alkali metal 'ate complexes

3.1. Solution and reactivity studies

The sterically demanding tri-coordinate Lewis acid aluminium tris(2,6-diphenylphenoxide) has been employed as a selective activator of saturated carbonyls towards α-alkylation by organolithium species [170–173]. It has also been noted that in the presence either of the same tri-coordinate species [174–178] or else of methylaluminium bis(2,6-di-*tert*-butyl-4-alkylphenoxide) [179–181] the addition of organolithium reagents to α,β-unsaturated ketones occurs not at the 1,2-positions [182,183] but at the 1,4-positions instead (Scheme 3). These observations have led to studies in which monomeric bis(aryloxy)methylalanes, MeAl(OAr)_2 (Ar = aryl) [184], have been reacted with various organolithium reagents to afford lithium aluminate monomers, $\text{Li}[(\mu_2\text{-O})\text{Ar}]_2\text{AlMe}_2$, of a type which are implicated in the conjugate addition process [185]. The asymmetric Li(μ-O)Al-based complex

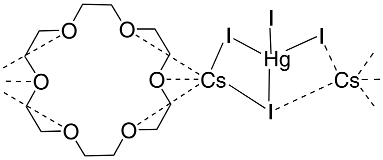


Fig. 19.

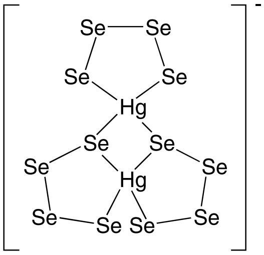
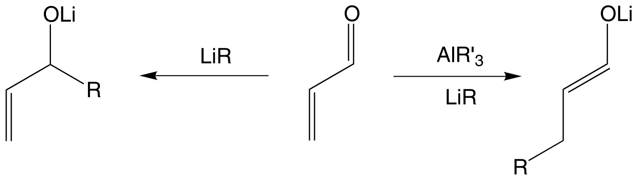


Fig. 20. Anionic HgSe-cluster, the charge on which is counter-balanced by an (18-crown-6)·Cs^+ moiety [169].

$C_6H_8O\cdot(THF)_2\cdot LiAl[(R)\text{-binol}]_2$ (binol-H_2 = 2,2′-dihydroxy-1,1′-binaphthyl) is worthy of particular note in this context because it acts as a heterobimetallic catalyst [186,187] in such reactions (Fig. 21) [188,189]. Synthetically useful [190] epoxide ring-opening has, in fact, been the subject of much study. Whereas treatment with organoaluminium reagents has led to the formation of 1,2-diols [191] the employment of mixed Li–Al systems has afforded a diverse set of products. Ring-opening of heterosubstituted epoxides in the presence of both $AlMe_3$ and alkynyllithium reagents has been the subject of much recent study. Results have indicated that the alkynylation reaction proceeds via a chelation-mediated process in which the Al centre of the alane reagent is rendered penta-coordinate by virtue of interaction with the functionalised epoxide [192,193]. The addition of '$LiR_3AlSn^nBu_3$' (R = Me, Et; afforded by treating $LiSn^nBu_3$ [194–196] with the corresponding trialkylaluminium) to an epoxide has been noted to result in the formation of alkenes via that of a β-oxido stannane intermediate [197]. Work which sought to rationalise the catalytic action of $GaMe_3$ in the context of epoxide ring-cleavage by alkynyllithium reagents [198] has been followed by investigations which have revealed that the gallium analogue of $C_6H_8O\cdot(THF)_2\cdot LiAl[(R)\text{-binol}]_2$ aids enantioselective epoxide ring-opening by thiols, affording significant enantiomeric excesses upon both catalytic and stoichiometric application [199].

The reactions of gallanes and indanes with alkali metal hydrides have been investigated [200,201] with a view to elucidating whether or not reductive elimina-



Scheme 3.

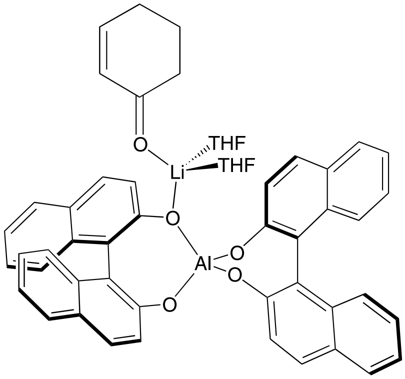
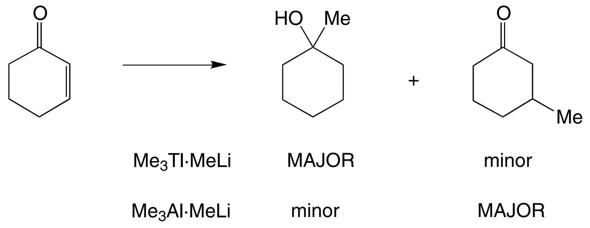


Fig. 21.

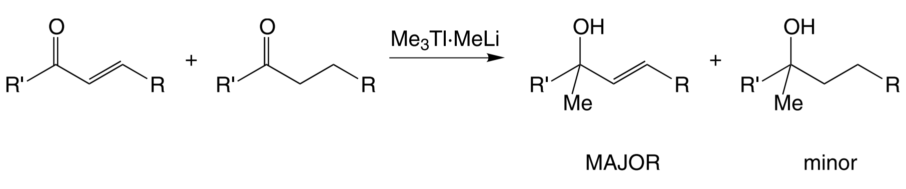
tion processes were active during their reported conversion to σ-bonded complexes of the type $\mathrm{MM'(CH_2SiMe_3)_2}$ (M = Li, Na, K, M′ = Ga [202]; M = Na, M′ = In [203]). The prevailing view, based on the isolation of $\mathrm{KGa(CH_2SiMe_3)_3H}$ and $\mathrm{KIn(CH_2SiMe_3)_3H}$ and an inability to reproduce the syntheses of $\mathrm{MM'(CH_2SiMe_3)_2}$, is now that dissociation and reaction of alkali metal alkyl species rather than reductive elimination is the path-determining factor in the chemistries of these systems [200].

The indium hydride $\mathrm{K\{H[In(CH_2^tBu)_3]_2\}}$, obtained by the treatment of $\mathrm{In(CH_2^tBu)_3}$ [204] with KH, reacts with a further equivalent of indane to yield $\mathrm{K[HIn(CH_2^tBu)_3]}$ [205]. Both of these potassium indates have been characterised in benzene solution by cryoscopic relative molecular mass techniques. Results suggest that whereas the first of these compounds exists as monomeric ion-pairs, the latter indate complex is dimeric. ^{1}H-NMR spectroscopy reveals broad signals attributable to the hydride ligands at δ 3.09 and 3.41, respectively [205]. The applications of indate species in organic synthesis have been explored in the context of conjugate addition of organolithium reagents to α,β-unsaturated ketones [206]. Results indicate that the combination of alkyllithium and allylic indium sesquihalides $\mathrm{[(allyl)_3In_2X_3]}$ afford ’ate complexes which promote the formation of head-to-tail 1,5-dienes [207] on treatment with the allylic bromide $\mathrm{R_2C{=}C(H)CH_2Br}$.

Tetraorganothallates, originally synthesised by the combination of $\mathrm{TlCl_3}$ with $\mathrm{RM/NH_3}$ (R = alkyl, M = alkali metal) [208], have been noted to exhibit the opposite regiospecificity to that demonstrated by their aluminate analogues with respect to their action on acyclic and cyclic enones (Scheme 4) [209]. Furthermore, it has been shown that they will preferentially react with enones in the presence of ketones (Scheme 5) [210]. The two heterocyclic anions $\mathrm{(SeTl)_2^{2-}}$ and $\mathrm{(TeTl)_2^{2-}}$ have been characterised both in the solid state (see below) and in solution. Both of these



Scheme 4.



Scheme 5.

ions, as well as the mixed thallate anion $Tl_2SeTe_2^{2-}$, have been studied by $^{203/205}$Tl [211,212], and ^{77}Se [212] NMR spectroscopies. Results point to the stability of the four-membered heterocycles and also to their significant flexibility about the inter-thallium axis with coupling suggesting that while the thallium–chalcogen interactions utilise only p-orbital overlap there is significant s-electron density residing along the Tl···Tl-axis. $^{203/205}$Tl-NMR spectroscopy resonances have also been reported for $TlSe_3^{3-}$ and $TlTe_3^{3-}$ ions [212,213].

3.2. Solid-state and theoretical structural studies

3.2.1. Lithium aluminates

3.2.1.1. Hydride bridges. The solid-state properties of organoaluminium [214] and, more saliently, of coordination [215] and inorganic [216] aluminium compounds, have been the subject of recent reviews. By far the most common motif in the structural chemistry of Group 1/Group 13 ’ate complexes is $M(\mu\text{-}X)_nM'$ ($M =$ Group 1 metal; $X = H, C, N, O$ etc.; $M' =$ Group 13 metal; $n = 1, 2$). For lithium aluminates structures in which a hydride bridges between alkali metal ions are rare. Such structures, based on a $(LiH)_2$ ring with respect to which the aluminium centres are exocyclic have been noted only for $[LiHAl{}^tBu_3]_2$ [217] and $[LiHAl(C_3H_3N_2)_2C(SiMe_3)_3]_2$ [218]. Several examples exist, however, in which hydride ligands are observed to bridge between the Group 1 and Group 13 metal centres. Thus the observation of simple $Li(\mu\text{-}H)_2Al$-based monomers (Fig. 22) $(Et_2O)_2 \cdot Li(\mu\text{-}H)_2AlR_2$ $\{R = N(SiMe_3)_2$ [219], $(2,6\text{-}{}^tBu_2)OC_6H_3$ [220]$\}$ was accompanied by that of $Li(\mu\text{-}H)AlRR'_2$-type monomers $\{R = R' = OCPh_3$ [220]; $R = {}^tBu$, $R' = C(H)(SiMe_3)_2$ [221]$\}$ and of $Li(\mu\text{-}H)AlHRR'$-based monomers $\{R = R' = (2,6\text{-}{}^tBu_2)OC_6H_3$ [220]$\}$ (viz. Fig. 22) and dimers $\{R = R' = H$ [222–224], $(2,6\text{-}{}^tBu_2)C_6H_3$ [220], $N(SiMe_3)_2$ [219], $NPhN(SiMe_3)_2$ [225]; $R = H$, $R' = N(SiMe_3)_2$ [219]; $R = H$, $R' = C(SiMe_2Ph)_3$ [226]; $R = H$, $R' = (2,4,6\text{-}Ph_3)C_6H_2$ [227]; $R = H$, $R' = (2,4,6\text{-}{}^tBu_3)C_6H_2$ [227]; $R = H$, $R' = C(SiMe_3)_2SiMe_2OMe$ [228]; $R = H$, $R' = C(SiMe_3)_2SiMe_2NMe_2$ [218]$\}$ (Fig. 23). More complex species are also known. A monomeric, THF-solvated bis(lithium) complex has been reported to incorporate the bis(aluminate) dianion $[(ArNH)_2AlH(NAr)AlH(ArNH)_2]^{2-}$ $[Ar = (2,6\text{-}{}^iPr_2)C_6H_3]$ [229] while a trianionic silylarsinoaluminate anion has been reported to contain three $Li(\mu\text{-}H)Al$ bridges. The X-ray crystal structure of this species reveals that two $(DME)_3 \cdot Li^+$ ions counter the charge on $\{DME \cdot Li[(\mu\text{-}H)AlHAsSiMe_2CMe_2^iPr]_3\}^{3-}$ [Al–As = 2.472(3) Å] [230]. An unsolvated tetranuclear 1,3,4-tri-*tert*-butyl-1,4-diazabutane complex which has been characterised incorporates both $Li(\mu\text{-}H)_2Al$ and $Li(\mu\text{-}H)Al$

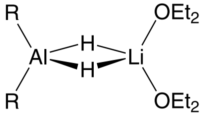


Fig. 22. $R = N(SiMe_3)_2$ [219], $(2,6\text{-}{}^tBu_2)OC_6H_3$ [220].

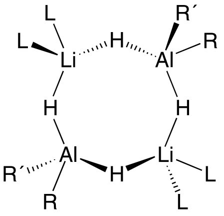


Fig. 23. See Refs. [219,222–230].

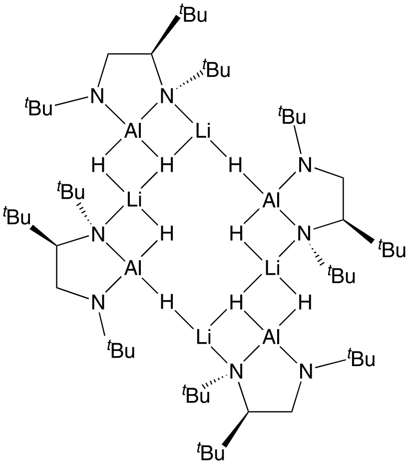


Fig. 24.

motifs (Fig. 24) [231]. Whereas hydride ligands have been seen to act as effective bridges between aluminium and both ring-core and exocyclic lithium centres, for bridging HNAr moieties fused tricyclic arrangements of six- and eight-membered heterobimetallic ring systems are observed [229].

3.2.1.2. Carbon bridges. The first solid-state structural characterisation of a simple lithium aluminate incorporated not bridging hydride but bridging methylene groups. Polymeric $LiAlEt_4$ is characterised by the stabilisation of each Li^+ ion by α-agostic interactions with two Al-bonded CH_2 units such as to afford infinite $Li(\mu\text{-}C)_2Al$ chains wherein mean M–(μ-C) distances are 2.30 Å (M = Li) and 2.02 Å (M = Al) [232]. In spite of this early observation of the $Li(\mu\text{-}C)_2Al$ motif, it has transpired that such fragments are rare in the solid state. Only three other reports of such a unit exist, all of them in an oligomeric context. Firstly, the reaction of $(Cl_2Al)_2CH_2$ with excess $LiCH_2SiMe_3$ yields $Li_2CH_2[Al(CH_2SiMe_3)_3]_2$; the unusual structure of which is based on a bowl shaped, CH_2-centred arrangement of four contiguous $Li(\mu\text{-}C)_2Al$ rings (Fig. 25) [233]. Secondly, both Li(μ-C)Al and Li(μ-

C)$_2$Al motifs are demonstrated by the dimer of LiN(SiMe$_2$CH$_2$P^{i}Pr$_2$)$_2$·LiAlMe$_4$ depending on whether the alkali metal centre is NP$_2$— or only N-stabilised (Fig. 26) [234]. Finally, the spirocyclic charged lithium bis(aluminate) complexes in the ion-separated main group interstitial hydride species [235] {Li$_8$(H)[N(2-C$_5$H$_4$N)Ph]$_6$}$^+$·[Li(Me$_2$Al^{t}Bu$_2$)$_2$]$^-$ {respective mean of Li–(μ-C) and Al–(μ-C) are 2.25 and 2.07 Å, viz. (LiAlEt$_4$)$_\infty$ [232]} and in weakly ion-bonded {Li$_4$[PhNCPhNPh]$_3$}$^+$·[Li(Me$_2$AlMe^{t}Bu)$_2$]$^-$ [respective mean Li–(μ-C) and Al–(μ-C) = 2.234 and 2.034 Å] have only very lately been reported [235–237].

