Aggregation of Metalated Organics by Hydrogen Bonding: Synthesis and Crystal Structures of 2-Aminophenoxy–Aluminum and Salen–Aluminum Ligand-Separated Ion Pairs[†]

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Received March 14, 1995[⊗]

Ion separation of $Al(2-H_2NC_6H_4O)_2Cl$ and of $Al(salen)X$ [X^- = Cl^-, I^-, $CF_3SO_3^-$; H_2salen = N,N'-bis-(salicylidene)ethylenediamine] is promoted by the addition of the strong Lewis base HMPA (hexamethylphosphoramide) which stabilizes the resulting cationic aluminum species. The X-ray structure of $[Al(2-H_2NC_6H_4O)_2(HMPA)_2]^+Cl^-$ (**2a**) shows it to be a dimer formed by two $[Al(2-H_2NC_6H_4O)_2(HMPA)_2]^+$ cations connected *via* two NH hydrogen bonded Cl^- ions. $[Al(salen)(HMPA)_2]^+Cl^-$ (**4a**) and $[Al(salen)(HMPA)_2]^+CF_3SO_3^-$ (**7a**) also form dimeric aggregates but by CH···X hydrogen bonds between the salen imine and ethylene protons and the anions, X^-. In contrast to the Cl^- and $CF_3SO_3^-$ derivatives, $[Al(salen)(HMPA)_2]^+I^-$ (**9**) forms a three-dimensional ionic lattice structure rather than distinct aggregates. If $[AlCl_4]^-$ is used as the counterion the weakly Lewis-basic THF is sufficient to stabilize the aluminum cation, as demonstrated by the structure of $[Al(salen)(THF)_2]^+[AlCl_4]^-$ (**10**). This compound also forms an ionic lattice-type structure. The crystal data are as follows. **2a**: $C_{12}H_{24}Al_{0.5}Cl_{0.5}N_4O_2P$, orthorhombic, *Pnnm*; a = 14.675(3), b = 15.059(3), c = 15.132(3) Å; Z = 8. **4a**: $C_{56}H_{100}Al_2Cl_2N_{16}O_8P_4\cdot2C_4H_8O$, triclinic, $P\bar{1}$; a = 10.821(2), b = 11.234(2), c = 32.974(7) Å; α = 84.99(3), β = 82.73(3), γ = 81.38(3)°; Z = 2. **7a**: $C_{29}H_{50}AlF_3N_8O_7P_2S\cdot2C_7H_8$, monoclinic, *C2/c*; a = 29.591-(6), b = 17.102(3), c = 18.018(4) Å, β = 97.98(3)°; Z = 8. **9**: $C_{56}H_{100}Al_2I_2N_{16}O_8P_4$, monoclinic, *Pn*; a = 10.552(2), b = 26.060(5), c = 14.030(3) Å, β = 104.39(3)°; Z = 2. **10**: $C_{24}H_{30}Al_2Cl_4N_2O_4$, monoclinic, *C2/c*; a = 28.474(6), b = 13.896(3), c = 15.532(3) Å; β = 111.80(3)°, Z = 8.

Introduction

In this paper, we report the synthesis and the solid-state structures of a cationic aminophenoxy–aluminum compound and four structurally similar H_2salen [N,N'-bis(salicylidene)-ethylenediamine] aluminum derivatives with varying counterions. Three of these structures exhibit dimer formation through weak NH···X or CH···X hydrogen bonding while the others form ionic lattice structures.

Although cationic aluminum species $(AlL_m)^{n+}$ are common in aqueous solution,[1] significant ion separation of AlR_3 compounds is not generally favored in nonpolar or weakly polar solvents such as hydrocarbons or ethers. For this reason, only a limited number of compounds containing $(AlRR'L_n)^+$ cations (R, R' = H, alkyl, NR''_2, OR'', Cl; L = neutral Lewis base) have been characterized in the solid state.[2] Of those that have, the cationic aluminum-containing moiety is usually, though not exclusively, stabilized by crown-ether complexation. Although such multidentate ligands seem to promote the formation of cationic aluminum compounds, they are not necessary, as can be seen from solid-state structures of $[AlCl_2(THF)_4]^+[AlCl_4]^-$ [3a] and $[AlCl_2(i-PrOH)_4]^+Cl^-$.[4] The formation of such cationic aluminum species from AlR_2X precursors depends on the Al–X bond strength on the one hand and on the stabilities of the aluminum cation (mediated by Lewis base solvation) and of the anion (e.g. $[AlCl_4]^-$) on the other hand. Thus, ion separation

of *monomeric* aluminum compounds (see eq 1) can be achieved

$$\text{(1)}$$
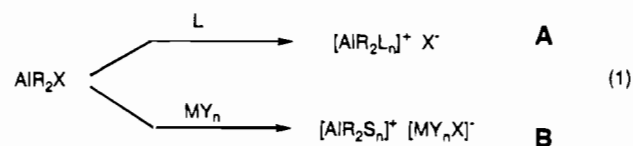
either by adding a strong Lewis base L to AlR_2X (route A) or by abstracting the anion X^- with a Lewis acid MY_n (route B) from AlR_2X.[2b] In the latter case, the coordination sphere of

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(2) (a) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: Weinheim, Germany, 1991; p 197 and references cited therein. (b) Lewinski, J.; Pasynkiewicz, S.; Lipkowski, J. *Inorg. Chim. Acta* **1990**, *178*, 113. (c) Atwood, J. L.; Robinson, K. D.; Jones, C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1697. (d) Self, M. F.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1991**, *10*, 36. (e) Knjazhansky, S. Y.; Nomerotsky, I. Y.; Bulychev, B. M.; Belsky, V. K.; Soloveichik, G. L. *Organometallics* **1994**, *13*, 2075. (f) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem.* **1993**, *105*, 1714. (g) Atwood, J. L.; Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom.* **1984**, *2*, 367. (h) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796. (i) Sangokoya, S. A.; Moise, F.; Pennington, W. T.; Self, M. F.; Robinson, G. H. *Organometallics* **1989**, *8*, 2584. (j) Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem.* **1987**, *99*, 476; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 485. (k) Engelhardt, L. M.; Kynast, U.; Raston, C. L.; White, A. H. *Angew. Chem.* **1987**, *99*, 702; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 681.

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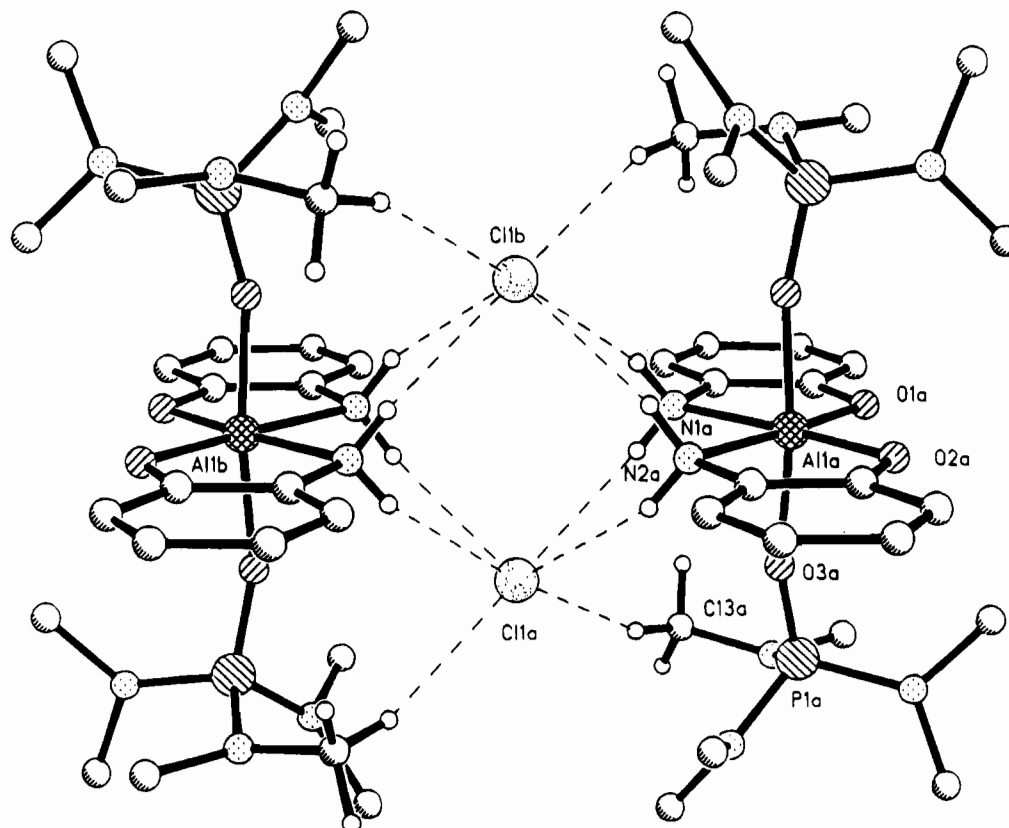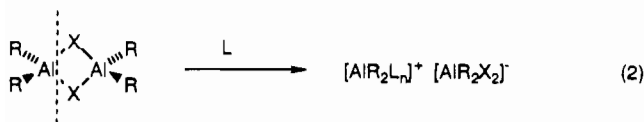(4) Yanovskii, A. I.; Bokii, N. G.; Struchkov, Y. T. *Koord. Khim.* **1976**, *2*, 1125.

Figure 1. Structure of **2a** in the solid state. Four asymmetric units are shown; the dimer has crystallographic C_{2h} symmetry. Only hydrogens involved in hydrogen bonding are drawn.

Table 1. Selected Hydrogen Bond Distances (Å) and Angles (deg) in **2a**

Y–H···X	Y–H	X···H	Y···X	∠Y–H···X	symmetry
N(1)–H(1)···Cl(1)	0.837(11)	2.576(10)	3.359(2)	156.13(32)	$x, y, -z + 1$
N(2)–H(2)···Cl(1)	0.867(7)	2.583(8)	3.369(2)	151.35(57)	$x, y, -z + 1$
C(13)–H(13c)···Cl(1)	0.98	2.846(7)	3.778(3)	161.17(1.69)	$x, y, -z + 1$

the aluminum cation is completed by weakly Lewis-basic solvent molecules S. Starting from a *dimeric* aluminum compound (eq 2), ion separation involves the asymmetric

$$R_{'''}\underset{R}{\overset{X}{\underset{\diagdown}{A}}}\underset{X}{\overset{R}{\underset{\diagup}{A}}}\overset{R}{\underset{R}{\diagdown}} \xrightarrow{\quad L \quad} [AlR_2L_n]^+ \; [AlR_2X_2]^- \qquad (2)$$

cleavage of the dimer by a Lewis base.[3] In this case the counteranion is invariably an aluminate ion.

The formation of supramolecular structures *via* strong hydrogen bonds (NH and OH bonds) is commonplace among organic and inorganic compounds and has been widely investigated,[5] especially with regard to the specific design of solid-state structures with distinct chemical and physical properties such as second harmonic generation.[6] However, the importance of CH hydrogen bonding among organic compounds has only recently gained more attention.[7] Thus, much less is known about the influences of weak CH hydrogen bonding on the solid-state structures of organometallic derivatives and metalated organics.[8]

Thus, our aim was twofold: first, to assess the factors which lead to ion pair formation in monomeric 2-aminophenoxy–aluminum and salen–aluminum compounds and, second, to investigate the influences of the counterion on the aggregation of the resulting aluminum cations *via* hydrogen bonding. 2-Aminophenol (R) and H_2salen (R_2) were used as ligands for aluminum since their high acidity and their chelating properties promised a high stability (thermodynamic as well as kinetic) of monomeric aluminum derivatives AlR_2X and hence are a good starting point for a comparative study.

Results and Discussion

$[Al(2\text{-}H_2NC_6H_4O)_2(HMPA)_2]^+Cl^-$ (2). The reaction of 2-aminophenol with $AlMe_2Cl$ in methylene chloride afforded,

(5) (a) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960. (b) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968. (c) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. (d) Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 397. (e) Bernstein, J.; Etter, M. C.; Leiserowitz, L. In *Structure Correlation*; Bürgi, H.-B., Dunitz, J. D., Eds.; VCH: Weinheim, Germany, 1994; Vol. 2, p 431. (f) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1993**, *115*, 4540. (g) Desiraju, G. R.; Kashino, S.; Coombs, M. M.; Glusker, J. P. *Acta Crystallogr., Sect. B* **1993**, *49*, 880. (h) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

