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Review

Hydrogen-bond supramolecular structure of group 13 Schiff base complexes

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Contents

Abstract

The structural features of the group 13 element complexes of general formula $R_2M(O,N)$ and $RM(O,N)_2$ (R = alkyl, M = B, Al, Ga, In), supported by bidentate and multidentate Schiff base ligands are discussed and considered in relation to the hydrogen-bond networks. Detailed structural analysis was performed for crystal structures of complexes retrieved from the Cambridge Structural Database (CSD) (version 5.25) and compounds recently characterized by our group. It was demonstrated that the intra- and intermolecular non-covalent interactions like the $C-H_{imino}\cdots O$, $C-H_{aryl}\cdots O$, $C-H_{aliph}\cdots O$, and $C-H\cdots\pi$ hydrogen bonds, and π-stacking appear very frequently. Various structural motifs for the group 13 Schiff base complexes were delineated ranging from monomeric species, hydrogen bond dimers, linear polymers, helicates, layers to 3D network architectures. Such diversity in the supramolecular architecture arises from the ligands identity and both the coordination geometry and the nature of the metal center.

Keywords: Group 13 elements; Schiff bases; Self-assembly; Hydrogen bonds; Helical structures

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1. Introduction

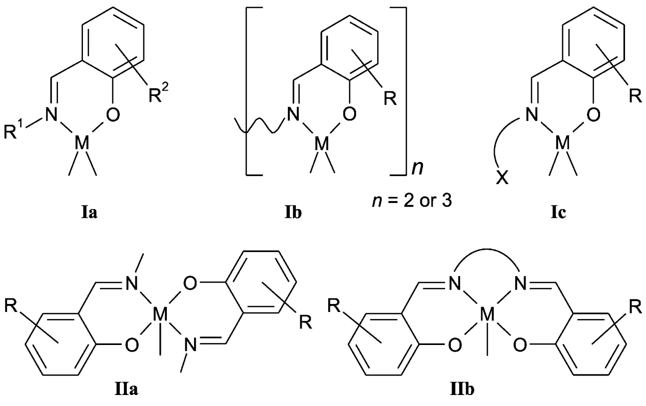
In Schiff base metal complexes, the environment at the coordination center can be modified by attaching different substituents to the ligand, which provides a useful range of steric and electronic properties essential for the fine-tuning of structure and reactivity. Therefore, Schiff base ligands are among the most fundamental chelating systems in coordination chemistry [1,2] and complexes of both transition and p-block metals based on this type ligands have been shown to catalyze a wide variety of reactions [3,4]. For instance, the aluminum complexes, which are of particular relevance to this paper, have been used as catalysts in polymerization of ethylene [5], methacrylate [6], lactide[7] and other heterocyclic monomers [8]. However, the vast majority of investigations focus on the metal first-coordination sphere, while the ligand frameworks have various donor and acceptor sites capable to participate in an internal hydrogen bond to an adjacent metal-bound ligand or an incoming substrate, and the fundamental structural consequences exhibited by the second-sphere hydrogen bonding interactions on the reactivity and properties of these type complexes are not a well-developed area. The importance of hydrogen bonding may lies in the numerous supporting roles for processes taking place at metal sites as well as in the rapidly developing field of crystal engineering and material chemistry. In our opinion the cooperation between the coordination center and non-coordinating active-site residues plays very often important (thought often yet unrevealed) role in the molecular recognition and activation processes involving catalysts supported by Schiff bases as well as it may be of fundamental importance in the design of well-organized solid-state materials with desired properties involving Schiff base ligands. The latter expectation is supported by recent studies, which have highlighted the potential importance of hydrogen bonding in tuning the properties of materials based on Schiff base metal complexes [9,10]. Undoubtedly, apart from wide application of Schiff base metal complexes in various fields of chemistry, exploitation of non-covalent interactions inherently exhibited by this group of compounds is an emerging area of research.

In the past few years, we have been engaged in an investigation of relationships between intra- and intermolecular secondary donor–acceptor interactions and hydrogen bonding using the group 13 alkoxides [11] and carboxylates as model complexes [12]. These studies revealed that minor differences in the subunit structure could have a profound effect on the molecular and crystal structure. An integral part of this work has been a study of the structure of group 13 organometallic chelate complexes (M = B, Al, Ga and In) with the salicylideneiminate anion as the *O*,*N*-bidentate ligand [13,14] The latter compounds were found to be a good basic model system for exploiting the role of hydrogen bonding on the supramolecular structure of Schiff base metal complexes. The purpose of this contribution is to present extended studies on the identification and characterization of supramolecular interactions in the group 13 Schiff base complexes based on detailed structural analysis of crystal structures retrieved from the Cambridge Structural Database (CSD) and recently published by our group. In particular, our crystal structure analyses focus on the identification of the hydrogen bond preferred modes for Schiff base metal complexes as well as an understanding their relative importance on the supramolecular architecture. It is also pertinent to note that a significant part of the revealed structural motifs and supramolecular structures had been not considered by the original authors.

1.1. *Method of database analysis*

The Cambridge Structural Database (CSD, version 5.25, April 2004) [15] was interrogated to extract all reliable structures of the group 13 element Schiff base complexes. The searches were performed for four-coordinate and five-coordinate complexes containing the $C_2M(O,N)$ (**I**) and $CM(O,N)_2$ (**II**) central core, respectively (where M = B, Al, Ga or In, and *O*,*N* denotes the skeleton of a salicylideneiminate ligand). The basic structural types **I** and **II** were further classified into distinct categories (Scheme 1). The category **Ia** contains mononuclear tetrahedral $R_2M(O,N)$ molecules. Bi- and tri-nuclear compounds with two or three tetrahedral $R_2M(O,N)$ units joined by an aliphatic backbone were categorized separately as **Ib** due to the distinguished supramolecular structure. Mononuclear derivatives of potentially tridentate salicylideneiminate ligands with the terminal Lewis base termini attached to the imine nitrogen constitutes a particular case and were categorized as **Ic**. On the other hand, the monomeric five-coordinate monoalkyl $RM(O,N)_2$ or $RM(O_2N_2)$ complexes, i.e., derivatives of *O*,*N*-bidentate salicylideneiminate or *O*,*O*,*N*,*N*-tetradentate Salen-type ligands, are denoted as **IIa** and **IIb**, respectively (Scheme 1).

The CSD searches were restricted to non-charged compounds and entries with the *R*-factor greater than 0.08 and those with an unresolved error were rejected (with one exception for NIXTOD because of its structural importance). Details concerning the data retrieval from the CSD file, and the list of CSD ref. codes with references and selected geo-



Scheme 1. Schematic representation of the structural types of the group 13 element Schiff base complexes analyzed in this work.

metrical parameters can be found in the supporting information. Essentially, there is more than one intermolecular non-covalent interaction per molecule for many of these structures. The applied atom-numbering scheme is consistent with labeling used in the CSD records.

2. Supramolecular structure of Schiff base derivatives with the $C_2M(O,N)$ core: four-coordinate complexes of type I

2.1. Type **Ia** complexes

For a simple monometallic Schiff base derivatives of formula $R_2M(O,N)$ (**Ia**) (M = B, Al, Ga, and In), total of 12 crystal structures are available. These compounds exist in the solid state as monomeric tetrahedral chelate complexes. The exception is the only one structurally characterized indium compound which forms dimers through the $In_2(\mu\text{-}O)_2$ bridges, and therefore contains the five-coordinate metal center (vide infra). Mononuclear complexes containing Schiff base ligands can be assembled into various supramolecular architectures by means of intermolecular non-covalent forces. The crystal structure analysis of these compounds provides interesting data concerning the effect of the nature of coordination center and both the M-alkyl and the *N*-alkyl substituents on the molecular assembly of the tetrahedral Schiff base complexes [13,14].

Two structurally characterized complexes of type **Ia** based on *N*-methyl-salicylideneimine (HsaldMe) have been described, namely Et_2B(saldMe) [14] and Me_2Ga(saldMe) [13,16]. Both compounds crystallize as the four-coordinate species; however, the crystal structures exhibit an extensive network of hydrogen bonds. The boron compound crystallizes in the orthorhombic space group *Pbca* with a simple 1D secondary chain structure. Adjacent monomeric moieties of Et_2B(saldMe) are held together in chains by the double C–H···O hydrogen bridges (Fig. 1). Both the imine hydrogen atom H(7) and the hydrogen atom H(12a) of the methyl group are involved in hydrogen bond interactions with the aryloxide oxygen O(1′) of an adjacent molecule [H(7)···O(1′): 2.57 Å; C(7)–H(7)···O(1′): 152° and H(12A)···O(1′): 2.50 Å; C(12)–H(12A)···O(1′): 160°]. The infinite H-bonded chain is propagated by the *a*-glide

