N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE

STRUCTURE OF COMPLEXES BETWEEN ALUMINUM
CHLORIDE AND OTHER CHLORIDES, II
ALKALI-[CHLOROALUMINATES]. GASEOUS COMPLEXES

Magdolna Hargittai

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546   APRIL 1980

1. Report No. NASA TM 75762	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle STRUCTURE OF COMPLEXES BETWEEN ALUMINUM CHLORIDE AND OTHER CHLORIDES, II. ALKALI-[CHLOROALUMINATES]. GASEOUS COMPLEXES		5. Report Date April 1980
		6. Performing Organization Code
7. Author(s) Magdolna Hargittai		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, Calif. 94063		11. Contract or Grant No. NASw-3199
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes   Translation of "Az Alumínium-Klorid Más Fém-Kloridokkal Alkotott Komplexeinek Szerkezetéről II. Alkáli-[Kloro-Aluminátik]. Gáz-Halmazállapotú Komplexek," Kémiai Közlemények Vol. 50, No. 4, 1978, pp 489-514

16. Abstract   The structural chemistry of complexes between aluminum chloride and other metal chlorides is important both for practice and theory. Condensed-phase as well as vapor-phase complexes are of interest. Structural information of such complexes is reviewed. The first emphasis is given to the molten state because of its practical importance. Aluminum chloride forms volatile complexes with other metal chlorides and these vapor-phase complexes are dealt with in the second part. Finally, the variations in molecular shape and geometrical parameters are summarized.

17. Key Words (Selected by Author(s))		18 Distribution Statement Unclassified-Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 36	22. Price

STRUCTURE OF COMPLEXES BETWEEN ALUMINUM
CHLORIDE AND OTHER CHLORIDES, II.[1]
ALKALI-[CHLOROALUMINATES]. GASEOUS COMPLEXES

Magdolna Hargittai
Central Research Institute of Chemistry of the
Hungarian Academy of Sciences, Budapest

In the first part of this study, I presented information   /489[*]
concerning the structure of aluminum chloride itself, and the capacity
of aluminum chloride to stabilize the lower oxidation state of other
metals and its relations to molecular structure, and finally, the
results of structural studies concerning the complexes of aluminum
chloride with transition metal chlorides.

In this, second, part of the study, I am discussing the alkali-
(chloro-aluminates) which are the most widely investigated compounds
of the complexes of aluminum chloride with other halides. This is
due to practical reasons, because these systems are encountered in a
great variety of chemical processes (for instance, in the preparation
of aluminum). This is the only class of compounds among the aluminum
chloride-metal chloride complexes, the structure of which has been
investigated in all three phases.

For practical reasons, I am devoting most of the attention to
studies carried out in the solution phase.

Further on, I present a review of the results of the structural
studies of gaseous aluminum chloride-metal chloride complexes. The
significance of these complexes for the preparation of various metals
is being increasingly recognized.

Alkali-(chloro-aluminates)

---

[*]Numbers in the margin indicate pagination in the foreign text.

In the crystalline phase, only the structure of sodium-
(tetrachloro-aluminate) was determined [2]. It was found that the
crystal structure is based on Na^+ and $AlCl_4^-$ ions. The aluminum has
a tetrahedral coordination, the Na^+ ions occupy the vacancies between
the tetrahedra. The tetrahedra have the following geometric parameters:
$r(Al-Cl) = 2.13$ Å, $r(Cl...Cl) = 3.48$ Å. The $Cl...Cl$ distance between
adjoining tetrahedra ranges from 3.80 to 3.87 Å. The distance of the
Na+ ions from the peaks of the tetrahedra is: 2.79--3.29 Å (the only
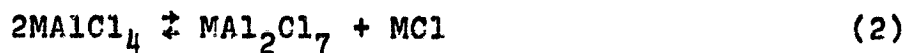distance $Na...Cl = 3.72$ Å).