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(8) (a) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem.* **1990**, *102*, 960; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888. (b) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 3210.
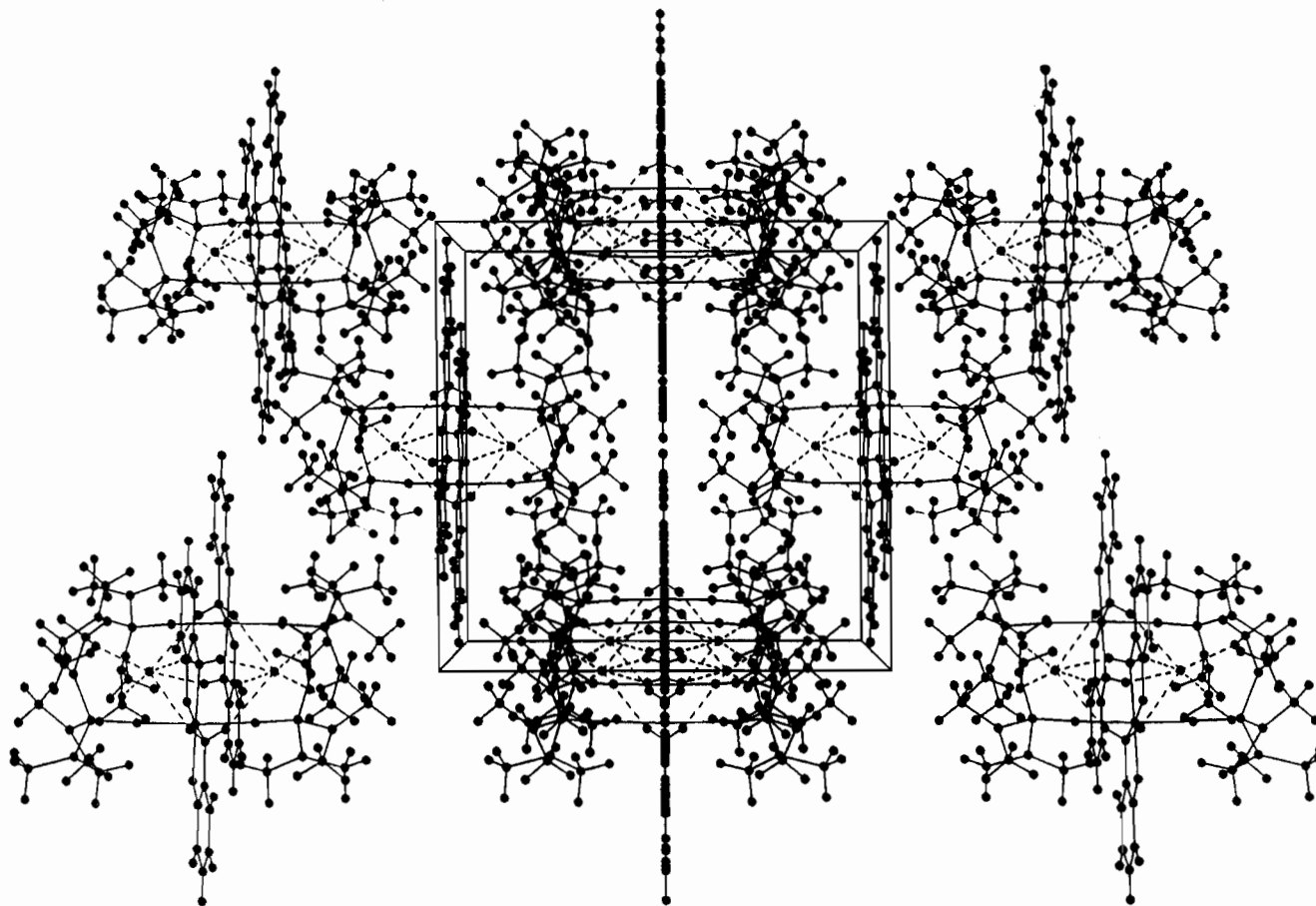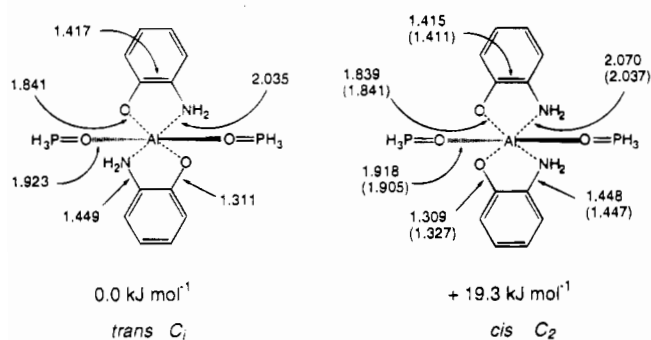
Figure 2. Packing plot of **2a**.

Figure 3. PM3-calculated structures of the cation of **2** (with H_3PO as model ligand) in *cis* and *trans* configurations. Distances are in angstroms (experimental distances in parentheses).

Table 2. Selected Hydrogen Bond Distances (Å) and Angles (deg) in **4a·2THF**

Y–H···X	Y–H	X···H	Y···X	∠Y–H···X	symmetry
Intraaggregative Hydrogen Bonds					
C(9)–H(9a)···Cl(1)	0.99	2.717(6)	3.639(6)	155.0(1)	$x − 1, y, z$
C(10)–H(10)···Cl(1)	0.95	2.788(5)	3.570(5)	140.1(1)	$x − 1, y, z$
C(35)–H(35)···Cl(1)	0.95	2.617(6)	3.512(6)	157.1(1)	x, y, z
C(7)–H(7)···Cl(2)	0.95	2.559(6)	3.464(6)	159.3(1)	$x − 1, y, z$
C(37)–H(37a)···Cl(2)	0.99	2.689(6)	3.622(6)	157.3(1)	x, y, z
C(38)–H(38)···Cl(2)	0.95	2.800(5)	3.655(5)	150.3(1)	x, y, z
THF···Cl⁻					
C(58)–H(58a)···Cl(1)	0.99	2.843(8)	3.813(8)	166.7(2)	$x − 1, y, z$
Interaggregative Hydrogen Bonds					
C(21)–H(21c)···Cl(1)	0.98	2.724(7)	3.690(7)	168.5(2)	x, y, z
C(56)–H(56a)···Cl(2)	0.98	2.779(6)	3.708(6)	158.3(1)	$x − 1, y, z$

after methane generation, a white precipitate (**1**). Filtration and suspension of the solid in toluene, followed by addition of excess of the strong Lewis base HMPA (hexamethylphosphoramide), gave a clear solution from which colorless crystals of [Al(2-

$H_2NC_6H_4O)_2(HMPA)_2]^+Cl^-$ (**2**) were obtained (eq 3). Although
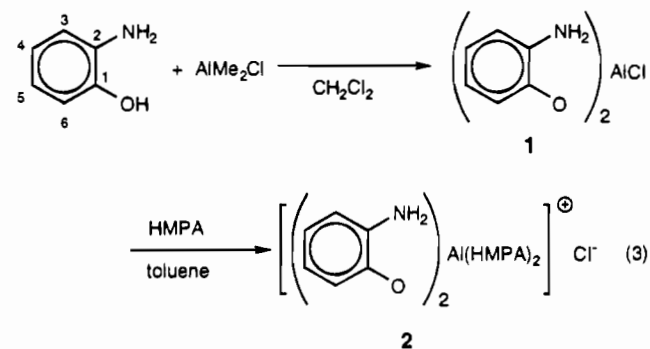
it was not possible to characterize **1** fully due to its insolubility in any common organic solvent, its stoichiometry seems reasonable in view of the reaction and the formation of **2**.

Figure 1 shows the solid-state structure of **2**. The aluminum cations are pseudooctahedrally coordinated by two bidentate 2-aminophenoxy anions in the equatorial plane and by two HMPA molecules in axial positions. The mean (2-aminophenoxy)O–Al distance is 1.841 Å, and the mean (2-aminophenoxy)NH₂–Al distance is 2.037 Å, roughly in agreement with other six-coordinate aluminum compounds with anionic oxygen and neutral amine donor ligands.[9] There is no precedent for HMPA–aluminum complexation in the solid state (d(O–Al) = 1.905 Å).

Two of the $[Al(2-H_2NC_6H_4O)_2(HMPA)_2]^+$ cations are connected *via* hydrogen-bonded chloride counterions to form a discrete dimeric aggregate (**2a**). These dimers do not interact

(9) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: Weinheim, Germany, 1991; p 1.
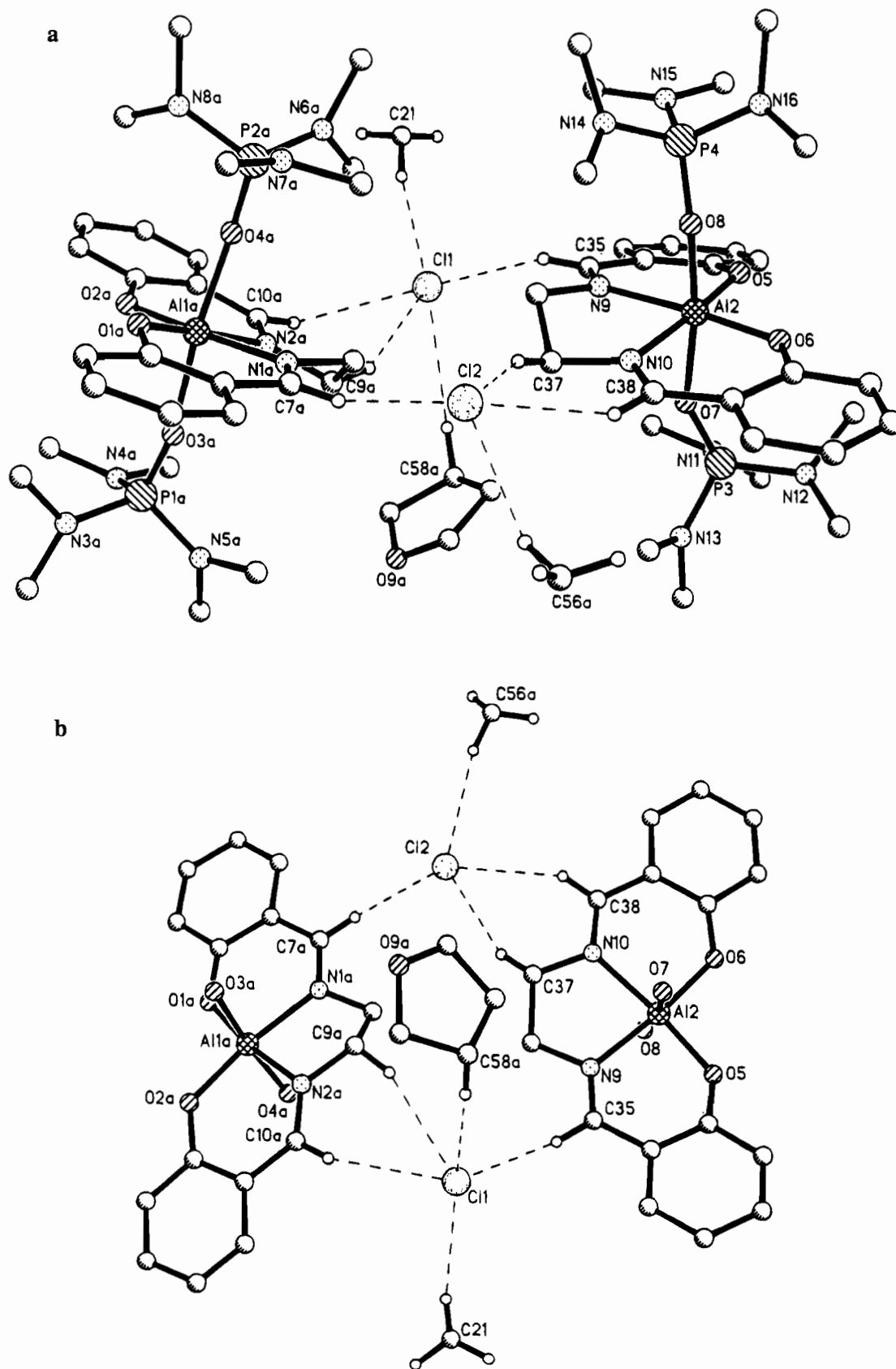
Figure 4. (a) Structure of **4a·2THF** in the solid state. The asymmetric unit (with only one of two THF molecules) is shown; only hydrogens involved in hydrogen bonding are drawn; C(21)H₃ and C(30)H₃ are methyl groups of HMPA molecules of adjacent dimers. (b) View perpendicular to the plane of the salen ligands. HMPA molecules are omitted for clarity.

with each other, as can be seen from a packing plot (Figure 2). Any direct electrostatic Al···Cl interactions in the dimer are mediated by the NH₂ groups which are squeezed between: R₂Al⁺···N^(δ−)—H^(δ+)···Cl⁻, thus forming a ligand-separated ion

pair.[10] Weak intramolecular CH···Cl hydrogen bonds from the HMPA molecules contribute to the solvation sphere of the chloride anions. The NH···Cl and CH···Cl hydrogen bond distances and angles (Table 1) lie in the range generally expected
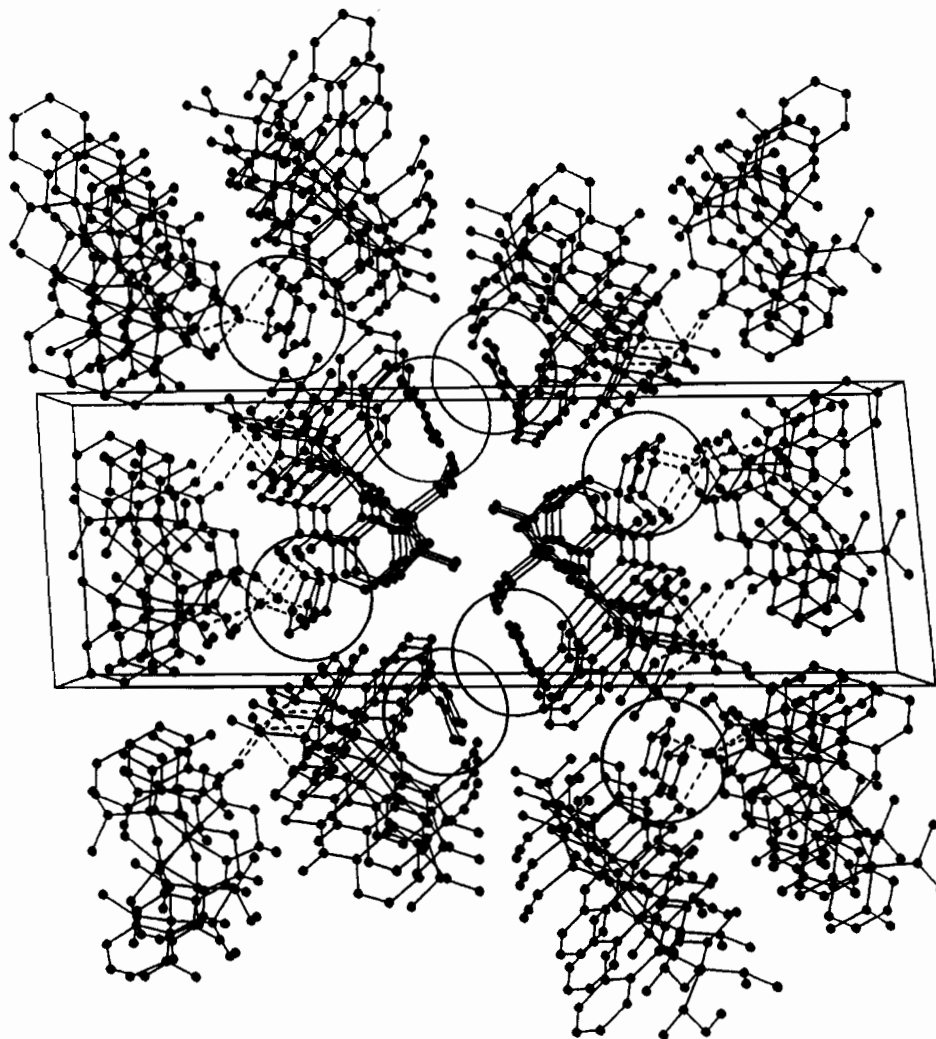
Figure 5. Packing plot of **4a**·2THF. THF molecules are in the circles; interaggregative hydrogen bonds are omitted for clarity.

