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Review

Organic ammonium halides as analogues of main-group amide/imide complexes in the solid state: Extension of ring-laddering and ring-stacking principles

Andrew D. Bond

Department of Chemistry, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

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Contents

Abstract

The structural chemistry of primary, secondary and tertiary ammonium halides is reviewed with emphasis on application of ring-laddering and ring-stacking concepts in the organic solid state. Similarities between motifs observed in the crystal structures of the ammonium halides and in amide/imide complexes of main-group elements suggest a general analogy between $R_xNH_{4-x}^+X^-$ (X = Cl, Br, I) and $R_xN^{(3-x)-}M^{(3-x)+}$ (M = principally Group 1/Group 2 cations and derivatives of Group 13 elements, e.g. $[AlR]^{2+}$, $[AlR_2]^+$, $[GaR]^{2+}$, $[GaR_2]^+$, etc.). The origin of the analogy lies in comparable directional preferences for association of the cations and anions in both the organic and main-group systems. Although similar motifs are observed amongst the organic and main-group structures, directly comparable ammonium and amide/imide moieties (i.e. $R_xNH_{4-x}^+$ and $R_xN^{(3-x)-}$ with identical R groups) rarely form comparable motifs. This is attributed primarily to different metric features: $N^+(-H)\cdots X^-$ distances in the organic sample are significantly longer than $N\cdots M$ distances in the main-group complexes. This affects the balance between electrostatic forces that promote further association of the cationic and anionic moieties and the (principally steric)

E-mail address: adb@chem.sdu.dk.

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interactions between the amine moieties that hinder further association. Additional factors that contribute to the observed differences include greater electrostatic energy for divalent $RN^{2-}M^{2+}$, directional bonding preferences for the M^{n+} cation and the influence of solvation in the main-group systems.

Keywords: Ring-laddering; Ring-stacking; Crystal structures; Ammonium halides; Amide/imide complexes

1. Introduction

This review describes and develops an analogy between the structural chemistry of organic ammonium halides and amide/imide complexes of monovalent and divalent main-group elements in the solid state. The study arose initially from serendipitous preparation and crystallographic study of a tetrahydrofuran solvate of 2,6-di(*iso*-propyl)aniline hydrochloride, which contains discrete hydrogen-bonded cubanes [1].[1] The significance of this compound at the time was not the observation of hydrogen-bonded cubanes as such – similar motifs had been observed on several previous occasions [2–4] – but rather the fact that comparable cubanes exist in the structures of the Sn^{2+} and Pb^{2+} complexes with the dianion derived from the same organic moiety [5]. Furthermore, similarities between the geometrical attributes of the cubanes in both the organic and inorganic systems suggested that the driving forces responsible for self-assembly are comparable in the two cases. This is perhaps not surprising: both the organic and inorganic systems are essentially ionic solids with similar tendencies to aggregate, maximising the coordination numbers of the cations and anions, thereby maximising Coulombic energy. In both cases, aggregation is limited to some degree by the influence of the amide/imide moieties, and the same amide/imide moieties might be expected to exert similar influence in both the organic and inorganic systems. Such concepts are of course familiar to main-group structural chemists, forming the essence of the ring-laddering and ring-stacking principles developed by Snaith and co-workers during the mid-1980s [6–8], with significant later contributions by Mulvey [9,10]. They are considerably less familiar, however, to organic solid-state chemists who concentrate more commonly on structural motifs formed via directional hydrogen bonds. One principal purpose of the articles concerning the organic ammonium halides [11,12] was to demonstrate that the concepts of main-group chemistry – in particular ring-laddering and ring-stacking – find utility in the organic solid state, in fact providing a more complete global perspective for the ammonium halides compared to a more conventional analysis based on hydrogen bonds alone. In the first part of this article, the structural chemistry of the organic ammonium halides is reviewed, with emphasis placed on ring-laddering and ring-stacking principles. In the second part, the analogy between organic ammonium halides and main-group amide/imide complexes is developed, and some conclusions and predictions are made by transfer of information between the relatively extensive organic sample and the main-group arena. Throughout the article, compounds are labelled using the CSD reference code.

[1] I am grateful to Drs. Emma L. Doyle and Dominic S. Wright, University of Cambridge (UK), the former for preparation of the compound and the latter for encouraging examination of the analogy in a more general sense.

2. Structural chemistry of organic ammonium halides: ring-laddering and ring-stacking in the organic solid state

2.1. Directional preferences of $N(-H)\cdots X^-$ contacts in $R_xNH_{4-x}{}^+X^-$

Application of ring-laddering and ring-stacking principles in organic ammonium halides, $R_xNH_{4-x}{}^+X^-$, was described initially in two articles [11,12]. The first considered secondary ammonium moieties, $R_2NH_2{}^+$ and the second considered both primary and tertiary moieties, $RNH_3{}^+$ and R_3NH^+. The concepts were developed in each case by considering in a general sense the geometrical distribution of X^- with respect to the N^+ centre. In all of the samples, the shortest $N^+\cdots X^-$ contacts (ca. 3.0–3.2, 3.2–3.4 Å for X = Cl, Br) display geometrical attributes typical of strong hydrogen bonds: the $N{-}H\cdots X^-$ angles are close to linear and inversely correlated with the $N^+\cdots X^-$ distances. In all cases, the hydrogen-bonding capacity of the $R_xNH_{4-x}{}^+$ moiety is utilised in full, i.e. tertiary ammonium moieties form one $N{-}H\cdots X^-$ hydrogen bond, secondary ammonium moieties form two, and primary ammonium moieties form three. Thus, the "first coordination sphere" around N^+ in each case resembles a *pseudo*-tetrahedral arrangement. In R_3NH^+, this comprises three R groups and one $N{-}H\cdots X^-$ hydrogen bond; in $R_2NH_2{}^+$, two R groups and two $N{-}H\cdots X^-$ hydrogen bonds and in $RNH_3{}^+$, one R group and three $N{-}H\cdots X^-$ hydrogen bonds (Fig. 1). The *next* longest (i.e. non-hydrogen-bonded) $N^+\cdots X^-$ contacts naturally display a rather greater spread in both distance and directionality. The shortest of these contacts, however, are clustered around several specific regions. For primary ammonium moieties, $RNH_3{}^+$, the shortest $N^+\cdots X^-$ contacts of all (ca. 3.3–3.4 for X = Cl, Br) approach N^+ from the same side as the $N^+{-}H$ bonds, along an axis extending directly outwards from the $C{-}N^+$ bond. Considering the $RNH_3{}^+$ unit as a *pseudo*-tetrahedral moiety, this corresponds to approach towards the centre of the H_3 face (Fig. 1(a)). For secondary ammonium moieties, $R_2NH_2{}^+$, contacts of comparable magnitude (ca. 3.2–3.5, 3.2–3.9 Å for X = Cl, Br) approach N^+ in the plane of the $H{-}N^+{-}H$ group, along the bisector of the $H{-}N^+{-}H$ angle. This corresponds to approach towards the midpoint of the $H\cdots H$ edge of the *pseudo*-tetrahedral $R_2NH_2{}^+$ moiety (Fig. 1(b)).

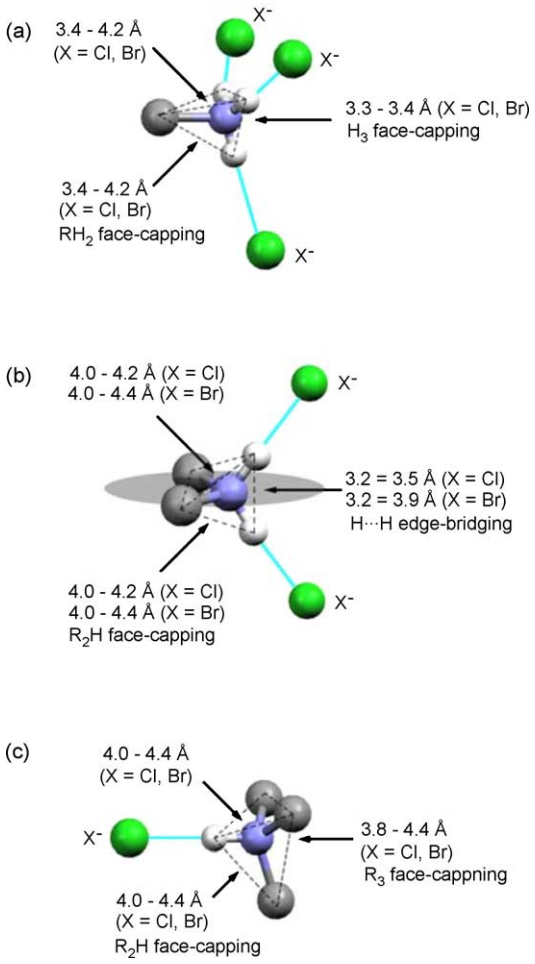


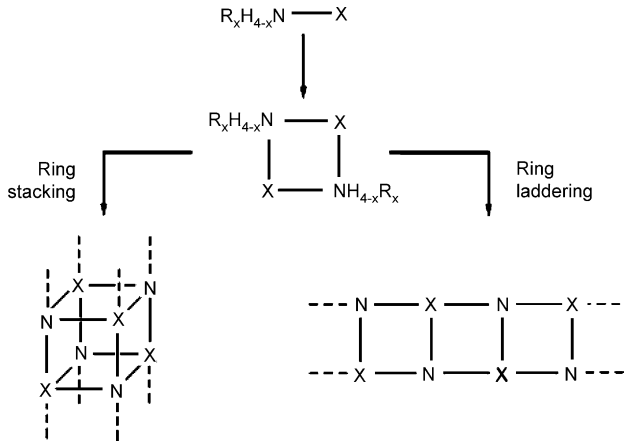
Fig. 1. Directional preferences for non-hydrogen-bonded approach of X^- towards: (a) primary ammonium moieties RNH_3^+; (b) secondary ammonium moieties $R_2NH_2^+$; (c) tertiary ammonium moieties R_3NH^+.

Thus, the shortest non-hydrogen-bonded $N^+\cdots X^-$ contacts serve to cap the H_3 face in RNH_3^+ and bridge the H···H edge in $R_2NH_2^+$. For each of the primary, secondary and tertiary ammonium moieties, slightly longer $N^+\cdots X^-$ contacts (ca. 3.4–4.2 for $RNH_3^+X^-$, 4.0–4.4 Å for $R_2NH_2^+X^-$ and $R_3NH^+X^-$) are also observed close to the directions that cap the RH_2 or R_2H faces (Fig. 1).

2.2. Association of $R_xNH_{4-x}^+X^-$ in the solid state

2.2.1. Ring-laddering

Since electrostatic energies display a reciprocal relationship to charge separation, the closest directions of approach lead to the greatest attractive electrostatic contributions to the lattice energy, and there is, therefore, some driving force for $R_xNH_{4-x}^+X^-$ ion pairs to associate so that the $N^+\cdots X^-$ contacts lie within the regions of space described above. From this perspective, ring-laddering and ring-stacking concepts evolve naturally. Derivation of the ring-laddering principle is particularly clear for secondary ammonium halides:



Scheme 1. Ring-laddering and ring-stacking in organic ammonium halides. R groups and H atoms bound to N are omitted from the laddered and stacked motifs to assist clarity.

$R_2NH_2^+X^-$ ion pairs may be envisaged to align side-by-side in an anti-parallel manner to form dimeric rings (Scheme 1). In some cases, the (principally steric) influence of the R groups of the ammonium moieties hinders any further association of these rings, and discrete $\{R_2NH_2^+X^-\}_2$ dimers are observed (e.g. CUNVUC [13] and HALOXN [14]). Since the dimers are formed from N^+–H···X^- hydrogen bonds alone, all four $N^+\cdots X^-$ distances are relatively short. Where further association occurs, each of the preferred directions of approach for X^- towards $R_2NH_2^+$ are co-planar with the H–N^+–H group of the ammonium moiety (Fig. 1(b)), thereby leading commonly to formation of one-dimensional ladders that are close to planar (Fig. 2). The existence of two different preferred directions of approach (H···H edge-bridging and R_2H face-capping) gives rise to two distinct types of ladder. In the first – referred to as Type 1 – two N^+–H···X^- hydrogen bonds make up the ladder arms, and a third N^+–H···X^- contact lying along the H–N^+–H bisector forms the ladder rungs (Fig. 2(a)). This third contact is apparently largely electrostatic in nature, but N^+–H···X^- angles greater than 90° also suggest some degree of hydrogen-bond character. Thus, Type 1 ladders may be considered to contain bifurcated and non-bifurcated N^+–H···X^- hydrogen bonds. In the second ladder type – referred to as Type 2 – two N^+–H···X^- hydrogen bonds make up the ladder rungs and one section of the ladder arms, and a third $N^+\cdots X^-$ contact lying to the backside of one N^+–H bond makes up the second section of the ladder arms (Fig. 2(b)). The nature of the third-shortest contact in this case is unequivocally electrostatic;[2] N^+–H···X^- angles of 90° and below are not consistent with a hydrogen-bond interaction. Thus, Type 2 ladders contain two non-bifurcated N^+–H···X^- hydrogen bonds and one electrostatic $N^+\cdots X^-$

[2] Although the direction of approach might possibly suggest some degree of overlap between the filled valence orbitals of X^- and the σ^*(N–H) or σ^*(N–C) orbitals of the ammonium moiety, $N^+\cdots X^-$ distances of 4 Å and above clearly preclude any significant orbital interaction.