Comparing the data with the Pauling-type covalent or ionic
radii [3], we found that: within the individual tetrahedra, the
Al-Cl or the Cl...Cl distances are smaller than the sum of the
tetrahedral covalent radii $(\Sigma r_{kov}(Al-Cl) = 2.25$ Å$)$, or of the
van der Waals radii $(2r_{vdw}(Cl) = 3.60$ Å$)$. At the same time, the distance
between the chlorine atoms belonging to different tetrahedra is larger
than the double of the van der Waals radius of Cl or of the Cl^- ion
$(2r_{vdw}(Cl) = 3.60$ Å, $2r_{ion}(Cl^-) = 3.62$ Å$)$, respectively).
The same thing applies to the distance between Na...Cl distances also
(c.f. Σr_{ion} $(Na^+...Cl^-) = 2.76$ Å$)$. Thus, in the crystal, the bonds
within the $AlCl_4^-$ tetrahedron are stronger, while the relations between
the tetrahedra and the Na^+ ion and between the individual tetrahedra
are loose. This finding agrees with the result of the structural
investigation by electron diffraction, in the gas phase carried out by
Spiridonov et al [4]. According to these findings, in the vapor phase
of the related $KAlCl_4$, the $AlCl_4$ tetrahedra form a tight unit, while
the connection between the tetrahedra and the alkali atoms is quite
weak (see below).

In the vapor phase over the $KCl-AlCl_4$ solutions, Grothe [5]
found that complexes with a composition of $KAlCl_4$ and KAl_2Cl_7 are
present. According to the thermodynamic studies of Morozov and
Toptyigin [6], the sodium and potassium-(tetrachloro-aluminate)
evaporates without decomposition. A. Morozov [7] determined by
partial vapor pressure measurements the composition of the vapor phase
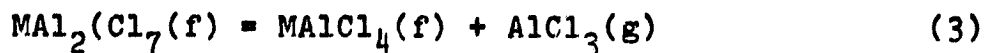
2

of the solutions as a function of temperature. According to their findings, aluminum chloride and alkali-(tetrachloro-aluminate) molecules are present in the vapor phase, and the relative partial vapor pressure of the tetrachloro aluminate increases from the lithium toward the cesium. The partial pressure of aluminum chloride over the $LiAlCl_4$ melt within the temperature interval under study is larger than the partial pressure of the complex. The partial pressures of the two components in the vapor phase of $NaAlCl_4$ are nearly identical, while in the vapor phase of the potassium, rubidium and cesium tetrachloro-aluminates, to a large extent, complex molecules are present. The thermal decomposition of the alkali-(tetrachloro-aluminates) takes place according to the following reaction:

$$2MAlCl_4(f) = MAlCl_4(g) + AlCl_3(g) + MCl(f) \qquad (1)$$
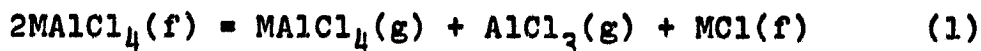
In addition, another equilibrium occurs in the melt:

$$2MAlCl_4 \rightleftarrows MAl_2Cl_7 + MCl \qquad (2)$$

and

$$MAl_2(Cl_7(f) = MAlCl_4(f) + AlCl_3(g) \qquad (3)$$

The thermal stability of the complex MAl_2Cl_7 molecules increases with the increase of the ionic radius of the alkali metal cation. The $LiAl_2Cl_7$ molecules are easily decomposed, and according to the above reactions, this is the reason for the large partial pressures of aluminum chloride in the vapor phase. On the other hand, the $CsAl_2Cl_7$ is very stable, and therefore, mostly tetrachloro-aluminate molecules are present in the vapor phase.

According to the observations of A. Morozov and I. Morozov, addition of alkali chloride to the melt results in the considerable reduction of the partial pressure of aluminum chloride. This can easily be understood on the basis of the above reactions, because if the concentration of the chloride ion is increased, the reaction (2) is shifted towards the left, and, on the basis of (3), the formation of $AlCl_3$ (g) does not take place. The authors underline the fact that the presence of aluminum chloride in the gas phase is the consequence of the above reactions (2) and (3), and not of the eventual decomposition of the $MAlCl_4$ molecules in the gas phase.