3.2.1.3. Oxygen and sulfur bridges. The carbon-bridged lithium bis(aluminates) just discussed are immediately comparable to only one other charged lithium 'ate complex. Calculations point to the favourability of an oxo-bridging motif in the solvent-separated ion pair [(DME)$_3$·Li]$^+$(Li{[(μ-O)Ph]$_2$AlEt$_2$}$_2$)$^-$ [238]. The propensity of oxygen for stabilising Group 1 metal centres means that neutral lithium aluminates based on O-centred ligands have been known for some time and have generally been based on either Group 13 homometallic cyclic (AlO)$_n$ ($n = 2$, 3) [239] or cage (AlO)$_6$ [240] structures or — more commonly — heterobimetallic Li(μ-O)Al [188,228,239,241–245], Li(μ-O)$_2$Al [185,220,242,245–255] or LiO(AlO)$_2$ [243] cyclic cores. The catalytically important complex C$_6$H$_8$O·(THF)$_2$·LiAl[(*R*)-binol]$_2$ (Section 3.1) reveals a Li(μ-O)AlO$_3$ motif in which the alkali metal centre interacts with just one of the four Al-bonded oxygen centres [188]. Of the Li(μ-O)$_2$Al systems all but three display external solvation by etherate solvent of the Group 1 metal centre. The exceptions are the unique lithium ion in the complex

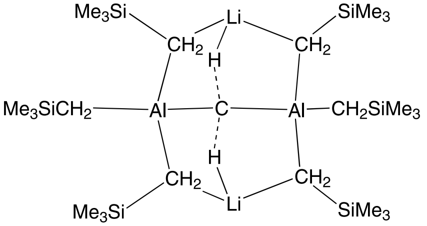


Fig. 25.

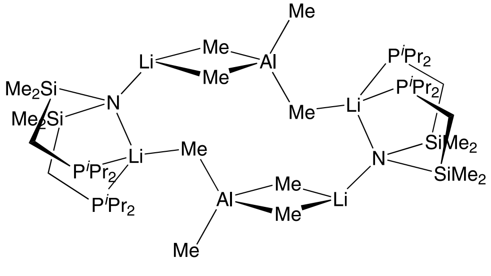


Fig. 26.

Li-capped heterocyclic structure of $(\mu_4\text{-Li})[(\text{THF})_2\cdot\text{Li}(\mu\text{-O})_2\text{AlMe}_2]_4$ [239], monomeric $\text{Li}[\mu\text{-OC}(\text{CF}_3)_2\text{Ph}]_2\text{Al}[\text{OC}(\text{CF}_3)_2\text{Ph}]_2$ wherein internal stabilisation via $\text{Li}\leftarrow\text{F}$ interactions is observed [249], and the more recently noted structure of $\text{Li}[(\mu\text{-O})\text{Ar}]_2\text{AlMe}_2$ (Ar = 2,6-di-*tert*-butyl-4-methylphenyl, see Section 3.1) which demonstrates stabilisation of the otherwise merely two-coordinate lithium centre by the formation of agostic bonds [185]. In this compound the Group 1 metal centre is rendered pseudo-octahedral by bonding interactions which, while they compare with those attributed to strong agostic bonds in compounds with formally two-coordinate lithium centres {e.g. $[\text{LiN}(\text{SiMe}_3)_2]_n$ ($n = 2$, 3) [256] and *anti*-$(\text{Et}_2\text{O}\cdot\text{Li})_2[{}^t\text{Bu}_6\text{Al}_6(\text{O})_6\text{Me}_2]$ [240]}, are the shortest yet observed in lithium aluminate structural chemistry. More recently studies into the controlled oxygenation of heterobimetallic complexes of alkali metals [257–259] have been undertaken for systems containing pre-formed lithium aluminates. The lithium ’ate species $[\text{PhCONMeAlMe}_2^t\text{Bu}]\text{Li}$ affords a mixed-anion compound $[\text{PhCONMeAlMe}^t\text{BuOMe}]\text{Li}\cdot[\text{PhCONMeAlMe}({}^t\text{OBu})\text{OMe}]\text{Li}$ on treatment with dry air (Fig. 27). In the solid state this species dimerises to give a tetranuclear $(\text{LiO})_4$ ladder structure in which terminal mono(oxygenated) aluminate ligands and tripodal bis(oxygenated) aluminate ligands span end and central Li^+ ions, respectively [260]. Employment of the more sterically congested lithium ’ate complex $[\text{PhCONPhAlMe}_2^t\text{Bu}]\text{Li}$ in an analogous reaction sequence in turn yields the mixture $[\text{PhCONPhAlMe}(\text{OR})\text{R}']\text{Li}$ ($\text{R} = {}^t\text{Bu}$, $\text{R}' = \text{Me}$ and $\text{R}' = {}^t\text{Bu}$, $\text{R} = \text{Me}$) [261]. The solid-state structures of the last three complexes reveal, unusually, a predilection for a lithium–oxygen structural core [251] rather than a bimetallic or else a uniquely Group 13-containing one (see above). Lastly, the esoteric structures of several lithium oligosiloxane aluminates have lately been reported. They are based on eight-membered heterocyclic cores composed of four oxo-bridged aluminium centres which are supplemented by a further four annelated $\text{Li}(\mu\text{-O})_2\text{Al}$ rings (Fig. 28) [262].

Recently, $[(\text{THF})_2\cdot\text{Li}(\mu\text{-H})\text{AlH}_2\text{C}(\text{SiMe}_3)_3]_2$ [226] has been reacted with Me_2S_2 and with ${}^t\text{BuSH}$ to give the organodi- and organotri(thiolato)aluminates $\text{THF}\cdot\text{Li}[(\mu\text{-S})\text{Me}]_2\text{AlHC}(\text{SiMe}_3)_3$ and $(\text{THF})_2\cdot\text{Li}[(\mu\text{-S})\text{Me}]_2\text{Al}(\text{SMe})\text{C}(\text{SiMe}_3)_3$, respectively [263].

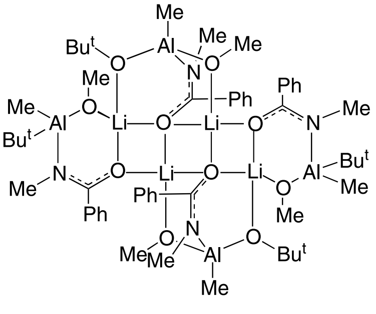


Fig. 27.

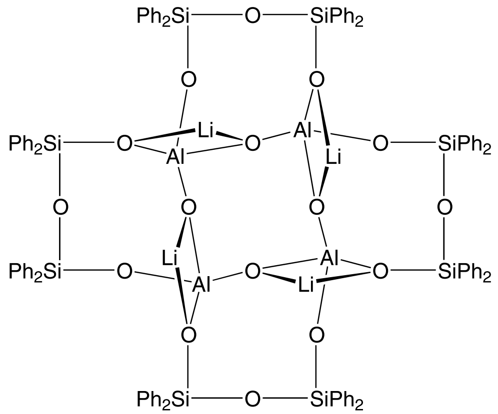


Fig. 28.

3.2.1.4. Nitrogen bridges. The favourability of Li(μ-X)Al motifs, demonstrated above for X = O, extends to Group 15-centred ligands also. For X = N, as for the other elements discussed, the majority of structures incorporate external Lewis bases in the solid state; $(PhCH_2)_2NH\cdot Li(\mu\text{-}N)Al$ [264], $(THF)_3\cdot Li(\mu\text{-}N)Al$ [265], $[(THF)_n\cdot Li(\mu\text{-}N)Al]_2$ ($n = 1$, 2) [266,267], and $L_n\cdot Li(\mu\text{-}N)_2Al$ ($n = 1$, L = THF, Et_2O, C_5H_5N [268–271]; $n = 2$, L = HNC_4H_8, THF [267,272–274]). In only a very few cases have structures been recorded in the absence of external donor. The first of these, the internally coordinating lithium tetra(imido)aluminate $Li[(\mu\text{-}N)C^tBu_2]_2Al(NC^tBu_2)_2$ is based on a $Li(\mu\text{-}N)_2Al$ core [275], as are the monomeric amido species $Li[(\mu\text{-}N)HSiPh_3]_2Al^tBu_2$ (wherein weak Li···Ph interactions are observed) [276], internally stabilised $Li[(\mu\text{-}N)^tBu(CH_2)_2N^tBu]_2Al$ [268] and $Li[(\mu\text{-}N)^tBuCH_2CHN^tBu]_2AlH_2$ [224], and polymeric $Li[(\mu\text{-}N)HMe]_2Al(NHMe)_2$ [277]. The association of two $Li(\mu\text{-}N)_2Al$ heterocycles has been reported to afford fused networks of four- and eight-membered rings [the latter also incorporating Li(μ-N)Al interactions] in $\{Li[(\mu\text{-}N)H^tBu]_2Al^tBu[(\mu\text{-}N)H^tBu]\}_2$ [278]. A similar duality of N-bridging has been recorded in the lithium 'ate-^{n}BuLi co-complex $(Li^nBu)_2Li_3Al_2[NH^tBu]_3(N^tBu)_3$ (Fig. 29) [279]. This species forms by the combination of Li^nBu with the potential $Al(NR)_3^{3-}$ precursor $[Al(NH^tBu)_3]_2$ and contains unsolvated $(Li^nBu)_2$ wherein the metal centres are tri-coordinate.

Whereas polymerisation via the formation of infinite $Li(\mu\text{-}N)_2Al$ chains has been observed in only one instance [280], other species — $LiN(SiMe_3)_2AlMe_3$ [281], $Li(TMP)AlMe_3$ [282] and $Li[N(SiMe_3)_2]Al[N(2\text{-}C_5H_4N)Ph]Me_2$ [283] — incorporate Li(μ-N)Al motifs into infinite linear chains resulting from stabilisation of the Li^+ ion in each monomeric unit by an aluminium-bonded Me group in an adjacent monomer. An unusual feature noted in both of the latter two structures is the adoption, by the bridging N-centre, of modified sp^2-hybridisation [284]. The existence of exocyclic lithium ions in compounds of the type discussed here has been observed not only in a simple dimeric context [266] but also in the more

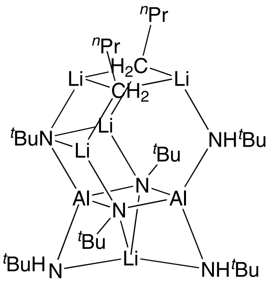


Fig. 29.

complicated η^3-,η^6-Li sandwich dimer of Li{^{i}Pr$_2$Al[(2,4,6-Me$_3$)NC$_6$H$_2$]}{[Al[(2-CH$_2$)(4,6-Me$_2$)NC$_6$H$_2$]}, based as it is on three contiguous Al(μ-N)$_2$Al rings (Fig. 30) [285].

Ion-separation is extremely rare in lithium aluminates containing aluminium-bonded N-centres. However, the extrusion of lithium (as a diethyl ether solvate) has been noted to afford an unusual aluminate anion which incorporates Al(μ-N)$_n$Al ($n = 1$, 2) motifs (Fig. 31) [286].

3.2.1.5. *Phosphines and arsines*. In contrast to lithium aluminate structures incorporating N-centred organic residues, those which utilise higher Group 15 elements are much less common and have been isolated exclusively from donor media. In one example a protic phosphine has acted as a Lewis base but has otherwise been excluded from the lithium 'ate product of reaction: hence, agostic bonding between

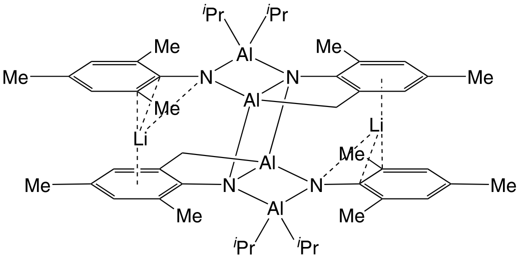


Fig. 30.

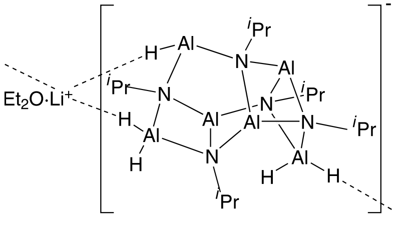


Fig. 31.

lithium and the single, terminal aluminium-bonded methyl group is responsible for the polymerisation of $(C_6H_{11})_2PH\cdot Li[(\mu\text{-}C)Me]_2Al(Me)^tBu$ [282]. However, simple heterocyclic monomers $Li[P(SiMe_3)_2]_2AlH_2$, $Li[PMe_2CH_2]_2AlMe_2$ and $LiPMe_2CH(SiMe_3)_2AlMe_2Cl$ have been isolated as bis(diethyl ether) [287] and mono(TMEDA) [288–291] solvates. The precise analogue of the first of these three compounds has also been achieved with arsenic in place of phosphorus [287]. The third, TMEDA-incorporating species has been found to undergo opening of the central six-membered $Li(PC)_2Al$ ring in the presence of THF, the result being $THF\cdot TMEDA\cdot LiPMe_2CH_2AlMe_3$ [289]. The significantly more complex dianionic phosphinidine species $\{(THF\cdot Li)_2P(C_6H_{11})[P(C_6H_{11})AlMe]_2\}_2$ has also been reported to result from the reaction of the Al(III) imide $[AlMeNMes]_4$ and $LiPHC_6H_{11}$ (Fig. 32) [292] with the arsenic-based analogue $\{(Et_2O\cdot Li)_2AsSi^iPr_3[As(Si^iPr_3)AlH]_2\}_2$ having been more recently reported [293].