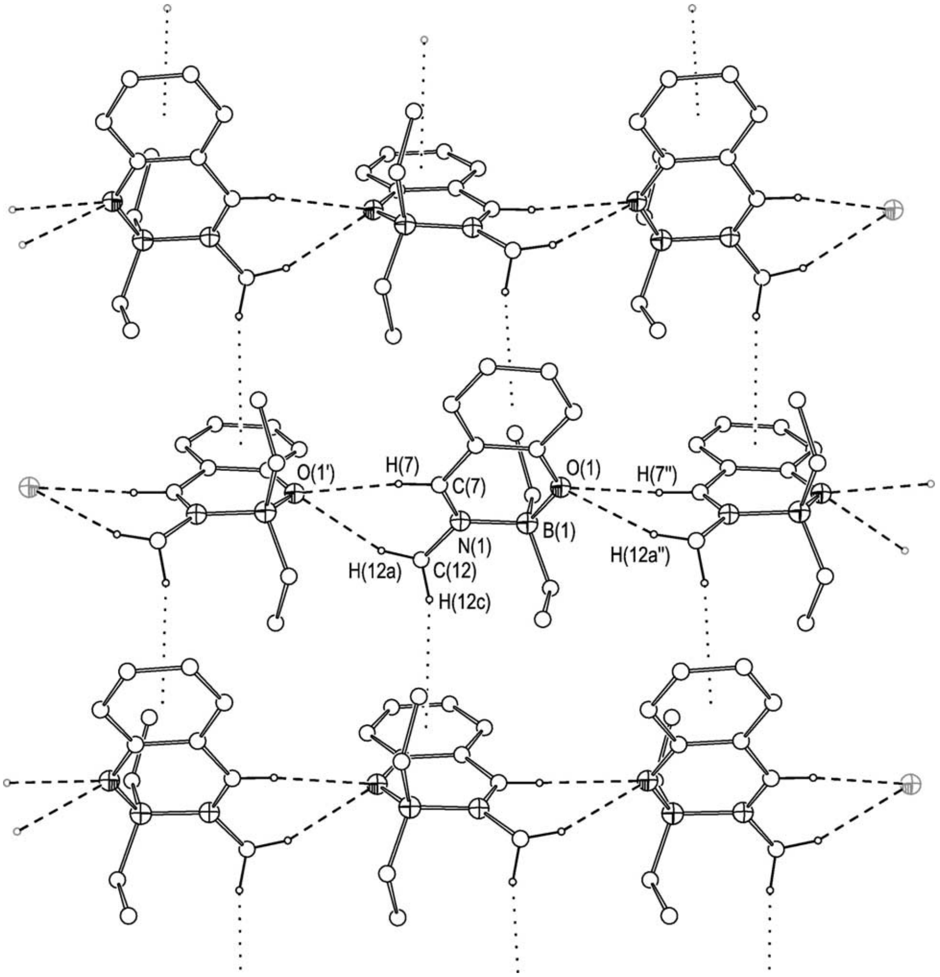


Fig. 1. A view of the 2D hydrogen bonding in the crystal structure of Et_2B(saldMe). The dashed and the dotted lines represent C—H···O and C—H···π(Ph) hydrogen bonds, respectively. Hydrogen atoms are omitted excluding those involved in the H-bond formation. Adapted from ref. [14].

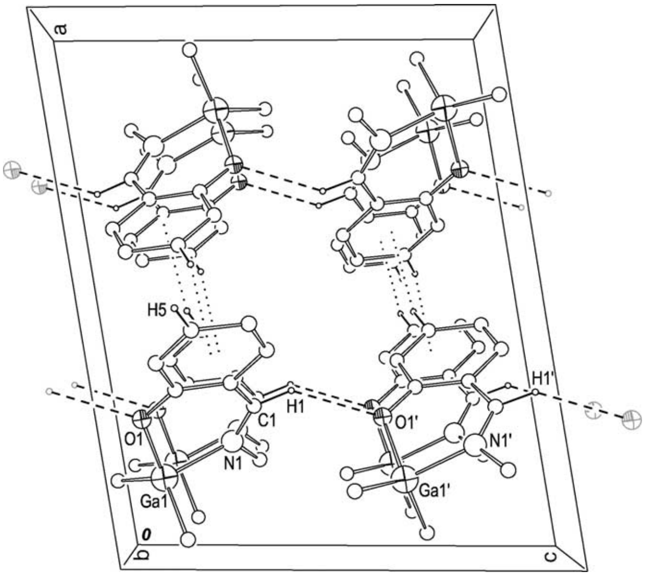


Fig. 2. A view of the crystal packing of *N*-methyl-salicylideneiminato-dimethylgallium (MSCGAA), along *b*-axis showing the intermolecular C—H· · ·O (dashed lines) and C—H· · ·π(Ph) (dotted lines) hydrogen bonds. Only hydrogen atoms involved in the H-bond formation are depicted. Adapted from ref. [13].

plane with the glide vector equal to 6.1205(5) Å. Further analysis of intermolecular contacts showed that the tertiary structure of Et_2B(saldMe) is achieved through C–H· · ·π(Ph) interactions (dotted lines in Fig. 1) between parallel chains leading to grid-like 2D network lying on the (0 0 1) crystallographic plane.

The arrangement of molecules in the crystal structure of *N*-methyl-salicylideneiminato-dimethylgallium, Me_2Ga(saldMe) (MSCGAA) [13] is also achieved by the C–H_{imino}· · ·O and C–H· · ·π interactions (Fig. 2). The imine hydrogen atom is close to the aryloxide oxygen atom O(1′) [H(1)· · ·O(1′) = 2.44 Å] of a second molecule related by a glide plane (the length of the glide vector = 6.0343(5) Å) and this type of interaction results in the formation of an infinite H-bonded chain, like in the boron analogue. The tertiary structure of Me_2Ga(saldMe) is different than that in Et_2B(saldMe), and parallel H-bonded chains are further assembled by C–H· · ·π(Ph) interactions (dotted lines in Fig. 2) into the 2D double layers lying on the (1 0 0) crystallographic plane; the appropriate H(5)· · ·$\pi_{centroid}$ separation is equal ∼2.60 Å. Thus, in the presence of the *N*-Me substituent, non-covalent interactions lead to the formation of the 2D framework of closely packed slabs without guest molecules, and the nature of the metal center does not affect the hydrogen-bond supramolecular structure of the tetrahedral R_2M(*O*,*N*) chelate complexes.

Interestingly, the replacement of the *N*-methyl to the *N*-phenyl group in the bidentate salicylideneiminate ligand leads to significant changes in the molecular assembly of R_2M(*O*,*N*) complexes, which have revealed detailed structural analyses of the complete series of organometallic derivatives of the group 13 elements, Et_2B(saldPh) [14] Me_2Al(saldPh) (OKUJIN) and Me_2Ga(saldPh) (OKUJOT) [13]. The latter two complexes are isostructural, except for the different ionic radii of aluminum and gallium, and crystallize in the tetragonal space group $I4_1/a$ as solvates with disordered molecules of *n*-hexane. Adjacent monomeric moieties are linked by the C–H_{imino}· · ·O hydrogen bonds with the aryloxide oxygen acting as the hydrogen acceptor. This leads to the formation of infinite helices as depicted in Fig. 3a for Me_2Al(saldPh). Parallel alternating left- and right-handed helical chains are thus further joined by C–H· · ·π(Ph) interactions to form a tetragonal net (Fig. 3b). In both structures the intermolecular C–H· · ·$\pi_{centroid}$ separations are equal ∼3.03 Å and lie in the accepted distance range for this type of contacts [17]. The examination of the space-filling model indicates the existence of oblate spheroidal cavities (about 200 $Å^3$ in volume) into which the disordered guest molecules (*n*-hexane) are included [13].

Surprisingly, the completely different supramolecular structure was found for diethylboron derivative of *N*-phenyl-salicylideneimine, which crystallizes in the monoclinic space group *C*2/*c* [14]. The adjacent tetrahedral Et_2B(saldPh) species are interconnected by the pair of intermolecular C–H_{arom}· · ·O hydrogen bonds between the aryloxy-oxygen atom and the *ortho*-positioned hydrogen of the salicylideneimine aromatic ring (H· · ·O: 2.54 Å; C–H· · ·O: 171°) leading to the H-bonded dimer as depicted in Fig. 4. In addition, the dimeric species are further linked by C–H_{arom}· · ·π(Ph) interactions to form infinite layers parallel to the *bc* plane, and both aromatic rings are engaged in the latter interaction (Fig. 5). Thus, in the case of the group 13 *N*-phenyl-salicylideneimine derivatives, the nature of the coordination center significantly affects the molecular assembly of the group 13 tetrahedral R_2M(*O*,*N*) complexes. As mentioned above, the observed intermolecular hydrogen bond motifs for R_2M(saldPh) are entirely different from that found for R_2M(saldMe) analogues; however, this issue is discussed more detail in the next part of this report.

In contrast to the four-coordinate hydrogen bonded structures of the group 13 lower element complexes, the indium analogue Me_2In(saldPh) (OKUJUZ) forms dimeric molecules without any notable intermolecular contacts in the solid structure (Fig. 6) [13]. The indium center In(1) strongly interacts with the aryloxide oxygen O(1′) on the fifth coordination site forming hypercoordinate dimeric complex with In(1)–O(1′) bridging bond of distance 2.477(3) Å, and with the imine nitrogen N(1) atom and the bridging oxygen O(1′) atom occupying the axial sites Thus, in the indium complex the secondary metal–ligand interactions preclude the formation of potentially C–H· · ·O hydrogen bonds. Nevertheless, the higher coordination of indium is fully consistent with our earlier reported conclusion regarding the Lewis acidity of the group 13 metal centers in the four-coordinate complexes [11a].