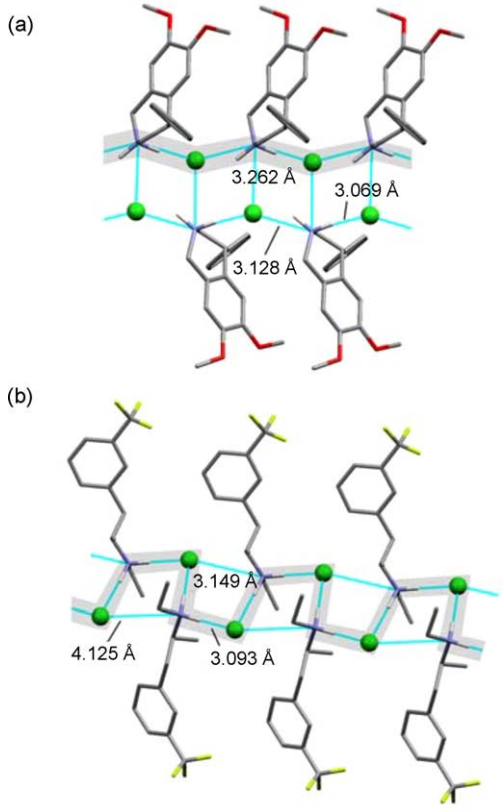


Fig. 2. Ladders in secondary ammonium halides, $R_2NH_2^+X^-$: (a) Type 1 ladder in PEFCUY [15], in which the third-shortest $N^+\cdots X^-$ contact lies along the bisector of the H–N^+–H angle and the hydrogen-bond motif (shaded) forms a *cis*,*cis* arrangement; (b) Type 2 ladder in BUHCIQ [16], in which the third-shortest $N^+\cdots X^-$ contact lies to the backside of one N^+–H bond and the hydrogen-bond motif forms a *trans*,*trans* arrangement. H atoms bound to C are omitted.

contact. The arrangement of contacts is reflected in the distribution of $N^+\cdots X^-$ distances in each case: Type 1 ladders contain three relatively short contacts, while Type 2 ladders contain two short and one significantly longer contact (Fig. 2).

On the basis of the observed distance distributions, and considering again that electrostatic energies display a reciprocal relationship to charge separation, it may be concluded that *in terms of electrostatic interactions between N^+ and X^- alone*, formation of Type 1 ladders in $R_2NH_2^+X^-$ is energetically preferable to formation of Type 2 ladders, which is in turn preferable to non-association of $\{R_2NH_2^+X^-\}_2$ dimers.[3] Of course, the electrostatic contribution must be in balance with all other contributions to the lattice energy (e.g. interactions between the R groups of the ammonium moiety, etc.), but it is likely to be the dominant contribution in the majority of these structures. In both Type 1 and Type 2 ladders, the underlying manner of association of $R_2NH_2^+X^-$ ion pairs and the resulting spatial distribution of the N^+ and X^- centres is comparable and is described effectively by the ring-laddering principle. Ring-laddering in fact provides a unifying concept that is more effective than conventional analysis of hydrogen bonds alone: although Type 1 and Type 2 ladders appear to form quite different hydrogen-bond motifs – a *cis*,*cis* arrangement in the first case and a *trans*,*trans* arrangement in the second (Fig. 2) – they are quite clearly related by ring-laddering. The different arrangements of the N^+–H$\cdots X^-$ hydrogen bonds within the two types of ladder demonstrate that ring-laddering within organic ammonium halides does not necessarily imply lateral association of *hydrogen-bonded* dimers, but rather lateral association of $\{R_2NH_2^+X^-\}_2$ units. The distinction between Type 1 and Type 2 ladders in $R_2NH_2^+X^-$ lies in the orientation of the organic moiety with respect to the ladder motif: in Type 1 ladders, the C–N^+–C plane lies approximately perpendicular to the ladder arms (and the bisector of H–N^+–H angle lies parallel to the ladder rungs), while in Type 2 ladders the C–N^+–C plane lies closer to 20° to the ladder arms (and one N^+–H bond lies parallel to the ladder rungs). The adoption of the Type 1 or Type 2 arrangement is driven by optimisation of the interactions between the R groups of the ammonium moieties – both within and between ladders – and the resulting distribution of $N^+\cdots X^-$ distances may be considered to be a "fine tuning" effect dependent on the orientation of $R_2NH_2^+$. From this perspective, directional N^+–H$\cdots X^-$ hydrogen bonds provide only a "secondary" influence on the solid-state structures of $R_2NH_2^+X^-$. Of course, the practice of segregating and ranking intermolecular forces is fraught with pitfalls; observed crystal structures reflect a balance between *all* forces. Nonetheless, envisaging the electrostatic contribution as the principal driving force – and implementing this within the framework of ring-laddering – proves fruitful in this system, particularly when the discussion is widened to consider primary and tertiary ammonium moieties.

In primary ammonium halides, $RNH_3^+X^-$, ladders (being inherently 3-connected motifs) may be constructed from N^+–H$\cdots X^-$ hydrogen bonds alone. In contrast to the planar $R_2NH_2^+X^-$ ladders, $RNH_3^+X^-$ ladders display a "sawtooth" conformation on account of the approximately tetrahedral disposition of the N^+–H bonds in RNH_3^+. The ladders are in most cases fully *transoid*, i.e. equivalent R groups lie on opposite sides of the ladder plane at each subsequent organic moiety along the ladder (e.g. HABXAK [17], Fig. 3(a)). One *cisoid–transoid* conformation also exists in adamantamine hydrochloride (FINVAZ [18]), giving rise to a sinusoidal ladder arrangement (Fig. 3(b)). This accommodates one bulky adamantamine unit, lying exclusively to the outside of the ladder curvature. Discrete dimers are not observed amongst the primary ammonium halides; the hydrogen-bonding capacity of the RNH_3^+ moiety is always utilised in full.

In tertiary ammonium halides, $R_3NH^+X^-$, discrete dimers are evident in several cases, e.g. HIJDEJ [19], MOATPB10

[3] Although the Type 1 ladders contain shorter attractive $N^+\cdots X^-$ contacts, of course they also contain shorter repulsive $N^+\cdots N^+$ and $X^-\cdots X^-$ contacts. A simple evaluation of the net interaction (along the lines of the derivation of Madelung constants for extended 3D ionic solids) can be made to confirm that Type 1 ladders are indeed more stable in electrostatic terms than Type 2 ladders, which are in turn more stable than isolated $\{R_2NH_2^+X^-\}_2$ dimers.

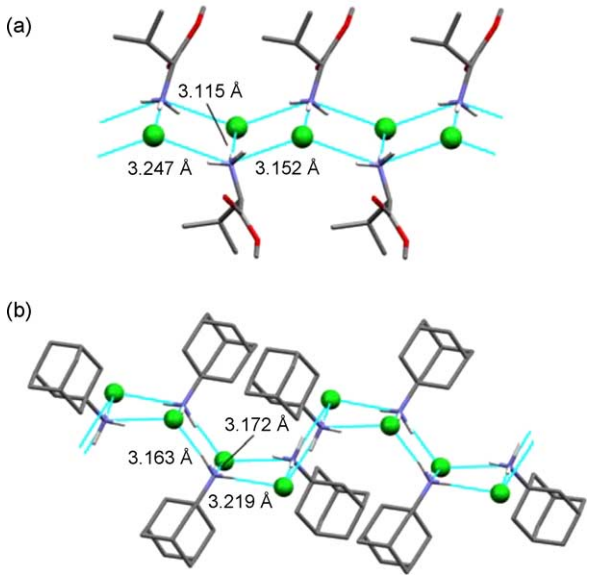


Fig. 3. Hydrogen-bonded ladders in primary ammonium halides, $RNH_3^+X^-$: (a) *transoid* sawtooth ladder in HABXAK; (b) *cisoid–transoid* sinusoidal ladder in FINVAZ. H atoms bound to C are omitted.

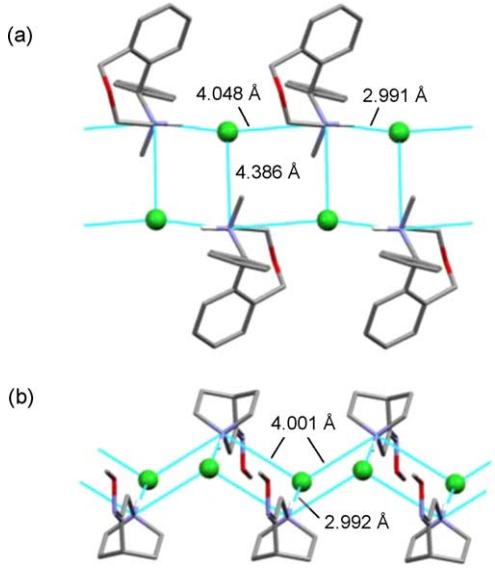


Fig. 4. Type 1 and Type 2 ladders in tertiary ammonium halides, $R_3NH^+X^-$: (a) projection onto the planar Type 1 ladder in POLCEY; (b) sawtooth Type 2 ladder in LEBHAB. H atoms bound to C are omitted.

[20] and VALJOH [21]. Most commonly, each ammonium moiety within such dimers forms one N^+–H···X^- hydrogen bond that is close to linear and one electrostatic R_2H face-capping contact lying approximately perpendicular to it. In other cases (e.g. VALJOH), the N^+–H vector points between the two X^- anions so that bifurcated N^+–H···X^- hydrogen bonds may be envisaged. Again, the distinction lies only in the orientation of the ammonium moiety with respect to the dimer motif; the underlying manner of association of the $R_3NH^+X^-$ ion pairs is comparable in each case. Where further laddering association takes place, two distinct types of $R_3NH^+X^-$ ladder are formed, again reflecting two distinct preferred directions of approach for X^- towards the R_3NH^+ moiety. In the first ladder type, denoted Type 1, the ladder arms are formed by N^+–H···X^- hydrogen bonds and N^+···X^- contacts that cap the R_3 face of the R_3NH^+ moiety (e.g. POLCEY [22]; Fig. 4(a)). The ladder rungs are formed by N^+···X^- contacts that cap one R_2H face and the resulting ladders are planar. In a second type of ladder – denoted Type 2 – the ladder rungs comprise N^+–H···X^- hydrogen bonds and the ladder arms are formed by two N^+···X^- contacts that cap R_2H faces (e.g. LEBHAB [23]; Fig. 4(b)). Since the normals to these faces lie at ca. 120° to each other, these ladders form "sawtooth" conformations, broadly comparable to those in hydrogen-bonded *transoid* $RNH_3^+X^-$ ladders (Fig. 3(a)). The fact that ladder motifs are observed for each of the primary, secondary and tertiary ammonium halides confirms the unifying nature of the ring-laddering principle and reiterates that the principal driving force for association of $R_xNH_{4-x}^+X^-$ in the solid state is electrostatic. The influence of N^+–H···X^- hydrogen bonds may be perceived to be secondary, affecting the conformation of the ladder motifs and the N^+···X^- distance distributions.

2.2.2. *Ring-laddering in two dimensions*

In many structures, amongst each of the primary, secondary and tertiary samples, laddering association occurs in two directions to form extended two-dimensional (2D) nets. Several distinct classes of net may be classified, the most common being the 4^4 (square) net [24]. For secondary ammonium halides, the co-planar approaches preferred for X^- give rise to planar 4^4 nets in which each N^+ centre forms two N^+–H···X^- hydrogen bonds and two relatively longer R_2H face-capping contacts. The relative orientation of the $R_2NH_2^+$ moieties within the net varies between structures. In some cases, the nets resemble Type 2 ladders that are associated further via face-capping contacts (e.g. MAESCI [25]; Fig. 5(a)). In others, the distinction is less clear (e.g. YUWWIW [26]; Fig. 5(b)). This reiterates that ring-laddering should not necessarily be considered in terms of lateral association of *hydrogen-bonded* $\{R_2NH_2^+X^-\}_2$ dimers, and that the orientation of the N^+–H bonds within the 4^4 net – and therefore, the resulting N^+···X^- distance distribution – is a consequence of optimisation of interactions between R groups, both within and between nets. The interactions between R groups can in fact exert an apparent influence on the nature of the nets themselves. In SEFWAB [27], for example, one R_2H face-capping N^+···X^- contact from each N^+ centre is particularly long (ca. 5.45 Å) as a result of the presence of one bulky R group on the $R_2NH_2^+$ moiety (Fig. 5(c)). This produces an apparent 3-connected 4.8^2 net rather than a 4-connected 4^4 net. The nets are fundamentally comparable: the 4.8^2 net is simply a 4^4 net in which one of the face-capping N^+···X^- contacts around each N^+ centre is significantly elongated.