3.2.1.6. Halide bridges. Although examples of lithium 'ate complexes containing aluminium-bonded halogen atoms have been described previously [290,291] the paucity of structural data regarding $Li(\mu\text{-}X)_nAl$ ($X =$ halogen) is, perhaps, surprising. The only Li ← F-containing species, notwithstanding previously mentioned (see Section 3.2.1.3) monomeric $Li[(\mu\text{-}O)C(CF_3)_2Ph]_2Al[OC(CF_3)_2Ph]_2$ [249], are $[(PhMe)_3\cdot Ag]^+$ $(Li\{[(\mu\text{-}F)AlF]_2F\}_2)^-$ [294] and tetrameric $THFLi\cdot(\mu\text{-}F)_3\text{-}AlC(SiMe_3)_3$ [250]. For the higher halogens examples are equally uncommon. A complex arrangement of contiguous heterobimetallic ring systems incorporating $Li(\mu\text{-}Cl)_nAl$ ($n = 1$, 2) motifs dominates the structural chemistry of tetrameric $LiAlCl_3C(SiMe_3)_3$, two of the four lithium centres being η^6-solvated by toluene (Fig. 33) [295]. In the case of X = Br, the simple dimer $Li(\mu\text{-}Br)_2AlBrAr$ [Ar = $(2,6\text{-}Mes_2)C_6H_3$] reveals similar η^6-stabilisation of the otherwise merely two-coordinate alkali metal centres — this time by one of the mesityl components of each Ar group [296].

3.2.1.7. Miscellaneous lithium aluminates. Ion-separated lithium aluminates have been reported almost uniquely in the presence of strongly coordinating Lewis bases. While THF is generally insufficiently strongly bonding to incur ion-separation, $[(THF)_4\cdot Li]^+[Al(NHPh)_3C(SiMe_3)_3]^-$ [274], $[(THF)_4\cdot Li]^+\{Al^tBu[NH(2,6\text{-}$

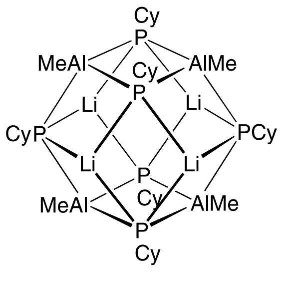


Fig. 32. THF omitted for clarity [292].

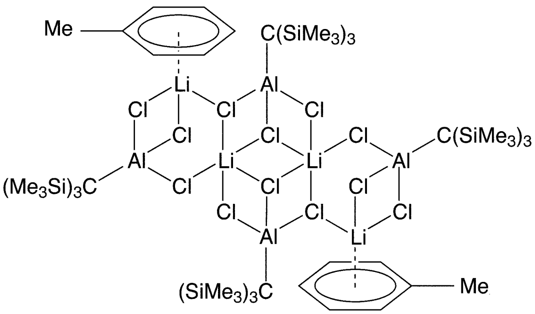


Fig. 33.

$^{i}\mathrm{Pr_2)C_6H_3]}^{i}\mathrm{Pr_2\}^-}$ [267] and $\mathrm{[(THF)_4\cdot Li]^+\{Al[Si(SiMe_3)_3]Cl_3\}^-}$ [297] have all been characterised. In a similar vein, bi- and tridentate ligands may incur ion-separation, as in internally deprotonated $\mathrm{[(TMEDA)_2\cdot Li]^+Al[CH(SiMe_3)_2]_2[CH(SiMe_3)\text{-}SiMe_2CH_2^-]}$ [298] (Fig. 34) and $\mathrm{(L_2\cdot Li)^+\{Al[CH(SiMe_3)SiMe_2CH_2][CH\text{-}(SiMe_3)_2]R\}^-}$ (L = 1,3,5-trimethyl-hexahydro-1,3,5-triazine, R = ^{t}Bu [299], $\mathrm{CH_2^{\,t}Bu}$ [299], $\mathrm{CH_2SiMe_3}$ [300]), the mixed ligand 'ates $\mathrm{[(TMEDA)_2\cdot Li]^+\{AlH[CH\text{-}(SiMe_3)_2]_2^{\,t}Bu\}^-}$ [301], $\mathrm{[(TMEDA)_2\cdot Li]^+\{Al(S^tBu)_3[C(SiMe_3)_3]\}^-}$ [263] and $\mathrm{(TMEDA\cdot Li)^+[AlH_3C(SiMe_3)_3]^-}$ [274], and also in the homoleptic species $\mathrm{[(L)_2\cdot Li]^+AlR_n^-}$ (L = $\mathrm{^tBuN(CH)_2N^tBu}$, R = $\mathrm{^tBuN(CH_2)_2N^tBu}$, $n = 2$ [268]; L = TMEDA, R = $\mathrm{^tBuN(CH_2)_2N^tBu}$, $n = 2$ [268]; L = TMEDA, R = H, $n = 4$ [222]). However, ion-bonded structures may still pertain — for example in $\mathrm{(TMEDA\cdot LiAlH_4)_2}$ (see above) [222] and $\mathrm{Al(\mu\text{-}N)_2Al}$-containing $\mathrm{(LiH)_2[HAlN(CH_2)_3NMe_2]_6}$ (Fig. 35) [302]. A similar duality of behaviour is recorded for cyclopentadienyl derivatives with the ion-bonded, Al–Cl–Al bridged η^5-sandwich complex $\mathrm{Li[(Me_4C_4N)AlMe_2]_2Cl}$ [303] (Fig. 36) and the ion-separated species $\mathrm{[Li(CpR_5)_2]^-(AlCp_2^*)^+}$ (R = benzyl) [304] both known. More strongly coordinating crown ethers [241] and cryptands [305] almost invariably yield ion-separated species [241].

It is noteworthy that lithium alane-aluminates, already alluded to in an ion-bonded context [303], show a significant predilection for ion-separation. The anionic components of these compounds assume a variety of basic forms. Direct Al–Al interactions have been recorded in $\mathrm{[(TMEDA)_2\cdot Li]^+[R_2Al\text{–}AlR_2R']^-}$ {R = $\mathrm{CH(SiMe_3)_2}$, R′ = H, Me [306]; R = $\mathrm{CH(SiMe_3)_2}$, R′ = Br [307]} (Fig. 37). Investigations in the field of homonuclear multiple bonding between Group 13 elements

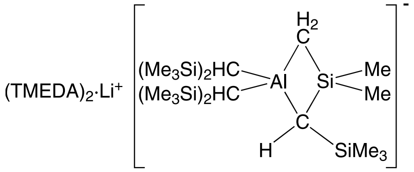


Fig. 34.

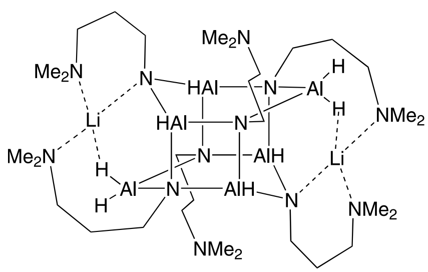


Fig. 35. Dimeric structure of $(LiH)_2[HAlN(CH_2)_3NMe_2]_6$ [302].

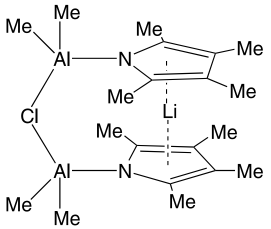


Fig. 36.

[308,309] have led to the observation that the reduction of Al–Al bonded species is capable of affording stable radical anions. Thus, $Al_2[CH(SiMe_3)_2]_4$ reacts with Li(0) in Et_2O/TMEDA to give $\{[(TMEDA)_2 \cdot Li]^+(R_2Al\overset{\cdots}{-}AlR_2)^{\bullet -}$ [$R = CH(SiMe_3)_2$] in which a single electron reduction has led to strengthening of the inter-aluminium bond [$Al\overset{\cdots}{-}Al = 2.53(1)$ Å] by virtue of a one-electron π-bond between the Group 13 metal centres [310]. In a similar vein, the treatment of R_2AlBr [$R = (2,4,6\text{-}{}^iPr_3)C_6H_2$] with elemental potassium affords $R_2Al–AlR_2$ [$Al–Al = 2.647(3)$ Å] which, in turn, reacts with lithium metal in TMEDA to yield $[(TMEDA)_2 \cdot Li]^+(R_2Al\overset{\cdots}{-}AlR_2)^{\bullet -}$ [$Al\overset{\cdots}{-}Al = 2.470(2)$ Å] [311]. Al–Al bonds have also been observed in a heterocyclic context in the case of $[(TMEDA)_2 \cdot Li]^+[R_2AlCH_2SiMe_2CHSiMe_3AlR]^-$ $\{R = CH(SiMe_3)_2\}$ (Fig. 38) [312]. While an ion-bonded species containing an Al(μ-H)Al unit has been reported [218], bridged Al(μ-X)Al motifs are more common in an ion-separated context and may take symmetric or asymmetric forms. While the former type include examples in which X = Cl [303] or $NN{\equiv}CP(N^iPr_2)_2$ [313] the latter category includes $(L_2 \cdot Li)^+[R_2Al(\mu\text{-}CH_2)AlR_2R']^-$ {L = TMEDA, R =

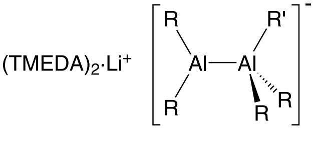


Fig. 37. $R = CH(SiMe_3)_2$, R′ = H, Me; [306] $R = CH(SiMe_3)_2$, R′ = Br, [307].

$CH(SiMe_3)_2$, $R' = CH_2^tBu$ [314]}. Further, Al(μ-CH_2)(μ-X)Al bridging units have also been reported: hence $[L_2\cdot Li]^+((\mu\text{-}CH_2)(\mu\text{-}X)\{Al[CH(SiMe_3)_2]_2\}_2)^-$ (L = TMEDA, X = H [315]; L = TMEDA, X = PMe_2CHPMe_2 [316]; L = 1,3,5-trimethyl-hexahydro-1,3,5-triazine, X = SMe [317]; L = 1,3,5-trimethyl-hexahydro-1,3,5-triazine, X = O_2NO [318]) (Fig. 39).

The ion-separated lithium alane-aluminate Li^+ $\{Al_{12}[N(SiMe_3)_2]_8\}^{\bullet -}$ comprises a much more complex radical anion and is synthesised by the direct combination of AlCl with $LiN(SiMe_3)_2$ [319]. Similarly, the largest metal cluster yet observed was isolated from the reaction of Al(I) iodide [320] and $LiN(SiMe_3)_2$. The Al_{77} core of the ion-separated species $\{[(Et_2O)_3\cdot Li(\mu\text{-}I)Li\cdot(OEt_2)_2]^+\}_2\{Al_{77}[N(SiMe_3)_2]_{20}\}^{2-}$ is comprised of an essentially metallic core in which aluminium adopts a coordination number of 12 [akin to the fcc packing in Al(0)] [321].

3.2.2. Sodium, potassium and higher aluminates

A sodium 'ate complex incorporating the Na(μ-H)Al motif has been observed as a tris(THF)-solvate {cf. $(THF)_3\cdot Li(\mu\text{-}H)AlH(OAr)_2$ [220]} in $(THF)_3\cdot Na(\mu\text{-}H)Al(OCPh_3)_3$ (Fig. 40) [220]. Examples have also been reported in which an aliphatic group, rather than a hydride, forms the basis of the intermetallic bridge. The polymeric sodium complex of $\{AlEt_3[N(SiMe_3)Ar]\}^-$[Ar = $(2,6\text{-}^iPr_2)C_6H_3$] results from the formation of weak intermolecular interactions not only between aryl rings and sodium cations but also between these metal centres and the CH_2-components of two of the three aluminium-bonded ethyl groups (Fig. 41) [229]. Polymerisation has also been reported to result from the 1,3-bridging action of an azide group in $(THF)_2\cdot Na(\mu\text{-}N_3)Al(N_3)_3\cdot(THF)_2$ [322].

Whereas M(μ-X)$_n$Al (X = O, N; $n = 1, 2$) units are common for M = Li, the lack of structural analogues for M = Na is notable. The tetrameric sodium 'ate complex

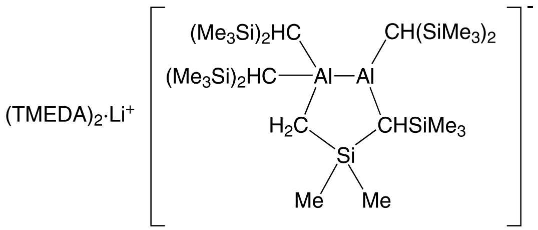


Fig. 38.

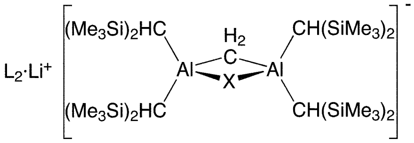


Fig. 39. L = Lewis base; X = H, [315] PMe_2CHPMe_2, [316] SMe, [317] O_2NO [318].

$(THF\cdot Na)_4[EtAlO_3SiN(SiMe_3)Ar]_4$ [$Ar = (2,6\text{-}{}^iPr_2)C_6H_3$] has been reported [323]. Whereas it is intriguing that while the THF-solvated $NaAlH(OCPh_3)_3$ monomer shows a single hydride-bridge between metal centres, its analogue, $NaAlH_2(OCPh_3)_3$, is based on a monomeric $Na(\mu\text{-}O)_2Al$ motif with two exocyclic aluminium-bonded hydride ligands [220]. Similar four-membered heterocycles are to be found in the complex dimeric tris(sodium) salt of the cyclic aluminophosphonate ligand $[Et_2AlOP{}^tBuO_2]_3$ (Fig. 42) [324]. A $Na(\mu\text{-}N)Al$ bridge has been reported in the sodium [sodium bis(aluminate)] $Na^+\{Na[N(SiMe_3)_2AlMe_3]_2\}^-$ (Fig. 43) [325]. A similar mono-nitrogen bridging motif has also been observed in the contiguous bicyclic arrangement at the core of $Na(\mu_2\text{-}N)H{}^tBu(\mu_3\text{-}N){}^tBu(\mu_3\text{-}Si)Me(\mu_2\text{-}N){}^tBuAlMe_2$ (Fig. 44) [326].