Among type **Ia** complexes is a number of mononuclear molecules with a bulky substituent in the vicinity of the aryloxide oxygen atom. Detailed examination of the structural

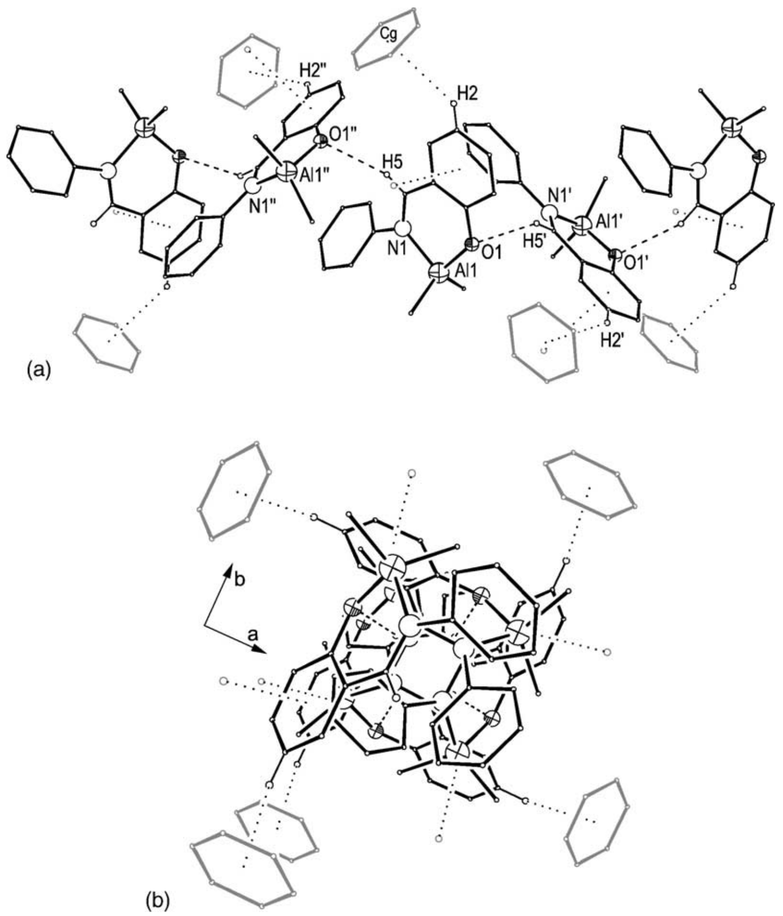


Fig. 3. (a) A view of the helical chain structure of $Me_2Al(saldPh)$ and (b) along *c*-axis. The dashed and the dotted lines represent C—H···O and C—H···π(Ph) hydrogen bonds, respectively. Disordered solvent molecules are omitted. Hydrogen atoms are omitted excluding those involved in the H-bond formation.

data retrieved from CSD (see, Appendix A) showed that in this case there is not any notable intermolecular hydrogen bonding interactions. The bulky group effectively shields the aryloxy-oxygen atom and essentially prevents any intermolecular contacts either to the hydrogen donor groups or the Lewis-acid metal centers. This is the reason why the association of monomeric species via hydrogen bonding or donor–acceptor bonds does not occur. However, for complexes with *tert*-Bu substituent, the short distances between two hydrogen atoms of *tert*-Bu groups and the oxygen atom (∼2.35 Å) are observed in all the analyzed structures (cf. the structure of RAJYUW [18] presented in Fig. 7). Taking into

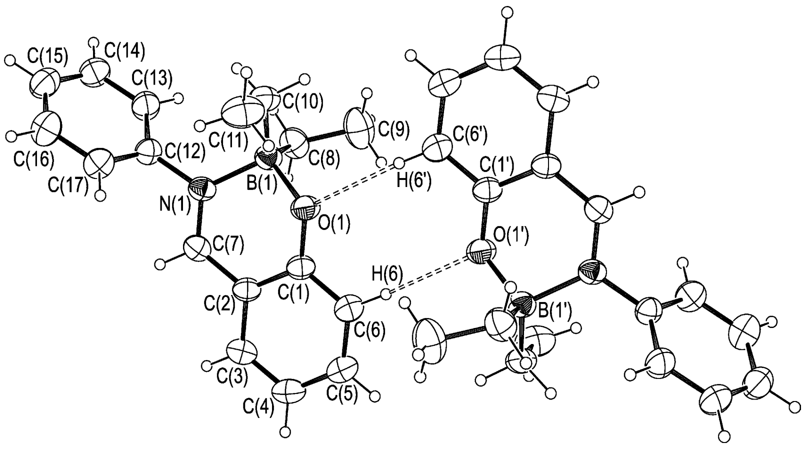


Fig. 4. An ORTEP diagram of hydrogen bonded dimer of $Et_2B(saldPh)$ in the solid state showing a 30% probability of thermal ellipsoids. Adapted from ref. [14].

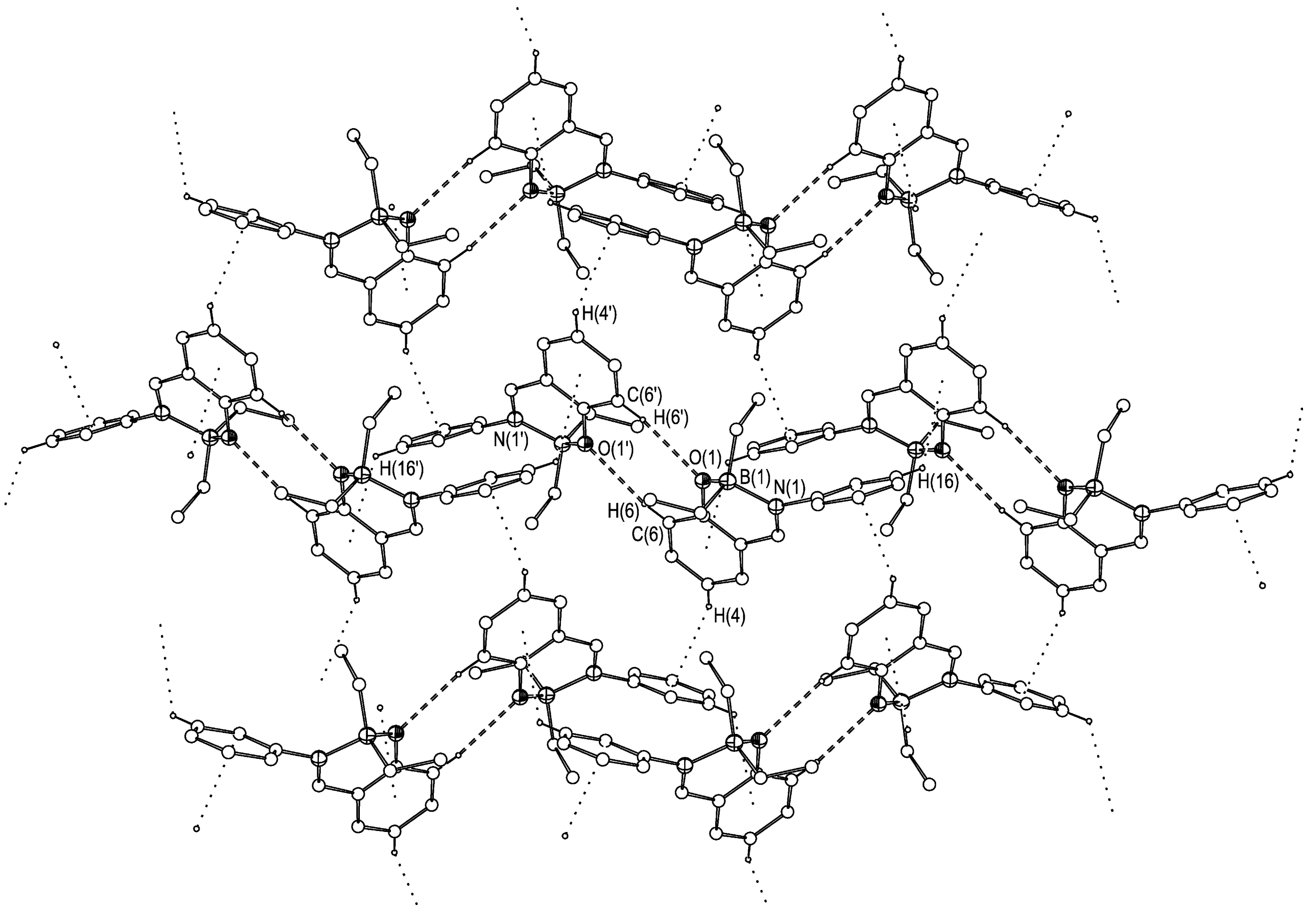


Fig. 5. A view of the 2D hydrogen bonding network in the crystal structure of Et_2B(saldPh). The dashed and the dotted lines represent C—H···O and C–H···π(Ph) hydrogen bonds, respectively. Hydrogen atoms are omitted excluding those involved in the H-bond formation. Adapted from ref. [14].