4^4 nets are also observed amongst tertiary and primary ammonium halides. For tertiary ammonium moieties, these

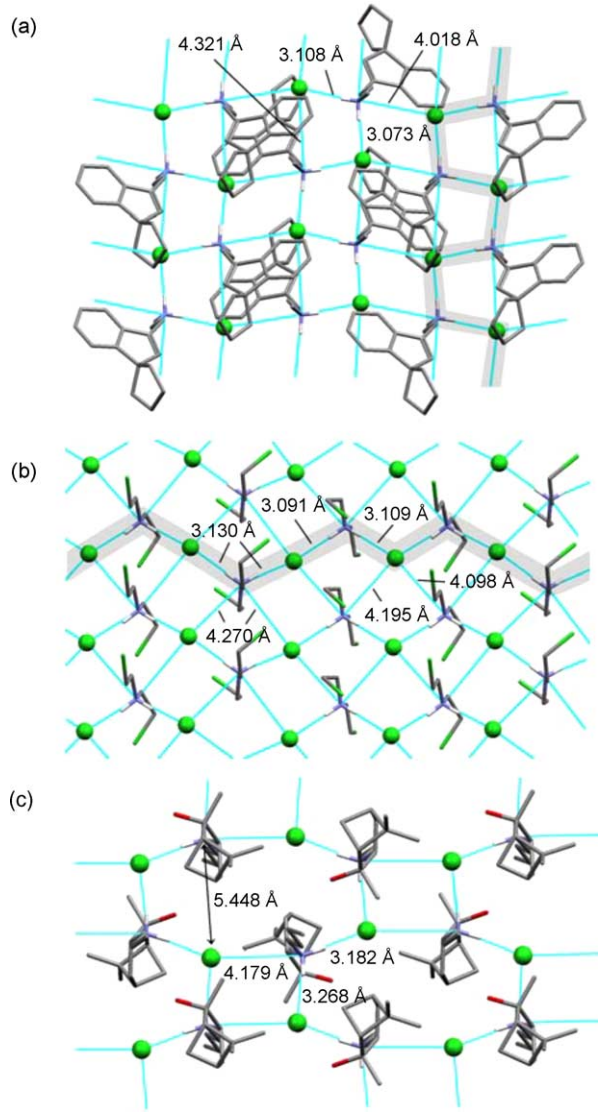


Fig. 5. Projection onto the planar 2D nets in secondary ammonium halides, $R_2NH_2^+X^-$: (a) 4^4 net in MAESCI in which Type 2 ladders (containing a *trans*,*trans* hydrogen-bond arrangement) may be clearly visualised; (b) 4^4 net in YUWWIW containing an unusual *cis*–*trans* hydrogen bond arrangement; (c) 4.8^2 net in SEFWAB derived from elongation of one R_2H face-capping $N^+\cdots X^-$ contact. H atoms bound to C are omitted.

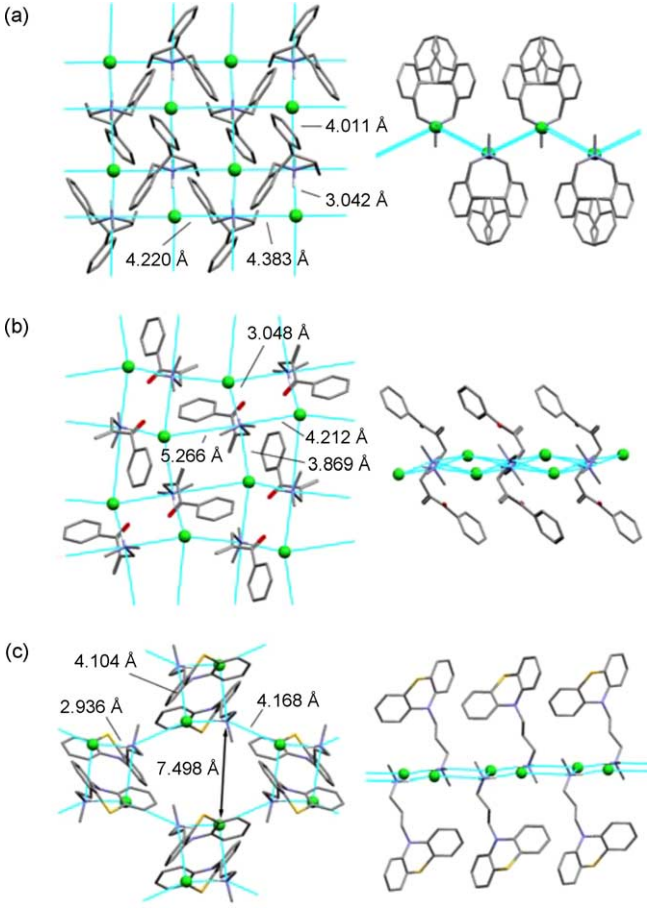


Fig. 6. Projections onto the plane and perpendicular to the plane of the 2D nets in tertiary ammonium halides, $R_3NH^+X^-$: (a) 4^4 net in POLCIC in which all N^+—H vectors are parallel and the net displays a sawtooth conformation in projection along that direction; (b) 4^4 net in SITJAG in which the arrangement of $N^+\cdots X^-$ contacts is less regular; (c) 4.8^2 net in PROMZC01 in which one face-capping $N^+\cdots X^-$ contact is significantly elongated. H atoms bound to C are omitted.

contain one N^+–$H\cdots X^-$ hydrogen bond and three R_2H face-capping contacts. Since the face-capping contacts lie at ca. 120° to each other, these nets are non-planar. In some cases, all of the N^+–$H\cdots X^-$ hydrogen bonds are aligned in a parallel manner so that the nets appear indistinguishable from sawtooth Type 2 ladders when viewed in projection along the N^+–$H\cdots X^-$ vectors (e.g. POLCIC [28]; Fig. 6(a)). Where the N^+–$H\cdots X^-$ hydrogen bonds within the net are not parallel, the conformation and $N^+\cdots X^-$ distance distribution is less regular (e.g. SITJAG [29]; Fig. 6(b)). Instances are again observed in which one $N^+\cdots X^-$ contact from each N^+ centre is elongated, giving rise to apparent 4.8^2 nets. In PROMZC01 [30], for example, one contact around each N^+ centre is elongated to ca. 7.5 Å, much too long to be simply a consequence of interactions between R groups *within* the net (Fig. 6(c)). This elongated contact arises as a consequence of interactions between R groups in *adjacent* nets: the R groups are interdigitated in such a manner that those of the adjacent net project into the gaps formed by the elongated $N^+\cdots X^-$ contacts. This example shows clearly that the nature of the structural motif may be influenced significantly by interactions between the R groups in *adjacent* motifs.

In the primary ammonium halides, regular 4^4 nets are relatively rare but are observed in some structures, e.g. DEAMMC02 [31], DODAMB [32], DOMBOW01 [33], HECBEW [34], ZZZLWK02 [31]. The interactions around each N^+ centre comprise three N^+–$H\cdots X^-$ hydrogen bonds and one RH_2 face-capping contact. In each case, the nets may be envisaged as $RNH_3^+X^-$ sawtooth ladders associated further in a lateral manner. In projection along one set of $N^+\cdots X^-$ vectors, the nets are indistinguishable from sawtooth ladders. In the primary 4^4 nets, the R groups of the ammonium moieties are either long *n*-alkyl chains or small

aromatic groups, each of which present minimal steric hindrance to lateral association in the plane of the net. Crucially, these groups also present minimal steric hindrance to interdigitation of adjacent nets, i.e. the R groups of adjacent nets interdigitate without requiring expansion of the $N^+\cdots X^-$ contacts within the nets.

A second more common class of net exists amongst the primary ammonium halides, in which each N^+ centre forms three N^+–H$\cdots X^-$ hydrogen bonds that are close to linear, giving rise to 3-connected 6^3 nets. Several conformations are observed for such nets, the principal variation lying in the coordination geometry of X^-. In one type, exemplified by EDUGUF and UFAJAM [35], the three-fold coordination sphere of X^- is approximately planar so that the six-membered rings of the 6^3 net form an "envelope" arrangement in which the three N^+ centres and two of the X^- anions lie in a common plane and the third X^- anion lies out of this plane (Fig. 7(b)). Viewed along the direction of the $N^+\cdots N^+$ vectors, a "sawtooth" arrangement is observed, although not exactly comparable to the $RNH_3{}^+X^-$ sawtooth ladders on account of the approximately linear $N^+\cdots X^-\cdots N^+$ angles. In a second conformation, exemplified by FINVED [36] and PUDKUU [37], the coordination geometry of X^- is pyramidal and the six-membered rings form a boat arrangement (Fig. 7(c)). When viewed along one set of N^+–H$\cdots X^-$ hydrogen bond vectors, these nets resemble closely the *cisoid–transoid* conformation of the sinusoidal ladder FINVAZ (Fig. 3(b)). In a third conformation, observed in VEDCOW [38], the six-membered rings of the 6^3 net form a chair arrangement. This also gives rise to an undulating net, in this case viewed most clearly in projection along the $N^+\cdots N^+$ vectors (Fig. 7(d)).

The directional characteristics of the $N^+\cdots X^-$ contacts in the 6^3 net clearly resemble those in the 4^4 net: the cross-hexagon contacts in the 6^3 net may be visualised simply as elongated RH_2 face-capping contacts. Thus, the 4^4, 4.8^2 and 6^3 nets are fundamentally comparable, the latter two being derived from the first by elongation of one or more face-capping contacts. This facilitates a genuine global perspective of the 2D nets in the tertiary, secondary and primary ammonium halides. On the basis of electrostatic interactions between N^+ and X^- alone, the regular 4^4 net – predicted by straightforward application of the ring-laddering principle – is most stable.[4] If no other forces were in operation, the 4^4 net would, therefore, be expected for all 2D motifs. The observation of 4.8^2 and 6^3 nets arises from the influence of other interactions in the solid, namely those between the R groups of the organic moieties, coupled with the drive for primary ammonium moieties to form three linear N^+–H$\cdots X^-$ hydrogen bonds, i.e. the balance between isotropic electrostatic forces and directional N^+–H$\cdots X^-$ hydrogen bonds. Observation of regular 4^4 nets amongst the primary sample illustrates – perhaps surprisingly – that the directional hydrogen bonds are by no means dominant. The fact that 6^3 nets are rather more common than 4^4 nets in $RNH_3{}^+X^-$ illustrates primarily that formation of the latter is rarely compatible with efficient interaction between the R groups of the ammonium moieties.

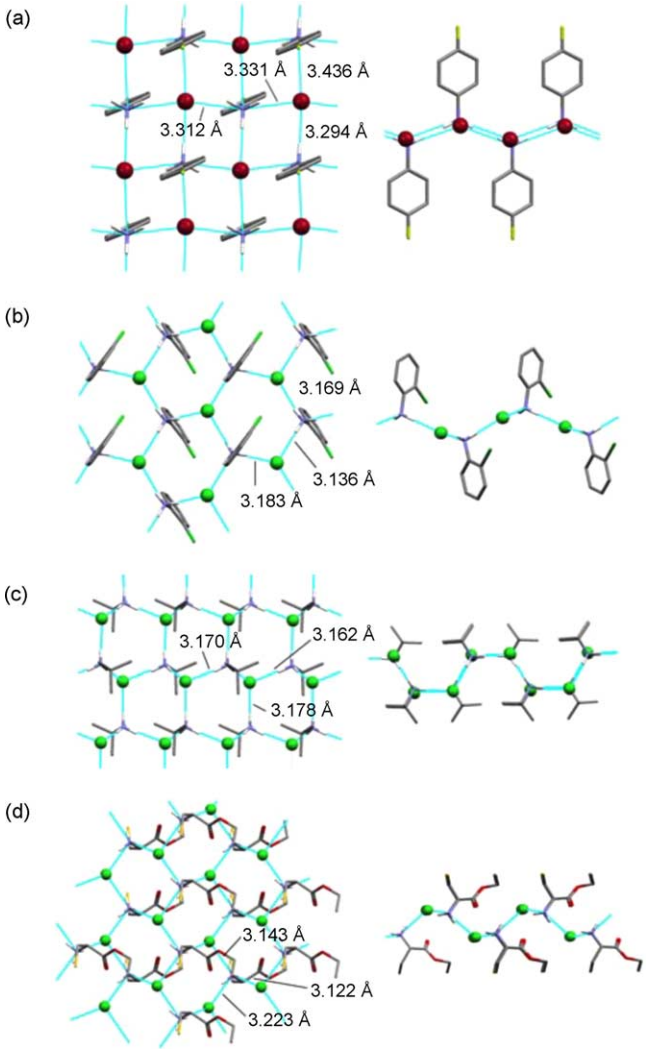


Fig. 7. Projections onto the plane and perpendicular to the plane of the 2D nets in primary ammonium halides, $RNH_3{}^+X^-$: (a) 4^4 net in DOMBOW01 displaying a sawtooth conformation in projection along one set of $N^+\cdots X^-$ vectors; (b) 6^3 net in UFAJAM in which the six-membered rings adopt an "envelope" arrangement; (c) 6^3 net in FINVED resembling a sinusoidal ladder, in which the six-membered rings adopt a boat arrangement; (d) 6^3 net in VEDCOW in which the six-membered rings form a chair arrangement. H atoms bound to C are omitted.

2.2.3. *Ring-stacking*

Stacking association is observed amongst each of the primary, secondary and tertiary ammonium halides, being most prevalent in the primary sample. For primary ammonium moieties, three N^+–H$\cdots X^-$ hydrogen bonds are suf-

[4] Again, although the 4^4 net clearly has the largest attractive electrostatic energy since it contains the greatest number of short $N^+\cdots X^-$ contacts, it also has the largest repulsive electrostatic energy. Simple evaluation of the net energy (based on idealised planar nets) confirms the intuitive notion that the nets do indeed become less stable *in electrostatic terms* in the order $4^4 > 4.8^2 > 6^3$.