Sodium aluminates show a more pronounced affinity for ion-separation in the solid state than do their lithium analogues. For the simple homoleptic, aliphatic 'ate species $Na^+AlR_4^-$ monomeric examples exist for R = Me [327], Et (in both the absence [327] and in the presence [328] of external Lewis base), ${}^nPr$ and ${}^nBu$ [327].

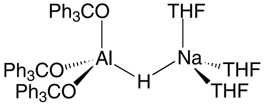


Fig. 40.

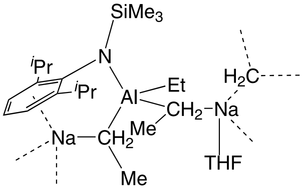


Fig. 41.

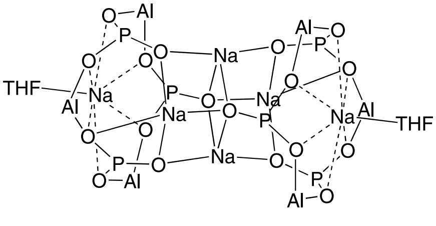


Fig. 42. Core of the dimeric tris(sodium) salt of the cyclic aluminophosphonate ligand $[Et_2AlOP{}^tBuO_2]_3$ [324].

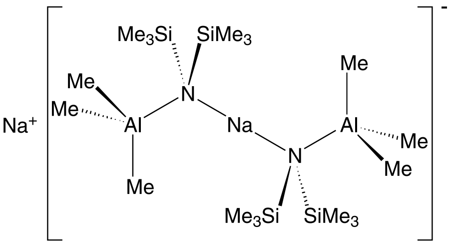


Fig. 43.

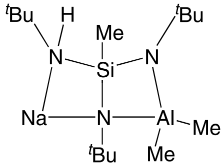


Fig. 44.

While ion-separation has been retained in cases where R contains electron-*poor* heteroatoms such as boron [329,330] it has, more surprisingly, also been noted when R incorporates electron-rich heteroatoms. Examples of the latter type are simple $Na^+\{(MeOH)_2\cdot Al[(O_2C)_2CHMe]_2\}^-$ [331], $Na^+\{Al[(O_2CCH_2)_2NMe]_2\}^-$ [332], the mixed-cation species $Na^+[MeN(CH)_2NMeCH]^+(AlCl_4^-)_2$ [333], the mixed-anion tris(sodium) bis(aluminate) compound $(Na^+)_3[Al(O_2CCH_2OH)_2(O_2CCH_2O)]^-[Al(O_2CCH_2OH)(O_2CCH_2O)_2]^{2-}$ (Fig. 45) [334], its hydrogen bonded analogue [335], and finally $Na^+\{Al[O(CH_2)_2O]_2[O(CH_2)_2OH]\}^-$ and its close relative $Na^+(\{Al[O(CH_2)_2O]_2[O(CH_2)_2OH]\}_2\{Al[O(CH_2)_2O]\})^-$ (Fig. 46) [336].

Sodium alane–aluminates exist as separated ions. Just as bridging hydride ligands have been observed in an ion-bonded context [220] so too are they known in the ion-separated species $Na^+[Me_3Al(\mu\text{-}H)AlMe_3]^-$ [337]. The bridging of two

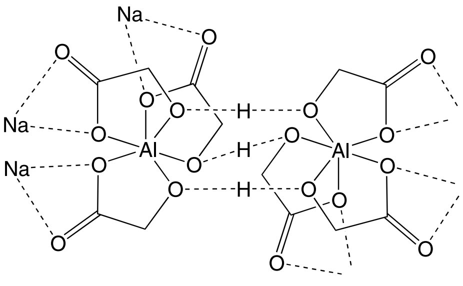


Fig. 45.

Al centres by a methylene unit (cf. Fig. 39) is observed in the cyclic anion $[(Me_3Si)_2HC]_2Al(\mu\text{-}CH_2)(\mu\text{-}X)Al[CH(Me_3Si)_2]_2$ ($X = ONO^-$ [318], $MeCO_2^-$ [338], N_3^- [338]) wherein the Group 1 metal ion is no longer uncoordinated but instead is solvated by THF [318], TMEDA [318] or a combination of an ether and 18-crown-6 [318,338]. Analogous oxo-bridging between aluminium centres is observed in the tris(aluminium) anion $\{Me_2Al[(\mu\text{-}O)AlMe_3][(\mu\text{-}O_2C)Ph]AlMe_2\}^-$ for which the separated sodium counter-ion is calyx[4]arene-encapsulated [339]. Bis(sodium) bis(aluminates) have also been observed, again in an ion-separated context, in $[(THF)_2 \cdot Na^+]_2$ $[Me_2Al(\mu\text{-}Ar)_2AlMe_2]^{2-}$ (Ar = 1,4-dihydro-1,4-naphthylene [340], 9,10-dihydro-9,10-anthrylene [341]).

The homoleptic potassium 'ate species $KAl[CH_2^iPr]_4$ is found to be a polymer in the solid state by virtue of the formation of extensive agostic interactions between the anion and the Group 1 metal centre [342]. This example notwithstanding, it is generally found that ion-bonded potassium aluminate complexes exist only when the 'ate moiety contains electron-rich heteroatoms, as in the $K(\mu\text{-}O)_2Al$- and $K(\mu\text{-}F)Al$-based dimers of $K[OMe(CH_2)_2O]_2Al[CH(SiMe_3)_2]_2$ [343] and of $(THF)_2 \cdot K\{(\mu\text{-}F)AlF[C(SiMe_3)_3]\}_2F$ [344], respectively. The apparently simple heteroleptic potassium aluminate $(^iPrOH)_2 \cdot KAl(O^iPr)_4$ forms a $K(\mu\text{-}O)_2Al$-based polymer but is rendered more complicated by the migration of two anionic ligands to the Group 1 metal centre such that the monomeric unit is more accurately described as $(^iPrO)_2K[(\mu\text{-}O)H^iPr]_2Al(O^iPr)_2$ (Fig. 47) [345]. Similarly K ← O interactions result not only in ion-association but also in polymerisation of the complex

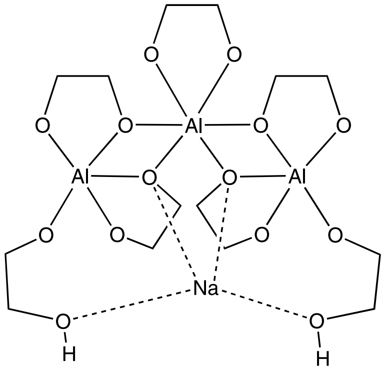


Fig. 46.

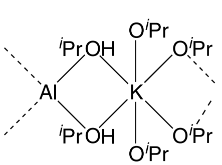


Fig. 47.

$\{DME\cdot KO(CH_2)_2OAl[CH(SiMe_3)_2]_2\}$ (Fig. 48) [346]. Whereas intramolecular oxo-chelation of the potassium ions is demonstrated by $DME\cdot KOMe(CH_2)_2OAl[CH(SiMe_3)_2]_2Me$ it is interesting to note that the formation of infinite chains in this species has a different origin — the existence of weak bonds between the Group 1 metal ion and the aluminium-bonded Me group of an adjacent ion-pair [346]. Lastly, polymerisation of the dimeric complex $\{K(\mu\text{-}Cl)_2Al[CH(SiMe_3)_2]_2\}$ results in the observation of both intra-dimer $K(\mu\text{-}Cl)_2Al$ and inter-dimer $K(\mu\text{-}Cl)Al$ motifs (Fig. 49) [347].

The isolation both of $KAlMe_3CN$ [348] and of $K^+AlMe_3ONO_2^-$ from non-donor solvents result in the observation of interactions between the alkali metal centre and ligand heteroatoms in the solid state. In the former case these manifest themselves as bonds to the cyanide N-centres while the second complex features oxo-bridging to the potassium ion [349]. Likewise, $KAl(\text{cyclooctene-3,8-diyl})_2$ features a potassium centre which is rendered tetra-coordinate by virtue of weak K···C interactions [350]. However, for the other AlR_3R' containing potassium 'ates to be synthesised in non-donor media, ion-separation is preferred — examples include the $AlMe_3H^-$ [351], $AlMeCl_3^-$ [352], $AlMe_2(OPh)_2^-$ [353] and $Al[(O_2CCH_2)_2NMe]_2^-$ anions [332]. Analogous complexes have been isolated from donor media and have demonstrated both solvated {in $(PMDETA)_2\cdot K^+[Al(Me)_3O^tBu]^-$, the formation of which is in competition with that of dimeric $PMDETA\cdot K[Al(Me)_3O^tBu]$ [354]} and unsolvated {in $K^+[Al(desferriferrithiocin)]^-$ [355]} motifs.

Potassium 'ates containing poly-aluminium anionic moieties are well known. These complexes display a range of bridging units between the Group 13 metal centres with one ion-bonded compound, $(THF)_2\cdot K\{(\mu\text{-}F)AlF[C(SiMe_3)_3]\}_2F$, having already been discussed [344]. Further, whereas it is known [356] that the

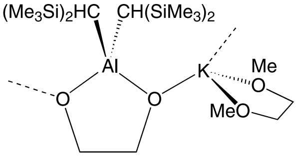


Fig. 48.

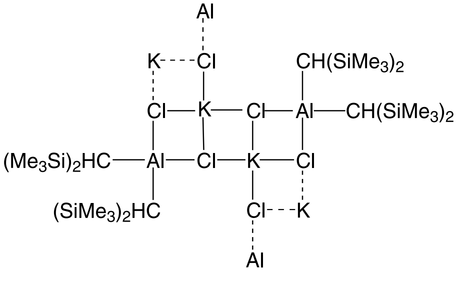


Fig. 49.

reduction of Al^{i}Bu$_2$Cl with elemental potassium affords ^{i}Bu$_2$Al–Al^{i}Bu$_2$ and a mixture of other species, it has recently been found that one of these by-products is the unique potassium 'ate K$_2$(Al^{i}Bu)$_{12}$ [357]. This complex incorporates *closo*-dodecahedral Al$_{12}$-cluster monoanions (the icosahedral structure of which contrasts with that of (fcc) $\{Al_{12}[N(SiMe_3)_2]_8\}^{\bullet -}$ [319]). These negatively charged clusters are bridged by trigonal antiprismatic K$^+$ centres that are bonded to three α-carbon atoms on each monoanion (mean K···C = 3.23 Å). The icosahedra reveal three types of Al–Al interaction in the solid state [2.679(5), 2.680(4) and 2.696(5) Å] [357]. However, ion-separated poly-aluminium anion species are also known. Examples exist not only of compounds which incorporate essentially naked potassium ions {e.g. K$^+$(AlMe$_3$)$_2$F$^-$ which reveals only weak interactions between alkali metal centres and lattice benzene molecules [358]} but also of (dibenzo-18-crown-6) solvated Group 1 metal centres in which the negatively charged moieties contain two {e.g. (Et$_3$Al)$_2$X where X = F$^-$ [359], (Me$_3$Al)$_2$X where X = O$_2$NO$^-$ [349], SCN$^-$ [360], O$_2^-$ [361,362] Cl$^-$, [361,363], OPh$^-$ [353], N$_3^-$ [364,365]} (Fig. 50), three {in (Me$_3$Al)$_2$X where X = SeMeAlMe$_3^-$ [366]} and four {e.g. (Me$_3$Al)$_2$X where X = O$_2$S[(OAlMe$_3$)$_2$]$^-$ (Fig. 51) [367]} aluminium centres, with more complex hepta(aluminium) monoanions having also been reported [368].

Rubidium aluminate complexes are extraordinarily rare. To our knowledge, the only solid-state characterisation of such a species is that of the simple ion-separated monomer Rb$^+$AlMe$_3$N$_3^-$ [369], a complex with a precise caesium analogue [370]. Similar ion-separated caesium aluminates have also been reported; Cs$^+$ AlMe$_3$NCS$^-$ [371] and Cs$^+$AlMe$_2$I$_2^-$ [372,373]. The relative of the potassium 'ate incorporating the (Me$_3$Al)$_2$N$_3^-$ [364,365] moiety has been reported to feature unsolvated caesium [365]. Two Cs$^+$ ions, solvated by 18-crown-6, exist in the same lattice as — but fail to interact with — the tris(aluminium) sulfate dianion [Me$_3$AlO]$_2$S(=O)OAlMe$_3$ [374]. Two examples exist of ion-bonded caesium aluminates. The dimerisation of CsAlMe$_3$F affords a central (CsF)$_2$ ring, with respect to which the two aluminium centres are exocyclic (Fig. 52) [375]. More recently, a

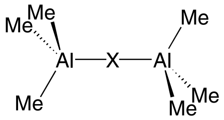


Fig. 50. X = O$_2$NO$^-$, [349] SCN$^-$, [360] O$_2^-$, [361,362] Cl$^-$, [361,363] OPh$^-$, [353] N$_3^-$, [364,365].

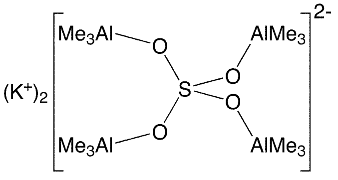


Fig. 51.

complicated caesium aluminophosphonate aggregate has been characterised. It is based on two tricyclic, capped six-ring $(THF)_3 \cdot Cs_3F(O_3P^tBu)_4(Al^iBu)_3$ moieties fused by a central $(^iBuAl)_2Al_2(\mu\text{-}F)_2(O_3P^tBu)_4$ cube-like unit (Fig. 53) [376].