3

According to the above-cited [4] electron diffraction studies of Spiridonov et al., the KAlCl$_4$ molecules in the gas phase have a C$_{2v}$ symmetry (Figure 1). The following geometric parameters were found:

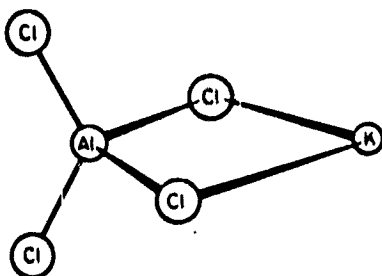|	
r(Al—Cl), Å	2.16 ± 0.02
r(K—Cl), Å	2.84 ± 0.02
∢Cl—Al—Cl	109,5 ± 5° (tetrahedral)
∢Cl—K—Cl	77°

Figure 1. The gas-phase configuration of the KAlCl$_4$ molecule [4]

The difference between the lengths of the two types of Al-Cl bonds is not more than 0.1 Å.

As we indicated above, within the molecule, the AlCl$_4$ group is exceptionally stable, which is supported by the fact that it has the same structure in all three phases, and phase transitions do not change the tetrahedral symmetry of the group. On the other hand, the bond between the tetrahedron and the potassium atom is quite loose. This is proven by the increase of the K-Cl distance with respect to the length of the bond of the K-Cl molecule (r(K-Cl) = 2.6666 ± 0.0001 Å [8]). The K-Cl distance in the complex is by 0.18 Å larger than in the vapor phase of K-Cl; at the same time, the average amplitude of oscillation, l(K-Cl) = 0.13 Å, is considerably larger than that of the bonds in general (0.04 - 0.07 Å).

A structure similar to potassium-(tetrachloro-aluminate) was found in the vapor phase of other mixed halides. The following similar systems were investigated by electron diffraction: NaAlF$_4$[9], KYCl$_4$ [10] and TlInCl$_4$ [11]. According to Spiridonov [12], in these molecules, instead of the static bridged structure presented in Figure 1, a dynamic structure is formed, in which the M metal atom belongs with equal probability to all four halide atoms of the MeX$_4$ group. This is implied by the structural representation

$$M^{\delta+}[MeX_4]^{\delta-}$$

which, at the same time, expresses the polar character of the bond.

The melts of alkali(chloro-aluminates), especially the sodium and potassium derivatives, are examined in many studies. I only mention some of these investigations [13-22]; the results of some of them were examined more closely in the first part of this study [1]. At this time, I present in greater detail only the results of the more recent and more complete investigations. Torsi et al. [23] examined the NaCl-AlCl$_3$ system by Raman spectroscopy [23], while Cyvin, Øye et al. studied the AlkCl-AlCl$_3$(Alk = Li, K and Cs) [24-26].
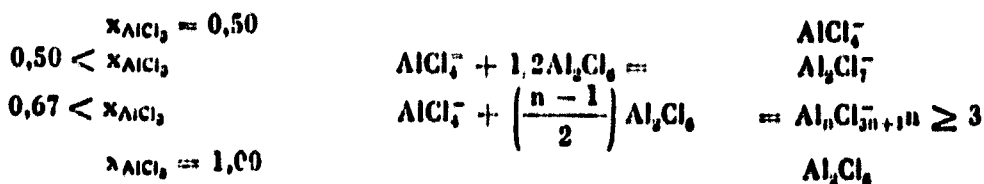
The Raman spectra of alkali-(chloro-aluminates) were determined in various concentration ranges (AlCl$_3$ between 50 and 100%), in order to study the composition changes of the melt. The experimental temperatures were varied from 170 to 400°C, but control measurements revealed that in the investigated range, the spectra are independent of the temperature. The uncertainty in the composition of the melt was estimated at $\pm$ 0.3 mol percent.