for NH···Cl hydrogen bonding.[7a,11,12] While the (N)H···Cl distances (2.58 Å) are appreciably shorter than the sum of the van der Waals radii of H and Cl (2.95 Å), the (C)H···Cl distances (2.85 Å) are only slightly shorter, indicating considerably weaker bonds.[13]

The ion separation of the aluminum cation and the chloride anion in **2a** is facilitated by strong aluminum solvation *and* by chloride solvation. The chelating 2-aminophenoxy ligands and the strongly basic HMPA molecules complete the ligand sphere

of the highly Lewis-acidic $[Al(RO)_2]^+$ cation. The need for the strong Lewis base HMPA to effect ion separation is stressed by the fact that several other, weaker Lewis donors (acetone, DMSO, DMPU, tetramethylurea) fail to react with **1** in a similar manner and, in addition, that **1** is insoluble in THF. The chloride anions are solvated by NH···Cl and CH···Cl hydrogen bonding to the 2-aminophenoxy amino groups and to one methyl group of each HMPA molecule, respectively. These bonds give rise to the supramolecular dimeric arrangement *via* hydrogen bonding, a unique feature in the coordination chemistry of aluminum. Normally, aluminum alkoxides form Al—O—Al—O four-membered rings with bridging alkoxide anions.[14]

Electrostatically, one would expect the 2-aminophenoxy ligands in $[Al(2-H_2NC_6H_4O)_2(HMPA)_2]^+$ to be *trans* rather than *cis*, an expectation confirmed by semiempirical PM3 calculations on the model complex $[Al(2-H_2NC_6H_4O)_2·2O=PH_3]^+$ which

(10) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, VCH: Weinheim, Germany, 1988; p 233.

(11) We regard hydrogen bonds as being attractive if the (C)H···X distance is shorter than the sum of the van der Waals radii of hydrogen and the heteroatom, X (see refs 5b (Chapter 1.7), 5e, and 7). van der Waals radii used: H, 1.20; C, 1.70; N, 1.55; O, 1.52; F, 1.47; Cl, 1.75; I, 1.98 Å (Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441). When comparing the H···X distances from this paper with sums of van der Waals radii and with distances from neutron diffraction experiments, one has to take into account that N—H and C—H hydrogen bonds derived from X-ray diffraction measurements are shorter by about 0.1 Å than the ones derived from neutron diffraction (Taylor, R.; Kennard, O. *Acta Crystallogr., Sect. B* **1983**, *B39*, 133). Hence, the "true" H···C distances are about 0—0.1 Å shorter than those reported in this paper (see ref 8b). Since hydrogen bonds are regarded to be the stronger the more linear they are, we only give the data for H···X interactions which are shorter or slightly longer than the sum of the H and X van der Waals radii and which have a C—H···X angle greater than about 130°. This criterion is to some extent arbitrary since hydrogen bonds are mainly electrostatic and may be attractive even beyond the van der Waals cutoff distance (see refs 5e, 7).

(12) Hamilton, W. C.; La Placa, S. J. *Acta Crystallogr., Sect. B* **1968**, *24*, 1147.

(13) A search in the Cambridge Crystallographic Database revealed that, among the four structures of metal—2-aminophenolate compounds reported, two show hydrogen bonds of the NH₂ groups, however, to the oxygen atoms of adjacent molecules. Ga(2-H₂NC₆H₄O)(CH₃)₂: Gracey, G. D.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1987**, *65*, 2469. MoO₂(2-H₂NC₆H₄O)₂: Griffith, W. P.; Koh, T. Y.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3459.

(14) (a) Oliver, J. P.; Kumar, R.; Taghiof, M. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: Weinheim, Germany, 1991; p 167. (b) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982, Vol. 1, p 555. (c) Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409.

Table 3. Selected Hydrogen Bond Distances (Å) and Angles (deg) in **7a·2C₇H₈**

Y−H···X	Y−H	X···H	Y···X	∠Y−H···X	symmetry
		Intraaggregative Hydrogen Bonds			
C(8)−H(8b)···O(5)	0.99	2.55(2)	3.33(2)	136.3(5)	$1 - x, y, 0.5 - z$
C(9)−H(9b)···O(5)	0.99	2.43(2)	3.42(2)	175.3(5)	x, y, z
C(10)−H(10)···O(6)	0.95	2.46(2)	3.37(2)	161.1(4)	x, y, z
C(7)−H(7)···O(7)	0.95	2.59(1)	3.51(1)	164.3(3)	$1 - x, y, 0.5 - z$
		Toluene···CF₃SO₃⁻			
C(04)−H(04a)···O(5)	0.96	2.58(3)	3.49(3)	160.1(6)	x, y, z
		Interaggregative Hydrogen Bonds			
C(20)−H(20c)···O(6)	0.98	2.64(2)	3.53(2)	150.9(5)	$1 - x, 2 - y, -z$
C(21)−H(21a)···O(7)	0.98	2.54(2)	3.46(2)	156.5(3)	$1 - x, 2 - y, -z$
C(24)−H(24c)···F(1a)	0.98	2.72(3)	3.54(13)	141.9(8)	$1 - x, 1 - y, -z$
C(24)−H(24c)···F(1b)	0.98	2.56(11)	3.48(13)	157.1(53)	$1 - x, 1 - y, -z$

show the *trans* isomer to be ca. 19 kJ mol⁻¹ more stable than the *cis* isomer (see Figure 3).[15] In **2a**, this energy difference is overruled by the favorable NH···Cl⁻ hydrogen bonds which require and enforce the *cis* configuration. As can be seen from the calculated and the observed structural parameters, the PM3 calculations model the ligand sphere of the aluminum ion very well.

[Al(salen)(HMPA)₂]⁺Cl⁻ (4). To clarify the influence of the NH protons of 2-aminophenol on the structural features found in **2a**, H₂salen was chosen as a ligand which provides a similar coordination sphere for aluminum but which does not have NH protons. Reaction of H₂salen in toluene with AlMe₂-Cl afforded a white precipitate (eq 4) identified as Al(salen)Cl
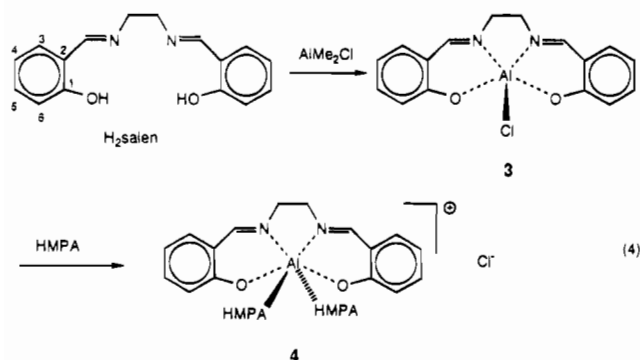
(3) by ¹H NMR spectroscopy in DMSO solution. HMPA added to a toluene suspension of **3** afforded a clear solution from which colorless crystals of [Al(salen)(HMPA)₂]⁺Cl⁻ (**4**) separated. Weaker Lewis donors (MeCN, THF, acetone) did not dissolve the precipitate, once again highlighting the necessity of the very strong donor HMPA to overcome the favorable "hard−hard" Al−Cl interaction and thus to promote ion separation.

Recrystallization of **4** from THF gave X-ray-quality crystals of a clathrate inclusion compound[16] of **4a** and 2 equiv of THF: {[Al(salen)(HMPA)₂]⁺Cl⁻}₂·2THF (**4a·2THF**). Figure 4 shows **4a·2THF** to be a dimeric aggregate of six-coordinate [Al(salen)-

(15) The PM3 calculations were carried out using the VAMP 4.30 program by T. Clark, Erlangen. *cis*-[Al(2-H₂NC₆H₄O)₂·2O=PH₃]⁺: C_2, ΔH_f = −825.5 kJ mol⁻¹. *trans*-[Al(2-H₂NC₆H₄O)₂·2O=PH₃]⁺: C_i, ΔH_f = −844.8 kJ mol⁻¹. The use of H₃P=O as a model for HMPA is supported by *ab initio* calculations which gave almost the same Mulliken charge on oxygen in H₃P=O as in (H₂N)₃P=O: Armstrong, D. R.; Davidson, M. G.; Martin, A.; Raithby, P. R.; Snaith, R.; Stalke, D. *Angew. Chem.* **1992**, *104*, 1662; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1634. Armstrong, D. R.; Bennet, S.; Davidson, M. G.; Snaith, R.; Stalke, D.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1992**, 262.
(16) (a) Vögtle, F. *Supramolecular Chemistry*; Wiley: New York, 1991; p 171. (b) Atwood, J. L.; Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom.* **1984**, *2*, 367.

Figure 6. Structure of **7a·2C₇H₈** in the solid state (view perpendicular to the plane of the salen ligands). Two asymmetric units with only one of two toluene molecules are shown; the dimer has crystallographic C_2 symmetry. Only hydrogens involved in hydrogen bonding are drawn. The HMPA molecules are omitted for clarity; C(20b)H₃, C(21b)H₃, and C(24c)H₃ are methyl groups of HMPA molecules of adjacent dimers. The toluene molecule in the center of the dimer and one fluorine atom of the CF₃SO₃⁻ anion are disordered in two positions.

(HMPA)₂]⁺ moieties connected by hydrogen-bridged Cl⁻, superficially similar to **2a**. Although NH groups are lacking in **4a·2THF**, solvation of the Cl⁻ ions is now provided by CH···Cl hydrogen bonds from the imine and ethylene hydrogens of the salen moiety (Table 2). However, these hydrogen bonds force the Cl⁻ ions to sit in the plane of the salen ligands rather than above and below as in **2a**. Also unlike the case of **2a**, each Cl⁻ ion in **4a·2THF** is hydrogen bonded to a CH₃ group of an HMPA ligand of a *neighboring* dimer. One of the two THF molecules which are also in the lattice is weakly bonded to a Cl⁻ ion sitting in a cavity formed by the dimer. The second THF molecule is sitting in a tunnel between the **4a** dimers (see also packing plot, Figure 5). All CH and CH₂ groups of the salen ligands involved in hydrogen bonding are adjacent to an N atom as this acidifies the CH bond.[7a] Although the aggregation of **4a·2THF** is essentially dimeric [short intraaggregative imine and ethylene CH···Cl bonds; $d((C)H···Cl) = 2.56–2.80$

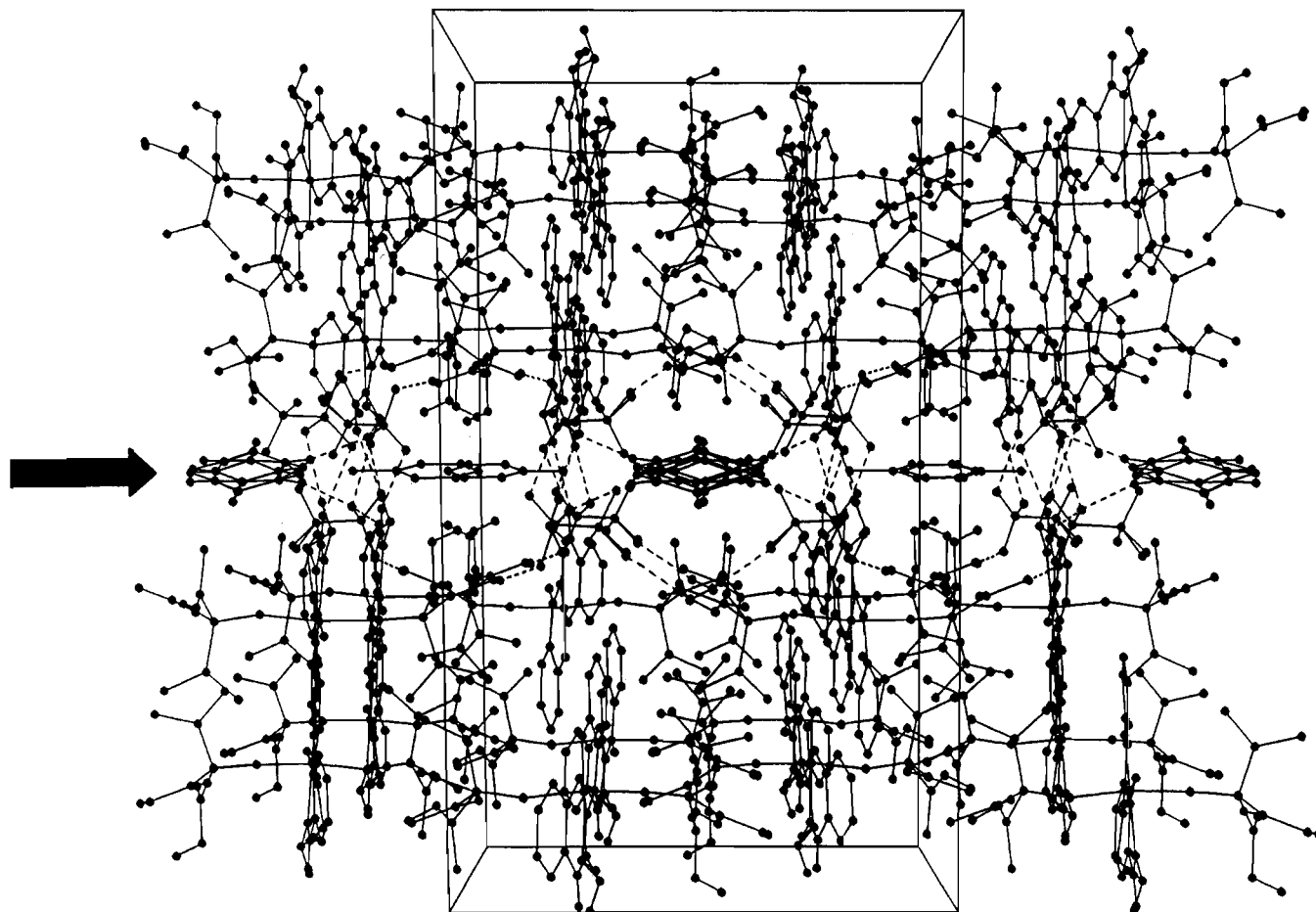**Figure 7.** Packing plot of **7a**·2C₇H₈. The arrow indicates the channel with the toluene molecules oriented along their C_{2v} axes. The toluene molecule in the center of the picture is disordered and sits in the cavity of two **7a** dimers.
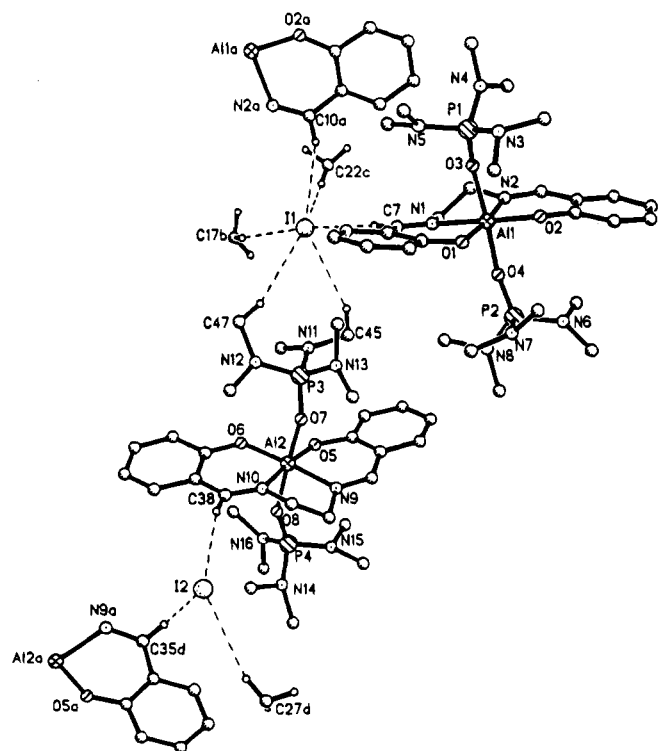
Figure 8. Structure of **9** in the solid state. The asymmetric unit together with fragments H-bonded to the two iodide anions is shown; only hydrogens involved in hydrogen bonding are drawn.