3.2.3. *Lithium gallates, indates and thallates*

The majority of simple complexes of lithium and gallium replicate the ion-bonded $Li(\mu\text{-}X)_nAl$ (X = O, N, C etc.; $n = 1, 2$) motifs described above for lithium aluminates. Oxo-bridging is observed in the monomeric tris(THF) solvate of $Li[(\mu\text{-}O)H]GaMes_3$ [239], the dimeric bis(THF) relative of which is the precise structural analogue of the previously described lithium aluminate $[(THF)_2 \cdot LiOAlMes_2]_2$ [239] — the Group 1 metal centres residing exocyclic to a core $(MO)_2$ ring (M = Al, Ga). Inversion of this motif, affording an $(LiO)_2$ core with exocyclic gallium centres, is observed in the dimer $\{Li[(\mu\text{-}O)H]Ga(OH)_2[Si(SiMe_3)_3]\}_2$ wherein each monomeric component is supported by the coordination of two equivalents of the gallane precursor $(HO)_2Ga[Si(SiMe_3)_3]$, affording four six-membered $MO(M'O)_2$ (M = Li, M′ = Ga) arrangements (Fig. 54) [377]. The reaction of $[Ga^tBu_2(\text{neol-H})]_2$ (neol-H_2 = 2,2-dimethylpropane-1,3-diol) with LiOH in hexane results in the formation of $Li(\mu\text{-}O)Ga$-based $Li(Ga^tBu_2OH)(\text{neol-H})$ [378]. Whereas a lithium aluminate complex incorporating the chiral ligand binol has been shown to incorporate a $Li(\mu\text{-}O)Al$ motif [186,187], reaction of dilithiated (*S*)-binol with $GaCl_3$ in THF or with $PhCH_2GaCl_2$ in THF/DME has lately afforded the tris-$Li(\mu\text{-}O)_2Ga$ complexes $[(THF)_2 \cdot Li]$-

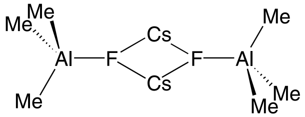


Fig. 52.

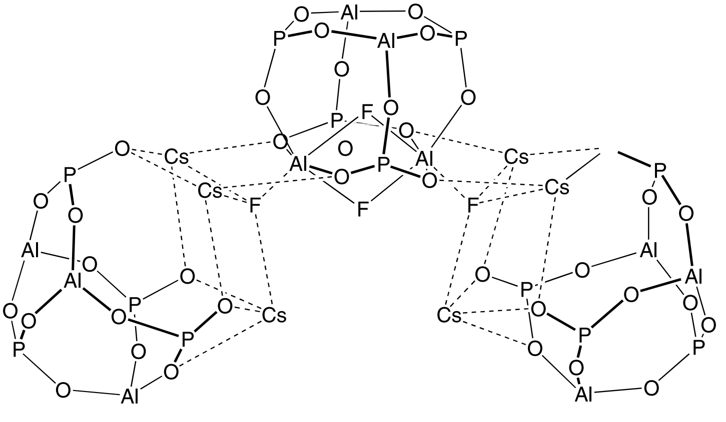


Fig. 53. The core of a recently characterised caesium aluminophosphonate aggregate [376].

$(\mathrm{THF}\cdot\mathrm{Li})\mathrm{Ga(binol)}_3$ and $[(\mathrm{DME})_3\cdot\mathrm{Li}]\mathrm{Ga(binol)}_3$, respectively [379]. Whereas an isolated $\mathrm{Li}(\mu\text{-O})_2\mathrm{Ga}$ ring-core has been noted in the monomeric bis(THF) lithium complex of the $\mathrm{Ga(OSiMe_3)_2[N(SiMe_3)_2]Cl^-}$ ion, comparable N-bridged—in $\mathrm{Et_2O\cdot Li[(\mu\text{-N})HAr]_2Ga^{n}Bu_2}$ $[\mathrm{Ar} = (2,6\text{-}\mathrm{Me_2})\mathrm{C_6H_3}]$ [380], $\mathrm{Et_2O\cdot LiGa\{[(\mu\text{-}N)(SiMe_3)CH_2]_2CMe_2\}}$ [381] and $\mathrm{(THF)_2\cdot Li[(\mu\text{-N})H^{t}Bu]_2Ga(C_6H_{11})_2}$ [382] — NC-bridged — in $\mathrm{LiGa(CN)_4}$ [383] — Cl-bridged — in $\mathrm{(THF)_2\cdot Li(\mu\text{-Cl})_2Ga\text{-}[Si(SiMe_3)_3]_2}$ [384], $\mathrm{(THF)_2\cdot Li(\mu\text{-Cl})_2Ga[C(SiMe_3)_3]Cl}$ [385], $\mathrm{[(Et_2O)_2\cdot Li(\mu\text{-}Cl)]_2Ga(C_4Ph_4)}$ [386] and $\mathrm{(^{i}PrOH)_2\cdot Li(\mu\text{-Cl})_2Ga^{t}Bu_2}$ [387] — and Br-bridged — in $\mathrm{Li(\mu\text{-Br})_2GaBr_2}$ [388] and $\mathrm{(THF)_2\cdot Li(\mu\text{-Br})_2Ga[Si(SiMe_3)_3]_2}$ [389] — motifs have also been reported. A more complex arrangement, based on a four-membered $\mathrm{(LiCl)_2}$ ring supported by four $\mathrm{Li(\mu\text{-Cl})_2Ga}$ heterocycles, is afforded by the trichlorogallate ion $\mathrm{Ga[2,4,6\text{-}^{i}Pr_3)C_6H_2]Cl_3^-}$ (Fig. 55) [390]. The association of lithium gallate monomers in the presence of a bifunctional Lewis base to afford an unusual dinuclear aggregate has been observed for the Li–(1,4-dioxane)–Li bridged complex $\mathrm{(1,4\text{-dioxane})_3\cdot\{Li[(\mu\text{-C})H_2SiMe_3]_2Ga(CH_2SiMe_3)_2\}_2}$ [391] in which the Lewis base adopts both bridging and terminal behavioural modes (Fig. 56). Higher aggregation state lithium gallates have been synthesised by, for example, the direct combination of $\mathrm{GaMe_3}$ with $\mathrm{LiN(SiMe_3)_2}$. The product, a polymer in the solid state, is based on intra-monomer $\mathrm{Li(\mu\text{-C})(\mu\text{-N})Ga}$ and inter-monomer $\mathrm{Li(\mu\text{-C})Ga}$ bridging motifs and is the precise structural analogue of $\mathrm{LiN(SiMe_3)_2AlMe_3}$ [281]. Although phosphorus- and arsenic-bridged analogues of lithium gallates have been reported to reproduce the $\mathrm{Li(\mu\text{-X})Al}$ motif on isolation as the solvates

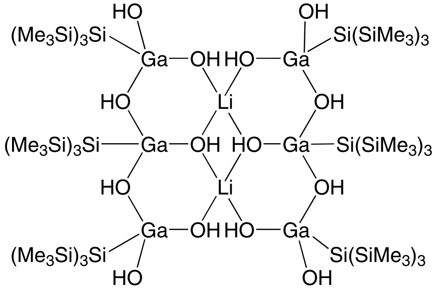


Fig. 54.

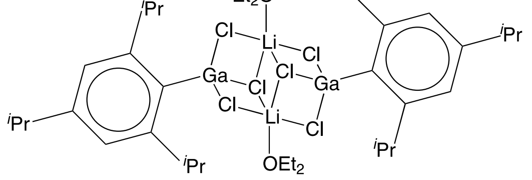


Fig. 55.

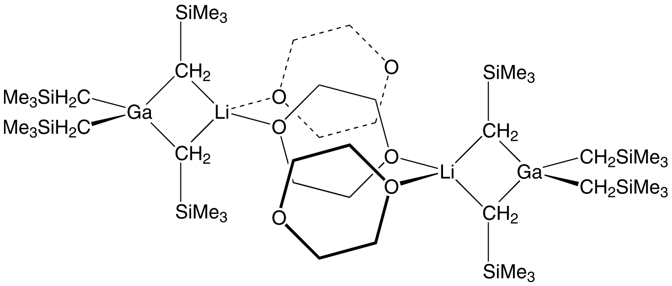


Fig. 56.

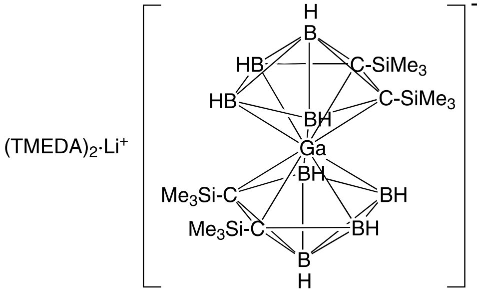


Fig. 57.

$(Et_2O)_2 \cdot Li[(\mu\text{-}X)(SiMe_3)_2]_2GaH_2$ (X = P, As) [392], the contiguous triheterocycle $(Et_2O)_2 \cdot Li[(\mu\text{-}P)^tBu]_2(GaMe_2)_2$ has also been reported [393].

More strongly coordinating crown ethers have been found to incur ion-separation in lithium gallate chemistry, as exemplified by the solid-state structure of $THF \cdot (12\text{-crown-}4) \cdot Li^+Ga\{[CPhCPh]_2\}_2^-$ [394]. Similarly, ion-separation has been observed in $(TMEDA)_2 \cdot Li^+GaR_2^-$ where R is the carborane cluster $\{[C(SiMe_3)]_2(BH)_3\}BH$ (Fig. 57) [395]. More unusual is the recent report of a low-coordinate lithium centre in $(Et_2O)_n \cdot Li^+Ga(Cl)_3[(2,4,6\text{-}Ph_3)C_6H_2]^-$ ($n = 1$, 2) [396]. Tri- and tetrasolvation of the lithium ion is noted in the straightforward complexes $(^iPrOH)_4 \cdot Li^+Ga^tBu_2Cl_2^-$ [387] and $L_n \cdot Li^+$ $Ga(fluorenyl)_4^-$ (L = DME, $n = 3$; L = THF, $n = 4$) in which the fluorenyl anions act as η^1-donors to the gallium centre (Fig. 58) [397]. Likewise $(THF)_4 \cdot Li^+Ga(XPh_2)_4^-$ (X = P, As) has been reported [398].

Directly gallium–gallium bonded species are less common than their aluminium analogues. Nevertheless, single Ga–Ga bonds have been noted in the ion-separated species $(THF)_4 \cdot Li^+ArClGa\text{–}GaCl_3^-$ [399] and ion-bonded $Li(\mu\text{-}Br)_2BrGaGaBr_3$ [388]. Notably, the inclusion of higher Group 13 elements introduces the possibility of multiple bonding between p-block metal centres in polymetallic anions [308,309] — a structural phenomenon largely unvisited for aluminate species [310,311]. Thus, reaction of R_2MgBr [$R = (2,4,6\text{-}^iPr_3)C_6H_2$] with $(1,4\text{-dioxane})_2 \cdot Ga_2Cl_4$ has resulted in the isolation and solid-state characterisation of $\mathrm{R_2Ga{-}GaR_2}$ [Ga–Ga = 2.515(3) Å] [400]. This species is reduced by elemental lithium to the ion-separated complex $(\text{12-crown-4})_2\cdot\mathrm{Li^+}$ $(\mathrm{Ar_2Ga}\overset{\cdots}{-}\mathrm{GaAr_2})^{\bullet -}$ ($\mathrm{Ga}\overset{\cdots}{-}\mathrm{Ga}$ = 2.343(2) Å, bond order = 1.5) {cf. $\mathrm{Al}\overset{\cdots}{-}\mathrm{Al}$-based radical anions [310,311]} [400]. A slightly longer inter-aluminium distance of 2.401(1) Å has been reported in the similar radical species $[\mathrm{(CH_2)_3(NMe)_3}]_2\cdot\mathrm{Li^+}(\mathrm{R_2Ga}\overset{\cdots}{-}\mathrm{GaR_2})^{\bullet -}$ [$\mathrm{R = CH(SiMe_3)_2}$], synthesised by the reaction of $\mathrm{(R_2Ga{-}GaR_2)_2}$ with LiEt [401]. More complicated gallate clusters have been noted lately. A $\mathrm{Ga_3}$-fragment has been observed to constitute part of the four-membered heterocyclic $\mathrm{Si(\mu\text{-}Ga)_2Ga}$ ring-core of the monoanion in the solid-state structure of $\mathrm{(THF)_4\cdot Li^+(Me_3Si)_2Si[(\mu\text{-}Ga)Si(SiMe_3)_3]_2Ga[Si(SiMe_3)_3]SiMe_3^-}$ (mean Ga–Ga = 2.541 Å, mean Ga–Si = 2.509 Å) (Fig. 59) [402]. Furthermore, arrangements of four gallium centres have twice been observed. The former of these reports details the synthesis — by the combination of gallium metal with iodine to yield a subhalide which can then be treated with $\mathrm{(THF)_3\cdot LiSiMe_3}$ — and characterisation of a convoluted seven-centre gallium–iodine ion in $\mathrm{(THF)_4\cdot Li^+}$ $\{\mathrm{I_3[GaSi(SiMe_3)_3]_4}\}^-$ wherein the anionic moiety is based on a fused array of three Ga–Ga edge-sharing $\mathrm{I(\mu\text{-}Ga)_2Ga}$ rings (mean Ga–Ga = 2.532 Å, Ga–I = 2.854 Å) (Fig. 60) [403,404]. In a similar vein, reaction of the subhalide '$\mathrm{Ga_2I_3}$' with $\mathrm{(THF)_3\cdot LiSiMe_3}$ has afforded $\mathrm{(THF)_4\cdot Li^+\{(Me_3Si)Si[GaSi(SiMe_3)_3]_3GaSiMe_3\}^-}$, the solid-state structure of which has revealed a weakly bonded [405] trigonal $\mathrm{Ga_3(SiMe_3)_3}$ arrangement [$\mathrm{Ga_{eq}{-}Ga_{eq}}$ = 2.790(1) Å] bis(capped) by $\mathrm{XSiMe_3}$ groups [X = Ga, Si such that $\mathrm{Ga_{ax}{-}Ga_{eq}}$ = 2.440(1) Å and $\mathrm{Ga_{eq}{-}Si_{ax}}$ = 2.402(2) Å] (Fig. 61)

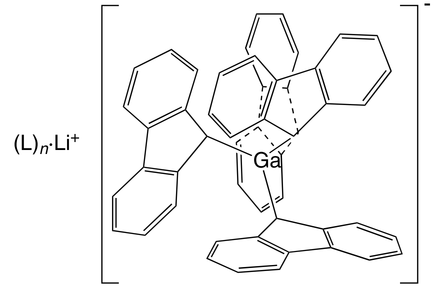


Fig. 58. L = DME, n = 3; L = THF, n = 4 [397].