In Figure 2, I present the Raman spectra of the melts of the NaCl-AlCl$_3$ system, according to Torsi, Mamantove and Begun [23]. The data given below are characteristic for the spectra of all investigated materials. The maxima of the spectra taken in the 100 mol% aluminum chloride were attributed to the Al$_2$Cl$_6$ dimeric molecules (cf. Persina and Raskin [27]) and were designated with lower case letters a-j. The peaks are discernibly decreased, and finally, disappear completely as the AlCl$_3$ concentration is decreased (at the 63% mol% of the AlCl$_3$, they are not observed at all). The spectrum of the melt containing 50 mol percent of AlCl$_3$ was ascribed to AlCl$_4^-$ ion (designated on the picture with Greek letters α-δ). These peaks are gradually decreased and finally disappear, as the AlCl$_3$ concentration increases. In the meantime, new peaks appear and gradually increase in the spectrum. They belong to the dimeric Al$_2$Cl$_7^-$ ion (designated with upper-case characters: A-D). Finally, as the aluminum chloride concentration is further increased (66.7 → 73.0 mol%), new maxima appear, which were ascribed to the thus-formed, higher-level polymeric

5

anions, $Al_nCl_{3n}^-$ + n $\geq$ 3, primarily $Al_3Cl_{10}^-$ (on the spectra, they are designated by x-z). On the basis of the above, the composition of the alkali chloride-aluminum chloride melts in the acid range may be characterized in the following way:

AlCl$_3$ concentration   reactions taking place   groups in excess

$$x_{AlCl_3} = 0,50 \qquad\qquad\qquad\qquad\qquad AlCl_4^-$$
$$0,50 < x_{AlCl_3} \qquad AlCl_4^- + 1,2Al_2Cl_6 = \qquad Al_2Cl_7^-$$
$$0,67 < x_{AlCl_3} \qquad AlCl_4^- + \left(\frac{n-1}{2}\right)Al_2Cl_6 \quad = Al_nCl_{3n+1}^- n \geq 3$$
$$x_{AlCl_3} = 1,00 \qquad\qquad\qquad\qquad\qquad Al_2Cl_6$$

As a result of the aluminum chloride concentration of the melt, two
types of complex ions are preferentially created in the solution, $AlCl_4^-$, and $Al_2Cl_7^-$. Higher than the second order associated states (such as the Al_3Cl_{10} anion) could not be definitely identified on the basis of spectra. On the other hand, the vibrational analysis of the two most important ions was carried out, drawing conclusions concerning bond relations from these measurements.

Table 1.

The Raman frequencies of the $AlCl_4^-$ ion in various alkali-(tetrachloro-aluminate) melts.

	LiCl—AlCl$_3$ (1)	NaCl—AlCl$_3$ (2)	(3)	(4)	KCl - AlCl$_3$ (1)	CsCl—AlCl$_3$ (1)
σ_2	119	146	145	121	122	120
σ_4	182	180	183	184	182	178
σ_1	348	349	349	351	350	344
σ_5	498	575	580	490	487	483

(1) — Rytter, Øye, Cyvin, Cyvin & Klæboe [26].
(2) — Gerding & Houtgraaf [13].
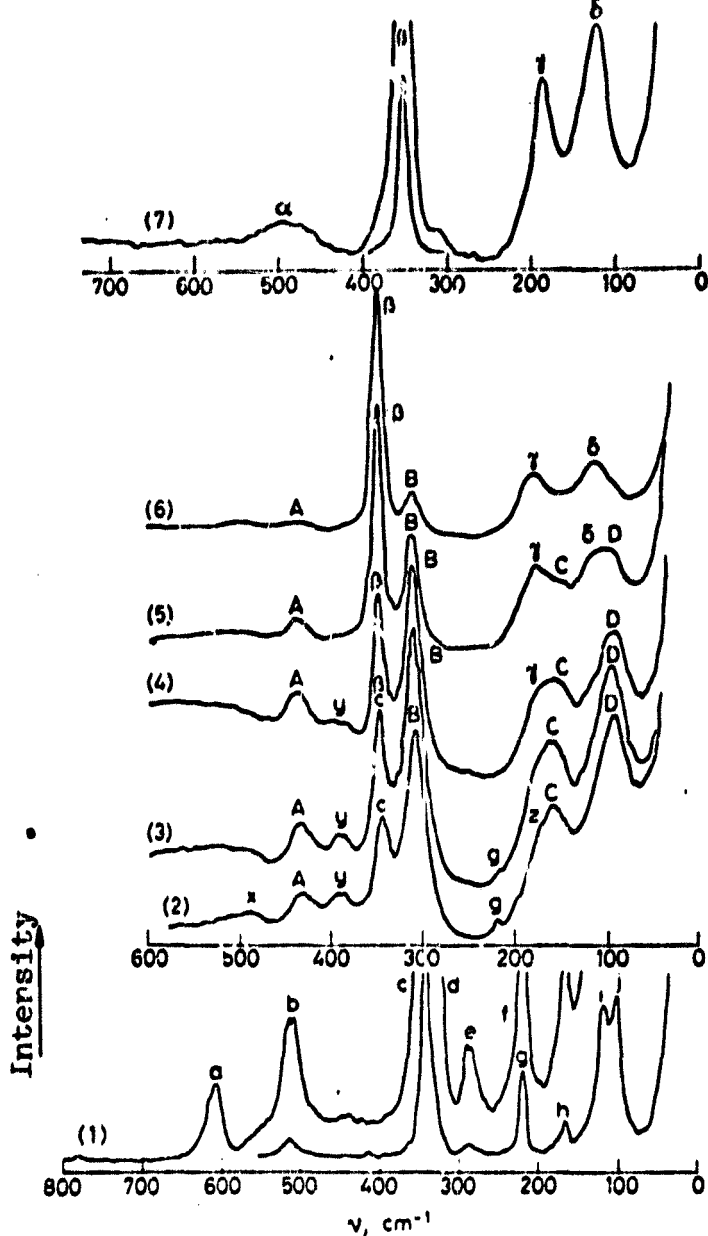(3) — Balasubrahmanyam & Nanis [19].
(4) — Torsi, Mamantov & Begun [23].