Å],[7a,11] a three-dimensional network is formed by the weak interaggregative hydrogen bonds [d((C)H···Cl) = 2.72 and 2.78

Å] of the chloride ions of one dimer to the HMPA molecules of other ones. The C—H···Cl angles scatter without any correlation with the (C)H···Cl distances between 140 and 169° (average angle = 157°), roughly in agreement with the values from ref 7a (average angle = 147°).[17,19]

[Al(salen)(HMPA)₂]⁺CF₃SO₃⁻ (7). In order to investigate the influence of the counterion on the aggregation of the [Al-(salen)]⁺ cations we chose CF₃SO₃⁻ as a "hard" but "non-spherical" anion. Since no dimethylaluminum triflate precursor

(17) Although our data set is too limited for a statistical evaluation, the lack of correlation of the C—H···Cl angles with the (C)H···Cl distances can be explained by the low angle forces in these bonds: assuming a purely electrostatic interaction, the bond energy can be modeled by a dipole (C—H bond) and a point charge (Cl⁻). The interaction energy then is proportional to cos θ(C—H···Cl). This means that, even at a C—H···Cl angle of 130°, the hydrogen bond energy is lowered by only ca. one-third of that of a linear arrangement. Considering the overall bond energy of ca. 4—8 kJ mol⁻¹ (see refs 7b and 18), the loss of energy due to angle deformation is very small and might easily be overruled by other factors. In fact, a search of a subset of the Cambridge Crystallographic Database (1000 randomly chosen crystal structures with CH···Cl distances between 2.2 and 3.2 Å) gave 3470 CH···Cl interactions but no indication for a correlation of the (C)H···Cl distances with the C—H···Cl angles. The same arguments hold true for CH···O hydrogen bonds. CH···O bonds tend to have a linear arrangement although the angles cover a wide range. The preference of a linear bond is independent of the H···O bond lengths (see ref 7b and: Desiraju, G. *J. Chem. Soc., Chem. Commun.* **1989**, 179; **1990**, 454). This behavior contrasts with the stronger N—H···O hydrogen bonds, which tend to be more linear the shorter the bond is (Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320. Taylor, R.; Kennard, O.; Versichel, W. *Acta Crystallogr., Sect. B* **1984**, *B40*, 280). For a thorough discussion of electrostatic potentials of hydrogen bonds, see: Taylor, R. *J. Mol. Struct.* **1981**, *71*, 311. Berkovitch-Yellin, Z.; Leiserowitz, L. *J. Am. Chem. Soc.* **1980**, *102*, 7677. Berkovitch-Yellin, Z.; Leiserowitz, L. *J. Am. Chem. Soc.* **1982**, *104*, 4052.
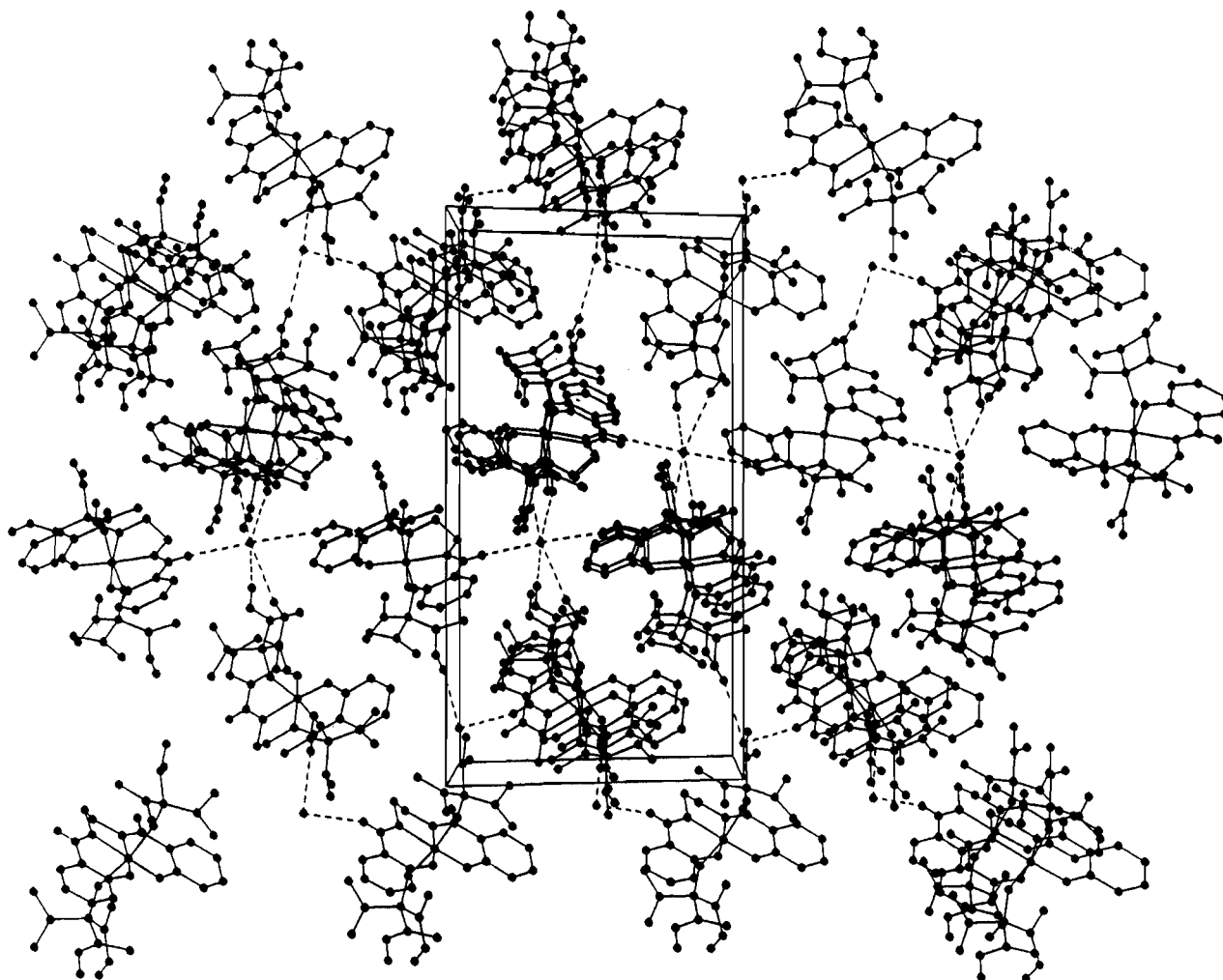
Figure 9. Packing plot of **9**. The compound forms a lattice structure of [Al(salen)(HMPA)$_2$]$^+$ cations and I$^-$ anions without any discrete aggregates. The anions are weakly H-bonded (dotted lines).

Table 4. Selected Hydrogen Bond Distances (Å) and Angles (deg) in **9**

Y−H···X	Y−H	X···H	Y···X	∠Y−H···X	symmetry
C(7)−H(7)···I(1)	0.95	2.961(8)	3.908(8)	175.4(2)	x, y, z
C(10)−H(10)···I(1)	0.95	3.060(9)	3.847(9)	141.1(1)	$x - 0.5, 3 - y, z - 0.5$
C(17)−H(17a)···I(1)	0.98	3.154(11)	4.048(11)	152.5(3)	$x, y, z - 1$
C(22)−H(22c)···I(1)	0.98	3.243(16)	4.187(11)	162(3)	$x + 0.5, 3 - y, z - 0.5$
C(45)−H(45b)···I(1)	0.98	3.225(35)	3.939(10)	131.1(3)	x, y, z
C(47)−H(47b)···I(1)	0.98	3.140(10)	4.087(10)	162.9(1)	x, y, z
C(27)−H(27c)···I(2)	0.98	3.212(11)	4.158(10)	163(1)	$x - 0.5, 2 - y, z - 0.5$
C(35)−H(35)···I(2)	0.95	3.132(8)	3.930(8)	142.7(1)	$x - 0.5, 2 - y, z - 0.5$
C(38)−H(38)···I(2)	0.95	2.985(9)	3.886(9)	158.8(1)	x, y, z

Table 5. Selected Hydrogen Bond Distances (Å) and Angles (deg) in **10**

Y−H···X	Y−H	X···H	Y···X	∠Y−H···X	symmetry
C(20)−H(20a)···Cl(1)	0.97	2.94(2)	3.89(2)	168.1(3)	$x, 1 - y, z - 0.5$
C(20)−H(20a)···Cl(1a)	0.97	3.03(3)	3.94(3)	156.7(5)	$x, 1 - y, z - 0.5$
C(21)−H(21b)···Cl(1a)	0.97	2.66(2)	3.34(2)	127.6(3)	x, y, z
C(22)−H(22a)···Cl(1a)	0.97	2.50(2)	3.21(2)	130.0(4)	x, y, z
C(9)−H(9b)···Cl(3)	0.97	2.821(7)	3.740(7)	158.6(2)	x, y, z

is available, a different synthetic route was used (eq 5): reaction

$$\text{H}_2\text{salen} + \text{AlMe}_3 \xrightarrow[\text{THF}]{-\text{CH}_4} \underset{\mathbf{5}}{\text{Al(salen)CH}_3}$$

$$\xrightarrow[\text{THF}]{+\text{NH}_4\text{CF}_3\text{SO}_3, -\text{CH}_4, -\text{NH}_3} \underset{\mathbf{6}}{\text{Al(salen)CF}_3\text{SO}_3} \xrightarrow[\text{THF/toluene/CH}_2\text{Cl}_2]{\text{HMPA}}$$

$$[\text{Al(salen)(HMPA)}_2]^+\text{CF}_3\text{SO}_3^- \cdot \text{C}_7\text{H}_8 \quad (5)$$
$$\mathbf{7 \cdot \text{C}_7\text{H}_8}$$
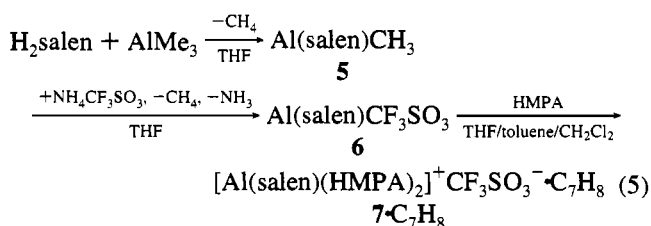
of H$_2$salen with AlMe$_3$ in THF gave Al(salen)CH$_3$ (**5**),[20] which

in turn reacted with NH$_4$CF$_3$SO$_3$ to give insoluble Al(salen)CF$_3$-SO$_3$ (**6**), methane, and ammonia. Subsequent addition of HMPA, toluene, and CH$_2$Cl$_2$ resulted in a clear solution from which colorless crystals of [Al(salen)(HMPA)$_2$]$^+$CF$_3$SO$_3^- \cdot$C$_7$H$_8$ (**7·C$_7$H$_8$**) grew.