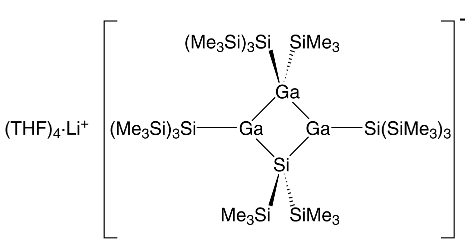


Fig. 59.

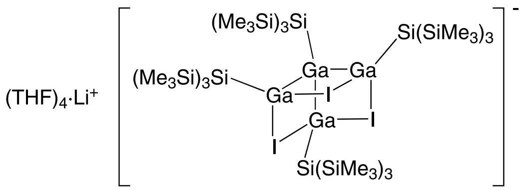


Fig. 60.

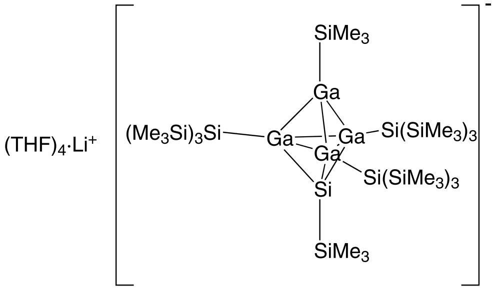


Fig. 61.

[406]. The relative bond lengths point, along with calculations, to the existence of both 2e2c and 2e3c bonding in the cluster, making it the first example of a *closo*-silagallane compound. Isolated from the same reaction mixture as $(THF)_4\cdot Li^+\{I_3[GaSi(SiMe_3)_3]_4\}^-$ (see above), the higher order gallate monoanion $Ga_9[Si(SiMe_3)_3]_6^-$ [for which $Li\cdot(THF)_4$ is the separated counter-ion] (Fig. 62) is based on a pentagonal bipyramid of gallium atoms of which the axial (Ga_{ax}) and two of the equatorial [$Ga_{eq(Si)}$] metal centres are each coordinatively saturated by a single $Si(SiMe_3)_3$ group [Ga_{ax}–$Ga_{eq(Si)}$ and $Ga_{eq(Si)}$–$Ga_{eq(Si)}$ = 2.803 Å (mean) and 2.465(2) Å, respectively]. The remaining three equatorial gallium centres (Ga_{eq}) are linked [$Ga_{eq(Si)}$–Ga_{eq} and Ga_{eq}–Ga_{eq} = 2.425(1) Å and 2.793(1) Å, respectively] and

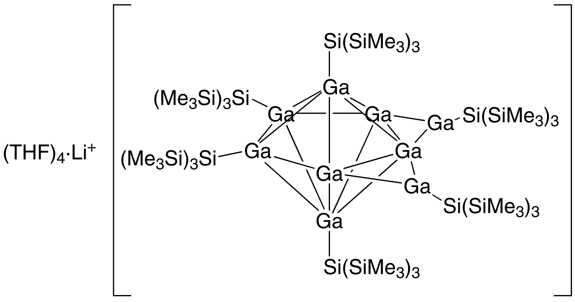


Fig. 62.

interact with the final two Ga-centres (Ga) to afford two triangular bonded $GaGa_{eq}Ga_{eq}$ arrays [mean $Ga–Ga_{eq} = 2.361$ Å] [403].

Whereas the reaction of $[Ga^tBu_2(neol-H)]_2$ with LiOH in hexane affords $Li(Ga^tBu_2OH)(neol-H)$, the solvent dependency of this process is demonstrated by the isolation of $THF\cdot Li_4[Ga^tBu_2(neol)]_3$ — which incorporates a complex array of $Li(\mu-O)_nAl$ ($n = 1, 2$) heterocycles — if the same process is attempted in THF [378]. Just one more example of a polygallium array in which no Ga–Ga bonds are noted has been reported. The core of this ion-bonded compound shows similarities to certain of the lithium bis(aluminates) discussed previously [235,236,238] insofar as it describes a spirocyclic arrangement. The THF-intercepted fragment $(THF)_2\cdot Li(\mu-O)_2Li(\mu-O)_2Li(\mu-O)_2Li\cdot(THF)_2$ incorporates the oxygen centres from two tripodal gallium phosphate $(OP^tBu\{[(\mu-O)GaMe][(\mu-O)GaMe]\}_{\frac{1}{2}})_3O^{2-}$ anions (Fig. 63) [407].

The lithium indate analogue of bis(Cl-bridged) $(THF)_2\cdot Li(\mu-Cl)_2GaClC(SiMe_3)_3$ is mono(Cl-bridged) $(THF)_2\cdot Li(\mu-Cl)InCl_2C(SiMe_3)_3$ [385]. While $(THF)_3\cdot Li(\mu-Cl)InCl_2N(SiMe_3)[(2,6-^iPr_2)C_6H_3]$ also contains a single Cl-bridge [408], the bis(-bridged) $Li(\mu-X)_2In$ (X = heteroatom) motif has been observed more frequently. Thus $(THF)_2\cdot Li(\mu-Cl)_2In[Si(SiMe_3)_3]_2$ has been noted [384] and is not dissimilar to $TMEDA\cdot Li(\mu-Br)_2In[CH(SiMe_3)_2]_2$ [409]. More recently, the combination of 1,4-dilithiotetraphenylbutadiene with $InBr_3$ in Et_2O has afforded $(Et_2O)_2\cdot Li(\mu-Br)_2In(C_4Ph_4)_2In(\mu-Br)_2Li\cdot(OEt_2)_2$ [410]. Oxygen bridges have been reported in monomeric $Li[(\mu-O)Ar]_2InCl_2\{Ar = [2,4,6-(Me_2NCH_2)_3]C_6H_2,\ In–(\mu-O) = 2.136(4)$ Å$\}$ [411]. For X = N it has been found that the 2:1 treatment of $Li_2(NSiMe_3)_2SiMe_2$ with $InCl_3$ yields monomeric $Li[(\mu-N)SiMe_3SiMe_2NSiMe_3]_2In$ [In–N = 2.055(3) Å, In–(μ-N) = 2.223(3) Å] [412] (Fig. 64) whereas four equivalents of $LiNMeSiMe_3$ react with one equivalent of $InCl_3$ in the presence of *para*-(*N*,*N*-

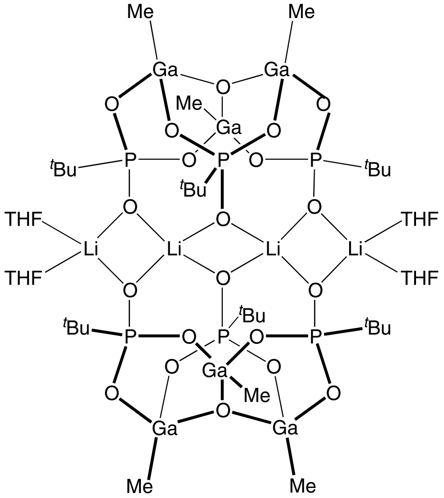


Fig. 63.

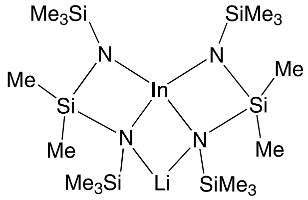


Fig. 64.

dimethyl)aminopyridine (= L) to afford L·Li[(μ-N)MeSiMe$_3$]$_2$In[N(SiMe$_3$)$_2$]$_2$ [413]. A more complex array of contiguous heterocycles is reported in the product of reaction between LiNMeSiMe$_2$NMeH and InCl$_3$. The result is the ion-bonded lithium indate dimer Li$_2$In$_2$(MeNSiMe$_2$NMe)$_2$(MeNSiMe$_2$NHMe)$_4$ which is Li(μ-N)In-bridged (mean In–N = 2.108 Å, mean In–(μ-N) = 2.163 Å) (Fig. 65) [414]. Just as the treatment of dilithiated (*S*)-binol with GaCl$_3$ in THF has yielded the tris-Li(μ-O)$_2$Ga complex [(THF)$_2$·Li](THF·Li)Ga(binol)$_3$, so the employment of InCl$_3$ affords the precise indium analogue [379].

In spite of the structures discussed thus far, ion-separation remains the prevalent motif in the structural chemistry of lithium indates. Simple (THF)$_4$·Li$^+$InR$_4^-$ (R = η^1-fluorenyl [415]; C≡CPh [92]; PPh$_2$ [398]), (THF)$_4$·Li$^+$InRR$_3'^-$ (R = Cl, R′ = η^1-fluorenyl [415,397], R = Cl, R′ = NPh$_2$ [413], R = C(SiMe$_3$)$_3$, R′ = Br [416]) and (15-crown-5)·Li$^+$InMe$_4^-$ [417] have all been observed to incorporate heavily solvated lithium ions and/or sterically congested indium centres. Worthy of particular note is the trimetallic complex {(THF)$_2$·Li[(μ-O)^{t}Bu]$_2$Al[(μ-O)^{t}Bu]$_2$Li·(THF)$_2$}$^+$InCl$_4^-$ which, while it is ion-separated, features an unusual bis(lithium)aluminate cation [255]. Interestingly, hydride-bridged bis(indates) have been observed in both ion-bonded and ion-separated contexts. Hence, both Li(μ-H)In and In(μ-H)In motifs are observed in the six-membered heterocyclic core of (THF)$_2$·Li{(μ-H)InH[C(SiMe$_3$)$_3$]}$_2$(μ-H) in the solid state (Fig. 66) [418]. However, TMEDA solvation of the Group 1 metal centre affords ion-separated

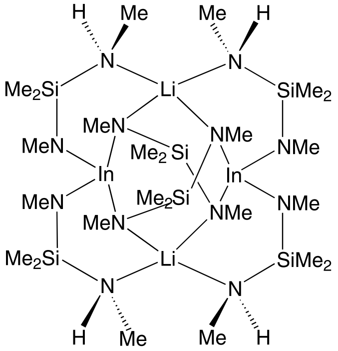


Fig. 65.

$(TMEDA)_2\cdot Li^+$ $Me_3In(\mu\text{-}H)InMe_3^-$ (mean In–H = 1.87 Å) and results in the observation of a non-linear [In–H–In = 148.6(10)°] homobimetallic anion in the solid state [419]. Only two more substantial lithium indate complexes exist-both of them, significantly, featuring p-block heteroatoms. In an attempt to model catalytically useful indium zeolites [420,421] the tetraanion $[InMeO_3SiNSiMe_3Ar]_4^{4-}$ [Ar = $(2,6\text{-}^iPr_2)C_6H_3$] has been synthesised by the treatment of $Me_3Si[(2,6\text{-}^iPr_2)\text{-}C_6H_3]NSi(OH)_3$ with one equivalent of $Li^+InMe_4^-$. The product can be viewed as being based on an $(InSi)_4$ pseudo-cubane structure which features In(μ-O)Si motifs (mean In–O = 2.053 Å) by virtue of its twelve edge-bridging oxygen centres [422]. Four of the cube faces are μ_4-capped by square-based pyramidal Group 1 metal centres (Fig. 67). The largest solid-state lithium indate aggregate reported is that incorporating the hexameric anion $[(InCl)_2InCl_2(As^tBu)_3]_2^{2-}$. This cluster adopts a structure in which two $(InAs)_3$ heterocycles stack on top of one another such that the two charged, tetra-coordinate In centres reside at diametrically opposite points of the hexamer (mean intra-trimer In–As = 2.622 Å, mean inter-trimer In–As = 2.669 Å) (Fig. 68) [423].

Four lithium thallates have been characterised in the solid state. A simple monomeric $Li(\mu\text{-}N)_2Tl$ fragment, akin to that observed profusely for the lower Group 13 elements exists in $(THF)_2\cdot LiTlR$ [R = 1,8-bis(trimethylsilylamido)naphthalene] [424]. However, a more complex $LiTl_4$ cluster containing both N(μ-Tl)N, N(μ-Tl)Tl and $N(\mu\text{-}Tl)_2Tl$ motifs has also been reported (Fig. 69) [425].

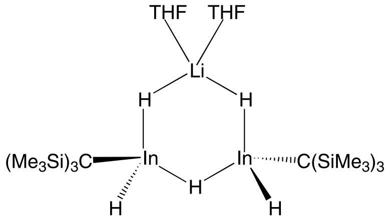


Fig. 66.

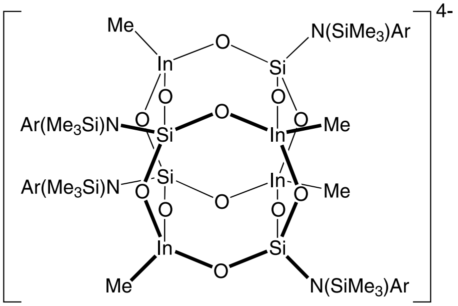


Fig. 67. The pseudo-cubic $[InMeO_3SiNSiMe_3Ar]_4^{4-}$ anion [Ar = $(2,6\text{-}^iPr_2)C_6H_3$], four $In_2Si_2O_4$-faces of which are capped by $THF\cdot Li^+$ (not shown for clarity) [422].

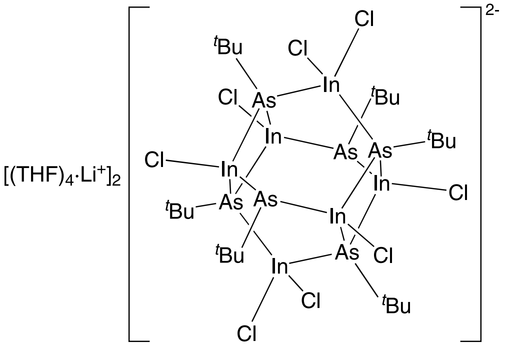


Fig. 68.

Whereas the cyclopentadienide-bridged complex PMDETA·Li(η^5-Cp)TlCp retains ion-association [426], separation is observed {in (12-crown-4)$_2$·Li$^+$CpTl-(η^5-Cp)TlCp$^-$} if a more strongly coordinating Lewis base is employed instead [427].