6

Figure 2. The Raman spectrum at 225°C of the melt of the NaCl-AlCl₃ system as a function of the composition [23].

	NaCl	AlCl₃
	mól%	
1		100
2	27	73
3	33	67
4	36	64
5	46	54
6	48	52
7	50	50

The frequency assignment is given in the text.

7

$AlCl_4^-$ ion

A tetrahedral symmetry was tentatively assigned to the tetra-chloro-aluminate ion, to which correspond 4 active Raman frequencies, $\sigma_1(A_1)$, $\sigma_2(E)$, $\sigma_3(F_2)$ and $\sigma_4(F_2)$. The four maxima in the Raman spectra of the melts containing 50 mol% aluminum chloride may be ascribed to them.[1]

A summary of the frequencies belonging to the $AlCl_4^-$ ion, and the calculated force constant, respectively, is presented in Tables 1 and 2. By now it may be assumed as proven that the $AlCl_4^-$ ion has a regular or only slightly distorted tetrahedral configuration in the melt. The slight distortion of the tetrahedra may be due, for example, to the strongly polarizing effect of the cation (see below).

Table 2.

Some of the force constants of the $AlCl_4^-$ ion (mdin $Å^{-1}$)

	(1a)	(1b)		(2a)	(2b)
f_f	1.76	1.704	K	2.06	1.67
f_{ff}	0.28	0.285	F	0.31	0.23
f_a	0.17	0.193	H		0.08
f_{aa}	0.01	0.020	F'		0.01

(1) Valence-force space:
   a - Müler and Krebs [29];
   b - Øye, Rytter, Klaeboe and Cyvin [25];

(2) Urey-Bradley force space:
   a - Gerding and Houtgraaf [13];
   b - Müler and Krebs [29]

$Al_2Cl_7^-$ ion

Øye and Gruen were the first to assume [18] that the $Al_2Cl_7^-$ ion consists of two distorted tetrahedra, which are in contact with each other at one of their peaks. The following symmetry types may be

---

[1] Balasubrahamanyam and Nanis [19] observed nine maxima in the Raman spectrum of the melt of the KCl-AlCl3 system, and derived a distorted tetrahedral C_{2v} symmetry. However, later Bredig [28] and then Øye and collaborators [25] pointed out that the appearance of the excessively large number of maxima is probably due to electric noise, and the KCl-ACl3 system has a regular tetrahedral symmetry, just like the other compounds of similar type.

atcributed to the dimeric tetrachloro-aluminate ion [25]:

1. Assuming a linear Al-Cl-Al bridge, D_{3h}, D_{3d} or D_3, depending whether the two final $AlCl_3$ groups have an open (D_{3d}) or covered (D_{3h}) position with respect to each other, or whether they are able to rotate freely (D_3). The active Raman frequencies 6 (D_{3d}), 10 (D_{3h}) or 11 (D_3) belong to these frequencies.
2. In the case of a non-linear Al-Cl-Al bridge, C_{2v}, C_s, C_2 or C_1, similarly as a function of the orientation of the final $AlCl_3$ groups. 21 active Raman frequencies belong to these symmetry types.