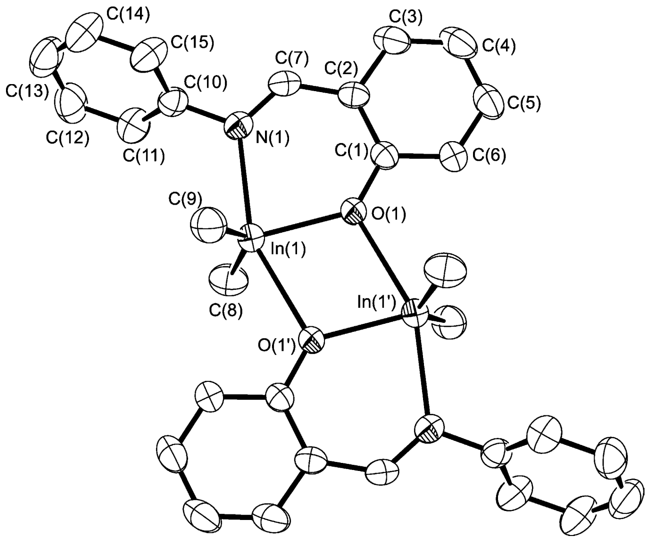


Fig. 6. The molecular structure of bis(*N*-phenyl-salicylideneiminato-dimethylindium), Me_2In(saldPh). Hydrogen atoms are omitted for clarity. Adapted from ref. [13].

account the C–H···O angles of about 124° and the orientation of the *tert*-Bu group there is evidence that monomers are stabilized by a pair of C–H_{aliph}···O intramolecular hydrogen bonds.

Similar intramolecular C–H_{aliph}···O contacts, and additional intramolecular C–H_{aliph}···N_{imine}(pπ) interactions due to the bulky 2,6-dialkylphenyl pendant group at the imine nitrogen, exist in two aluminum complexes, QOLDIE and QOLDOK [19]. In both cases, the five-membered HCCCN

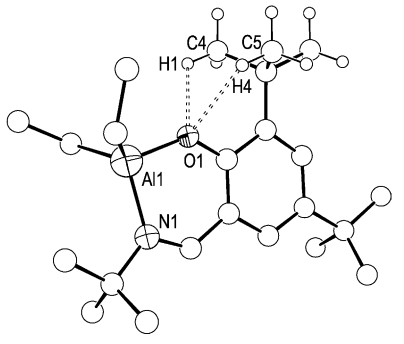


Fig. 7. A view of the molecular structure of (4,6-bis(*tert*-butyl)-*N*-*tert*-butyl-salicylideneiminato)-diethyl-aluminum with short intramolecular C—H···O contacts designated by dashed lines.

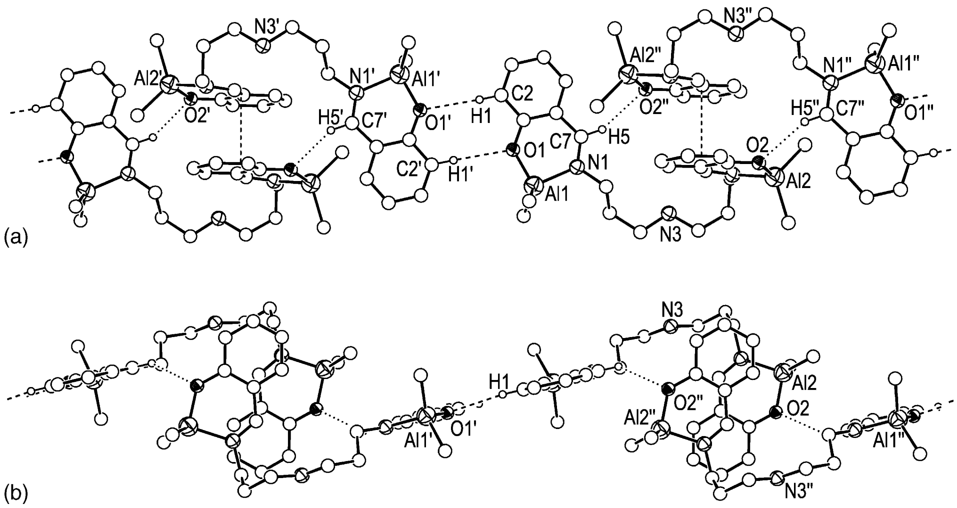


Fig. 8. A view of the hydrogen-bonded molecular chain in (amino-bis(*N*-propylene-salicylideneiminato))-tetramethyl-dialuminum (LOGYEL) showing (a) the intermolecular C—H···O (dashed and dotted lines) hydrogen bonds and (b) π···π-stacking. For clarity, hydrogen atoms are omitted excluding those involved in the H-bond formation.

rings are formed with short H···N distances (∼2.4 Å) and C–H···N angles about 110°.

Another one boron Schiff base derivative of type **Ia** has also been encountered, namely *N*-methyl-2-oxy-1-naphthaldiminato-diphenylboron, MONALB [20]. Analysis of the structural data for this compound demonstrates that the presence of phenyl groups bonded to the boron center prevents the association of molecular complexes through intermolecular C–H···O interactions. Instead of, both boron bonded phenyl rings, adopting appropriate orientations, are engaged in the intramolecular $C–H_{phen}\cdots O$ and $C–H_{phen}\cdots N$ interactions. The observed $H_{phen}\cdots O$ and $H_{phen}\cdots N$ contacts are 2.48 and 2.62 Å, respectively. The molecules are arranged into a 2D sheet in the (1 0 0) plane, which are sustained by several $C–H_{arom}\cdots\pi$ interactions involving both the Schiff base ligand and the phenyl rings.

2.2. *Type **Ib** complexes*

Diversified types of intermolecular contacts are observed in bi- and tri-nuclear complexes of a series of bis- and tris-salicylideneimine derivatives with the $C_2M(O,N)$ central core, i.e., the $SalenH_2$ or $SaltrenH_3$ derivatives, where two or three tetrahedral $R_2M(O,N)$ moieties are joined by an aliphatic backbone (type **Ib** complexes, Scheme 1). So far only one boron compound of this type has been structurally characterized, namely (*N*,*N*-ethylene-bis(salicylideneiminato)-bis(diphenylboron), REVQUE [21]. Owing to the presence of two phenyl groups bonded to the boron center, the aryloxy oxygen atom is engaged only in the formation of intramolecular hydrogen bonds. However, the molecular assembly in REVQUE is attained through $C–H_{arom}\cdots\pi$ interactions between ligand aromatic hydrogen atoms and phenyl rings of adjacent molecules (the distance $H\cdots\pi_{centroid} = 2.71$ Å). Molecules are organized in 1D chains along the crystallographic *a*-axis.

An interesting supramolecular linear assembly has been perceived in the structure of (amino-bis(*N*-propylenesalicylideneiminato))-tetramethyl-dialuminum (LOGYEL) [22]. We note that the original authors indicated only the presence of C–H···O interactions between two neighboring bimetallic molecules leading to hydrogen bonded dimeric units interconnected via the eight-membered ring with the H(1)···O(1′) distance of 2.52 Å and C(2)–H(1)···O(1′) angle ∼175° (Fig. 8).

This association mode corresponds exactly to that observed for diethylboron derivative of *N*-phenyl-salicylideneimine, $Et_2B(saldPh)$ (vide supra) [14]. However, our detailed analysis of intermolecular contacts for LOGYEL revealed a more complex supramolecular structure. The two molecules related by symmetry center are held together by two C–H···O bonds formed by the imino hydrogen and aryloxy-oxygen atoms [H(5)···O(2″): 2.68 Å and C(7)–H(5)···O(2″): 144°], which results in the formation of the hydrogen-bonded molecular chain as is illustrated in Fig. 8. In addition, the π–π-stacking interactions of the salicylideneiminate ligand of neighboring molecules (distance of about 3.5 Å) play a substantial role in the molecular organization in LOGYEL (Fig. 8).

In the case of the group 13 trimetallic $SaltrenH_3$ derivatives, the analysis of intermolecular contacts showed that the attachment of the third ligating arm to the ligand does not change significantly the molecular assembling modes. For example, molecules of $Saltren(GaEt_2)_3$ [(μ_3-tris(((2-oxybenzylidene)amino)ethyl)amine)–tris(diethyl-gallium), QILDOE] [23] form centrosymmetric dimers joined by the $C–H_{imino}\cdots O$ hydrogen bonds with H···O contacts of 2.60 Å and C–H···O angle ∼164°. Much weaker

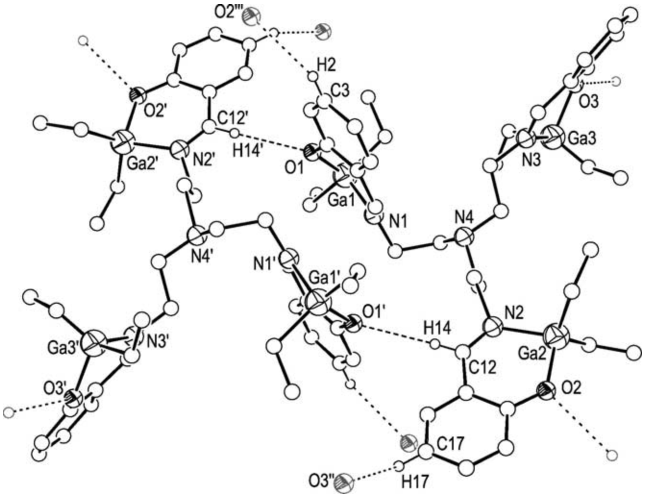
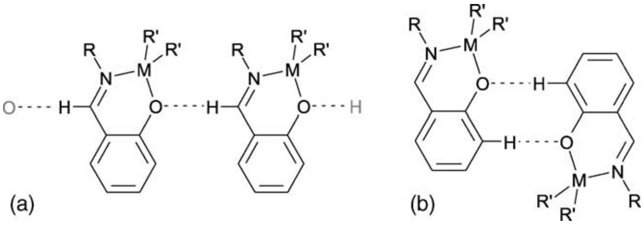


Fig. 9. A view of a portion of the 2D hydrogen bonding network in the crystal structure of Saltren$(GaEt_2)_3$ (QILDOE) showing a centrosymmetric dimer and its contacts with adjacent molecules. H-atoms are omitted excluding those involved in H-bond formation.

interactions between aryl protons and oxygen atoms of two remaining chelating groups lead to an extended 2D network lying parallel to the (0 0 1) crystallographic plane (Fig. 9). Interestingly, the central nitrogen atom, N(4), potentially a strong hydrogen bond acceptor, is not engaged in the H-bond formation.