3.2.4. *Sodium, potassium and higher gallates, indates and thallates*

Akin to its sodium and potassium aluminate analogues, the simple gallate Na$^+${Ga[(O$_2$CCH$_2$)$_2$NMe]$_2$}$^-$ reveals a naked sodium ion in the crystal lattice in spite of the presence of four potentially coordinating carbonyl fragments in each mono-anion [332]. The sodium analogue of (TMEDA)$_2$·Li$^+$GaR$_2^-$ (R = {[C(SiMe$_3$)]$_2$(BH)$_3$}BH) [395] has been reported for the related carborane cluster R = {C(SiMe$_3$)BHC(SiMe$_3$)(BH)$_2$}BH (Fig. 70) [395]. The solid-state structure of K$^+$GaH(CH$_2$SiMe$_3$)$_3^-$ rather than incorporating a K(μ-H)Ga motif, instead reveals a naked potassium ion [200] whereas ion-separation in the presence of a crown ether has been reported only for the potassium gallate (THF)$_2$·(12-crown-4)·K$^+$ Ga{[N^{t}BuCH]$_2$}$_2^-$ [428]. The reduction of Ga$_2$Te$_3$ with K/NH$_3$ affords a species which demonstrates variable Group 1 metal ion behaviour in the solid state. Whereas several straightforward alkali metal 'ates incorporating MSi(SiMe$_3$)$_3$ groups (M = Group 13 metal) have been synthesised, only one has been characterised crystallographically; the participation of η^6 toluene-capped sodium ions in

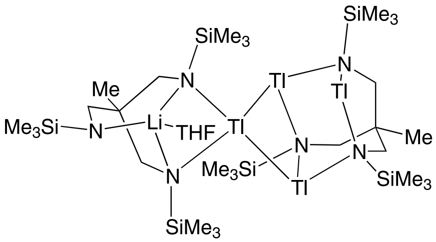


Fig. 69.

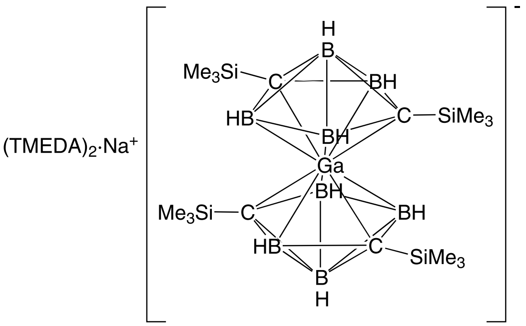


Fig. 70.

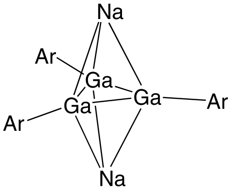


Fig. 71. Ar = (2,6-Mes$_2$)C$_6$H$_3$ [436,437].

weak GaMe···Na···MeGa interactions affording polymeric chains of PhMe·Na(μ-Me)$_n$GaMe$_{3-n}$–Si(SiMe$_3$)$_3$ ($n = 1, 2$) in the solid state [429]. The crystal structure of trimetallic K$^+$[(18-crown-6)·K$^+$]$_2$GaTe$_3^{3-}$ reveals distortions in the trigonal planar trianion [Ga–Te = 2.495(3)–2.513(2) Å] resulting from its proximity to the alkali metal centres [430]. More recently, the transition metal substituted species K(μ-Cl)$_2$GaClCo(CO)$_4$ has been reported [431]. Nitrogen bridges have also been noted in higher alkali metal gallate chemistry. Hence, whereas mono-bridged (THF)$_2$·Na(μ-N$_3$)Ga(N$_3$)$_3$·(THF)$_2$ is based on a two-dimensional polymeric structure in the solid state, so a double-bridged Na(μ-N)$_2$Ga motif [322] has been noted in the product of reaction between GaCl$_3$ and NaN$_3$; Na(μ-N$_3$)$_2$Ga(N$_3$)$_2$. This species has been shown to react with Et$_3$N to afford Et$_3$NGa(N$_3$)$_3$ [432] a precursor to GaN [433].

The tri- and tetrametallic species Na$_2$MM′[Mo$_3$O$_4$(O$_2$CEt)$_8$]$_2$ (M = M′ = Ga or M = Ga, M′ = Al) reveal isostructural chains in the solid state wherein each monomer contains two triangular propionate [Mo$_3$O$_4$(O$_2$CEt)$_8$]$^{4-}$ clusters which link Group 12/13 and Group 1 metal centres [434]. Empirically NaBF$_4$ and KCl are present in {[H$_2$C(NMe$_2$)O]$_2$·MGa$_2$R$_3$}$^+$X$^-$ [M = Na, K; R = 1,2-bis(8-oxyquinolin-7-yl)ethane; X = BF$_4$, Cl] wherein the cationic moiety incorporates two unassociated gallium centres [435]. However, anionic polygallium-containing clusters in which the Group 13 metal centres interact with each other are rather more common. The trigonal planar arrangement of bonded gallium centres in the Ga$_9$[Si(SiMe$_3$)$_3$]$_6^-$ ion described in Section 3.2.3 [403] is analogous to that observed in the delocalised C_{3v} cluster Ga$_3$Ar$_3^{2-}$ [Ar = (2,6-Mes$_2$)C$_6$H$_3$]. This has been isolated both with sodium (Fig. 71) [436,437] [$\mathrm{Ga}\overset{\cdots}{-}\mathrm{Ga} = 2.441(1)$ Å] and potassium [438] (mean $\mathrm{Ga}\overset{\cdots}{-}\mathrm{Ga} = 2.425$ Å) counter-ions by the reactions of $GaCl_3$ with $Na[(2,6\text{-}Mes_2)C_6H_3]$ [439] and of $[(2,6\text{-}Mes_2)C_6H_3]GaCl_2$ with K(0), respectively — both of the resultant Ga_3 clusters can be viewed as two π-electron metalloaromatic systems. The more extensive delocalised Ga_4-component of the ion-bonded cluster $Na_2Ga(GaAr_2)_3$ [$Ar = (2,4,6\text{-}{}^iPr_3)C_6H_2$] (Fig. 72), afforded by treating $Ar_2GaGaAr_2$ with sodium metal in triethylamine, contains a unique gallium centre which mutually bridges between each of the remaining three such metal atoms (mean $\mathrm{Ga}\overset{\cdots}{-}\mathrm{Ga} = 2.383$ Å) [440]. This compound can be reduced, in the presence of dry air, to the neutral species $Ga(GaAr_2)_3$ (mean $\mathrm{Ga}\overset{\cdots}{-}\mathrm{Ga} = 2.476$ Å) [440]. A remarkably higher bond order of three is claimed for an inter-gallium interaction in the sodium 'ate complex which results from the simple combination of $ArGaCl_2$ [$Ar = (2,6\text{-}Mes_2)C_6H_3$] with elemental sodium. The anionic moiety, $ArGaGaAr^{2-}$, displays a $\mathrm{Ga}{\equiv}\mathrm{Ga}$ distance of 2.319(3) Å in the solid state [437,441]. However, while π-interactions with the mesityl rings support the sodium counter-ion, the Ga···Na distances (mean = 3.08 Å) are also suggestive of a bonding interaction [436]. Hence the compound can be viewed as having a $(GaNa)_2$ heterocycle at its core. The gallium–gallium distance is not so low as to fail to compare with that of 2.343(2) Å in $(Ar_2\mathrm{Ga}\overset{\cdots}{-}\mathrm{Ga}Ar_2)^{\bullet -}$ [400] and some theoretical studies [309] have since suggested a lower bond order, with sodium–arene interactions responsible for the shortening of the inter-gallium bond. A polygallium cluster which lacks direct interactions between Group 13 metal centres is found in the triply bridged digallium hexaanion in the potassium gallate $(K^+)_6[Ga(\mu\text{-}Ar)_3Ga]^{6-}$ [Ar = bis(4-isopropylamido-2,3-dihydroxybenzamido)-*para*-phenylene] (Fig. 73) [442]. Finally no interactions exist between Group 13 elements in the structure of a potassium gallate which utilises gallium *tert*-butylphosphate ligands akin to those described above [407]. In this case, three eight-membered $(OP^tBu\{[(\mu\text{-}O)GaMe_2][(\mu\text{-}O)GaMe_2]\}_{\frac{1}{2}})_2^{2-}$ gallophosphonate heterocycles are situated on the periphery of a THF-solvated K_5O_6 cluster core which is based on a trigonal bipyramidal arrangement of alkali metal centres (Fig. 74) [443].

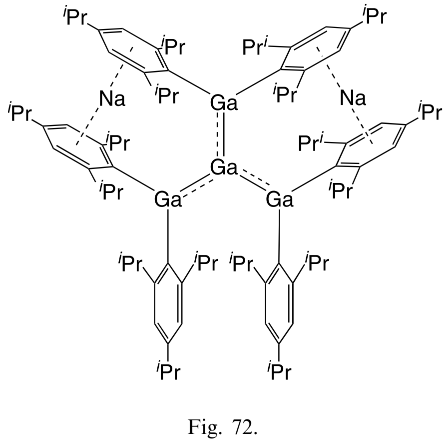


Fig. 72.

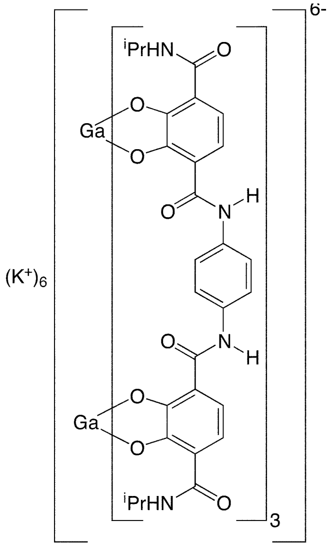


Fig. 73.

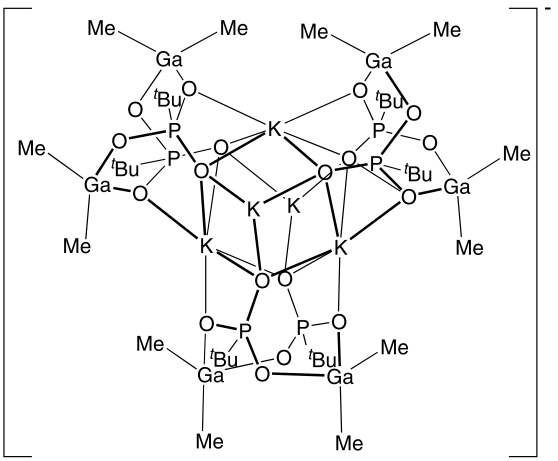


Fig. 74. A monoanion composed of three gallophosphonate ligands encapsulating a K_5O_6 core. THF and potassium counter-ions not shown [443].

Three sodium indates have been characterised in the solid state. At one extreme is simple, homoleptic sodium tetraphenylindate [444]. Just as the metathesis reaction of MCl_3 ($M = Al$, Ga) with NaN_3 has been shown to yield tetraazido complexes of both aluminium and gallium, so the indium analogue has been reported to be structurally analogous to the aluminium complex [322]. Altogether more complicated is the structure of the crystalline compound

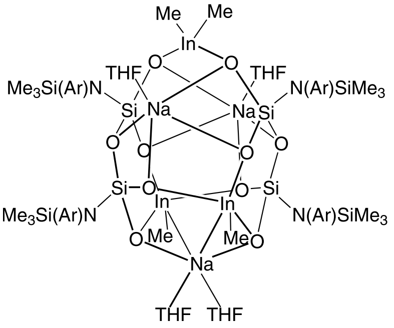


Fig. 75. Ar = (2,6-^{i}Pr$_2$)C$_6$H$_3$ [422].

$(THF)_4 \cdot Na_3\{[InMeO_3SiN(Ar)SiMe_3]_2InMe_2[SiO_2N(Ar)SiMe_3]_2\}$ [Ar = (2,6-^{i}Pr$_2$)-C$_6$H$_3$] {cf. [(THF)·LiInMeO$_3$SiN(Ar)SiMe$_3$]$_4$ [422]} (Fig. 75). This species, afforded by the 4:3 reaction of Me$_3$Si[(2,6-^{i}Pr$_2$)C$_6$H$_3$]NSi(OH)$_3$ [= Me$_3$SiArNSi-(OH)$_3$] with Na$^+$InMe$_4^-$, is based on the coordination of two formal $\{[NArSiMe_3]O_2(\mu\text{-}O)SiO_2NHAr\}^{4-}$ ions by two InMe^{2+}, one InMe$_2^+$ and three Na$^+$ moieties. This arrangement takes the form of two InO$_3$Si$_2$ six-membered rings linked by as many In(μ-O)Si bridges, each indate centre being tetrahedral and each sodium ion being either tetrahedral or square pyramidal [422].

Potassium indates are more common, with ion-separation having been observed in both simple homoleptic {in K$^+$InMe$_4^-$ [445], K$^+$In(CH$_2$SiMe$_3$)$_4^-$ [200], (benzo-15-crown-5)$_2$·K$^+$InX$_4^-$ (X = Br [446], I [447])}, more complex heteroleptic {in (18-crown-6)·K$^+$In(PC$_4$Me$_4$)$_2$Cl$_2^-$ [448], (15-crown-5)$_2$·K$^+$In(^{i}Pr)$_2$Cl$_2^-$ [449] and (Me$_2$SiO)$_7$·K$^+$InH(CH$_2^t$Bu)$_3^-$ [450]} and also mixed-anion {in [(18-crown-6)·K$^+$]$_2$InI$_2$ClMe$^-$InIClMe$_2^-$ [451]} contexts. In one case, however, both ion-bonded and ion-separated structures have been noted, depending on solvent conditions: treatment of KSCN with InCl$_3$ in the presence of (18-crown-6)/pyridine or of THF/bipyridyl affording either ion-separated (18-crown-6)·K$^+$ (C$_5$H$_5$N)$_2$·In(NCS)$_4^-$ [mean In–NCS = 2.184 Å] or ion-bonded (THF)$_5$·K(SCN)(C$_5$H$_4$N)$_2$·In(NCS)$_3$ [K–S = 3.327(4) Å, mean In–NCS = 2.162 Å], respectively [452]. Such ion-bonded potassium indates have been observed only rarely in the solid state, though a complex multi-dimensional polymer has been noted to result from the formation of an extensive K(μ-Br)$_2$In-based network between monomers of K(μ-Br)$_3$InMes (Fig. 76) [453]. Trimetallic potassium indates have also been observed. A mixture of activated In and KCl has been reacted with Fe$_3$(CO)$_{12}$ in the presence of THF to yield THF·KIn[Fe$_2$(CO)$_8$]$_2$ wherein the alkali metal ion interacts both with THF and two O-centres (one from each iron centre in an Fe$_2$(CO)$_8$ unit] from each of four anions [454]. The 3:1 reaction of K$_2$Te with In$_2$Te$_3$ affords the mixed potassium–indium–tellurium species (K$^+$)$_6$In$_2$Te$_6^{6-}$ which incorporates a binary telluroindate dimer anion [430,455] based on the association of two InTe$_3^{3-}$ units (cf. GaTe$_3^{3-}$ [430]). The result is the formation of a central In(μ-Te)$_2$In motif (mean

In–Te = 2.851 Å) about which four exocyclic Te-centres (mean In–Te = 2.740 Å) complete the distorted tetrahedral coordination spheres of the indium atoms [456]. Whereas TMEDA solvation of the Group 1 metal ion is necessary to stabilise ion-separated $(TMEDA)_2 \cdot Li^+Me_3In(\mu\text{-}H)InMe_3^-$ [419] the potassium analogue, $K^+({}^tBuCH_2)_3In(\mu\text{-}H)In(CH_2^tBu)_3^-$, reveals a Group 1 metal ion which, in the solid state, is weakly bonded both to the bridging hydride ligand [K···H = 2.71(9) Å] and to methylene and *tert*-butyl groups [205].