In part because of the appearance of few bands, and on the other hand, on the basis of geometric considerations, Øye and collaborators rejected the non-linear models [25,26] in spite of the fact that in two cases they found a curved Al-Cl-Al bridge, [30,31]. The normal coordinate analysis [25] agreed with the fact that the $Al_2Cl_7^-$ ion has an open position (D_{3d}), although the closed-position (D_{3h}) model cannot be excluded. The barrier to internal rotation may be assumed to be very low, and free rotation may be considered.

The effect of cations on the structure of the melts was also studied [26]. The Raman frequencies of the anions are in most cases nearly identical, although some remarkable exceptions were also found. In the case of $AlCl_4^-$ (or $AlCl_7^-$), the expansion frequency increases gradually from cesium to lithium (or potassium). The increase of the expansion frequency is a phenomenon which often accompanies the increase of the polarizing effect of the cation (see [26] and references given there).

The 498 cm^{-1} maximum in the spectrum of the $LiCl-AlCl_3$ system is split into three parts. This is attributed to the fact that the Li ion forms in part a covalent bond with the $AlCl_4^-$ ion, creating a molecule with a C_{2v} symmetry:
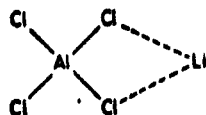
This decreases the strength of the bridged Al-Cl bonds, as a result of which the expansion frequency of the tetrahedra is split. The larger the polarizing strength of the cation (the smaller the cation), the more marked is this effect. After dimension of the cation increases, its polarizing strength is gradually decreased, and the $AlCl_4^-$ ion retains its tetrahedral symmetry. The tendency of the Li ion to create partially covalent Al-Cl ... Li bonds is proven by the electric conductivity measurements of the melts. According to these measurements, while the conductivity of the alkali(tetrachloro-aluminates) decreases gradually as expected in the Na→Rb direction, the conductivity in the $LiCl-AlCl_3$ system is lower than in the case of the $NaCl-AlCl_3$ melts [32].

Gaseous complexes

It was found a long time ago that aluminum chloride (and similarly the Fe(III) chloride) forms volatile complex compounds with sodium chloride [33]. However, during recent years, many studies were published suddenly, on the existence of new volatile metal chloride-aluminum chloride complexes.

The complexes are formed according to the following general formula:

$$m\ MCl_k + n\ Al_2Cl_6 \rightleftarrows (MCl_k)_m \cdot (Al_2Cl_6)_n,$$

where in most cases m = 1 (but not necessarily; see, for example, the complexes of CuCl) and n = 0.5-2.

The volatile complexes of metal dichlorides and aluminum chloride

Dewing has found that the volatility of metal dichlorides is considerably increased in the presence of aluminum chloride [34,35]. He investigated the complexes of the following metals: Ca, Mg, Mn, Co, Ni, Zn, Cd and Pd. Dewing's paper contains the detailed results of the evaporation of metal dichlorides in the presence of aluminum chloride. According to Dewing, two different types of complexes

are present in the vapor space according to the following reactions :

$$MCl_2 (s) + 2AlCl_3 (g) = MAl_2Cl_8 (g)$$
$$MCl_2 (s) + 3AlCl_3 (g) = MAl_3Cl_{11} (g) .$$
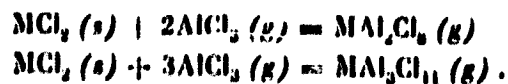
The temperature dependence of the equilibrium constants of the two reactions is shown in Figures 3 and 4.