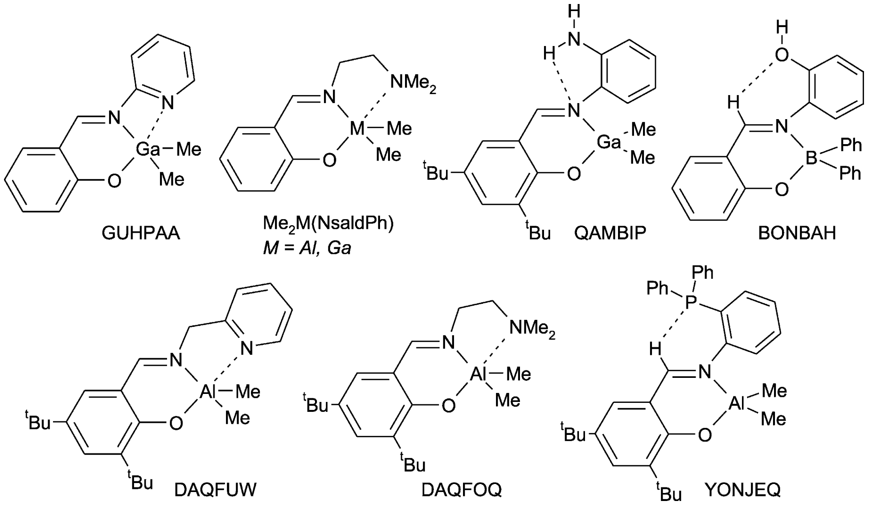
2.3. Factors affecting supramolecular structure of Schiff base complexes with the $C_2M(O,N)$ core

The analysis of the crystal structure of tetrahedral $R_2M(O,N)$ complexes presented above should suffice to illustrate not only the variety of structures that exist, but also allows for a discussion on the factors controlling the self-assembly process. Although the molecular structure of $R_2M(saldR')$ (where M = B, Al or Ga) complexes consists of isostructural monomeric species irrespectively of the character of the coordination center, their crystal structures differ significantly. In all cases, the supramolecular structure is determined by intermolecular hydrogen bonds, but the resulting hydrogen bond motifs are distinct. Depending on the *N*-alkyl substituent, the formation of H-bonded 2D double layer network that is build from 1D chains, or H-bonded 3D framework structure that is assembled from 1D helical chains is observed (Scheme 2a). Only for the boron derivative of *N*-phenylsalicylideneimine, it is the hydrogen-bonded dimer formed by a pair of intermolecular $C–H_{arom}\cdots O$ interactions between the aryloxide oxygen atom and the *ortho*-positioned hydrogen of the salicylideneimine aromatic ring (Scheme 2b).



Scheme 2. Hydrogen bond motifs in type **Ia** complexes: (a) 1D array and (b) H-bonded dimer.

Thus, a common feature of the observed hydrogen bond motifs is the aryloxide oxygen acting as the hydrogen acceptor and the difference concerns a competition between the $C–H_{imino}$ and the $C–H_{arom}$ hydrogen donor sites (these interactions are absent in the case of steric hindrances in the vicinity of the aryloxide oxygen atom). The latter observation rises the question: why is there a change in the hydrogen bond donor sites in the homologous series of *N*-phenylsalicylideneimine derivatives passing from boron to the heavier group 13 derivatives? In order to ascertain whether the observed hydrogen bond motifs are determined by the molecular shape, molecular size or other factors, we have considered the silent features of the molecular structures of $R_2M(saldR')$ complexes [14]. The analysis of the corresponding structural parameters have indicated that the steric congestion at the hydrogen bond donor and acceptor sites, as a result of changes in the coordination center environment or the *N*-alkyl substituents, affect the strength of the $C–H\cdots O_{aryloxy}$ hydrogen bond and may leads to the self-assembly switching of the bidentate Schiff base metal complexes. For instance, the radius of boron is significantly smaller than that of aluminum and gallium which result in a concomitant decrease in the B–O and B–N bond length in $Et_2B(saldPh)$. One consequence of this difference is the increase of steric congestion at the aryloxide oxygen in the boron complexes, and since as the formation of the $C–H_{imino}\cdots O_{aryloxy}$ hydrogen bond chains requires a relatively close approach of the –(Ph)N=C–H_{imino} hydrogen to the metal bonded aryloxide oxygen, this causes a more significant repulsion between the phenyl ring and the sterically congested Et_2BO tetrahedron face. In turn, a considerably greater congestion in the putative structure based on the $C–H_{imino}\cdots O_{aryloxy}$ hydrogen bond promotes the formation of the hydrogen-bonded dimer, where the cooperative $C–H_{arom}\cdots O$ interactions sufficiently compete with the potential chain array of $C–H\cdots O$ bonds involving the stronger hydrogen bond donor site. For the assembly of $Me_2Al(saldPh)$ and $Me_2Ga(saldPh)$, this steric congestion at the hydrogen acceptor site is relieved due to the larger radius of aluminum and gallium, and the formation of 1D chainlike structures is promoted. The substitution of the *N*-phenyl group with the *N*-methyl group in $R_2M(saldR')$ complexes gives similar effect, i.e., relives steric crowding at the hydrogen donor site and promotes 1D H-bonded chains. Furthermore, the observed differences in the crystal structure of the boron and gallium derivatives of *N*-methylsalicylideneimine, and aluminum and gallium derivatives of *N*-phenyl-salicylideneimine indicate that small differences in the molecular shape of $R_2M(saldMe)$ and $R_2M(saldPh)$ complexes alter additionally the mode of the molecular assembly. To compare, the *N*-Me complexes possess a relatively uncongested environment at the N=C–H hydrogen which promotes



Scheme 3. The selected complexes comprising salicylideneiminate ligands with the pendant neutral donor group.

the formation of infinite helices, while in the N–Ph complexes a considerably greater steric congestion imposed by the imine ligand leads to hydrogen bonded molecular chains. Thus, again changes in the steric congestion at the N=C–H hydrogen appear to greatly affect the spatial arrangement of the component molecules and change the hydrogen-bonding pattern. For the related SalenH_2 or SaltrenH_2 derivatives, where two or three tetrahedral $R_2M(O,N)$ moieties are joined by an aliphatic backbone, the inherent encumbers lead additionally to significant changes in the molecular assembly, and except the dominant $C–H_{imino}\cdots O$ interaction, the $C–H_{aryl}\cdots O$, $C–H_{aliph}\cdots O$ and $C–H\cdots\pi$ hydrogen bonds, and π-stacking play a substantial role in the molecular assembly.

2.4. Type **Ic** complexes

A particularly interesting case constitutes the group 13 complexes derived from potentially tridentate salicylideneiminate ligands bearing a pendant O, N, or P donor arm attached to the imine nitrogen, which are schematically depicted in Scheme 3.

These complexes exhibit a relatively large diversity of structural motifs, which are interesting in the context of both the hydrogen-bond networks and the secondary donor–acceptor interactions. For instance, a consideration of the extended structure for (*N*-salicylidene-2-aminopyridine)-dimethyl-gallium (GUHPAA) indicates that there is no notable intermolecular hydrogen bonding interactions in the presence of a pyridyl group bonded to the N_{imine} atom (Fig. 10) [24]. However, an analysis of the gallium coordination sphere shows that the metal center interacts with both the nitrogen atom of the pyridyl group [Ga(1)–N(2): 2.875(3) Å] (the considered interaction by the original authors) and with the aryloxy-oxygen atom of the adjacent molecule related by the center of symmetry [Ga(1)–O(1′): 3.362(3) Å] (the not considered contact, the dotted line in Fig. 10). Although both contacts are relatively long, the observed distances and the directionality of these contacts indicates that these are secondary interactions, which is in conformity with our recently published results for alkylaluminum alkoxides [11d]. Based on the above analysis, it is a reasonable assumption that the observed intermolecular secondary metal–ligand coordination effectively competes with the feasible $C–H\cdots O(1)$ hydrogen bond (cf. structures of Me_2Al(saldPh) and Me_2Ga(saldPh)). In this regard (*N*-salicylidene-2-aminopyridine)-dimethyl-gallium (GUHPAA) is closely related to the analyzed above the indium complex, Me_2In(saldPh).