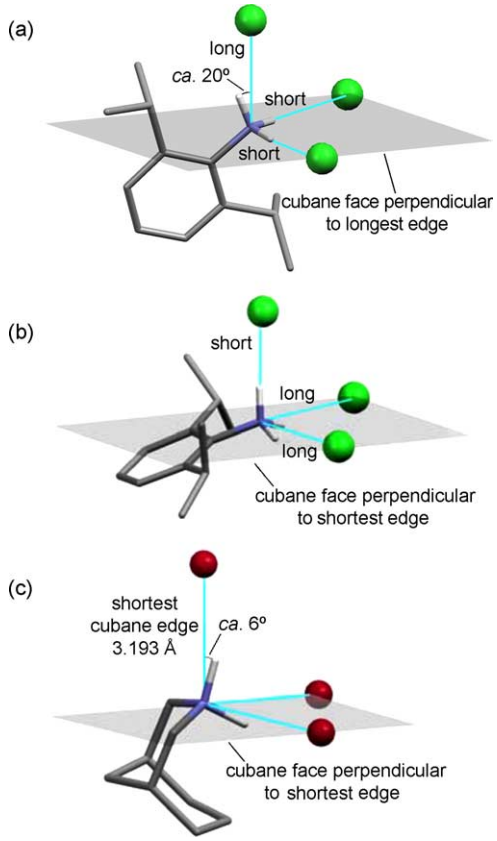


Fig. 8. Orientations of the ammonium moieties with respect to the cubane motif: (a) (*s*,*s*,*l*) orientation in 2,6-di(*iso*-propyl)aniline hydrochloride; (b) (*s*,*l*,*l*) orientation in 2,6-di(*iso*-propyl)aniline hydrochloride; (c) orientation in the secondary ammonium bromide AZNONB.

ficient alone to form cubanes, as observed for 2,6-di(*iso*-propyl)aniline hydrochloride [1]. To date, three other examples of discrete hydrogen-bonded $\{RNH_3^+X^-\}_4$ cubanes have also been reported, all of which are chlorides [2–4]. The cubane motif, with its approximate 90° $X^-\cdots N^+\cdots X^-$ angles, introduces some degree of "frustration" at the N^+ centre, since it is not possible to accommodate optimal linear geometries for all N^+–H$\cdots X^-$ hydrogen bonds. This is reflected in the distribution of $N^+\cdots X^-$ distances: each N^+ centre adopts either two short distances and one longer one (*s*,*s*,*l*) or one short distance and two longer ones (*s*,*l*,*l*). The pattern is correlated with the adoption of two distinct orientations of the organic moiety with respect to the cubane core. In one orientation, two N^+–H bonds lie approximately within one cube face, forming two short $N^+\cdots X^-$ distances. This forces the third N^+–H bond to lie out of the perpendicular cube edge, giving rise to one longer $N^+\cdots X^-$ distance (Fig. 8(a)). The alternative orientation includes one N^+–H bond lying exactly in one cube edge, giving rise to a short $N^+\cdots X^-$ distance, with the remaining two N^+–H bonds lying out of the perpendicular cube face, thereby forming longer contacts (Fig. 8(b)). Thus, the $N^+\cdots X^-$ distance distribution in $\{RNH_3^+X^-\}_4$ is again clearly controlled by the orientation of the ammonium moiety with respect to the cubane motif.

There is one example to date of a discrete cubane amongst secondary ammonium halides in the bromide AZNONB [39]. In this case, each N^+ centre forms one short N^+–H$\cdots Br^-$ hydrogen bond that coincides closely with one cubane edge, and one intermediate and one longer $N^+\cdots Br^-$ contact that are in essence RH_2 face-capping contacts (Fig. 8(c)). The N^+–H bond that does not lie in the shortest cubane edge points approximately along the diagonal of the perpendicular face, so that the latter two $N^+\cdots Br^-$ contacts may be considered to comprise a bifurcated hydrogen bond. The distribution of $N^+\cdots Br^-$ distances is identical to that in archetypal ring-stacked systems [9]: four short and four long distances can be considered to lie within dimers, and four intermediate distances can be considered to be *inter*-dimer, the latter defining the "ring-stacking direction". There are no examples to date of discrete $\{R_3NH^+X^-\}_4$ cubanes amongst tertiary ammonium halides.

There are several instances in which more extended stacks are formed, predominantly amongst the primary and secondary samples. For primary ammonium moieties, two examples exist. In WOWXOV [40], each RNH_3^+ moiety forms three N^+–H$\cdots X^-$ hydrogen bonds and one RH_2 face-capping contact (Fig. 9(a)), with the $N^+\cdots X^-$ distances distributed so that hydrogen-bonded cubanes can be envisaged within the stack. In ADOLIO [41], the distribution of N^+–H$\cdots X^-$ hydrogen bonds and the RH_2 face-capping contacts does not suggest discrete hydrogen-bonded cubanes (Fig. 9(b)). In fact, a more insightful analogy can be made if the motif is considered to comprise two ladders stacked one on top of the other. The ladders in such a description are in essence identical to the Type 2 ladders described for the secondary ammonium halides: they are planar with two N^+–H bonds of each RNH_3^+ moiety lying approximately within the plane, one forming the ladder rungs and the second forming one section of the ladder arms. The remaining section of the ladder arms is formed by a significantly longer (electrostatic) $N^+\cdots X^-$ contact (i.e. the RH_2 face-capping contact). With the RNH_3^+ moiety in ADOLIO, a third N^+–H bond projects close to perpendicular to the plane of the ladders, allowing them to stack one on top of the other via N^+–H$\cdots X^-$ hydrogen bonds. The distinction between the various descriptions of the motif is perhaps somewhat arbitrary; the key feature is the clear relationship between the motifs formed in the secondary and primary ammonium halides, and their description within the framework of ring-laddering and ring-stacking.

Several similar variants of the extended stack motif are found amongst secondary ammonium halides. The stacked motif in ZENJAD [42] again resembles most closely two Type 2 ladders stacked one on top of the other (Fig. 9(c)). The two N^+–H bonds of each $R_2NH_2^+$ moiety lie within the plane of these ladders, and stacking occurs via RH_2 face-capping contacts with geometrical attributes similar to those in the cubane AZNONB. A further clear example of stacked Type 2 ladders is found in POJVUF [43], in which the stacking contacts are significantly longer (4.81 Å) than the other $N^+\cdots X^-$ contacts within the motif. A less regular variant of

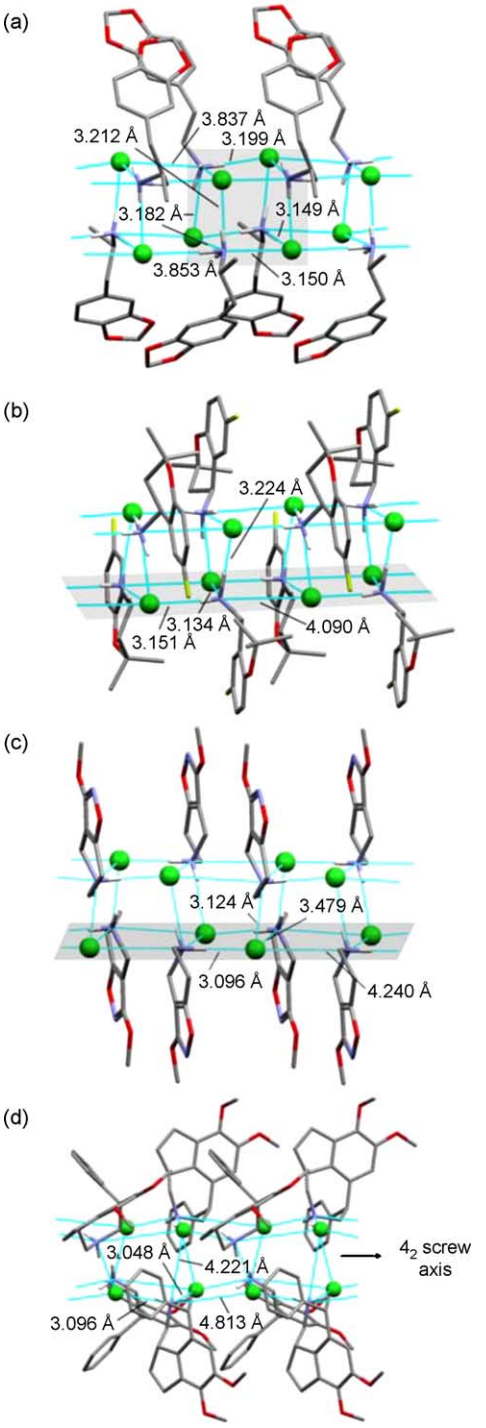


Fig. 9. Extended stack motifs in: (a) primary ammonium halide WOWXOV, in which hydrogen-bonded cubanes (shaded) can be envisaged; (b) primary ammonium halide ADOLIO, resembling Type 2 $R_2NH_2^+X^-$ ladders (shaded) associated further via N^+—H···X^- hydrogen bonds; (c) secondary ammonium halide ZENJAD, resembling Type 2 ladders (shaded) stacked one on top of the other; (d) secondary ammonium halide DUTKAE10, forming a more irregular arrangement about a crystallographic 4_2 screw axis. H atoms bound to C are omitted.

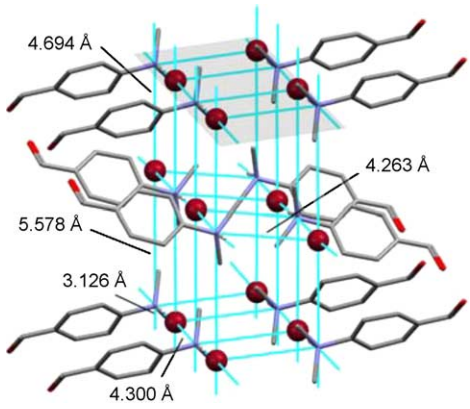


Fig. 10. Stacked Type 1 ladders (shaded) in the tertiary ammonium halide MABZAL10. H atoms bound to C are omitted.

the extended stack is observed in DUTKAE10 [44], where the motif is formed about a crystallographic 4_2 axis and displays a somewhat distorted geometry in which it is not possible to distinguish clearly either hydrogen-bonded dimers, cubanes or stacked Type 2 ladders. In this case, a "classic" ring-stacking description based on $\{R_2NH_2^+X^-\}_2$ units is probably most appropriate. In each instance, the extended stack motifs are inherently comparable and the $N^+\cdots X^-$ distance distributions simply reflect the number of N^+–H donors available for hydrogen bonding and the orientations of the organic moieties with respect to the motifs. Stacking association is considerably less common for tertiary ammonium moieties, consistent with the notion of increasing steric influence of the amide moieties as the number of R groups (≠H) increases. One example does exist in which Type 1 (planar) $R_3NH^+X^-$ ladders are stacked one on top of the other via relatively long R_2H face-capping contacts (MABZAL10 [45]; Fig. 10). The planes through adjacent ladders within the stack are not parallel, but form an angle of ca. 95°, presumably driven to some extent by the tendency for R_2H face-capping contacts to lie at ca. 120° to each other.

3. The analogy between organic ammonium halides and main-group amide/imide complexes

The laddered and stacked motifs observed in the ammonium halides are clearly reminiscent of those commonly observed in main-group complexes. The analogy between organic ammonium halides and main-group amide/imide complexes may be derived formally by considering that the directional bonding requirements of the amine moieties are comparable for both $R_xNH_{4-x}^+$ and $R_xN^{(3-x)-}$. Thus, primary ammonium moieties, RNH_3^+, may be compared to doubly-charged RN^{2-} imide moieties and secondary ammonium moieties, $R_2NH_2^+$, may be compared to singly-charged R_2N^- amide moieties. In each case, the N atom of the amine displays a tendency for tetrahedral coordination in its "first coordination sphere". For cationic ammonium moieties, the R groups and N^+–H bond vectors are oriented at ca. 109.5°

to each other and the strongest hydrogen bonds are formed to X^- when the N^+–H···X^- angles are close to linear. For amide/imide anions, the tendency towards tetrahedral coordination around N can be visualised in terms of sp^3 hybrid atomic orbitals on N (having predominantly lone-pair character), which are directed at 109.5° to each other and form the strongest, shortest bonds to cations (M^{n+}) when the M–N–M angles are close to 109.5° (i.e. the coordination geometry around N is closest to regular tetrahedral). In this respect, $R_xNH_{4-x}^+$ and $R_xN^{(3-x)-}$ moieties may be considered to be essentially "isolobal". In main-group complexes for which the bonding is principally ionic, the bonding requirements of the cations are also comparable to those of the X^- anions in $R_xNH_{4-x}^+X^-$: both form electrostatic contacts that are isotropic with respect to M^{n+} or X^-. Thus, primary ammonium halides, $RNH_3^+X^-$, may be considered to be analogues of imide complexes of divalent cations such as those of Group 2, Sn^{2+}, Pb^{2+}, etc. Secondary ammonium halides, $R_2NH_2^+X^-$, may be considered to be analogues of amide complexes of monovalent cations, principally those of Group 1. Logical extension of the analogy to include tertiary ammonium halides is complicated since R_3NH^+ may be compared only to neutral R_3N and any complex containing R_3N and a metal cation requires the presence of some other anion for charge balance. Tertiary ammonium halides, therefore, are not considered in the following comparison.

3.1. Primary amine moieties: $RNH_3^+X^-$ and $RN^{2-}M^{2+}$

Primary ammonium halides may be compared to imide complexes of Sn^{2+} and Pb^{2+}, and also to those of Group 13 derivatives such as $[AlH]^{2+}$, $[GaH]^{2+}$, $[AlCH_3]^{2+}$, $[GaCH_3]^{2+}$, etc. There are no examples to date in the Cambridge Structural Database [46] of *directly* comparable motifs containing Group 2 M^{2+} cations. Although the structural chemistry of Group 2 imides is encompassed by ring-laddering and ring-stacking principles, Group 2 M^{2+} cations always acquire additional solvation through, for example, THF (see Section 4.3). Cubanes are particularly abundant amongst imide complexes of Sn^{2+} and Pb^{2+}, and the complexes with 2,6-di(*iso*-propyl)aniline provide the most direct positive comparison to date between $RNH_3^+X^-$ and $RN^{2-}M^{2+}$ [1]. As outlined in the Introduction, the THF solvate of 2,6-di(*iso*-propyl)aniline hydrochloride contains discrete hydrogen-bonded cubanes that are analogous in all respects to those in the Sn^{2+} and Pb^{2+} complexes of the dianion derived from the same organic moiety [5]. The Sn^{2+} and Pb^{2+} complexes display (*s*,*s*,*l*) and (*s*,*l*,*l*) N–M distance distributions that are correlated with the orientation of the imide moiety in a manner identical to that in the hydrogen-bonded cubane (see Section 2.2.2). Interestingly, the isomorphous Sn^{2+} and Pb^{2+} structures contain two crystallographically independent cubane units, each with different combinations of N–M distances about the N centres. This indicates most clearly that the N–M distances in the main-group complexes are also influenced by interactions *between* cubane units. The fact that the organic hydrogen-bonded cubane crystallises as a THF solvate while the main-group complexes remain unsolvated may be significant: it is possible that lattice THF molecules are required in order for the metrically larger $\{RNH_3^+X^-\}_4$ cubanes to pack effectively in the solid state, while the smaller Sn^{2+}/Pb^{2+} cubanes pack effectively without requiring lattice solvent.[5] Of course, it is also possible that other crystalline forms are yet to be discovered; the Sn^{2+}/Pb^{2+} complexes were crystallised from *n*-hexane rather than THF [5] and attempts have not been made (at least by this author) to crystallise 2,6-di(*iso*-propyl)aniline hydrochloride from any solvent other than THF.