The X-ray structure of **7·C$_7$H$_8$** (Figure 6) shows again a dimeric aggregate (**7a·2C$_7$H$_8$**) built up from [Al(salen)-(HMPA)$_2$]$^+$ cations which are hydrogen bonded to triflate anions. All triflate oxygens are involved in hydrogen bonding to the imine and ethylene protons of the salen ligand. There
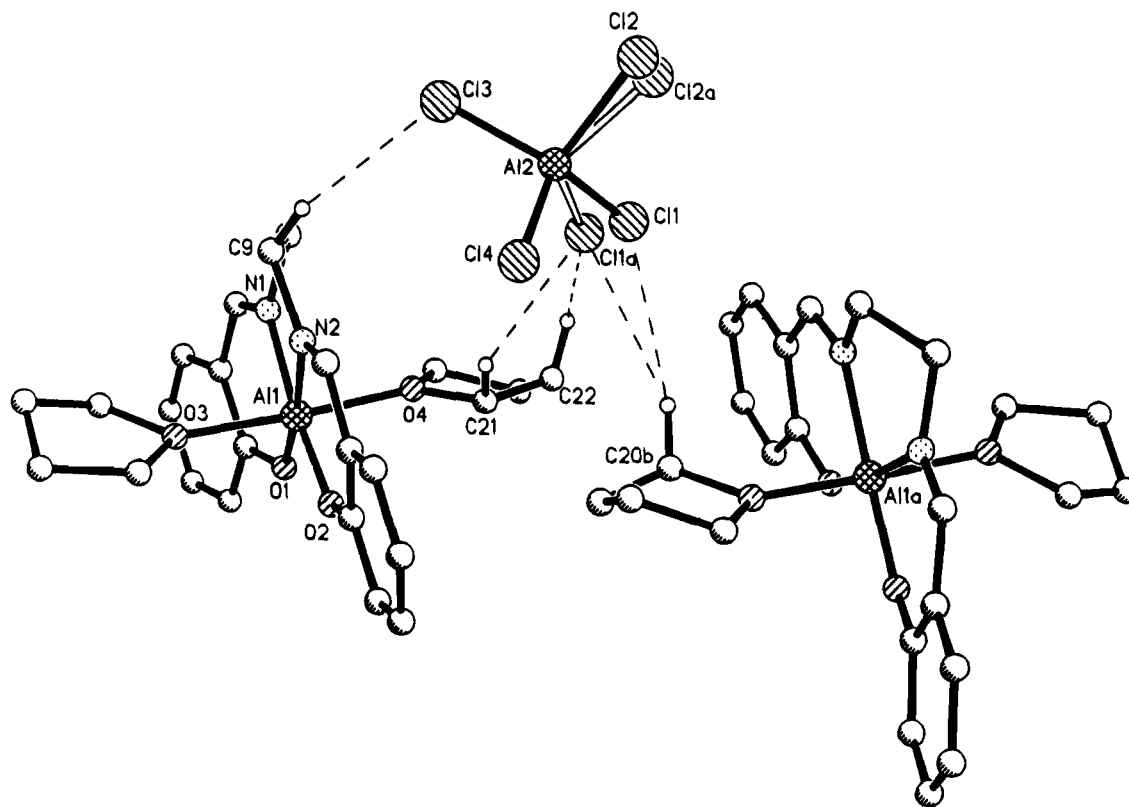
Figure 10. Structure of **10** in the solid state. The asymmetric unit together with one symmetry-equivalent $[Al(salen)(THF)_2]^+$ is shown; only hydrogens involved in hydrogen bonding are drawn. Two chlorine atoms of the $[AlCl_4]^-$ anion are disordered in two positions.

Table 6. Selected Bond Distances (Å) in the Aluminum Cation Moieties of **2a**, **4a·2THF**, **7a·2C$_7$H$_8$**, **9**, and **10**

$[Al(2-H_2NC_6H_4O)_2(HMPA)_2]^+$ of **2a**			
Al(1)—O(2)	1.834(2)	Al(1)—O(1)	1.847(2)
Al(1)—O(3)	1.905(2)	O(3)—P(1)	1.488(2)
Al(1)—N(1)	2.035(2)	Al(1)—N(2)	2.039(2)
O(1)—C(1)	1.325(3)	N(1)—C(2)	1.449(3)
N(2)—C(7)	1.445(3)	O(2)—C(8)	1.329(3)
$[Al(salen)_2(HMPA)_2]^+$ of **4a·2THF**			
Al(1)—O(2)	1.825(4)	Al(1)—O(1)	1.831(3)
Al(1)—O(3)	1.915(4)	Al(1)—O(4)	1.933(4)
Al(1)—N(1)	2.004(4)	Al(1)—N(2)	2.011(4)
P(1)—O(1)	1.506(4)	P(2)—O(4)	1.502(4)
Al(2)—O(5)	1.817(3)	Al(2)—O(6)	1.818(4)
Al(2)—O(8)	1.901(4)	Al(2)—O(7)	1.959(4)
Al(2)—N(9)	1.998(4)	Al(2)—N(10)	2.008(4)
P(3)—O(7)	1.502(4)	P(4)—O(8)	1.507(4)
$[Al(salen)_2(HMPA)_2]^+$ of **7a·2C$_7$H$_8$**			
Al(1)—O(1)	1.809(8)	Al(1)—O(2)	1.820(8)
Al(1)—O(4)	1.902(9)	Al(1)—O(3)	1.907(8)
Al(1)—N(1)	1.995(10)	Al(1)—N(2)	2.012(10)
P(1)—O(3)	1.490(8)	P(2)—O(4)	1.487(9)
$[Al(salen)_2(HMPA)_2]^+$ of **9**			
Al(1)—O(1)	1.814(6)	Al(1)—O(2)	1.816(5)
Al(1)—O(3)	1.920(6)	Al(1)—O(4)	1.928(6)
Al(1)—N(2)	2.021(7)	Al(1)—N(1)	2.024(7)
P(1)—O(3)	1.498(6)	P(2)—O(4)	1.509(6)
Al(2)—O(5)	1.819(6)	Al(2)—O(6)	1.824(6)
Al(2)—O(7)	1.912(6)	Al(2)—O(8)	1.917(6)
Al(2)—N(10)	2.008(7)	Al(2)—N(9)	2.018(7)
P(3)—O(7)	1.500(6)	P(4)—O(8)	1.492(6)
$[Al(salen)_2(THF)_2]^+$ of **10**			
Al(1)—O(2)	1.792(5)	Al(1)—O(1)	1.797(5)
Al—O(4)	2.001(4)	Al(1)—O(3)	2.000(4)
Al(1)—N(1)	1.991(6)	Al(1)—N(2)	2.002(6)

are weak interaggregative hydrogen bonds involving HMPA methyl groups of neighboring dimers and the oxygen and fluorine atoms of the triflate anion of a given dimer (see Table 3). The C—H···F bonds in **7a·2C$_7$H$_8$** (2.72 and 2.56 Å) lie within the range reported for interactions of neutral RCF$_3$ groups

(ca. 2.4—2.9 Å;[6b,21] sum of the van der Waals radii of H and F = 2.67 Å[11]). In this way, the dimeric arrangement of **7a·2C$_7$H$_8$** is quite similar to the one of **4a·2THF**. The four different (C)H···O hydrogen bond distances from the salen moiety (see Table 3) are within 2.43—2.59 Å (sum of the van der Waals radii of H and O = 2.72 Å[11]). Although the observed hydrogen bond separations are only moderately strong compared to CH···O bonding in other compounds,[7a,b,11] the dimeric aggregation in **7a·2C$_7$H$_8$** proves these interactions to be attractive. Again, the C—H···O angles show no correlation with the (C)H···O bond distances (136—175° range, average angle = 158°).[17]

Like **4a·2THF**, **7a** also forms a clathrate inclusion compound[16] with 2 equiv of solvent molecules, in this case toluene. As can be seen from the packing diagram (Figure 7), the two crystallographically different toluene molecules are arranged along their C_{2v} axes in tunnels between layers of the **7a** dimers. One of the toluene molecules is very weakly bonded by a hydrogen bond to the oxygen atom of one $CF_3SO_3^-$ anion and sits in the cavity of the dimer **7a** (Figure 6), similar to the position of one of the THF molecules in **4a·2THF**.

[Al(salen)(HMPA)$_2$]$^+$I$^-$ (9). Iodide is a "soft" counterion and, consequently, should disfavor hydrogen bonding. A reaction analogous to eq 4 with AlEt$_2$I instead of AlMe$_2$Cl gave first Al(salen)I (**8**) and then, after treatment with HMPA, $[Al(salen)(HMPA)_2]^+I^-$ (**9**). Indeed, the X-ray structure of **9**

(18) Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1993**, *97*, 7899.

(19) A search in the Cambridge Crystallographic Database revealed only one example of a metalated salicylaldehyde Schiff base complex which shows an N—CH hydrogen bond to Cl$^-$: bis((2-aminoethyl)salicyl-aldiminato)iron(III) chloride monohydrate, d(N—CH$_2$···Cl) = 2.93 Å (normalized), α(C—H···Cl) = 131.6° (Summerton, A. P.; Diamantis, A. A.; Snow, M. R. *Inorg. Chim. Acta* **1978**, *27*, 123).

(20) Gurian, P. L.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1991**, 1449.

(21) Shimoni, L.; Carrell, H. L.; Glusker, J. P.; Coombs, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 8162.
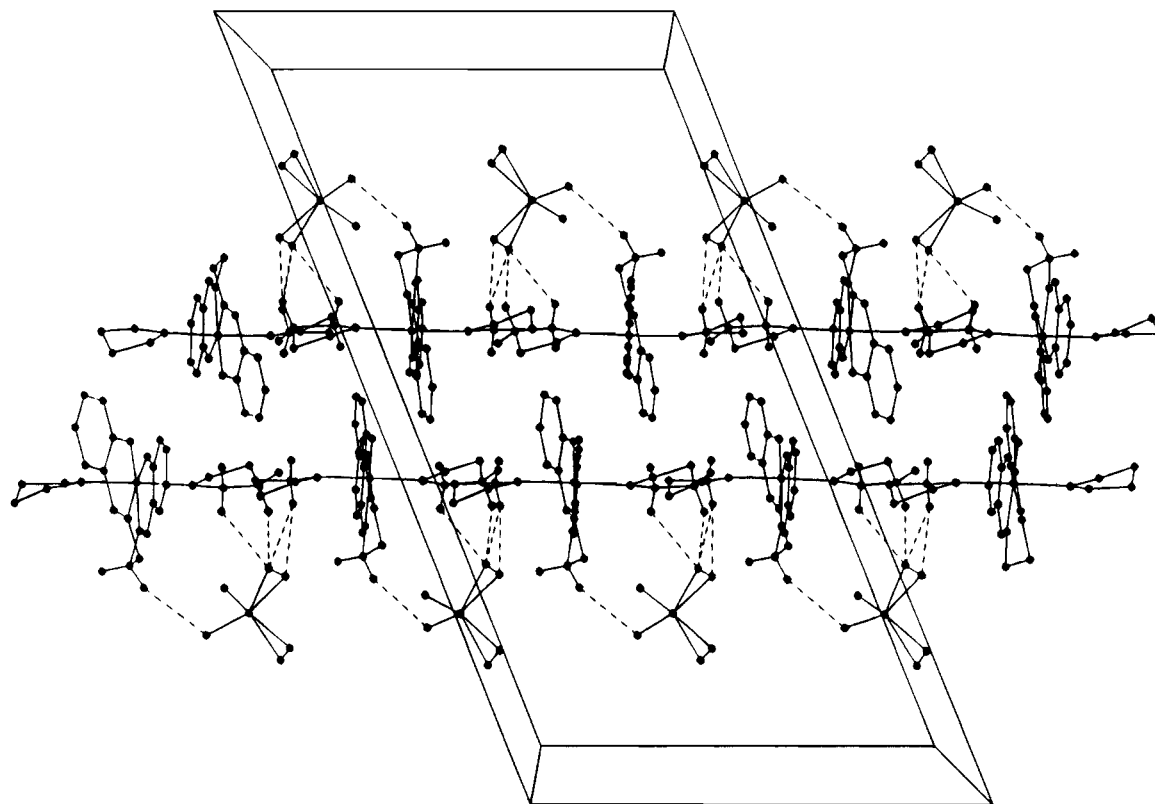
Figure 11. Packing plot of **10**. The compound forms polymeric strands of alternating [Al(salen)(THF)$_2$]$^+$ cations and [AlCl$_4$]$^-$ anions. The anions are weakly H-bonded by the cations (dotted lines).

Table 7. Crystallographic Details for **2a**, **4·2THF**, **7a·2C$_7$H$_8$**, **9**, and **10**

	2a	4a·2THF	7a·2C$_7$H$_8$	9	10
formula	C$_{12}$H$_{24}$Al$_{0.5}$Cl$_{0.5}$N$_4$O$_2$P	C$_{56}$H$_{100}$Al$_2$Cl$_2$N$_{16}$O$_8$P$_4$·2C$_4$H$_8$O	C$_{29}$H$_{50}$AlF$_3$N$_8$O$_7$P$_2$S·2C$_7$H$_8$	C$_{56}$H$_{100}$Al$_2$I$_2$N$_{16}$O$_8$P$_4$	C$_{24}$H$_{30}$Al$_2$Cl$_4$N$_2$O$_4$
fw	637.08	1518.47	885.87	1557.16	606.26
space group	Pnnm	P$\bar{1}$	C2/c	Pn	C2/c
a, Å	14.675(3)	10.821(2)	29.591(6)	10.552(2)	28.474(6)
b, Å	15.059(3)	11.234(2)	17.102(3)	26.060(5)	13.896(3)
c, Å	15.132(3)	32.974(7)	18.018(4)	14.030(3)	15.532(3)
α, deg	90	84.99(3)	90	90	90
β, deg	90	82.73(3)	97.98(3)	104.39(3)	111.80(3)
γ, deg	90	81.38(3)	90	90	90
V, Å^3	3344.0(12)	3921.7(13)	9030(3)	3737.0(13)	5706(2)
Z	8	2	8	2	8
ϱ_{calcd}, g cm^{-3}	1.265	1.286	1.303	1.384	1.411
μ, cm^{-1}	2.77	2.50	2.27	10.08	5.09
R_1, %^{a}	4.21	5.49	8.88	3.63	7.49
wR_2[$I > 2\sigma(I)$], %^{b}	14.70	14.15	22.57	11.01	21.24

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} w$R_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$.

shows a three-dimensional ionic lattice structure without any discrete aggregation (see packing plot, Figure 9). The two crystallographically different iodide anions are very weakly solvated by three or six CH hydrogen bonds involving the HMPA methyl groups and the salen imine protons (see Figure 8). The (C)H···I distances are 2.96–3.24 Å (see Table 4), and thus these interactions are very weak, given the sum of the van der Waals radii of H and I (3.18 Å).[11,22,23] The C−H···I angles vary over a broad range (131−175°, average angle = 154°) and again do not correlate with the (C)H···I distances.[17]

(22) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753.