The replacement of the *N*-pyridyl group to the *N*-dimethylaminoethyl functionality in the tridentate salicylideneiminate ligand leads to significant changes in the molecular assembly of $R_2M(O,N,N)$ complexes. For dimethylaluminum and dimethylgallium derivatives of *N*-(dimethylaminoethyl)salicylideneimine, Me_2Al(NsaldPh) and Me_2Ga(NsaldPh) (Scheme 3), the metal centers adopt distorted trigonal bipyramidal geometry with two methyl groups and the imine-nitrogen atom in the equatorial position, and the aryloxide oxygen and the pendant amino moiety in the axial positions [25]. The observed $Al–N_{amino}$ and

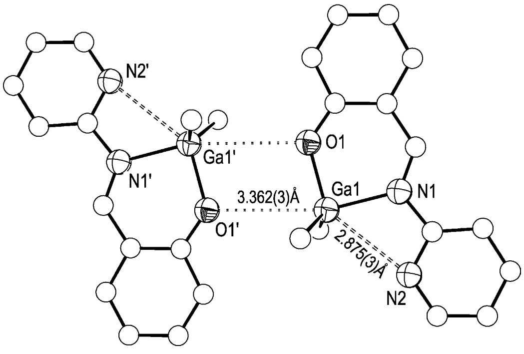


Fig. 10. A view of the structure of (*N*-salicylidene-2-aminopyridine)-dimethylgallium (GUHPAA). Dashed and dotted lines indicate the secondary donor–acceptor interactions. H-atoms are omitted for clarity.

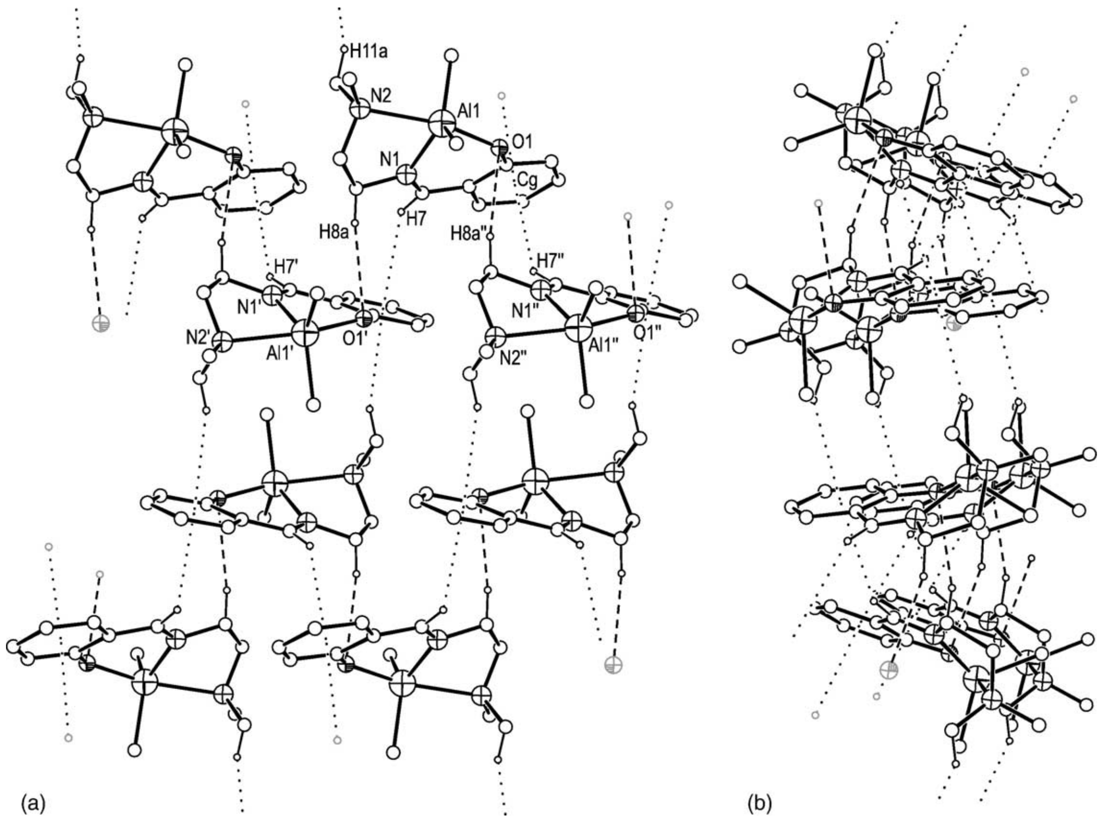


Fig. 11. A view of the 2D hydrogen bonding network in the crystal structure of $Me_2Al(NsaldPh)$. The dashed and the dotted lines represent C—H· · ·O and C—H· · ·π(Ph) hydrogen bonds, respectively. Hydrogen atoms are omitted excluding those involved in the H-bond formation.

$Ga–N_{amino}$ distances differ significantly and are equal to 2.297(4) and 2.806(2) Å, respectively, which clearly shows that the four-coordinate gallium center demonstrates a weaker Lewis acidity than the aluminum center. One consequence of this difference is an increase steric interaction between the substituents on the aluminum and the methyl groups on the amine. Hence, the five-membered AlNCCN chelate ring adopts an open-envelope conformation on N(2) atom in order to achieve the staggered positions of alkyl substituents bonded to the nitrogen and the metal center (Fig. 11), whereas the GaNCCN ring is twisted on the C(8)–C(9) bond with the eclipsed conformation (the elongation of the Ga–N bond reduces steric repulsion) (Fig. 12). For $Me_2Al(NsaldPh)$ and $Me_2Ga(NsaldPh)$ unlike for GUHPAA, the supramolecular arrangement is dictated by the $C–H_{aliph}$· · ·O and C–H· · ·π interactions leading to 2D lamellar structures (Figs. 11 and 12). Interestingly, the observed supramolecular hydrogen bond structures are different which is probably due to the mentioned small conformational changes of the five-membered MNCCN chelate rings in both compounds. In the aluminum complex, adjacent molecules related by *c* glide plane are double bridged by H-bonds to form a corrugated chain along the *c*-axis. As depicted on Fig. 11, the hydrogen atom H(8a) of the aliphatic backbone interacts with the oxygen O(1) atom (H· · ·O: 2.65 Å; C–H· · ·O: 161°) and the hydrogen atom H(7) of the imine group is engaged in the C–H· · ·π(Ph) interaction (H· · ·π: 2.96 Å; C–H· · ·π: 144°). The adjacent 1D zigzag chains are then linked via C–H· · ·π(Ph) interactions formed by the H(7) hydrogen atom of the amine methyl group (H· · ·π: 2.88 Å; C–H· · ·π: 143°). In contrast, molecules of the gallium complex are assembled by $C–H_{equatorial}$· · ·O bonds [H(8b)· · ·O(1): 2.62 Å, C(8)–H(8b)· · ·O(1): 138°] to yield a linear chain along the *b*-axis. The 2D framework arises from linking of these linear chains by C–H· · ·π interactions (H· · ·π: 2.72 Å; C–H· · ·π: 174°). Thus, the comparison of $Me_2Al(NsaldPh)$ and $Me_2Ga(NsaldPh)$ as well as GUHPAA crystal structures demonstrates that subtle changes of the coordination center properties and consequently an alteration of a weakest donor–acceptor bonds may lead to different molecular assemblies.

There are also a number of mononuclear molecules of type **Ic** with a bulky substituent in the vicinity of the aryloxide oxygen atom. Analogously to type **Ia** complexes, the bulky group effectively shields the aryloxy-oxygen atom and essentially prevents any intermolecular contacts either to hydrogen donor groups or the Lewis-acid metal centers. Good examples are provided by the aluminum compounds DAQFOQ and DAQFUW (Scheme 3) [26], where the pendant amino or pyridyl groups act as weakly coordinated fifth ligands with Al–N distances equal to 2.413(5) and 2.254(2) Å, respectively. For both compounds, the geometry at aluminum atoms is best described as a trigonal bipyramidal. The interaction of the additional nitrogen donor site with the aluminum center leads to appreciable weakening of the primary bonds,