There are no examples to date of infinite ladder motifs amongst main-group imides. There are, however, several examples of ladder fragments that contain four metal centres, based upon complex cations such as $[GaH]^{2+}$, $[AlCH_3]^{2+}$ or $[GaCH_3]^{2+}$. In the first example, CAFPEF [47], a $[Ga(H)N(iPr)]_2$ core is flanked by two $GaH_2(N=C(CH_3)_2)$ groups (Fig. 11(a)). The second two examples are comparable, containing $\{[MCH_3]N(tBu)\}_2$ cores, flanked by two $\{[Sn(CH_3)_2]N(tBu)\}$ groups (M = Al (RASDUK [48]), Ga (ZEVHAJ) [49]; Fig. 11(b)). The final example, JEZGOK [50], contains multi-dentate $[HN(CH_2)_3NH(CH_2)_3N]^{3-}$ ligands with both $[AlCH_3]^{2+}$ and $[Al(CH_3)_2]^+$ units (Fig. 11(c)). In each of these four cases, the ladder conformation is similar, and is comparable to the sawtooth arrangement observed in the organic ammonium halides. The sawtooth-type conformation of each ladder accommodates tetrahedral coordination about N in the RN^{2-} moieties of the central two ladder rungs, analogous to the tetrahedral arrangement of N^+–H···X^- hydrogen bonds about N^+ in RNH_3^+. The N–M distances about the central N atoms in the inorganic complexes lie in the approximate range 1.9–2.1 Å, compared with $N^+\cdots X^-$ distances of ca. 3.0–3.3 Å in the organic sample.

3.1.1. Direct comparison between $RNH_3^+X^-$ and $RN^{2-}M^{2+}$

In addition to the 2,6-di(*iso*-propyl)aniline examples, there are several other sets of crystal structures in the literature that facilitate direct comparison, i.e. $RNH_3^+X^-$ and $RN^{2-}M^{2+}$ having the same R groups. Amongst these, however, there are no other examples of directly comparable structure motifs. In complexes of cyclohexamine, for example, isostructural cubanes $\{C_6H_{11}N^{2-}M^{2+}\}_4$ are formed by Sn^{2+} and Pb^{2+} (ZAQHEE [51], POYFUE [52]), but the comparable chloride, $C_6H_{11}NH_3^+Cl^-$ (CYHACL [53]), forms a 2D net with a sinusoidal conformation comparable to that in FINVED (Fig. 7(c)).[6] These structures, together with the 2,6-di(*iso*-propyl)aniline examples, illustrate that minimal

[5] Although the cube edges are lengthened approximately isotropically in the organic cubane compared to the main-group cubane, the organic ligands themselves remain the same size(!). Thus, it is unlikely that the structures will simply "expand" as a whole while retaining the same packing arrangement.

[6] The net is probably best described as 6^3, but cross-hexagon contacts of ca. 4.5 Å cause it to resemble closely a 4^4 net.

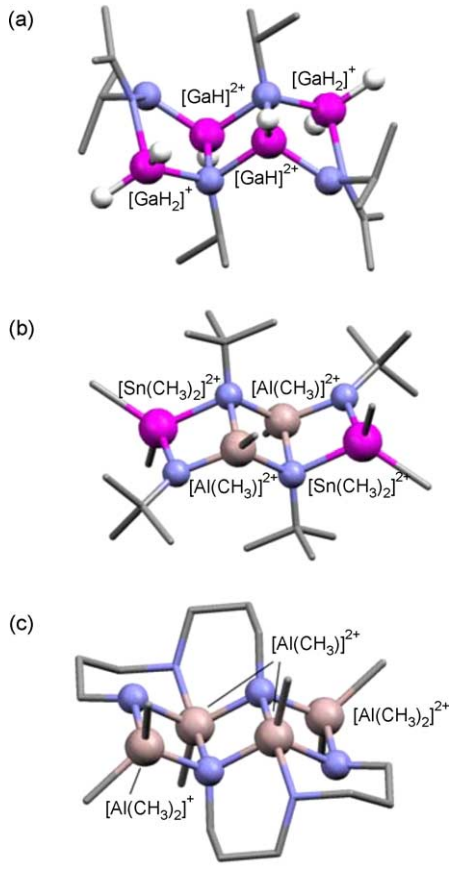
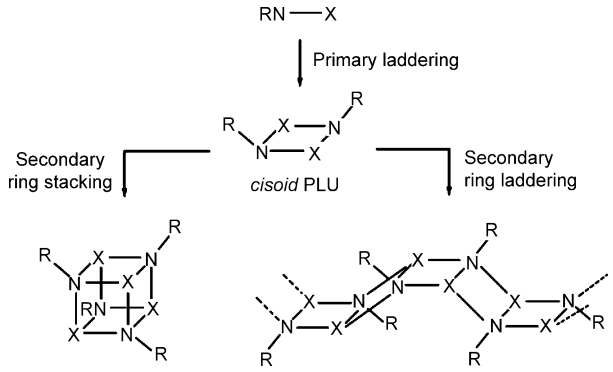


Fig. 11. Fragmented ladder motifs displaying sawtooth conformations in main-group primary imide complexes, $RN^{2-}M^{2+}$: (a) CAFPEF; (b) RASDUK (comparable to ZEVHAJ, containing Ga); (c) JEZGOK. H atoms bound to C are omitted.

variation in the organic moiety can lead to vastly different structures for the organic ammonium halides and main-group complexes. The 2D net in CYHACL and the cubanes in ZAQHEE and POYFUE exhibit some comparable features. The net in CYHACL can be envisaged to comprise laterally associated *cisoid–transoid* ladders (see Section 2.2.1), and both the *cisoid–transoid* ladder and the cubane can be considered to be constructed from $\{RNH_3{}^+X^-\}_2$ dimers that display a *cisoid* conformation. In the cubane, two *cisoid* $\{RNH_3{}^+X^-\}_2$ dimers associate in a face-to-face stacking manner, while in the *cisoid–transoid* ladder they associate in a laddering manner via only one edge (Scheme 2). Thus, the two structures can be reconciled to some extent by invoking a two-stage approach to ring-laddering and ring-stacking, as proposed by Downard and Chivers [54]. In the two-stage approach, primary and secondary association is distinguished: primary laddering describes initial lateral association of "monomeric" $R_xNH_{4-x}{}^+X^-$ ion pairs to produce dimeric primary laddering units (PLUs), which may (or may not) undergo secondary association to form more extended motifs. In both the organic structure and the main-group complexes of cyclohexamine, the primary laddering process is comparable, forming *cisoid* PLUs in both cases. Secondary association then proceeds in a



Scheme 2. The two-stage approach [54] describing association of *cisoid* primary laddering units (PLUs), highlighting the relationship between the cubane motif and the *cisoid–transoid* ladder in primary ammonium halides (H atoms not depicted).

laddering manner for CYHACL and in a stacking manner for ZAQHEE and POYFUE. The two-stage approach is clearly helpful for envisaging structural relationships in cases such as these.

One of the most extensive sets of directly comparable $RNH_3{}^+X^-$ and $RN^{2-}M^{2+}$ structures available in the literature includes *t*-butyl amine moieties, $(CH_3)_3CNH^+$ and $(CH_3)_3CN^{2-}$. Crystal structures have been reported for $(CH_3)_3CN^{2-}$ complexes of Sn^{2+} (both in an unsolvated form [55], and as a THF solvate [56]), $[AlH]^{2+}$, $[AlCH_3]^{2+}$, mixed $[Al(H)/(CH_3)]^{2+}$ [57], $[InCl]^{2+}$, $[InBr]^{2+}$, $[InI]^{2+}$ [58], $[InCH_3]^{2+}$ and $[GaCH_3]^{2+}$ (as isostructural benzene solvates [59,60]). A mixed $[AlH]^{2+}/Ca^{2+}$ complex is also known, in which the Ca^{2+} cation is coordinated by three additional THF molecules [61]. Cubane motifs are formed in every one of these main-group complexes. The solvated and unsolvated crystal forms of $\{(CH_3)_3CN^{2-}Sn^{2+}\}_4$ show that there is no exclusive distinction between efficient packing of this particular cubane moiety in the presence or absence of lattice solvent. In the organic analogues, the chloride (FINVED [36]), bromide (JORXIX [62]) and iodide (JAPLAN [63]) are isostructural, forming extended 2D (6^3-type) nets with sinusoidal *cisoid–transoid* conformations.

The majority of the remaining directly comparable $RNH_3{}^+X^-$ and $RN^{2-}M^{2+}$ structures are aniline derivatives. A full set of organic structures exists for aniline itself. The chloride (ANLINC01 [64]) forms a 6^3 net with a rare variant of the sawtooth conformation, in which all phenyl rings lie to the same side of the net to give a polar structure. The bromide and iodide each exist as two closely related polymorphs (orthorhombic form: ANLINB03 [65] and DOVVIT01 [66]; monoclinic form: ANLINB02 [67] and DOVVIT02 [66]), both containing 4^4 nets with a *transoid* sawtooth conformation (cf. Fig. 7(a)). For the main-group complexes, $C_6H_5N^{2-}Ge^{2+}$ contains cubanes [68], while the complex of $[AlCH_3]^{2+}$ contains hexameric $\{C_6H_5N^{2-}[AlCH_3]^{2+}\}_6$ units [69] (Fig. 12), with some unidentified solvent molecules also present in the lattice. The distribution of N–Al distances in the hexameric motif resembles closely the arrange-

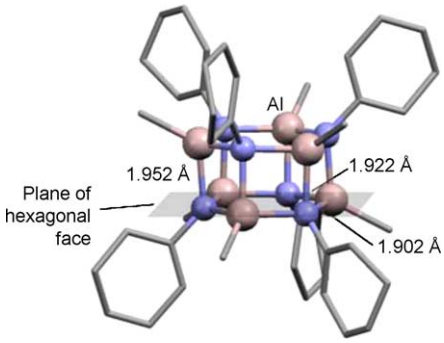


Fig. 12. Hexameric $\{C_6H_5N^{2-}[AlCH_3]^{2+}\}_6$ unit in DAYRUQ (H atoms omitted). The distribution of N–Al distances is comparable to the (*s*,*s*,*l*) arrangement described for cubanes of primary amides. The distorted geometry of the phenyl rings is derived from the published atomic coordinates [69].

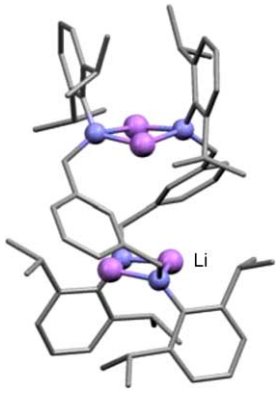


Fig. 13. Covalently linked $\{R_2N^-Li^+\}_2$ dimers in IHEXEY, containing 2-coordinate Li. H atoms bound to C are omitted.

ment in the cubanes $\{2,6\text{-}(i\text{Pr})_2C_6H_3N^{2-}Sn^{2+}\}_4$ and $\{2,6\text{-}(i\text{Pr})_2C_6H_3N^{2-}Pb^{2+}\}_4$: each N centre forms two relatively short N–Al contacts in the plane of one hexagonal face and one significantly longer contact perpendicular to this face (cf. Fig. 8(a)). Thus, description of the motif in terms of stacked trimeric units seems reasonable in this case. An alternative description as a cyclised 6-rung ladder might also be appropriate (see Section 3.2). In some respects, the distinction is arbitrary, although the latter description is clearly more consistent with a two-stage approach that describes secondary association of dimeric *cisoid* PLUs [54]. From the viewpoint of the analogy with the organic solid state, the principal point of interest is the relationship between the distribution of N–Al contacts and the orientation of the organic moiety with respect to the structural motif; this is consistent with the discussion of Section 2.2.3 (see Fig. 8).

Numerous additional direct comparisons are available for aniline derivatives containing substituents such as methyl, methoxy, halogen, etc. For the vast majority of these organic moieties, the Sn^{2+} and Pb^{2+} complexes form cubanes, the $[Al(R)]^{2+}$ and $[Ga(R)]^{2+}$ complexes form cubanes or hexamers, and the organic structures form 2D nets. One notable example is found for the anion derived from *para*-fluoroaniline: complexes with $[AlCH_3]^{2+}$ have been observed as both cubanes (ROMJIM) and hexamers (ROMJOS), the complex with $[GaCH_3]^{2+}$ forms a hexamer (ROMJUY) but with a crystal structure different from that of ROMJOS, and the $[InCH_3]^{2+}$ complex (ROMKAF) forms cubanes in which each In atom is further coordinated by a THF molecule [70]. The Al and Ga structures illustrate a somewhat delicate balance between the formation of cubane and hexamer motifs, and also their packing arrangements in the solid state. The adoption of 5-coordinate In in the latter structure clearly reflects the greater size of In compared to Al and Ga. In the organic structures, the comparable bromide (two polymorphs: DOMBOW and DOMBOW01 [71]) and iodide (DOMBUC [71]) both contain 4^4 nets (Fig. 7(a)), while the chloride (ANLCLA [72]) contains a complex 2D motif that resembles pairs of stacked 4^4 nets.