(23) A search in the Cambridge Crystallographic Database revealed no example of a metalated salicylaldehyde Schiff base complex with either N=CH or N−CH hydrogen bonds to I$^-$ but one complex with an N−CH$_2$··· bond to I$_5^-$: [(salen)VOVO(salen)[I$_5$]·MeCN, d(N−CH$_2$···I) = 2.85 Å (normalized), θ(C−H···I) = 149.7° (Hills, A.; Hughes, D. L.; Leigh, G. J.; Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1991**, 61).

Compound **8** is soluble in THF, forming the [Al(salen)(THF)$_2$]$^+$I$^-$ ion pair (by ^{1}H NMR spectroscopy in CDCl$_3$; see below). This demonstrates that THF is sufficiently Lewis-basic to overcome the "hard−soft" Al−I interaction and that the Al−I bond is distinctly weaker than the Al−Cl bond in Al(salen)Cl (**3**), which is insoluble in THF.

[Al(salen)(THF)$_2$]$^+$[AlCl$_4$]$^-$ (**10**). Pursuing route B of eq 1, reaction of a strong Lewis acid with Al(salen)Cl should abstract the Cl$^-$ ion and lead to ion separation without the need to apply a strong Lewis base like HMPA. This route was followed by adding 2 equiv of AlMeCl$_2$ to H$_2$salen in THF (eq 6). Since AlMeCl$_2$ in THF is equivalent to an equilibrium

$$H_2\text{salen} + 2\text{AlMeCl}_2 \xrightarrow{\text{THF}} [\text{Al(salen)(THF)}_2]^+[\text{AlCl}_4]^- \quad (6)$$
$$\mathbf{10}$$
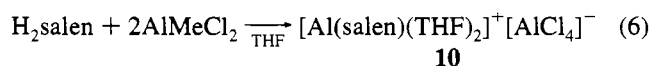
mixture of AlMe$_2$Cl and AlCl$_3$, H$_2$salen, in effect, is metalated by AlMe$_2$Cl to give Al(salen)Cl, which in turn reacts with AlCl$_3$ to give [Al(salen)(THF)$_2$]$^+$[AlCl$_4$]$^-$ (**10**).

Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **2a**

	x	y	z	U_{eq}		x	y	z	U_{eq}
Cl(1)	2337(1)	10000	3619(1)	36(1)	C(10)	1495(3)	5810(2)	5000	52(1)
Al(1)	2337(1)	9069(1)	5000	24(1)	C(11)	606(3)	6114(2)	5000	55(1)
O(1)	3452(1)	9637(1)	5000	31(1)	C(12)	432(2)	7020(2)	5000	38(1)
N(1)	1765(1)	10300(1)	5000	25(1)	O(3)	2264(1)	9085(1)	3743(1)	33(1)
C(1)	3391(2)	10515(2)	5000	26(1)	P(1)	2520(1)	9169(1)	2796(1)	29(1)
C(2)	2522(2)	10918(2)	5000	26(1)	N(3)	2808(1)	10173(1)	2476(1)	40(1)
C(3)	2424(2)	11831(2)	5000	35(1)	N(4)	3374(1)	8490(1)	2595(1)	40(1)
C(4)	3192(3)	12369(2)	5000	46(1)	N(5)	1668(1)	8887(1)	2163(1)	38(1)
C(5)	4059(2)	11974(2)	5000	41(1)	C(13)	2172(2)	10910(2)	2615(2)	46(1)
C(6)	4164(2)	11073(2)	5000	33(1)	C(14)	3757(2)	10454(2)	2471(2)	57(1)
N(2)	1045(1)	8571(1)	5000	26(1)	C(15)	4036(2)	8243(2)	3259(2)	51(1)
O(2)	2732(1)	7913(1)	5000	34(1)	C(16)	3640(2)	8280(2)	1694(2)	62(1)
C(7)	1148(2)	7616(2)	5000	27(1)	C(17)	1309(2)	9400(2)	1428(2)	56(1)
C(8)	2059(2)	7322(2)	5000	30(1)	C(18)	1096(2)	8151(2)	2439(2)	52(1)
C(9)	2229(2)	6398(2)	5000	41(1)					

^{a} U_{eq} is defined as one-third of the trace of orthogonalized U_{ij} tensor.

Table 9. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **4a**.^{a}

	x	y	z	U_{eq}		x	y	z	U_{eq}
Cl(1)	6859(1)	7324(1)	2386(1)	29(1)	O(6)	7396(3)	1495(3)	3955(1)	20(1)
Cl(2)	11719(1)	1296(1)	2375(1)	33(1)	O(7)	7876(3)	3837(3)	3834(1)	22(1)
Al(1)	968(1)	5802(1)	1126(1)	16(1)	O(8)	6524(3)	1642(3)	3233(1)	23(1)
P(1)	3200(1)	7383(1)	1282(1)	20(1)	N(9)	6941(4)	3968(4)	3098(1)	20(1)
P(2)	-1321(1)	4257(1)	960(1)	19(1)	N(10)	8811(4)	2303(4)	3257(1)	19(1)
O(1)	1960(3)	4771(3)	778(1)	19(1)	N(11)	7274(4)	5554(4)	4322(1)	26(1)
O(2)	629(3)	7037(3)	741(1)	20(1)	N(12)	7902(4)	3402(4)	4642(1)	28(1)
O(3)	2427(3)	6384(3)	1264(1)	19(1)	N(13)	9658(4)	4473(4)	4167(1)	24(1)
O(4)	-564(3)	5195(3)	1053(1)	19(1)	N(14)	6322(4)	1134(4)	2507(1)	26(1)
N(1)	1136(4)	4587(4)	1605(1)	18(1)	N(15)	4365(4)	2313(4)	2899(1)	27(1)
N(2)	-69(4)	6755(4)	1569(1)	19(1)	N(16)	4997(4)	145(4)	3206(1)	23(1)
N(3)	4452(4)	7102(4)	949(2)	31(1)	C(29)	4941(5)	4393(4)	3769(2)	18(1)
N(4)	2568(4)	8782(4)	1172(2)	29(1)	C(30)	4009(5)	4817(5)	4085(2)	26(1)
N(5)	3552(4)	7393(4)	1748(2)	30(1)	C(31)	3350(5)	5952(5)	4063(2)	28(1)
N(6)	-2668(4)	4455(4)	1255(1)	29(1)	C(32)	3539(5)	6731(5)	3716(2)	32(2)
N(7)	-759(4)	2831(4)	1046(1)	27(1)	C(33)	4442(5)	6348(5)	3397(2)	29(1)
N(8)	-1437(4)	4390(4)	463(1)	22(1)	C(34)	5156(5)	5201(4)	3423(2)	21(1)
C(1)	2765(5)	3800(4)	866(2)	18(1)	C(35)	6136(5)	4923(5)	3088(2)	21(1)
C(2)	3629(5)	3293(5)	547(2)	23(1)	C(36)	7905(5)	3762(5)	2742(2)	25(1)
C(3)	4428(5)	2227(5)	617(2)	28(1)	C(37)	9141(5)	3195(5)	2914(2)	26(1)
C(4)	4417(5)	1623(5)	1003(2)	29(1)	C(38)	9628(5)	1383(5)	3339(2)	20(1)
C(5)	3596(5)	2113(5)	1321(2)	27(1)	C(39)	9447(5)	517(5)	3681(2)	21(1)
C(6)	2773(5)	3201(5)	1261(2)	19(1)	C(40)	10413(5)	-445(5)	3735(2)	26(1)
C(7)	1920(5)	3607(5)	1613(2)	21(1)	C(41)	10332(5)	-1308(5)	4062(2)	31(1)
C(8)	275(5)	4886(5)	1972(2)	25(1)	C(42)	9254(5)	-1215(5)	4339(2)	27(1)
C(9)	87(5)	6229(5)	1991(2)	23(1)	C(43)	8283(5)	-284(5)	4297(2)	24(1)
C(10)	-884(5)	7693(5)	1512(2)	20(1)	C(44)	8339(5)	614(4)	3972(2)	17(1)
C(11)	-1079(5)	8294(4)	1112(2)	19(1)	C(45)	7017(6)	6472(5)	3991(2)	37(2)
C(12)	-2027(5)	9293(5)	1094(2)	24(1)	C(46)	6874(6)	6001(6)	4731(2)	47(2)
C(13)	-2241(5)	9929(5)	732(2)	30(2)	C(47)	6605(5)	3061(6)	4759(2)	38(2)
C(14)	-1489(5)	9590(5)	372(2)	31(1)	C(48)	8893(6)	2535(5)	4816(2)	36(2)
C(15)	-550(5)	8619(5)	383(2)	25(1)	C(49)	10631(5)	3716(6)	3912(2)	37(2)
C(16)	-312(5)	7942(4)	751(2)	18(1)	C(50)	10138(6)	5282(6)	4411(2)	45(2)
C(17)	5484(6)	7840(6)	928(2)	52(2)	C(51)	7656(5)	608(5)	2463(2)	32(2)
C(18)	4487(6)	6409(6)	588(2)	41(2)	C(52)	5661(6)	789(6)	2186(2)	35(2)
C(19)	2570(6)	9289(5)	750(2)	41(2)	C(53)	4339(6)	3279(5)	2569(2)	39(2)
C(20)	1580(5)	9427(5)	1457(2)	37(2)	C(54)	3258(5)	2488(5)	3215(2)	37(2)
C(21)	3929(6)	8445(6)	1928(2)	52(2)	C(55)	5827(5)	-753(5)	3429(2)	30(1)
C(22)	3704(6)	6264(6)	2014(2)	36(2)	C(56)	4073(5)	-392(5)	3014(2)	31(1)
C(23)	-2981(5)	5367(5)	1556(2)	34(2)	O(9)	1517(6)	7445(7)	2854(3)	121(3)
C(24)	-3664(6)	3675(6)	1258(2)	50(2)	C(57)	461(11)	8235(8)	2773(3)	89(3)
C(25)	-865(6)	2219(5)	1460(2)	39(2)	C(58)	-590(8)	7760(8)	3038(3)	69(3)
C(26)	229(5)	2192(5)	764(2)	30(1)	C(59)	-112(9)	6507(9)	3168(4)	105(4)
C(27)	-2161(6)	3627(5)	269(2)	33(2)	C(60)	1219(8)	6317(7)	3018(3)	67(2)
C(28)	-1409(5)	5588(5)	248(2)	27(1)	O(10)	12461(4)	1645(4)	4659(2)	53(1)
Al(2)	7092(1)	2709(1)	3562(1)	17(1)	C(61)	13795(8)	1513(7)	4579(3)	66(2)
P(3)	8162(1)	4278(1)	4224(1)	21(1)	C(62)	14229(7)	280(9)	4459(3)	90(3)
P(4)	5585(1)	1331(1)	2972(1)	20(1)	C(63)	13149(7)	-141(6)	4318(3)	59(2)
O(5)	5541(3)	3286(3)	3805(1)	19(1)	C(64)	12014(6)	649(6)	4509(2)	47(2)

^{a} U_{eq} is defined as one-third of the trace of orthogonalized U_{ij} tensor.

The solid-state structure of **10** is shown in Figure 10. The free coordination positions of aluminum are filled by two THF solvent molecules, and a pseudooctahedral ligand sphere similar to the ones in **4a·2THF**, **7a·2C₇H₈**, and **9** results for aluminum in **10**. A packing plot (Figure 11) shows that one-dimensional polymeric chains are formed *via* weak CH···H bonds from THF

Table 10. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **7a**[a]