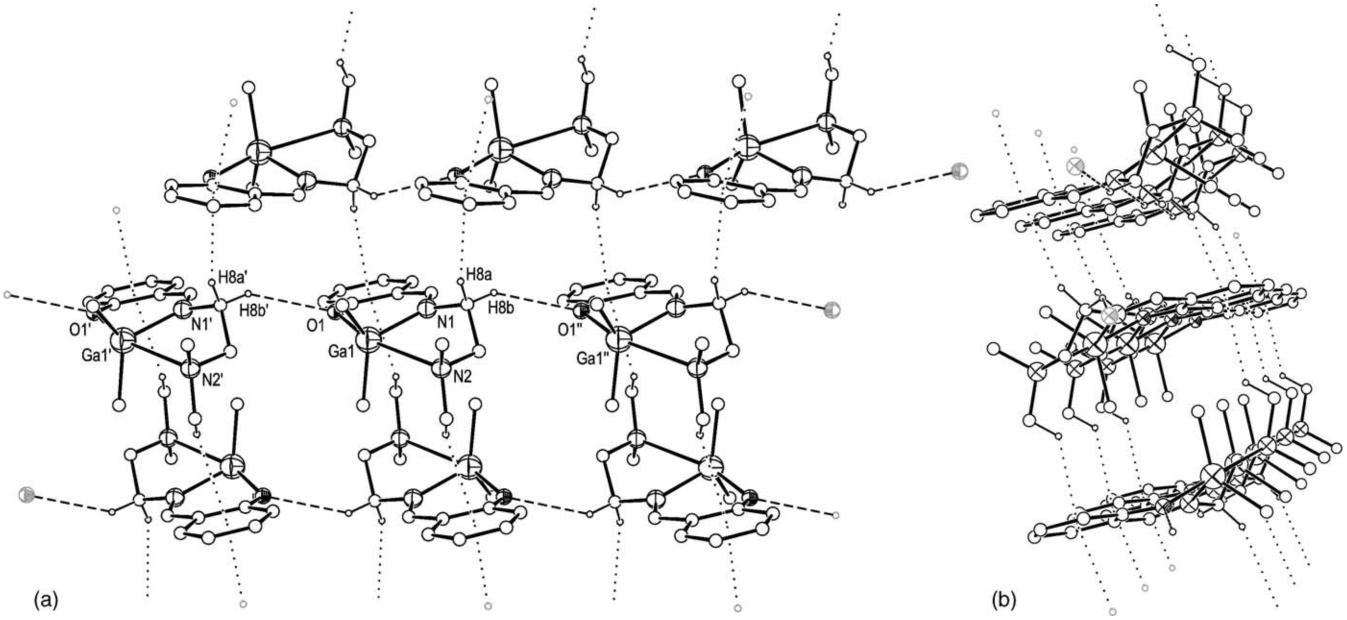


Fig. 12. A view of the 2D hydrogen bonding network in the crystal structure of $Me_2Ga(NsaldPh)$. The dashed and the dotted lines represent C—H···O and C—H···π(Ph) hydrogen bonds, respectively. Hydrogen atoms are omitted excluding those involved in the H-bond formation.

mainly *trans*-located Al—O ones, which is in accord with the structural *trans*-effect [27,28]. The Al—O bond distances in both structures are equal 1.854 Å, and are about 0.09 Å longer than their counterparts in simple four coordinate analogues (an average value of 1.766 Å). For DAQFOQ, there are no notable intermolecular contacts observed, while for DAQFUW is observed a pair of short $C—H_{aliph}\cdots\pi$ contacts between one of the methylene hydrogen atoms and the phenyl ring of the adjacent molecule related by the center of symmetry (H···π: 2.56 Å; C—H···π: 174°).

Another structural motif has been observed for (3,5-di-*tert*-butyl-*N*-(2-(diphenylphosphino)phenyl)-salicylideneiminato)-dimethyl-aluminum (YONJEQ) [26] and (3,5-di-*tert*-butyl-*N*-(2-aminophenyl)salicylideneiminato)-dimethyl-gallium (QAMBIP) [29], where potentially tridentate ligands are coordinated to the metal centers in a bidentate fashion. For YONJEQ, the pendant phosphine group is not coordinated to the aluminum center and acts as an acceptor in intramolecular hydrogen bonding with the $C–H_{imino}$ group. The H···P distance is equal 2.72 Å (C–H···P: 100°) and is much less than the sum of the van der Waals radii (3.00 Å [30]). The distinctive behavior of the phosphine functionality results probably from steric factors brought about by aryl substituents and from relatively weak and soft basic properties. Similarly for QAMBIP, the noncoordinated pendant aminophenyl group is oriented away from the gallium atom and acts as a donor in the intramolecular hydrogen bond with the imino nitrogen atom (H···N: 2.45 Å; N–H···N: 104°) (see Fig. 13). Thus, the comparison of QAMBIP and $Me_2Ga(NsaldPh)$ structures demonstrates that the intramolecular $N–H\cdots N_{imino}$ hydrogen bond can effectively compete with the intramolecular secondary metal–ligand coordination. Consequently, YONJEQ and QAMBIP are closely related to the discussed type **Ia** complexes with a bulky substituent in the vicinity of the aryloxide oxygen atom.

Complexes comprising salicylideneiminate ligands with the non-coordinated pendant group are able also to generate supramolecular organizations with quest organic molecules. For example, the crystallization of (*N*-(2-hydroxyphenyl)-salicylideneiminato)-diphenylboron in the presence of the methanol (strong hydrogen bond donor and acceptor) gives a 1:1 H-bonded solvate, BONBAH [31]. The crystal structure of BONBAH features molecular chains along a crystallographic *b*-axis with molecules of organoboron compound interconnected through bridging methanol hydroxyl groups [O(3)–H(21)] (Fig. 14). Strong O–H···O hydrogen bonds are formed by both the aryloxy-oxygen atom O1 [H(21′)···O(1): 2.00 Å; O(3′)–H(21′)···O(1): 163°] and the pendant hydroxy group attached to the *N*-phenyl ring [H(10)···O(3): 1.97 Å; O(2)–H(10)···O(3): 172°]. The $C–H_{imino}$ group is engaged in the formation of intramolec-

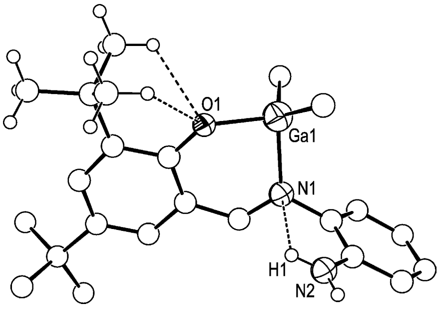


Fig. 13. A view of the molecular structure of (3,5-di-*tert*-butyl-*N*-(2-aminophenyl)-salicylideneiminato)-dimethyl-gallium (QAMBIP) with intramolecular N—H···N and C—H···O contacts.

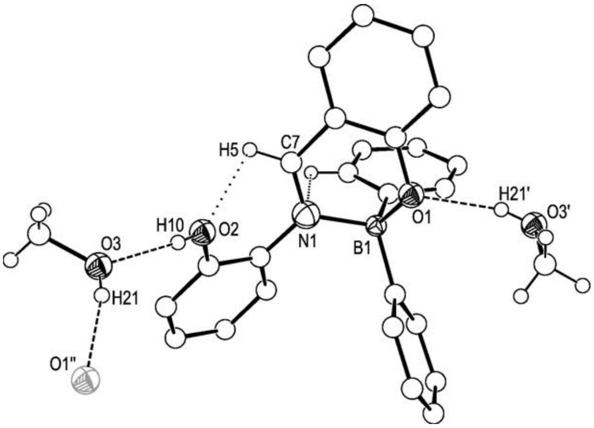


Fig. 14. Structure of the 1D hydrogen bonding array formed in the solid state by *N*-(2-hydroxyphenyl)-salicylideneiminato-diphenylboron methanol solvate (BONBAH).

ular hydrogen bond with the pendant hydroxy oxygen atom [H(5)···O(2): 2.35 Å; C(7)–H(5)···O(2): 102°]. In addition, the intramolecular C–H$_{\text{phen}}$···N interactions are also observed in this structure, like in other diphenylboron derivatives (vide supra).

3. Supramolecular structure of Schiff base derivatives with the CM(*O*,*N*)$_2$ central core: five-coordinate complexes of type II

3.1. Type **IIa** complexes

The CSD search revealed that the five-coordinate compounds of type **IIa**, i.e., the monomeric salicylideneimine derivatives with the CM(*O*,*N*)$_2$ core, are lacking, and the aluminum complex MeAl(saldPh)$_2$, OKUKAG, described recently by our group is the first example [13]. The geometry at aluminum atom in OKUKAG is best described as trigonal bipyramidal with the aryloxy-oxygen atoms and carbon atom occupying the equatorial positions. For this *N*-phenyl-salicylideneiminate derivative the weaker interactions of π-stacking type mediate the assembly of molecules via stronger C–H$_{\text{aryl}}$···O hydrogen bonds (Fig. 15). These interactions organize molecules into the H-bonded dimers in the solid state. As may be seen from Fig. 15, the phenyl group bonded to the N(1) nitrogen atom is oriented in such a way that the C–H$_{\text{aryl}}$···O hydrogen bonds are formed with both aryloxy-oxygen atoms of the neighboring molecule, related by the center of symmetry.

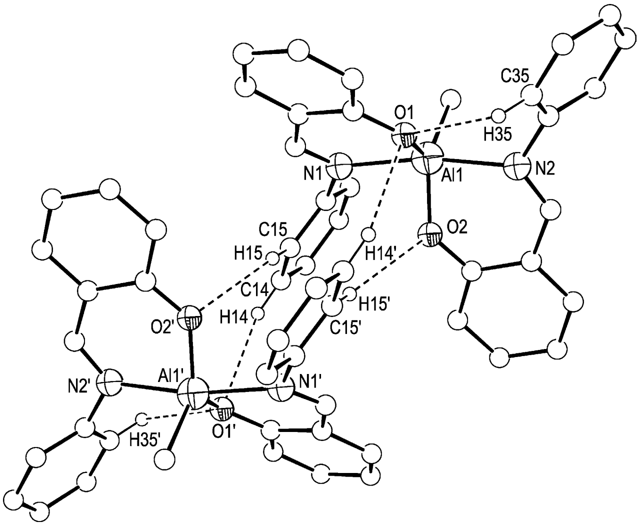


Fig. 15. Hydrogen bonded, centrosymmetric dimer of MeAl(saldPh)$_2$ (OKUKAG) in the solid state. The dashed lines represent intra- and intermolecular C–H···O hydrogen bonds. Hydrogen atoms are omitted excluding those involved in the H-bond formation.