3.2. Secondary amine moieties: $R_2NH_2^+X^-$ and $R_2N^-M^+$

Secondary ammonium halides may be compared to amide complexes of Group 1 cations (principally Li^+ and Na^+), and also to those of Group 13 derivatives such as $[AlH_2]^+$, $[GaH_2]^+$, $[Al(CH_3)_2]^+$, $[Ga(CH_3)_2]^+$, etc. The main-group complexes $R_2N^-M^+$ exhibit structural chemistry somewhat more diverse than that of their primary counterparts. Dimeric units analogous to hydrogen-bonded $\{R_2NH_2^+X^-\}_2$ motifs exist in many $R_2N^-M^+$ structures. Directly comparable discrete $\{R_2N^-M^+\}_2$ dimers containing Group 1 M^+ cations with no further coordination (i.e. forming only two M–N contacts) occur only in more sterically demanding systems. Examples are found for all Group 1 cations Li^+–Rb^+ (with the curious – and surely coincidental – exception of Na^+) with R_2N^- moieties in which the R groups are Si-based, e.g. $SiMe_3$, $SiPh(Me)_2$, $SiH(t\text{Bu})_2$, etc. [73–76]. A smaller number of examples are found in which only one R group is Si-based, restricted at present to Li^+ complexes, e.g. GEQSEA [76], POPYOI [77], SOLXUM [78]. There is also one example where two dimers containing 2-coordinate Li^+ are linked covalently via bidentate $C_6H_4(CH_2N^-)_2$ moieties (IHEXEY [79]; Fig. 13). There are no discrete $\{R_2N^-M^+\}_2$ examples to date in which 2-coordinate M^+ is found with R_2N^- moieties in which both R groups are carbon-based; in all dimeric examples containing Group 1 cations, the metal centres are further coordinated by neutral Lewis bases such as THF, Et_2O, C_5H_5N, $(i\text{Pr})_2NH$, etc., so that M^+ adopts approximately trigonal planar coordination (e.g. CISQAW [80], DOZHEF [81], HOLSUW [82], IDOQIB [83], TOMXEY [84]; Fig. 14(a)). In several cases, bidentate ethylenediamine moieties bridge between $\{R_2N^-M^+\}_2$ dimers (FIWBAO [85], KUFFEW [86], XENYEU [87]; Fig. 14(b)) and one structure has been reported where dimers are linked through 1,4-dioxane (YIXYOT [88]). For the Group 13 derivatives, $[AlR_2]^+$, $[GaR_2]^+$ and $[InR_2]^+$, discrete dimers are common, with a wide variety of R groups bound to the metal ion (e.g. H, CH_3, CH_2CH_3, $N(CH_3)_2$, halogen, etc. [see for example, [89–93]]). In every case, the metal acquires approximately

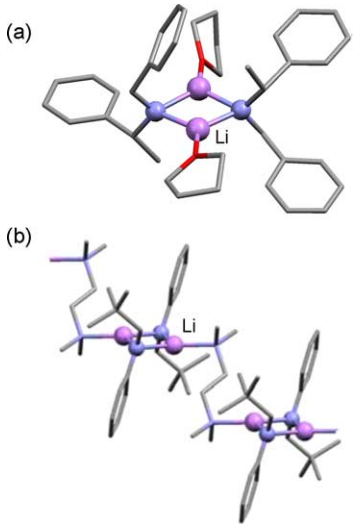


Fig. 14. (a) $\{(PhCH_2)(PhCH(CH_3))N^-Li^+\cdot THF\}_2$ dimer in CISQAW, in which Li acquires trigonal planar 3-coordination through "solvation" by THF; (b) section of an infinite $\{(Ph)((CH_3)_3CCH_2)N^-Li^+\cdot TMEDA\}_\infty$ coordination polymer in XENYEU, in which neutral tetramethylethylenediamine (TMEDA) moieties link $\{R_2N^-Li^+\}_2$ dimers. H atoms bound to C are omitted.

regular tetrahedral coordination. The extent to which these motifs can be compared to $\{R_2NH_2^+X^-\}_2$ dimers is questionable since the additional substituents bound to the metal centre clearly add to the steric constraints that prevent further association of $\{R_2N^-M^+\}_2$.

Some higher-order discrete cyclic motifs are also found amongst main-group $R_2N^-M^+$ complexes. For Group 1 cations, the crystal structures of two $\{R_2N^-Li^+\}_3$ trimers have been reported, each with carbon-based R groups and without further coordination to Li^+: CISPEZ [80], ZEGNII [94]. The fact that Li^+ remains 2-coordinate in the trimers while it invariably adopts 3-coordination in the comparable dimers (R based on carbon) may be rationalised by considering that the "coordination arc" around Li^+ is smaller in the trimeric rings than in dimeric units, so that any further coordination of Li^+ is effectively prevented by the steric influence of the amide moieties (Fig. 15) [9]. One trimeric example is known in which Li^+ is further coordinated, but this incorporates the multi-dentate lig-

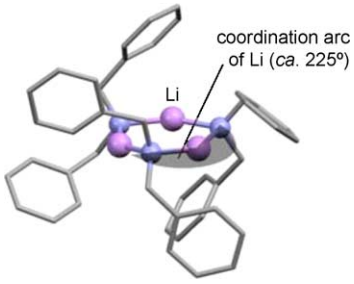


Fig. 15. Trimeric $\{(PhCH_2)_2N^-Li^+\}_3$ motif in ZEGNII. The coordination arc (shaded) of Li is less than that in dimeric motifs (ca. 270°), hindering further solvation by Lewis bases [9]. H atoms bound to C are omitted.

and $CH_3N(CH_2)_2N(CH_3)(CH_2)_2N^-$ (LOXZAZ [95]). In this case, the coordination geometry of Li^+ resembles a tetrahedron, heavily distorted by the constraints of the chelating ligand. For Group 13 derivatives, several trimeric examples are known (e.g. with $[AlH_2]^+$ (CASNEP [96]), $[GaH_2]^+$ (AZGALT [97], XICKOJ [98]), $[BH_2]^+$ (DMABTR [99]), $[Al(CH_3)_2]^+$ (EIMEAL [100])), in each case with the metal centre adopting approximately regular tetrahedral coordination. There are no examples to date of discrete cyclic trimers amongst organic ammonium halides. Two cyclic $\{R_2N^-Li^+\}_4$ tetramers have also been reported amongst the main-group complexes, described in more detail subsequently together with their directly comparable organic counterparts (Section 3.2.1).

Where extended laddering association takes place in $R_2NH_2^+X^-$, the $N^+\cdots X^-$ contacts either bridge the H···H edge or cap the R_2H faces of the *pseudo*-tetrahedral $R_2NH_2^+$ moieties (Section 2.1). Examination of the coordination geometries of M^+ in ring-laddered Group 1 amides [11] reveals that the N–M contacts occur exclusively from the least-hindered side of the R_2N^- moiety, most closely comparable to H···H edge-bridging contacts rather than R_2H face-capping contacts. Thus, all ring-laddered structures in inorganic complexes resemble Type 1 ladders of secondary ammonium halides and there are no examples to date of Type 2 ladders amongst main-group amides. This observation appears to be attributable to the relative importance of steric effects in the two ladder types, coupled with the intervention of other Lewis-base species in the main-group sample (see Section 4.3). In electrostatic terms, Type 1 $R_2NH_2^+X^-$ ladders are more stable than their Type 2 counterparts. However, Type 1 ladders introduce more severe steric constraints between the R groups of the amine moiety on account of the fact that they include shorter $N^+\cdots N^+$ contacts across the diagonals of each ladder section. These factors are reflected by the prevalence of Type 1 ladders for cyclic ammonium moieties such as pyrrolidinium and piperidinium, and Type 2 ladders for acyclic ammonium moieties: the R groups of acyclic $R_2NH_2^+$ project to a greater degree above and below the ladder plane (rather than to the outside of the ladder arms), increasing the relative significance of the steric constraints for these moieties within Type 1 ladders. As the steric influence of the R groups becomes relatively greater, Type 2 ladders become more prevalent. In the main-group systems, intervention by other Lewis-base species (i.e. "solvation") competes favourably with formation of Type 2 ladders: while each M^+ centre would be forced to adopt one relatively long N–M contact in a Type 2 ladder, the formation of smaller solvated ladder fragments allows all contacts to M^+ to be shorter, thereby maximising electrostatic energy. The majority of main-group amide ladders observed to date are fragmented, either by multi-dentate amines that act as "capping" groups (e.g. DOKBOU [7,101] (Fig. 16(a)), KARTOM [101], TETGOO, TETHAB [102], XEWFEK, XEWFIO [103], ENAWUL [104]) or by neutral Lewis bases performing a "solvating" role (e.g. diethyl ether in the mixed

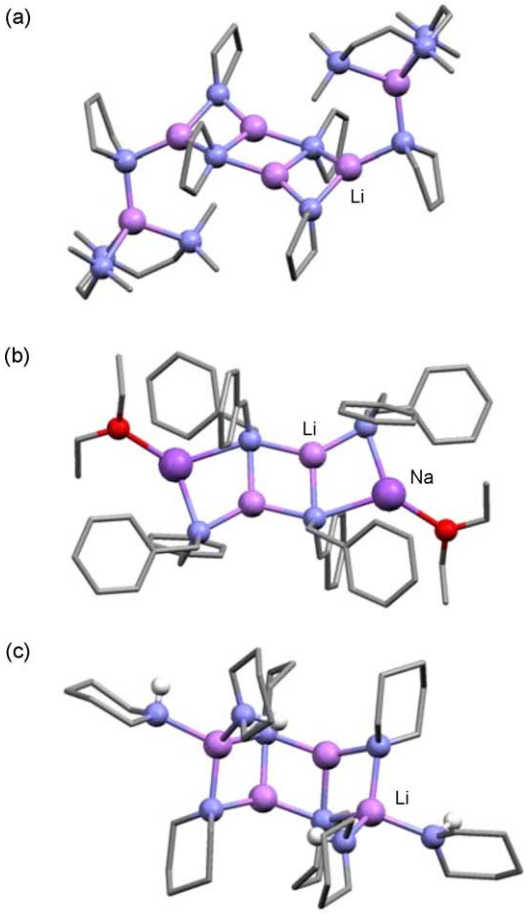


Fig. 16. (a) Ladder fragment in DOKBOU, in which neutral tridentate amine moieties "cap" the terminal Li^+ cations; (b) mixed Li^+/Na^+ ladder fragment in WASWOC, in which diethyl ether molecules "solvate" the terminal Na^+ cations; (c) ladder fragment $\{(C_5H_{10}N)_2Li_2{\cdot}2C_5H_{10}NH\}_2$ in KUPSET, in which the piperidide anions are the conjugate base of the neutral piperidine "solvent" molecules. H atoms bound to C are omitted.

Li^+/Na^+ complex WASWOC [105]; Fig. 16(b)). In one notable example, KUPSET, a 4-rung lithium piperidide ladder fragment is solvated by neutral piperidine moieties [106] (Fig. 16(c); see Section 4.3).

Some examples of infinite ladders are found amongst main-group amides, incorporating Li^+ (e.g. NECQER [107], JUPHAD [108], PIXVIB [109]) and Na^+ (NEXKOQ [110]). In each of these structures, one R group of the R_2N^- moiety is H so that the steric constraints associated with ladder formation are relaxed to some degree. The vastly different steric influence of the two groups bound to N has a significant effect on the ladder conformation: in PIXVIB, for example, sinusoidal *cisoid–transoid* ladders are formed in which relatively bulky R groups lie exclusively to the outside of the ladder curvature and H atoms lie exclusively to the inside. A comparable motif exists in the secondary ammonium halide CACVIM [111], in which one R group is the bulky 2,4-di((*t*Bu)phenyl) moiety and one R group is CH_3. In that case, the CH_3 groups lie exclusively to the inside of a sinusoidal ladder (Fig. 17). These arrangements clearly resemble

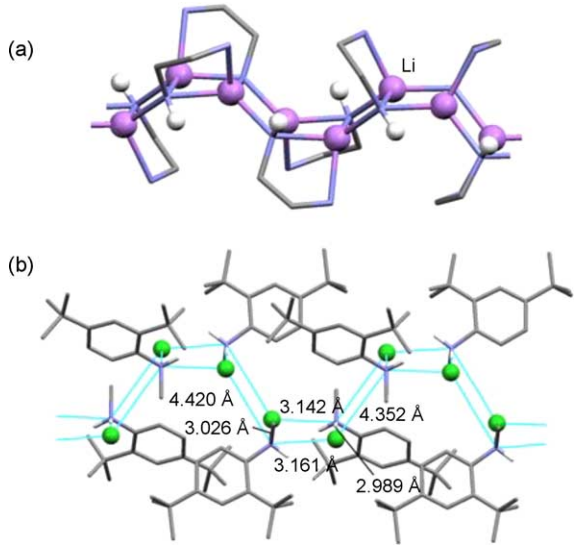


Fig. 17. Sinusoidal *cisoid–transoid* ladders in (a) $\{H_2NCH_2CH_2N(H)Li\}_\infty$ (PIXVIB) and (b) $\{(2,4\text{-}(t\text{Bu})C_6H_3)(CH_3)NH_2{}^+Cl^-\}_\infty$ (CACVIM) (H atoms bound to C omitted). In the main-group complex, H atoms bound to N lie to the inside of the ladder curvature, while methyl groups occupy these positions in the organic ladder. A second NH_2 group in the amide moiety completes the coordination sphere of Li^+ in PIXVIB.

that described previously for the primary ammonium halide FINVAZ (Fig. 3(b)). The sinusoidal ladder in CACVIM differs from archetypal Type 1 and Type 2 $R_2NH_2{}^+X^-$ ladders in that it is not planar. Here, the most appropriate description is probably based on two-stage association of *cisoid* dimers in the manner indicated in Scheme 2.