	x	y	z	U_{eq}		x	y	z	U_{eq}
Al(1)	6622(1)	7821(2)	1610(2)	31(1)	C(18)	7487(5)	9449(9)	1192(9)	64(4)
P(1)	6591(1)	9740(2)	1317(2)	34(1)	C(19)	6476(6)	9807(10)	−203(8)	77(5)
P(2)	6629(1)	5860(2)	1566(2)	39(1)	C(20)	5786(5)	9849(9)	413(9)	61(4)
O(1)	7185(2)	7784(5)	2150(5)	36(2)	C(21)	6178(5)	11093(7)	1665(8)	50(3)
O(2)	6818(2)	7786(4)	697(4)	33(2)	C(22)	6333(4)	10111(8)	2662(7)	42(3)
O(3)	6611(3)	8936(4)	1638(4)	35(2)	C(23)	5864(5)	5555(9)	666(10)	71(5)
O(4)	6553(3)	6716(5)	1622(6)	54(3)	C(24)	6571(6)	5259(10)	141(8)	65(4)
N(1)	6322(3)	7846(6)	2535(6)	38(2)	C(25)	6435(5)	5783(9)	2982(8)	62(4)
N(2)	5967(3)	7870(6)	1129(6)	40(3)	C(26)	6248(5)	4597(8)	2213(10)	66(5)
N(3)	7110(4)	10004(6)	1230(7)	53(3)	C(27)	7372(5)	4929(8)	1815(9)	61(4)
N(4)	6284(4)	9872(7)	493(6)	49(3)	C(28)	7495(4)	6228(7)	1318(10)	63(4)
N(5)	6347(3)	10309(5)	1879(6)	39(2)	S(1)	4401(1)	7828(2)	223(2)	50(1)
N(6)	6352(4)	5469(7)	807(7)	53(3)	O(5)	4562(4)	7550(9)	958(6)	88(4)
N(7)	6419(4)	5408(6)	2249(6)	48(3)	O(6)	4725(3)	8291(7)	−105(8)	88(4)
N(8)	7175(3)	5684(5)	1603(6)	44(3)	O(7)	3936(3)	8106(6)	112(5)	57(3)
C(1)	7329(4)	7903(7)	2876(7)	36(3)	C(100)	4376(7)	6964(13)	−351(12)	86(6)
C(2)	7792(5)	7878(7)	3148(7)	45(3)	F(1a)	4097(9)	6449(13)	−217(20)	90(11)
C(3)	7959(5)	8005(8)	3884(8)	52(4)	F(1b)	4051(31)	6465(77)	164(131)	254(77)
C(4)	7652(5)	8162(8)	4391(7)	56(4)	F(2)	4784(3)	6619(6)	−314(8)	109(4)
C(5)	7191(5)	8156(8)	4144(8)	52(4)	F(3)	4226(4)	7135(8)	−1075(7)	114(4)
C(6)	7017(4)	8028(7)	3393(6)	34(3)	C(101)	5000	9475(13)	2500	71(7)
C(7)	6527(4)	7962(7)	3202(7)	38(3)	C(102)	4920(5)	9879(11)	1839(10)	70(5)
C(8)	5818(4)	7729(9)	2394(8)	52(4)	C(103)	4919(5)	10687(9)	1847(9)	63(4)
C(9)	5651(4)	8096(9)	1657(7)	52(4)	C(104)	5000	11120(12)	2500	50(5)
C(10)	5814(4)	7738(7)	449(7)	39(3)	C(105)	5000	11995(13)	2500	82(7)
C(11)	6110(4)	7548(7)	−109(7)	37(3)	C(01)	5000	4424(15)	2500	74(7)
C(12)	5900(4)	7339(9)	−815(8)	53(4)	C(02)	4879(13)	4510(25)	1874(21)	79(10)
C(13)	6163(5)	7127(10)	−1378(8)	67(4)	C(03a)	4746(11)	5066(19)	1334(20)	67(9)
C(14)	6627(5)	7157(9)	−1232(8)	59(4)	C(03b)	4864(11)	5092(20)	1889(20)	60(8)
C(15)	6841(4)	7385(7)	−542(7)	43(3)	C(04)	4889(8)	5865(14)	1991(13)	38(6)
C(16)	6597(4)	7589(6)	51(6)	32(3)	C(05)	5000	5787(21)	2500	109(10)
C(17)	7226(6)	10819(9)	1103(12)	93(6)					

[a] U_{eq} is defined as one-third of the trace of orthogonalized U_{ij} tensor. F(1), C(02), C(03), and C(04) are in disordered positions. Occupancy factor for F(1) is equal to 0.68(9), and those for the other atoms are 0.5.

CH$_2$ groups and the salen ethylene group to the [AlCl$_4$]$^-$ counterion. The (C)H$\cdots$Cl distances (2.50−3.03 Å; see Table 5) are distinctly longer and thus weaker than the ones in **4a**·2THF. This is reasonable in view of the soft [AlCl$_4$]$^-$ anion (the negative charge is spread over four chlorides of the highly polarizable anion) compared to the "harder" Cl$^-$ ion. The C−H$\cdots$Cl angles (128−168°, average angle = 148°) cover a similarly broad range compared to the ones in **4a**·2THF.[17]

The stabilization of the abstracted Cl$^-$ counterion by a strong Lewis acid (AlCl$_3$ in this case) allows only weakly Lewis-basic solvent molecules (THF) to act as ligands toward the [Al-(salen)]$^+$ cation. That THF is bound more weakly to [Al-(salen)]$^+$ than HMPA can be seen from the long (THF)O−Al distances in **10** (average distance = 2.001 Å) compared to the average (HMPA)O−Al distance in **4a**·2THF, **7a**·2C$_7$H$_8$, and **9** (1.919 Å).

[Al(salen)(L)$_2$]$^+$ in Solution and in the Solid State. In contrast to neutral pentacoordinated Al(salen)X derivatives, which show two signals in the ^{1}H NMR spectrum for *exo* and *endo* protons of the ethylene bridge,[20,24] the ^{1}H NMR spectra of **4a**, **7a**·2C$_7$H$_8$, **9**, and **10** in CDCl$_3$ or DMSO-d_6 show only one signal for equivalent ethylene protons, indicating a symmetric six-coordinate [Al(salen)(L)$_2$]$^+$ cation in solution, similar to the cations in the solid state.

The Al−X distances in the [Al(salen)]$^+$ moieties of **4a**·2THF, **7a**·2C$_7$H$_8$, **9**, and **10** (see Table 6) lie within a narrow range [d(Al−O) = 1.791−1.831 Å, average value = 1.815 Å; d(Al−N) = 1.991−2.024 Å, average value = 2.008 Å] and are in good agreement with those of pentacoordinated Al(salen)X (X = Et, 2,4,6-trimethylphenoxy, μ-O) derivatives reported by

Goedken[24] and Barron.[20] The Al−O(HMPA) distances in **4a**, **7a**·2C$_7$H$_8$, and **9** also show a small range of values [d(Al−O) = 1.901−1.959 Å, average value 1.919 Å].

Conclusions

The solid-state structures of **2a**, **4a**·2THF, **7a**·2C$_7$H$_8$, and **9** are unusual on a number of counts: in these complexes the 6-fold, pseudooctahedral coordination of the metal center is completed by two HMPA molecules, a Lewis base common in the chemistry of alkali metals[25] but not seen previously in the solid-state structure of an aluminum complex; HMPA proves to be an ideal Lewis donor ligand to afford ion separation of aluminum compounds with "hard" counteranions (high Al−X bond strength) while (for **1**, **3**, and **6**) several other, weaker donor compounds fail. A strong Lewis base is necessary in cases where the Al−X bond strength is high ("hard" X$^-$ = Cl$^-$ or CF$_3$SO$_3^-$) since X$^-$ solvation by NH or CH hydrogen bonding (in **2a**, **4a**·2THF, and **7a**·2C$_7$H$_8$) is too weak to compensate for the loss of the strong Al−X bond. In contrast, if the Al−X bond strength is weak and the stability of the counterion is high ("soft" X$^-$ = I$^-$, [AlCl$_4$]$^-$; **8**, **10**) the weakly Lewis-basic solvent molecule THF is sufficient to solvate the [Al(salen)]$^+$ unit and to overcome the Al−X bond energy.

CH$\cdots$X hydrogen bonds generally are considered to be rather weak.[7] The energy for CH$\cdots$O hydrogen bonding is about 4−8 kJ mol^{-1}.[7b,18] Since the nature of CH hydrogen bonding is mainly electrostatic (r^{-1} dependence),[5e,7b,26] longer CH$\cdots$X bonds with X = Cl or I are likely to be even weaker; however, the distance dependence is not as strong as in (partially) covalent

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Table 11. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **9**[a]

	x	y	z	U_{eq}		x	y	z	U_{eq}
I(1)	7556(1)	14157(1)	7995(1)	31(1)	C(27)	2931(10)	11982(4)	4059(8)	40(2)
I(2)	9993(1)	9362(1)	9985(1)	32(1)	C(28)	4251(10)	12649(4)	5122(6)	37(2)
Al(1)	5568(2)	13787(1)	3150(2)	19(1)	Al(2)	6074(2)	11284(1)	9437(2)	18(1)
P(1)	7722(2)	14615(1)	2684(1)	21(1)	P(3)	7225(2)	12236(1)	8357(2)	18(1)
P(2)	3943(2)	12725(1)	3126(1)	19(1)	P(4)	4388(2)	10426(1)	10357(2)	24(1)
O(1)	6922(5)	13340(2)	3308(4)	21(1)	O(5)	4604(5)	11671(2)	9296(4)	24(1)
O(2)	4999(5)	13725(2)	1823(4)	24(1)	O(6)	6996(5)	11596(2)	10560(4)	22(1)
O(3)	6660(5)	14365(2)	3055(4)	22(1)	O(7)	6768(5)	11716(2)	8589(4)	25(1)
O(4)	4365(5)	13272(2)	3378(4)	23(1)	O(8)	5446(6)	10760(2)	10163(4)	25(1)
N(1)	6004(6)	13918(3)	4618(5)	21(2)	N(10)	7568(6)	10803(3)	9460(5)	20(2)
N(2)	4183(6)	14316(3)	3194(5)	21(2)	N(11)	6383(7)	12733(3)	8537(5)	26(2)
N(3)	8034(8)	14363(3)	1697(5)	33(2)	N(12)	8690(6)	12342(3)	9062(5)	25(2)
N(4)	7340(7)	15214(3)	2464(6)	35(2)	N(13)	7173(7)	12232(3)	7176(5)	23(2)
N(5)	9100(7)	14588(3)	3523(6)	35(2)	N(14)	4865(8)	9828(3)	10316(7)	45(2)
N(6)	2624(7)	12706(3)	2189(5)	27(2)	N(15)	2963(7)	10433(3)	9609(6)	37(2)
N(7)	4975(6)	12344(3)	2777(5)	23(2)	N(16)	4155(9)	10617(4)	11408(6)	48(2)
N(8)	3590(7)	12485(3)	4108(5)	26(2)	C(29)	3681(8)	11775(3)	8475(6)	25(2)
N(9)	5295(6)	10890(3)	8191(5)	18(2)	C(30)	2807(8)	12175(3)	8490(6)	26(2)
C(1)	8003(7)	13315(3)	4028(6)	21(2)	C(31)	1852(9)	12307(4)	7669(7)	35(2)
C(2)	9104(8)	13041(3)	3873(7)	28(2)	C(32)	1721(9)	12043(4)	6788(7)	39(2)
C(3)	10260(9)	13015(4)	4576(7)	31(2)	C(33)	2563(9)	11640(4)	6764(7)	38(2)
C(4)	10405(8)	13253(4)	5500(7)	35(2)	C(34)	3557(7)	11492(3)	7598(6)	22(2)
C(5)	9332(8)	13506(3)	5679(6)	28(2)	C(35)	4318(8)	11050(4)	7507(6)	26(2)
C(6)	8161(8)	13543(3)	4971(6)	23(2)	C(36)	6002(9)	10423(4)	8068(6)	30(2)
C(7)	7068(8)	13813(3)	5216(6)	24(2)	C(37)	7452(9)	10516(3)	8525(6)	28(2)
C(8)	4938(10)	14193(3)	4927(7)	35(2)	C(38)	8508(9)	10710(3)	10192(7)	26(2)
C(9)	4389(8)	14578(3)	4142(6)	26(2)	C(39)	8761(8)	10991(3)	11096(6)	22(2)
C(10)	3219(8)	14433(3)	2467(6)	25(2)	C(40)	9834(9)	10835(4)	11877(7)	34(2)
C(11)	2955(8)	14200(3)	1505(6)	21(2)	C(41)	10178(10)	11101(4)	12741(7)	40(2)
C(12)	1779(8)	14315(3)	848(7)	31(2)	C(42)	9503(9)	11541(4)	12857(7)	40(2)
C(13)	1389(9)	14090(4)	−83(7)	35(2)	C(43)	8472(8)	11710(4)	12125(6)	30(2)
C(14)	2294(9)	13748(4)	−346(7)	36(2)	C(44)	8023(8)	11434(3)	11232(6)	24(2)
C(15)	3471(8)	13642(3)	278(6)	25(2)	C(45)	5275(9)	12943(4)	7756(8)	40(2)
C(16)	3852(8)	13850(3)	1239(6)	23(2)	C(46)	6334(10)	12872(4)	9531(7)	40(2)
C(17)	7199(14)	14494(5)	733(8)	67(4)	C(47)	9277(8)	12843(4)	9293(8)	40(2)
C(18)	8395(11)	13817(4)	1706(8)	49(3)	C(48)	9574(8)	11907(4)	9407(7)	36(2)
C(19)	5976(10)	15407(4)	2247(8)	43(3)	C(49)	7809(9)	12652(4)	6783(7)	35(2)
C(20)	8260(12)	15591(4)	2301(10)	56(3)	C(50)	7165(11)	11747(4)	6650(6)	39(2)
C(21)	9070(11)	14790(5)	4483(7)	53(3)	C(51)	6268(10)	9702(4)	10610(8)	43(3)
C(22)	10393(9)	14541(5)	3351(9)	53(3)	C(52)	4027(13)	9384(5)	10395(12)	68(4)
C(23)	1610(8)	13080(4)	2157(7)	31(2)	C(53)	2641(12)	10148(6)	8675(8)	68(4)
C(24)	2245(9)	12287(4)	1520(7)	40(2)	C(54)	1977(14)	10826(6)	9642(14)	81(5)
C(25)	6013(9)	12088(4)	3531(7)	32(2)	C(55)	4985(11)	10981(4)	12039(7)	41(3)
C(26)	5372(8)	12460(3)	1849(6)	26(2)	C(56)	3304(16)	10316(6)	11888(10)	89(5)

[a] U_{eq} is defined as one-third of the trace of orthogonalized U_{ij} tensor.

bonds (r^{-6} dependence). While for the [Al(salen)]$^+$ ion, "hard" counterions like Cl$^-$ and CF$_3$SO$_3^-$ result in dimer formation *via* hydrogen bonding, "softer" anions like I$^-$ and [AlCl$_4$]$^-$ give ionic lattice structures with only very weak CH···X interactions. The formation of aggregates *via* hydrogen bonding with "hard" counteranions is due to highly favorable Coulomb interactions. Although CH···X bonds are weaker than NH···X bonds, these interactions are responsible for the formation of dimeric aggregates in **4a·2THF** and **7a·2C$_7$H$_8$**, similar to the one in **2a**. This type of dimer formation is unique in aluminum chemistry where dimers usually are formed by Al−Al-bridging anionic heteroatom substituents.[14] Thus, the structures of **2a** and (particularly) of **4a·2THF** and **7a·2C$_7$H$_8$** demonstrate the pronounced structure-forming influence even of weak CH hydrogen bonding in the coordination chemistry of main group elements.