3.2. Type **IIb** complexes

The CSD search revealed that so far the group 13 five-coordinate compounds of type **IIb**, i.e., the monomeric complexes with the CM(O_2N_2) core, are all derived from *O*,*O*,*N*,*N*-tetradentate Salen-type ligands (Scheme 3). These ligands feature two nitrogen and two oxygen donor sites situated in a nearly planar array. Depending on the nature of the ligand "backbone" (the connection between both nitrogen atoms) the resulting complexes contain a trigonal bipyramidal or square pyramidal metal coordination sphere, distorted to a different degree [32]. The analysis of the available structure data has proved that the association of molecular complexes is mainly attained through C–H···O interactions between aryloxy-oxygen atoms and hydrogen atoms of the aromatic or aliphatic ligand backbone. The incorporation of bulky *tert*-Bu groups around the phenol subunit causes appreciable shielding of oxygen atoms. However, in several cases these oxygen atoms do not fully confine the capabilities of H-bond formation from the side of the basal plane of the square pyramidal coordination sphere. For instance, Salen(*tert*-Bu) and Salomphen(*tert*-Bu) gallium derivatives (NIXTOD, NIXVAR and NIXVIZ) [33] show a propensity to the formation of hydrogen-bonded dimers by the C–H$_{\text{aliph}}$···O interactions, and the relevant C–H···O distances range from 2.50 to 2.85 Å. Such weakly bonded dimer of Salen(*tert*-Bu)GaEt (NIXTOD) formed through a pair of C–H$_{\text{aliph}}$···O interactions is displayed on Fig. 16. As a matter of fact, the original authors suggested that the dimerisation of compounds occurs due to Ga···H interactions (Ga···H distance of ~3.15 Å) [33]. However, the observed M···H contacts exceed the sum of the van der Waals radii (3.07 Å) [30] and this type interactions are not observed in analogous aluminum complexes with the more acidic metal center (RURPAV, RURPEZ) [34]. Therefore, it seems likely that the C–H$_{\text{aliph}}$···O hydrogen bonds have a predominant impact on the molecular arrangement. The revealed mode of crystal packing for NIXTOD is not unique to gallium derivatives. A similar situation was found in the crystal structure of Salen(*tert*-Bu)InMe, where a methylene hydrogen makes short contact with the oxygen atom (C···O distance

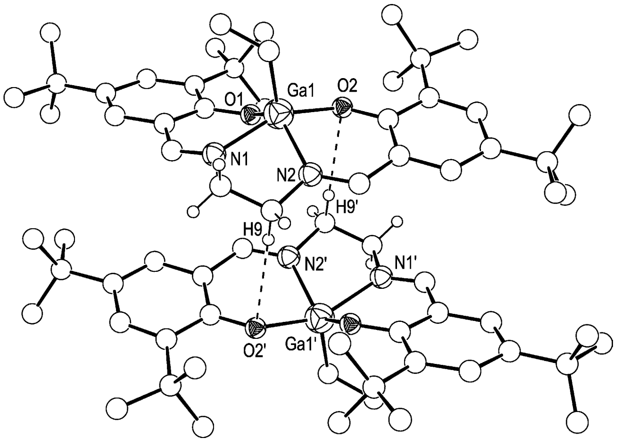


Fig. 16. Structure of the hydrogen bonded dimers of Salen(*tert*-Bu)GaEt (NIXTOD) showing the intermolecular C–H_{aliph}···O bonds (dotted lines).

~3.4 Å) of the adjacent Salen ligand to form a dimer.[32,35] In the complexes of type **IIb** without steric hindrances in the vicinity of the oxygen atom, the association of molecular units proceeds also through interactions of the oxygen with hydrogen atoms of the ligand backbone. It usually leads to 0D dimeric or 1D chainlike structures. For example, in the structure of (*N*,*N*′-bis(salicylidene)cyclohexane-1,2-diamine)-methylaluminum (KIQBIV) [36], the axial hydrogen atoms of the cyclohexane ring interact with the oxygen atoms forming a dimer and the appropriate C–H···O distances are equal 2.48 and 2.51 Å. The structure is additionally stabilized by π-stacking interactions between salicylideneiminate ligands of both molecules (the π–π contacts of ~3.4 Å). Furthermore, in crystalline (Salen)AlEt, DUCLIW [37] the hydrogen bonds between the methylene hydrogen and oxygen atom (H···O: 2.67 Å and C–H···O angle 148°) act jointly with the C–H···π interactions (the H···$\pi_{centroid}$ distance of 2.63 Å) forming chains of molecules related by the crystallographic two-fold screw axis. An interesting arrangement is observed in (Salophen)InMe (QUBJAY) [38]. The crystal structure features molecular chains linked via hydrogen-bonded seven-membered InO_2···H_2C_2 rings in which both oxygen atoms are engaged in the H-bond formation. The C···O contacts are relatively short and equal 3.43 and 3.41 Å (Fig. 17).

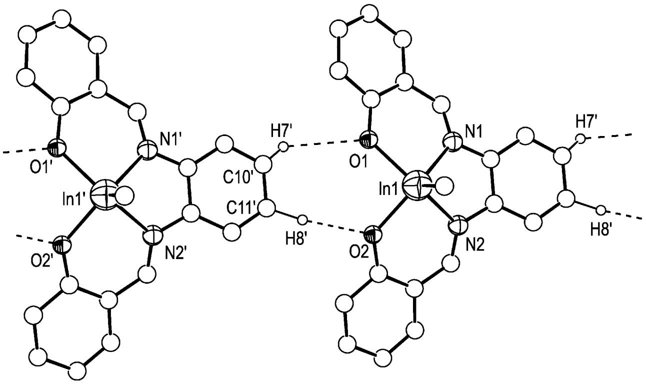
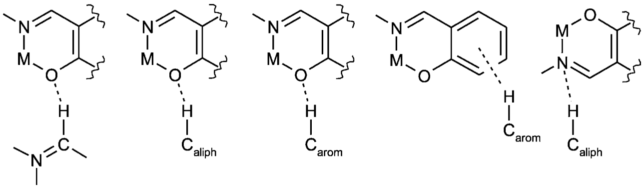


Fig. 17. A view of the structure of (Salophen)InMe (QUBJAY) illustrating the hydrogen-bonded chain running along *a*-axis.



Scheme 4. The observed intra- and intermolecular hydrogen bonding interactions in the group 13 metal Schiff base derivatives.

4. Conclusion

This contribution deals with the molecular and crystal structure of the group 13 complexes supported by bidentate and multidentate Schiff base ligands. The results presented show that the group 13 metal Schiff base complexes provide a means to study intramolecular and intermolecular non-covalent interactions. The observed most common non-covalent forces for the group 13 Schiff base complexes are depicted on Scheme 4 and involved the C–H_{imino}···O, C–H_{aryl}···O, C–H_{aliph}···O and C–H···π hydrogen bonds and π-stacking.

The molecular assembly of tetrahedral R_2M(*O*,*N*) (M = B, Al or Ga) complexes derived from bidentate Schiff bases is mediated by the intermolecular hydrogen bond systems established by the imine- and phenyl-hydrogen atoms. Depending on the *N*-alkyl substituent, the formation of H-bonded 3D framework structure that is assembled from 1D helical chains, H-bonded 2D double layer network that is build from 1D chains, or 0D H-bonded dimers is observed. The analysis of the structural parameters of R_2M(saldR’) complexes indicates that the steric congestion at the hydrogen bond donor and acceptor sites, as a result of changes in the *N*-alkyl substituents or the coordination centre environment, affect the strength of the intermolecular C–H···O hydrogen bond and may leads to the self-assembly switching of the bidentate Schiff base metal complexes. For the related $SalenH_2$ or $SaltrenH_2$ derivatives, where two or three tetrahedral R_2M(*O*,*N*) moieties are joined by an aliphatic backbone, the inherent encumbers lead to significant changes in the molecular assembly, and except the dominant C–H_{imino}···O interaction, the C–H_{aryl}···O, C–H_{aliph}···O, C–H···π hydrogen bonds and π-stacking play a substantial role in the self-assembly. The five-coordinate monomeric salicylideneimine derivatives with the CM$(O,N)_2$ core adopt a hydrogen-bonded dimeric structure where the weaker π-stacking interactions interplay with stronger C–H_{aryl}···O hydrogen bonds in the self-assembly process. For five-coordinate monoalkylaluminum, -gallium and -indium Schiff base derivatives of *O*,*O*,*N*,*N*-tetradentate Salen-type ligands, the molecular assembly is mainly attained through C–H···O interactions between the aryloxy-oxygen atoms and hydrogen atoms of the aromatic or aliphatic ligand backbone and these interactions usually lead to dimeric or 1D chainlike structures. Interestingly, in many cases steric hindrances close to the aryloxide oxygen atom do not fully confine the capabilities of H-bond formation from the side of the basal plane.

Finally, our observation represents an important impact that should be considered in the intentional design of inorganic-organic materials (with Schiff base ligands as the organic tecton) with specific function and properties. It seems likely that the non-covalent interactions which have been identified play a substantial role in the molecular assembly of Schiff base metal complexes and are also significant forces in the molecular recognition processes involving catalysts supported by Schiff base ligands.

Acknowledgments

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Appendix A. Supporting information

Supporting information associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2004.11.013.

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