One further main-group example of interest is a ladder fragment containing the multi-dentate ethylenediamine derivative $[(2,6\text{-di}(i\text{Pr})C_6H_3)N(CH_2)_2N(2,6\text{-di}(i\text{Pr})C_6H_3)]^{2-}$ (JIRTUZ [112]), in which the ladder geometry is constrained by the $(CH_2)_2$ linkage to form a centrosymmetric sawtooth arrangement with N–Li–N angles close to ca. 100° (Fig. 18). The interesting feature of this ladder fragment is the existence of terminal 2-coordinate Li^+ comparable to 2-coordinate X^- in $\{R_2NH_2{}^+X^-\}_2$ dimers. In this case, further coordination of Li^+ is prevented by the geometry of the ladder fragment, which causes

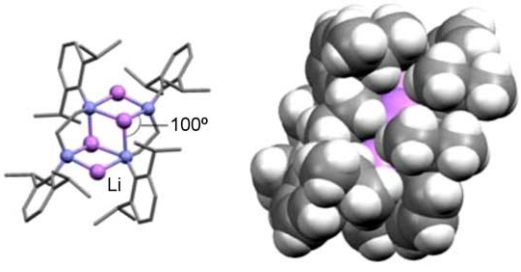


Fig. 18. Ladder fragment in JIRTUZ, in which the ladder geometry is constrained by a multi-dentate amide moiety and the terminal Li^+ cations remain 2-coordinate (H atoms omitted). The space-filling representation shows clearly that the terminal Li^+ cations are effectively encased by the 2,6-di(iPr)C_6H_3 groups.

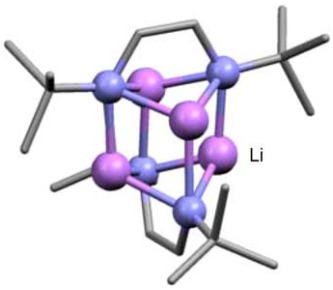


Fig. 19. $\{(t\text{Bu})\text{N}(\text{CH}_2)_2\text{N}(t\text{Bu})\text{Li}_2\}_2$ cubane in TETGUU (H atoms omitted). The top and bottom cubane faces are puckered to accommodate the relatively short constrained N···N distances.

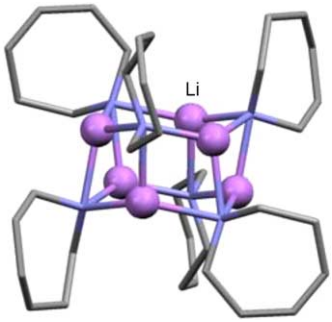


Fig. 21. Six-rung cyclised ladder $\{\text{H}_2\text{C}(\text{CH}_2)_5\text{NLi}\}_6$ in SEDVEC (H atoms omitted).

the 2,6-di(*i*Pr)C_6H_3 groups to "wrap around" the terminal Li^+ cation (Fig. 18). This structure suggests that discrete $\{\text{R}_2\text{N}^-\text{Li}^+\}_2$ dimers containing 2-coordinate Li^+ are likely to be observed with suitable organic ligands.

As is the case in the organic sample, stacking association to form cubanes occurs in only a limited number of $\text{R}_2\text{N}^-\text{M}^+$ structures. Both examples that exist at present, $\{(t\text{Bu})\text{N}(\text{CH}_2)_2\text{N}(t\text{Bu})\text{Li}_2\}_2$ (TETGUU, [102]) and $\{(t\text{Bu})\text{N}(\text{C(H)Me})_2\text{N}(t\text{Bu})\text{Li}_2\}_2$ (ZAXKUE, [113]), incorporate organic moieties derived from ethylenediamine. The geometrical aspects of these cubanes are influenced considerably by the presence of the bidentate organic units, with the faces bridged by the $(\text{CH}_2)_2$ linkages puckered to accommodate the relatively short constrained N···N distances (Fig. 19). There have not yet been any reported instances of discrete main-group $\{\text{R}_2\text{N}^-\text{M}^+\}_4$ cubanes that contain four independent monodentate organic moieties. There are, however, examples of more extended stacks: KIJFUE [114] contains a centrosymmetric $\{(\text{CH}_3)_2\text{NNa}\}_6$ double-cubane core that includes dimethylamide anions (Fig. 20). The steric constraints of stacking association are relaxed to some degree in this case on account of the relatively larger N–Na distances (ca. 2.4–2.5 Å, cf. 2.0–2.1 Å for N–Li) coupled with the minimal steric influence of the amide moieties. The N–Na distance distribution in the stack is not readily compared to

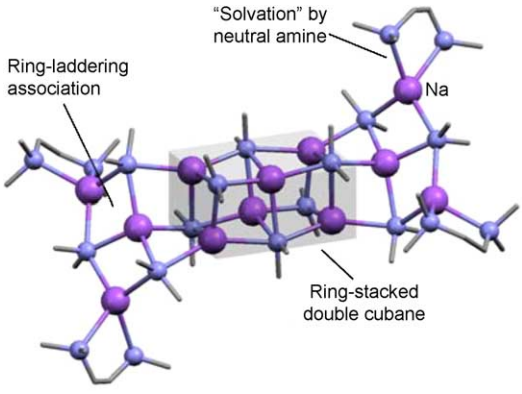


Fig. 20. Complex motif in KIJFUE incorporating a $\{(\text{CH}_3)_2\text{NNa}\}_6$ double-cubane core (shaded), flanked by regions of ring-laddering association and capped by neutral TMEDA moieties. H atoms are omitted.

any of the organic extended stacks described previously (Section 2.2.3). The complete motif in KIJFUE in fact contains a rather complex blend of ring-stacking and ring-laddering association, coupled with solvation of the terminal Na^+ cations by bidentate neutral amine moieties. In this case, the balance between electrostatic forces and steric effects is clearly rather difficult to predict.

One structural motif observed for $\text{R}_2\text{N}^-\text{M}^+$ structures that does not at present have an organic counterpart is the cyclised ladder. The archetypal example SEDVEC [115] forms a hexameric motif $\{\text{H}_2\text{C}(\text{CH}_2)_5\text{NLi}\}_6$ in which the coordination geometry around N resembles a distorted trigonal bipyramid (Fig. 21). A second comparable structure exists in PEBJAH [116], in which each of the hexagonal faces of the hexameric motif $\{\text{CH}_3\text{C}(\text{CH}_2\text{N}(i\text{Pr}))_3\text{Li}_3\}_2$ is capped by tridentate amide moieties. In these cases, the motifs are classified as "cyclised ladders" rather than "stacked trimeric rings" on the basis of the distribution of N–Li distances [9]. This description is supported by the analogy with Type 1 $\text{R}_2\text{NH}_2{}^+\text{X}^-$ ladders: all three N–Li distances about each N centre are of comparable magnitude and the mean planes of the cyclic organic moieties lie approximately perpendicular to the ladder arms (i.e. the motif adopts a "paddle–wheel" arrangement). This resembles closely the arrangement in Type 1 $\text{R}_2\text{NH}_2{}^+\text{X}^-$ ladders (Fig. 2(a)). The cyclised ladder in the main-group system presents an additional means by which to alleviate the steric constraints associated with planar Type 1 ladders: cyclisation relieves the steric congestion between R groups of the amide moieties by increasing the magnitude of the coordination arc around N [9]. The absence to date of cyclised ladders in $\text{R}_2\text{NH}_2{}^+\text{X}^-$ suggests that they do not compete favourably with the formation of Type 2 ladders. Observation of the *cisoid–transoid* ladder in CACVIM (Fig. 17), however, suggests that cyclised ladders may be attainable in the organic solid state; since ladder curvature is clearly introduced in that case, an appropriate ammonium moiety may encourage cyclisation rather than undulation.

3.2.1. Direct comparison between $\text{R}_2\text{NH}_2{}^+\text{X}^-$ and $\text{R}_2\text{N}^-\text{M}^+$

There are several direct comparisons between $\text{R}_2\text{NH}_2{}^+\text{X}^-$ and $\text{R}_2\text{N}^-\text{M}^+$ available in the current literature. Amongst

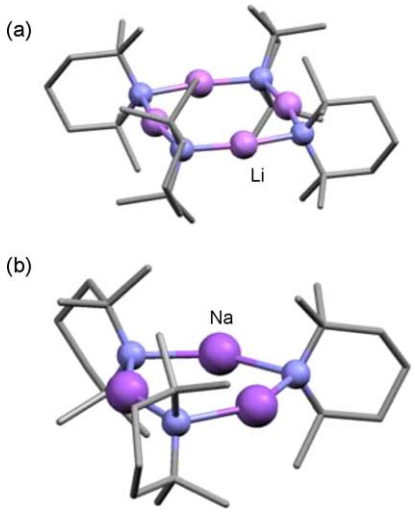


Fig. 22. (a) Planar $\{(CH_3)_2C(CH_2)_3C(CH_3)_2N^-Li^+\}_4$ tetramer in BUXNUD; (b) planar $\{(CH_3)_2C(CH_2)_3C(CH_3)_2N^-Na^+\}_3$ trimer in KENXOQ. H atoms bound to C are omitted.

these, however, there are no examples of directly comparable structural motifs. Two instances of cyclic $\{R_2N^-Li^+\}_4$ tetramers exist amongst the main-group complexes, one containing the dicyclohexylamide anion (ZALCUK [117]) and one containing 2,2,6,6-tetramethylpiperidide (BUXNUD [118]).[7] The cyclic tetramer motif, incorporating approximately linear N–Li–N links, imposes the greatest possible distance (ca. 4 Å) between two N centres coordinated to the same Li^+ cation, thereby accommodating relatively bulky R groups. In BUXNUD, the methyl groups bound to the α-C of the 2,2,6,6-tetramethylpiperidide moieties form an efficient four-fold arrangement above and below the plane of the tetrameric motif (Fig. 22(a)). A comparable Na complex also exists, in which cyclic $\{R_2N^-Na^+\}_3$ trimers are formed (KENXOQ [120]). In this case, the longer N–Na distances accommodate the methyl groups above and below the plane of the motif in a three-fold arrangement (Fig. 22(b)). In the organic analogues, dicyclohexylammonium chloride (ZENSUG [121]) contains hydrogen-bonded chains associated via relatively long $N^+\cdots X^-$ contacts (4.75 Å) into a 6^3 net arrangement. Formation of a 6^3 net by a secondary ammonium halide is rare in comparison to the occurrence of 4^4 nets, but elongation of the non-hydrogen-bonded $N^+\cdots X^-$ contacts clearly accommodates the steric requirements of the bulky cyclohexyl groups. The R groups in *adjacent* nets project into the gaps at the centre of each six-membered ring. In each of the 2,2,6,6-tetramethylpiperidinium halide structures, TEHDEP (Cl [122]) and CEFGEZ (Br [123]), Type 2 ladders are formed. A structure more closely comparable to that of BUXNUD is in fact found in the hydrochloride of triacetoneamine (TMPIPO [124]). The ammonium moiety in this case resembles closely 2,2,6,6-tetramethylpiperidide but also

[7] An interesting related structure also exists in which tetramers can be envisaged to be halved by the intervention of ethylenediamine capping groups (YAPCOH [119]).

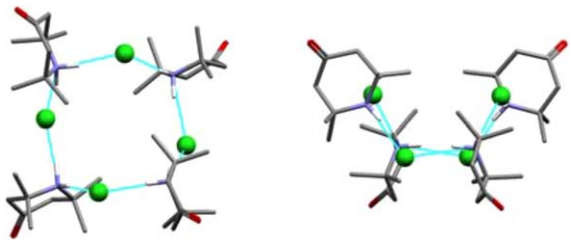


Fig. 23. Cyclic $\{(CH_3)_2CCH_2(C=O)CH_2C(CH_3)_2NH_2^+Cl^-\}_4$ hydrogen-bonded tetramer in TMPIPO (H atoms bound to C omitted). Viewed along the N^+—H$\cdots X^-$ vectors (right), the motif resembles closely one *cisoid* section from the *cisoid–transoid* ladder.

contains a carbonyl group in the 4-position relative to the ammonium group. In contrast to BUXNUD, the tetramers formed in TMPIPO are not planar, but resemble the "folded" arrangement of cyclooctatetraene [125]. When viewed along the N^+—H$\cdots X^-$ vectors, this motif resembles closely one *cisoid* section from the *cisoid–transoid* ladder (Fig. 23).

Two further direct comparisons exist. For the cyclic hexamethyleneamine (azepane), the amide complex with Li^+ forms the cyclised ladder $\{H_2C(CH_2)_5NLi\}_6$ (SEDVEC), while the ammonium chloride (HEXAMC [126]) forms an archetypal Type 2 ladder. For the non-cyclic ammonium moiety, $(PhCH_2)_2N^-$, the Li^+ complex forms the trimeric $\{(PhCH_2)_2NLi\}_3$ described previously (ZEGNII; Fig. 15), while the bromide of the comparable organic moiety forms a planar 4^4 net (GEQWUU [127]).