The ion-separated structure of the only fully characterised sodium thallate is based on a mixed-anion motif wherein three isolated $TlBr_4^-$ ions counter-balance a cationic (μ_4-Br)-incorporating $\{[(15\text{-crown-}5)\cdot Na]_4Br\}^{3+}$ cluster [457]. The stabilisation of two potassium ions by 2,2,2-cryptand facilitates the formation and structural characterisation of the two heterocycles $(SeTl)_2^{2-}$ and $(TeTl)_2^{2-}$ wherein the thallium–chalcogen bonds, at Se–Tl = 2.781(3) Å [212] and mean Te–Tl = 2.955 Å [212,458] are noticeably shorter than in comparable intermetallic species [459–462]. DFT calculations support NMR spectroscopic evidence (see Section 3.1) for the favourability of these cyclic dianions and their ability to deform readily about their Tl···Tl-axis. Lastly, the single reported rubidium thallate, $(15\text{-crown-}5)_2\cdot Rb^+$ $TlBr_4^-$, incorporates a heavily solvated cation and a straightforward, tetrahedral anion [463].

Of the few known caesium gallates almost all are ion-bonded in the solid state and of these a significant number have been found to incorporate $Cs(\mu\text{-}F)_nGa$ motifs. Whereas the crystal structure of $CsAlMe_3F$ reveals a central $(CsF)_2$ ring exocyclic to which are two aluminium centres [375], the gallium analogue is based on a one-dimensional ladder structure resulting from the association of monomeric units [mean ladder-edge Cs–F = 2.999 Å, mean ladder-rung Cs–F = 2.896 Å] [375]. However, a distorted trigonal bipyramidal core is observed for $Cs(\mu\text{-}F)_3GaMes$ [mean Cs–F = 3.223 Å] (Fig. 77). The extrusion of the alkali metal centre from the core of this structure is noticeable when its bonds to the F centres in adjacent molecules (resulting in the formation of a complex polymeric structure) are considered [Cs···F = 2.910–3.180 Å] [453]. Two-dimensional polymers based on $CsGaMe_2F_2$ units can be isolated both from non-donor [464] and Lewis base [465] media (Fig. 78). Both routes reveal products featuring complex arrays of edge-fused $Cs(\mu\text{-}F)_2Ga$ and $(CsF)_2$ rings [with one molecule of THF coordinated to each Cs centre in the latter structure, (Fig. 78b)]. A less simple bridging arrangment is noted

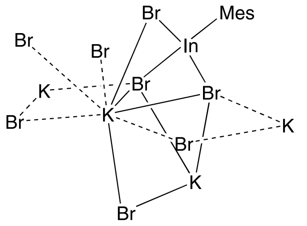


Fig. 76.

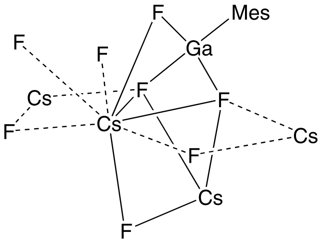


Fig. 77.

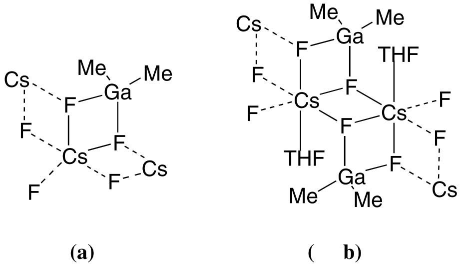


Fig. 78.

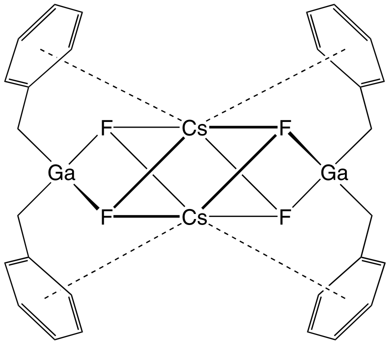


Fig. 79.

in the final polymeric caesium gallate to be discussed here. While the alkali metal centre in $CsGaN_3(CH_2Ph)_3$ is intramolecularly supported by interactions both with the azide α-N-centre and (η^6) with one benzyl π-system, it is intermolecularly stabilised by an azide γ-N-centre and by η^3-interaction with a benzyl π-system [466].

Oligomeric caesium gallates have also been reported. Thus $[Cs(\mu\text{-}F)_2Ga(CH_2Ph)_2]_2$ is based on four $Cs(\mu\text{-}F)_2Ga$ rings disposed about a non-bonded Cs_2 core (Fig. 79) with further stabilisation of the Group 1 metal centres being afforded by intra-dimer η^6-interaction with the aromatic components of the benzyl groups [467]. Also dimeric is $[Cs(\mu\text{-}F)Ga(CH_2Ph)_3]_2$ — a $(CsF)_2$-based aggregate in which exocyclic Group 13 metal centres are supported by both η^3- and η^6-interaction with the aromatic rings [465,468]. A similar dimeric motif, lacking π-interactions, has been noted in the solid-state structure of externally solvated $[(MeCN)_2\cdot Cs(\mu\text{-}F)Ga(CH_2Ph)_3]_2$ [468]. However, higher order tetrameric aggregates are also known. The simple heteroleptic 'ate complex $CsGa^iPr_3F$ is based on a $(CsF)_4$ pseudo-cubane [Cs–F = 2.924(2) Å, Ga–F = 1.970(4) Å] [469]. An ion-separated caesium gallate has been reported — a naked caesium ion existing in the lattice of the gallane–gallate species $Cs^+\ Me_3GaC{\equiv}NGaMe_3^-$ [470].

Ion-bonded caesium indate complexes representing close analogues of certain caesium gallates discussed above have been noted. Hence, the bis(acetonitrile) solvate of $Cs(\mu\text{-}F)InMes_3$ dimerises to form a $(CsF)_2$ ring with exocyclic indium centres (cf. $(MeCN)_2\cdot Cs(\mu\text{-}F)Ga(CH_2Ph)_3]_2$) [468]. Furthermore, tetrameric aggregates based on pseudo-cubane cores have been observed with the $Cs(\mu\text{-}F)_3In$ complex $[CsInR_3F]_4$ ($R = Et$, ^iPr) being the obvious analogue of the $CsGa^iPr_3F$ caesium gallate cluster [469]. Notably, however, the analogous pseudo-cubane $[CsInMe_3F]_4$ compares with the $(CsF)_2$ ring-based dimer and the one-dimensional ladder structure observed for both the corresponding aluminate and gallate [375]. A similarity between the propensity for formation of tetrameric pseudo-cubanes and infinite ladder structures is suggested by the observation that $CsIn^iPr_3F$ is capable of crystallising not only as a tetramer (see above) [469] but also as a one-dimensional ladder [471]. While a caesium indate analogue of the polymeric gallate $CsGaN_3(CH_2Ph)_3$ has been noted, it demonstrates several structural modifications. Thus intramolecular stabilisation of the Group 1 metal centre is no longer the result only of the formation of a bond to the azide α-N-centre and (η^6) with one benzyl π-system: instead it results from interactions with both the α- and β-azide N-centres and (η^4 and η^6) with two π-systems. Furthermore, polymerisation here results not from interaction with the azide γ-N-centre but merely by η^6-interaction with the third benzyl π-system on an adjacent monomer [466]. Chain formation via the association of dimeric units has been noted. Hence, the dimer of $CsInCl(CH_2Ph)_3$ is based on a four-membered $(CsCl)_2$ ring with exocyclic indium centres, the Group 1 metal ions being supported by η^6-coordination to phenyl rings at both an intra- and an interaggregate level [472].

Ion-separation in caesium indate structural chemistry has been known since the characterisation of straightforward, homoleptic $Cs^+InMe_4^-$ [445]. More recently, caesium ions stabilised only by weak interactions to lattice toluene molecules have been revealed in heteroleptic $Cs^+InF[N(SiMe_3)_2]_3^-$, in spite of the presence of a potentially donating fluoride ligand on the Group 13 centre [473]. The trimetallic species $(Cs^+)_5In[Se_3P(Se)P(Se)_2]_2^{5-}$ also exhibits an ion-separated structure in the solid state [474]. The anion is based on an $InSe_6$ core which incorporates two $In(\mu\text{-}Se)_2P$ (mean In–Se = 2.817 Å) and two $In(\mu\text{-}Se)P$ (mean In–Se = 2.665 Å) motifs (Fig. 80).

Finally, reaction of CsCl with $In(CH_2Ph)_3$ has recently afforded dimeric $Cs(\mu\text{-}Cl)In(CH_2Ph)_3$. The treatment of this species with dry oxygen has resulted in the isolation and crystallographic characterisation of the remarkable oxo-encapsulation product $Cs_2(\mu_4\text{-}O)In_4(CH_2Ph)_4(OCH_2Ph)_8$ (Fig. 81) [472]. This species is best viewed as comprising a cyclic In_4O_8 metalla(crown ether) through which is threaded a near linear Cs_2O [Cs–O = 3.4191(6) Å] molecule, the caesium ions each being further supported by η^6-interactions to four aromatic rings.

4. Overview

Group 1 ’ate complexes of Group 12 and Group 13 elements have been shown to be of great value to the preparative chemist. Although progress has been made towards rationalising the observed reactivities of Group 13 ’ate complexes, the synthetic utility of alkali metal triorganozincates makes the lack of detailed knowledge of their structural properties surprising. While ion-separated structures

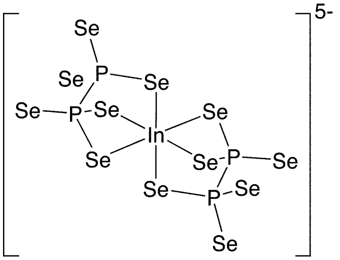


Fig. 80. Pentaanionic component of the trimetallic species $(Cs^+)_5\ In[Se_3P(Se)P(Se)_2]_2^{5-}$ [474].

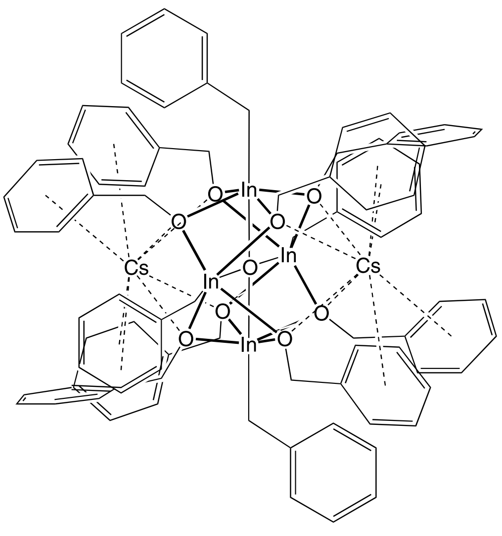


Fig. 81.

have been noted for a variety of alkali metals, heteroatomic (= X) zinc-bonded organic groups have afforded Li(μ-X)Zn bridges. This moiety is clearly related to the Li(μ-C)Zn and Li(μ-C)$_2$Zn units which dominate the remaining lithium zincate structures to have been reported — the latter of these motifs being synonymous with the formation of Li_2ZnR_4 spirocycles. Spirocyclic motifs have also been noted in a purely inorganic context with the observation of several ion-separated 'ate complexes which feature anions composed only of heavy chalcogen and Group 12 or Group 13 metal centres. For the higher alkali metals, Group 12 'ate complexes tend to reveal anion dimerisation and even polymerisation, as is demonstrated by the series of reported Group 1 thiocyanate complexes.

The principles of Group 1/Group 13 'ate complex structural chemistry are better understood than those which apply to 'ate complexes of Group 12 elements. Akin to the heterocyclic arrangements observed for alkali metal tetraorganozincates, the most commonly observed structural motif in Group 1/Group 13 'ate chemistry is $M(\mu\text{-}X)_nM'$ (M = alkali metal; X = H, C, N, O etc.; M′ = Group 13 metal; $n = 1$, 2), although homometallic rings [i.e. $M(\mu\text{-}X)_2M$] have been reported.

While the formation of polymetallic anions has been noted for both Group 12 and Group 13 'ate complexes, it is noteworthy that for the former Group direct metal–metal interactions have not been observed. Conversely, several Group 1/Group 13 'ate complexes feature direct inter-metal bonding between Group 13 metal centres. For Al-incorporating species such bonds have been generally found to be single. However, the reduction of an Al–Al bond has been noted to afford stable radical anions [310,311], while higher Group 13 elements show a more pronounced affinity for the formation of higher order inter-metal bonds. The ability of Group 13 elements to form inter-metal interactions has resulted in the observation of remarkable cluster anions — most notably in $\{Al_{77}[N(SiMe_3)_2]_{20}\}^{2-}$ [321].

Alkali metal 'ate complexes have been shown to exhibit a wide range of structural properties based on the coordinative requirements of one or both metal centres in both the solution and solid states. It is clear that their synthetic utility is also of significance, though not as well developed as it might be. Nevertheless, as our understanding of these unusual and versatile species advances, so too does the possibility of utilising their often-unique chemical reactivities.

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