Although the chloride anion in **4a·2THF** and the triflate anion in **7a·2C$_7$H$_8$** have quite different shapes, both compounds surprisingly crystallize in very similar fashions, not only concerning the dimeric aggregation and the presence of weak intermolecular hydrogen bonds from the HMPA molecules of neighboring dimers but also concerning the formation of inclusion compounds with 2 equiv of solvent molecules, one

of them sitting in the cavity of the dimer and the other outside in the crystal lattice. While **4a** prefers THF over toluene to yield **4a·2THF**, **7a** crystallizes out of a mixture of toluene, THF, and methylene chloride as **7a·2C$_7$H$_8$**.

Experimental Section

Table 12. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **10**[a]

	x	y	z	U_{eq}		x	y	z	U_{eq}
Al(1)	6006(1)	6896(2)	6340(1)	42(1)	O(3)	6001(2)	6887(4)	7624(3)	60(1)
O(1)	5455(2)	7652(4)	5966(3)	51(1)	C(19)	6037(3)	6509(8)	9110(5)	73(2)
O(2)	5672(1)	5776(4)	6055(3)	48(1)	C(17)	6076(5)	7725(10)	8303(8)	44(4)
N(1)	6464(2)	8034(5)	6641(3)	47(1)	C(18)	6274(6)	7350(12)	9256(8)	55(4)
N(2)	6671(2)	6208(5)	6839(3)	45(1)	C(20)	6034(6)	6014(10)	8196(9)	46(4)
C(1)	5399(2)	8574(6)	6150(4)	48(2)	C(17a)	5424(4)	6819(11)	7575(9)	55(4)
C(2)	4916(2)	8953(6)	5964(4)	55(2)	C(18a)	5510(5)	6298(11)	8471(9)	55(4)
C(3)	4845(3)	9901(6)	6154(5)	60(2)	C(20a)	6312(5)	6692(13)	8431(8)	53(4)
C(4)	5253(3)	10501(7)	6520(6)	79(3)	O(4)	6046(2)	6960(3)	5082(3)	55(1)
C(5)	5729(3)	10163(7)	6701(6)	84(3)	C(21)	6094(4)	6142(6)	4540(5)	79(3)
C(6)	5819(3)	9204(6)	6532(4)	53(2)	C(22)	6059(5)	6574(8)	3626(6)	109(4)
C(7)	6330(2)	8903(6)	6710(5)	57(2)	C(23)	5770(4)	7467(8)	3530(5)	93(3)
C(8)	6992(2)	7800(6)	6784(5)	62(2)	C(24)	5925(3)	7831(6)	4506(4)	65(2)
C(9)	7118(2)	6848(6)	7267(5)	59(2)	Al(2)	7834(1)	4942(2)	5296(1)	49(1)
C(10)	6736(2)	5295(6)	6871(4)	50(2)	Cl(1)	7316(6)	5355(11)	4028(6)	124(5)
C(11)	6339(2)	4588(5)	6567(4)	45(2)	Cl(1a)	7192(4)	5757(21)	4284(15)	120(6)
C(12)	6465(2)	3611(6)	6667(4)	53(2)	Cl(2)	8503(4)	4395(13)	5078(12)	124(4)
C(13)	6103(2)	2905(5)	6382(4)	51(2)	Cl(2a)	8322(10)	4709(9)	4690(17)	91(6)
C(14)	5598(3)	3176(5)	5984(4)	50(2)	Cl(3)	8079(1)	6045(2)	6306(2)	97(1)
C(15)	5458(2)	4122(5)	5879(4)	49(2)	Cl(4)	7534(1)	3796(2)	5834(2)	86(1)
C(16)	5822(2)	4863(5)	6170(4)	42(2)					

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. C(17), C(18), C(20), Cl(1), and Cl(2) in disordered positions. Occupancy factors for C(17), C(18), and C(20) equal to 0.48(1) and for Cl(1) and Cl(2) 0.67(3) in the first position.

by full-matrix least-squares based on F^2. All non-hydrogen atoms were refined anisotropically; the NH hydrogens in **2a** were located in a difference electron map and freely refined. All other hydrogens in **2a**, **4a·2THF**, **7a·2C7H8**, **9**, and **10** were refined isotropically using riding models since their positions were unambiguous. One F atom in the triflate anion of **7a·2C7H8** and two of the Cl atoms of the [AlCl4]⁻ ion in **10** exhibit disorder, as does one of the THF ligands in **10** and one of the two toluene molecules in **7a·2C7H8**. The disorder was resolved, and two sites were located for each disordered atom. These pairs of sites were refined with partial occupancies so that the total occupancy summed to unity. The toluene methyl group of the disordered molecule could not be located and was not included in the refinement. Calculations were carried out on a Viglen 486DX PC computer using the SHELXTL PLUS[27] and the SHELXL-93[28] packages. Crystallographic details of all structures are summarized in Table 7. Atomic coordinates of all structures are given in Tables 8–12.

[Al(2-H₂NC₆H₄O)₂(HMPA)₂]⁺Cl⁻ (2). 2-Aminophenol (240 mg, 2.20 mmol) was dissolved in 5 mL of CH₂Cl₂. AlMe₂Cl (2.2 mL of a 1.0 M solution in hexanes) was added at −78 °C. After warming to room temperature and addition of 5 mL of CH₂Cl₂, a white precipitate formed. To ensure completion of the reaction, this suspension was heated for a short time. The precipitate was filtered off and dried *in vacuo*. The residue (260 mg) was suspended in 4 mL of toluene, and HMPA (0.5 mL) was added, giving a colorless solution. Colorless crystals of **2** suitable for X-ray analysis (310 mg, 44%) were obtained after 1 d at −28 °C: mp 176 °C dec; ¹H NMR (400.1 MHz, DMSO-*d₆*, 25 °C) δ 6.99 (d, 7.3 Hz, 2 H; arom H), 6.93 (t, 7.6 Hz, 2 H; arom H), 6.56 (d, 6.2 Hz, 2 H; arom H), 6.45 (t, 7.4 Hz, 2 H; arom H), 5.31 (s (broad), 4 H; N*H*), 2.52 (d, 9.3 Hz, 36 H; HMPA); ¹³C NMR (100.6 MHz, DMSO-*d₆*, 25 °C) δ 159.8/128.1 (C(1)/C(2)), 127.3/116.4/115.7/114.3 (C(3)–C(6)), 36.5 (HMPA); IR (Nujol; cm⁻¹) 3250–3050 m, ν(NH). Anal. Calcd for C₂₄H₄₈N₈O₄P₂AlCl: C, 45.25; H, 7.60; N, 17.59. Found: C, 43.54; N, 7.72; N, 16.75.

[Al(salen)(HMPA)₂]⁺Cl⁻ (4). H₂salen (320 mg, 1.19 mmol) was dissolved in 10 mL of toluene. Addition of 1.19 mL of a 1.0 M AlMe₂-Cl/hexanes solution at room temperature resulted in a white precipitate, which was redissolved by addition of 0.42 mL of HMPA and 8 mL of toluene, followed by heating. Colorless crystals (760 mg, 93%) of **4** were obtained after 1 d at −28 °C: mp 215–218 °C; ¹H NMR (400.1 MHz, CDCl₃, 25 °C) δ 8.34 (s, 2 H; C*H*=N), 7.24 (t, 7.7 Hz, 2 H; arom H(5)), 7.16 (d, 7.7 Hz, 2 H; arom H(3)), 6.70 (d, 8.4 Hz, 2 H;

arom H(6)), 6.58 (t, 7.3 Hz, 2 H; arom H(4)), 4.06 (s, 4 H; C*H₂CH₂*), 2.32 (d, 9.7 Hz, 36 H; HMPA); ¹³C NMR (100.6 MHz, CDCl₃, 25 °C) δ 166.1 (*CH*=N), 165.5 (arom C(1)), 134.9/134.0 (arom C(5)/C(3)), 121.8/115.3 (arom C(4)/C(6)), 119.4 (arom C(2)), 54.5 (*CH₂CH₂*), 36.4 (HMPA). Anal. Calcd for C₂₈H₅₀N₈O₄P₂AlCl: C, 48.94; H, 7.33; N, 16.31. Found: C, 48.32; H, 7.43; N, 16.10. Crystals of **4a·2THF** suitable for X-ray analysis were obtained by recrystallization of **4** from a hot saturated THF solution.

[Al(salen)(HMPA)₂]⁺CF₃SO₃⁻ (7). H₂salen (330 mg, 1.23 mmol) was dissolved in 4 mL of THF. Addition of 0.62 mL of a 2.0 M AlMe₃/hexanes solution at room temperature gave after methane generation a bright yellow precipitate. NH₄⁺CF₃SO₃⁻ (205 mg) and 5 mL of THF were added. Heating initiated gas generation (CH₄, NH₃), and a white precipitate was obtained after 30 min of stirring. Addition of 0.5 mL of HMPA resulted in a clear solution and further gas generation (NH₃). The solution was heated and stirred for 1 h. Toluene (10 mL) and methylene chloride (3 mL) were added. Colorless crystals (488 mg, 44%) of **7a·2C₇H₈** suitable for X-ray crystallography precipitated at 5 °C after 2 d: mp 198–200 °C; ¹H NMR (400.1 MHz, CDCl₃, 25 °C) δ 8.29 (s, 2 H; C*H*=N), 7.26–7.13 (m, 9 H; salen arom H(5) and arom H(3), toluene arom H), 6.68 (d, 8.3 Hz, 2 H; arom H(6)), 6.60 (t, 7.4 Hz, 2 H; arom H(4)), 4.02 (s, 4 H; C*H₂CH₂*), 2.35 (d, 9.7 Hz, 36 H; HMPA), 2.34 (s, 3 H; toluene C*H₃*); ¹³C NMR (100.6 MHz, CDCl₃, 25 °C) δ 166.0 (*CH*=N), 165.5 (arom C(1)), 137.7 (toluene C(1)), 134.9/134.0 (arom C(5)/C(3)), 129.0 (toluene C(2)), 128.2 (toluene C(3)), 125.3 (toluene C(4)), 121.8/115.3 (arom C(4)/C(6)), 119.5 (arom C(2)), 54.5 (*CH₂CH₂*), 36.4 (HMPA). Anal. Calcd for C₃₆H₅₈N₈O₇P₂SF₃Al: C, 48.43; H, 6.55; N, 12.55. Found: C, 48.28; H, 6.29; N, 12.47.

[Al(salen)(HMPA)₂]⁺I⁻ (9). H₂salen (330 mg, 1.23 mmol) was dissolved in 5 mL of THF. Addition of 1.23 mL of a 1.0 M AlEt₂I/toluene solution at room temperature and initial heating resulted after ethane generation in an almost clear yellow solution. After addition of HMPA (0.5 mL) and heating, a yellow precipitate formed which dissolved upon adding 8 mL of THF and further heating. Colorless crystals (731 mg, 76%) of **9** were obtained at −28 °C after 1 d. X-ray-quality crystals were grown at room temperature from a hot saturated THF solution of **9**: mp 246 °C dec; ¹H NMR (400.1 MHz, CDCl₃, 25 °C) δ 8.44 (s, 2 H; C*H*=N), 7.28–7.24 (m, 4 H; arom H(5) and arom H(3)), 6.69 (d, 8.2 Hz, 2 H; arom H(6)), 6.59 (t, 7.4 Hz, 2 H; arom H(4)), 4.09 (s, 4 H; C*H₂CH₂*), 2.33 (d, 9.8 Hz, 36 H; HMPA); ¹³C NMR (100.6 MHz, CDCl₃, 25 °C) δ 165.8 (*CH*=N), 165.6 (arom C(1)), 134.9/134.0 (arom C(5)/C(3)), 121.8/115.3 (arom C(4)/C(6)), 119.5 (arom C(2)), 54.6 (*CH₂CH₂*), 36.4 (HMPA). Anal. Calcd for

(27) *SHELXTL PLUS, Program Version 4.0*; Siemens Analytical Instruments: Madison, WI, 1990.

(28) Sheldrick, G. M. *SHELXL-93, program for crystal structure refinement*; University of Göttingen:, Göttingen, Germany, 1993.

$C_{28}H_{50}N_8O_4P_2IAl$: C, 43.19; H, 6.47; N, 14.39. Found: C, 43.06; H, 6.60; N, 14.49.

[Al(salen)(THF)₂]⁺[AlCl₄]⁻ (10). H₂salen (350 mg, 1.30 mmol) was dissolved in 7 mL of THF. Addition of 2.60 mL of a 1.0 M AlMeCl₂/hexanes solution at room temperature generated methane and initially gave a yellow precipitate which dissolved upon adding the full amount of AlMeCl₂. The solution was stirred for 30 min and occasionally heated in order to complete the reaction; a white precipitate formed subsequently. This dissolved after the addition of 8 mL of THF and heating. Colorless crystals (260 mg, 33%) of **10** suitable for X-ray analysis formed at room temperature: mp >250 °C; ¹H NMR (400.1 MHz, DMSO-d_6, 25 °C) δ 8.73 (s, 2 H; C*H*=N), 7.40−7.35 (m, 4 H; arom H(5) and arom H(3)), 6.86 (d, 8.2 Hz, 2 H; arom H(6)), 6.73 (t, 7.3 Hz, 2 H; arom H(4)), 3.86 (s, 4 H; C*H₂*C*H₂*), 3.60 (m, 8 H; OC*H₂*CH₂, THF), 1.76 (m, 8 H, OCH₂C*H₂*, THF); ¹³C NMR (100.6 MHz, DMSO-d_6, 25 °C) δ 167.2 (*C*H=N), 164.6 (arom C(1)), 135.1/134.2 (arom C(5)/C(3)), 121.3/116.0 (arom C(4)/C(6)), 119.7 (arom C(2)), 67.1 (O*C*H₂CH₂, THF) 53.2 (*C*H₂*C*H₂), 25.2 (OCH₂*C*H₂, THF). Anal. Calcd for $C_{24}H_{30}N_2O_4Cl_4Al_2$: C, 47.55; H, 4.99; N, 4.62. Found: C, 45.55; H, 5.40; N, 4.58. Correct microanalysis could not be obtained since **10** loses THF upon drying.

Supporting Information Available: Full tables of crystallographic data, bond distances and angles, and anisotropic thermal parameters, as well as ORTEP plots of the aluminum-containing cations (39 pages). Ordering information is given on any current masthead page.

IC950302F