4. Applications and limitations of the analogy

The preceding discussion demonstrates that the structural analogy between organic ammonium halides and main-group amide/imide complexes functions at a basic level for both primary and secondary amine moieties. For primary amine moieties, comparable discrete cubanes and sawtooth ladders are observed in both the organic and main-group complexes. For secondary amine moieties, comparable stack motifs and planar ladders are observed in both systems, etc. The similarity between the organic and inorganic systems is a consequence of comparable *directional* properties of association in both cases and this is the key factor that facilitates transfer of ring-laddering and ring-stacking concepts to the organic solid state. There are, however, very few examples of directly comparable motifs. Indeed, in *most* cases, directly comparable amine moieties (i.e. containing the same R groups) do not form identical motifs. This distinction is attributed principally to metric differences between $N^+(-H)\cdots X^-$ and N–M contacts and clearly limits the analogy in a predictive sense: it is *not* possible to predict conclusively the motifs formed in main-group amides/imides by simple comparison with the analogous organic ammonium halides, and vice versa. However, the metric differences also present a valuable opportunity for comparison between the two systems. If the observed crystal structures represent a balance between electrostatic

energy and the steric influence of the organic moieties, there is potentially much to be learned from perturbing this balance. Since electrostatic energies (varying as $1/r$) and van der Waals interactions (attractive dispersion terms varying as $1/r^6$, repulsive terms varying approximately as $1/r^{12}$) display distinctly different distance characteristics, the metric features of the motif must influence the nature of the balance. Thus, recognition of the analogy facilitates examination of the balance between electrostatic energy and steric factors over a relatively large range of r.

4.1. The balance between electrostatic energy and steric factors

For secondary amine moieties, $R_2NH_2^+X^-$ and $R_2N^-M^+$, both the organic and main-group complexes incorporate singly-charged anions and cations so that the electrostatic forces are potentially comparable in the two cases.[8] The principal distinction in this system is, therefore, the metric difference between $N^+(-H)\cdots X^-$ and N–M contacts. The longer $N^+(-H)\cdots X^-$ contacts in the organic sample can be considered to diminish the steric influence of given R groups *within* structural motifs. A 4^4 net in an organic ammonium halide, for example, can accommodate larger R groups than a comparable net in the main-group system. Electrostatic energies are also diminished at greater r, but since electrostatic forces act over a much greater distance than steric effects, the influence of the former remains more closely comparable in the two systems. Thus, there is an inherent difference between the balance of electrostatic energy and steric factors in $R_2N^-M^+$ and $R_2NH_2^+X^-$ and it is unlikely that directly comparable motifs will be observed for analogous R_2N^- and $R_2NH_2^+$ moieties. However, if the organic system is considered to be a "scaled up" version of the main-group system, comparable structural motifs might be expected where the $R_2NH_2^+$ moiety in the organic system is a suitably scaled version of the R_2N^- moiety in the main-group complex. Support for this assertion is found in the comparable *cisoid–transoid* ladders PIXVIB and CACVIM (Fig. 17). In the main-group complex PIXVIB, H atoms bound to N of the amide moiety line the inside of the ladder curvature, while in CACVIM, relatively larger methyl groups perform an analogous role. Likewise, the R groups projecting to the outside of the ladder curvature in PIXVIB are relatively smaller than those in CACVIM. This hypothesis is difficult to quantify at a simplistic level, but it appears to present an interesting avenue for experimental study.

The primary system, $RNH_3^+X^-$ and $RN^{2-}M^{2+}$, differs fundamentally from its secondary counterpart in that primary ammonium halides are comparable to imide complexes of *divalent* main-group elements. The electrostatic energy (described as $-N_A z_+ z_- e^2/4\pi\varepsilon_0 r$) is greater by a factor of four (at the same r) in $RN^{2-}M^{2+}$ compared to $RNH_3^+X^-$ on account of the fact that $z_+ = z_- = 2$ in the main-group system. The metric difference between $N^+(-H)\cdots X^-$ and N–M contacts remains essentially as described for the secondary system. Thus, the balance between electrostatic energy and steric factors in the primary system is distinctly different from that in the secondary system. To some extent, the variation in the electrostatic energy and r act to "oppose" each other in $RN^{2-}M^{2+}$: while the electrostatic energy would be expected to dominate the motifs in the main-group complexes to a much greater degree than in the organic system, the shorter N–M contacts also "enhance" the steric influence of the amide moieties compared to the organic system. The observation of the only directly comparable main-group and organic motifs to date in the cubanes of 2,6-di(*iso*-propyl)aniline suggests that the balance between electrostatic energy and steric factors in the organic and main-group systems might be "closer" in the primary case than in the secondary. Indeed, considering that this balance is significantly different for the primary and secondary cases, and noting that directly comparable motifs *have* been observed for primary amine moieties, reiterates that directly comparable structures are unlikely ever to be observed for secondary ammonium moieties.

4.2. Directional bonding preferences at the cation

The ring-laddering and ring-stacking approaches as they are applied here concentrate principally on the coordination sphere of N and the directional characteristics of association with respect to the amine moiety. The directional bonding preferences of X^- in the organic system and M^{n+} in the main-group complexes are assumed to be isotropic. For the Group 13 and Group 14 elements, the validity of this assumption is questionable. For $[AlR]^{2+}$ and $[GaR]^{2+}$ with small R groups (e.g. H, CH_3), the Al or Ga atom invariably acquires approximate tetrahedral coordination in a cubane or hexameric motif. With more bulky R groups, dimers can also be formed in which the metal adopts approximate trigonal-planar coordination [129–133]. Clearly, the directional preferences and steric influence of $[AlR]^{2+}$ and $[GaR]^{2+}$ differ considerably from those of isolated Cl^- or Br^- anions in both of these situations. Thus, it is unlikely that directly comparable motifs will be observed for $RNH_3^+X^-$ and $RN^{2-}[Al/GaR]^{2+}$. Similarly, the Group 14 cations, Sn^{2+} and Pb^{2+}, rarely adopt structures typical of spherically symmetrical ions [134]. Amongst the main-group amide complexes discussed here, Sn^{2+} and Pb^{2+} most commonly adopt a pyramidal arrangement – as exemplified by the cubane motif – that can be viewed as tetrahedral with one "stereochemically active" non-bonding electron pair. Although this tendency towards pyramidal geometry is not fundamentally comparable to the isotropic nature of Cl^- or Br^- as a hydrogen-bond acceptor, the coordination geometries of Cl^- or Br^- do in fact approach

[8] The following discussion does not take any account of additional stabilisation provided by hydrogen bonding. Steiner has noted previously that hydrogen bonds with mainly ionic character such as $NH_3^+\cdots Cl^-$ might be considered as ionic interactions with a "moderate hydrogen bond formed on top" [128]. The associated energies for moderate hydrogen bonds are ca. 15–60 kJ mol^{-1}, a relatively small contribution to the lattice energy compared to the electrostatic energy.

pyramidal in many of the $RNH_3^+X^-$ motifs (e.g. cubanes, sawtooth ladders, *cisoid–transoid* ladders, etc.). Thus, the prospects for further observation of directly comparable motifs in $RNH_3^+X^-$ and $RN^{2-}Sn/Pb^{2+}$ are not necessarily diminished.

4.3. The influence of solvation

One further significant difference between the organic and main-group complexes is a chemical factor: inorganic chemistry is commonly undertaken in coordinating solvents and the inclusion of solvent molecules in the crystal structures of main-group complexes – either directly associated with the structural motif or as lattice solvent – is extremely common. Organic crystal structures, in particular those of relatively simple compounds such as ammonium halides, contain solvent molecules far less regularly. The influence of solvation often provides a critical difference between the motifs observed in the organic and main-group systems. The complete absence to date of Type 2 ladders in the main-group system, for example, appears to be attributable to the intervention of solvent (Section 3.2). Similar factors most likely account for the absence of 2D nets amongst the main-group systems. This is of course the very essence of the ring-laddering and ring-stacking concepts: extended association of the anionic and cationic moieties to form motifs such as infinite ladders and 2D nets is commonly prevented by the steric influence of the R groups of the amide/imide moieties. Solvent molecules, however, present steric constraints very different from those of the amide/imide anions so that further coordination to the metal centres by solvent molecules may become feasible. In this respect, solvent molecules may be considered to act as "space fillers" that are able to coordinate to metal cations in $\{R_xN^{(3-x)-}M^{(3-x)+}\}_n$ where coordination of further $R_xN^{(3-x)-}$ moieties is prevented on steric grounds. The strategy of promoting more extended association by exclusion of solvent has been exploited successfully – and deliberately – for main-group systems: each example to date of *infinite* alkali-metal amide ladders has been prepared either by avoiding coordinating solvents altogether (e.g. NECQER [107] and NEXKOQ [110], prepared from solution in *n*-hexane) or by employing only a stoichiometric amount of a coordinating ligand in an otherwise non-coordinating solvent system (e.g. $\{[PhCH_2N(H)Li]_2{\cdot}THF\}_\infty$ [108]). Infinite ladders have also been prepared from solution in the liquid amine itself (e.g. PIXVIB). Even this latter approach, however, does not guarantee a solvent-free structure: in KUPSET [106], for example, neutral piperidine molecules solvate a 4-rung lithium-piperidide ladder fragment (Fig. 16(c)).

The equivalent of "solvation" in organic ammonium halides is the introduction of some other neutral hydrogen-bond donor molecule that can compete for coordination to X^-. In the same way that neutral solvent molecules in main-group complexes are able to coordinate to the metal centres without invoking prohibitive steric penalties, so a second hydrogen-bond donor in the organic system might intervene in the association of the ammonium moieties and halide anions. One (serendipitous) glimpse of such a case is found for the dimeric species $\{FC_6H_4COCH(CH_3)N(tBu)H_2^+Cl^-\}_2$ (NUFSOW [135]; Fig. 24). The dimer crystallises as an ethanol solvate, in which the ethanol molecules form hydrogen bonds to the Cl^- anions. The resemblance of this arrangement to solvated main-group dimers such as $\{(PhCH_2)(PhCH(CH_3))N^-Li^+{\cdot}THF\}_2$ (CISQAW; Fig. 14(a)) is clear. It may be envisaged that systematic exploitation of multi-component ammonium halide systems containing additional hydrogen-bond donors will yield "solvated" motifs in the organic solid state, analogous to those in the main-group systems.

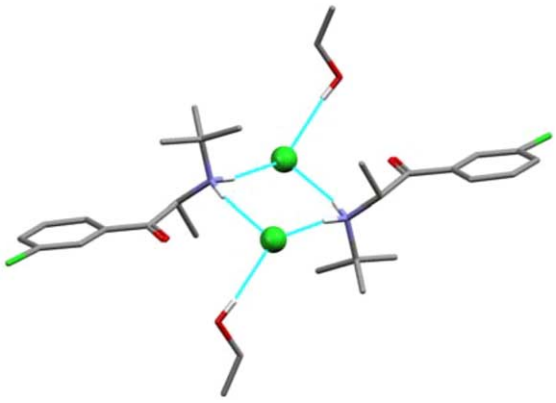


Fig. 24. Dimeric $\{R_2NH_2^+X^-\}_2$ unit in NUFSOW, in which ethanol solvent molecules form hydrogen bonds to Cl^- (H atoms bound to C omitted). The motif is comparable to that in Fig. 14(a).

5. Concluding remarks

Perhaps the most effective means to examine the validity and utility of the analogy described here lies in the pursuit of new targets in synthetic main-group chemistry and in the solid-state structures of organic ammonium halides. In general, many more crystal structures are required – particularly amongst the main-group complexes – to explore fully the extent of the analogy. The variety of amide/imide moieties amongst the main-group structures is currently rather limited in comparison to the range of ammonium halide structures. Of course, this reflects to some extent the relatively greater experimental challenges associated with preparation and characterisation of the main-group complexes, and the fact that they are in general prepared "deliberately" by chemists with a specific interest in their structural chemistry. Crystallisation of organic amines as hydrochloride salts is a rather more common practice in general, and many structures relevant to this study were provided indirectly by synthetic chemists pursuing entirely unrelated research. On the basis of the discussion here, it would seem that the best prospects for *directly* comparable motifs in the organic and main-group systems is offered by $RNH_3^+X^-$ and unsolvated complexes of Group

2 cations, since the electrostatic and steric factors are more closely balanced for the primary systems and the bonding preferences of Group 2 M^{2+} cations would be expected to be closest to isotropic. However, there is a definite shortage of Group 2 amide structures in the literature at present, and there are no examples to date in which Group 2 cations remain unsolvated. Recognition of the analogy may permit information derived from the organic solid state to be utilised to guide the preparation of such complexes.

Based on the structural chemistry of the main-group amides/imides, two main themes are immediately apparent for investigation in the organic solid state: examination of the organic ammonium halides as "scaled up" versions of main-group complexes, and consideration of the role of "solvents" in the organic system. In the first instance, there are several clear targets that have not yet been observed in the organic solid state, e.g. isolated cyclic trimers and cyclised ladders. A programmed study inspired by comparison with the main-group structures may yield such structures. For the second theme, systematic examination of multi-component ammonium halide systems incorporating additional hydrogen-bond donors may yield motifs comparable to the solvated dimers and fragmented ladders of the main-group complexes. In this case, there are a great many examples of Type 2 ladders and 2D nets amongst the organic structures in which several relatively long $N^+\cdots X^-$ contacts appear to offer prospective points for targeted intervention of "solvent" molecules. Realisation of such fragmented motifs would provide a most satisfying validation of the analogy.

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