All of the above reactions are exothermic, therefore, in the temperature range where the aluminum chloride is monomeric, the partial pressure of the complexes decreases with increasing temperature. At the same time, in view of the fact that the heat of reaction (ΔH), with the exception of the case of $MgAl_3Cl_{11}$) is lower than the heat of dimerization of aluminum chloride (14 kcal/$AlCl_3$), the reactions which take place in the presence of the dimer are endothermic. As a result of this, the partial pressure of the complexes passes through a maximum at the temperature of dissociation of the dimer (about $600°C$).
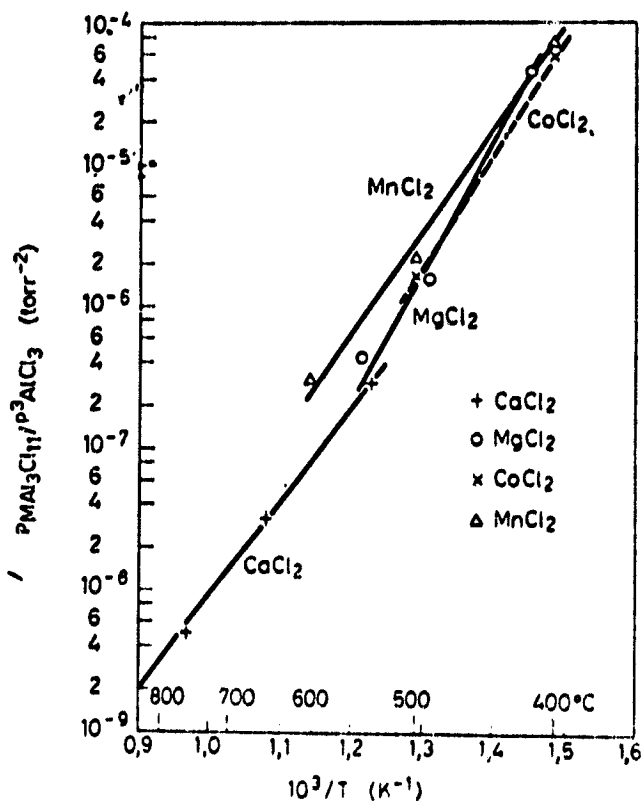

Figure 3. The temperature dependence of the equilibrium constants of the $MCl_2(s) + 2AlCl_3(g) = MAl_2Cl_8(g)$ reactions [35].

The $CoCl_2-Al_2Cl_6$ system

In addition to the above-mentioned one, the gas phase of the Co $Co_2-Al_2Cl_6$ system was examined in several studies. The vapor

11

pressure and certain thermodynamic parameters of the complex were determined by spectrophotometric measurements [36]. The spectrum of the gaseous phase is similar to that obtained with the molten complex [20], and on this basis, Papatheodorou assumes that the following equilibrium is established in the vapor phase:

I   2
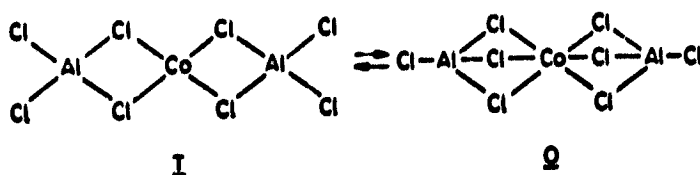
The two structures depend only on the spatial position of the $AlCl_4$ groups; in the T configuration, the tetrahedra are connected through their edges to the cobalt atom, forming a distorted tetrahedral coordination, while in the structure, the tetrahedra surround the cobalt atoms with their planes, thereby creating a distorted octahedral coordination. According to Papatheodorou [36], on the basis of the liquid space theory, the octahedral configuration may be expected to predominate in the gas phase

On the other hand, Dell'Anna and Emmenegger [37] propose another structure on the basis of these chemical transport experiments In their opinion, the following reaction takes place in the gaseous state:
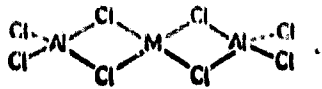
$$CoCl_2\ (s) +\ Al_2Cl_6\ (g) \rightarrow Co(AlCl_4)_2\ (g)$$
$$CoCl_2\ (s) + 2Al_2Cl_6\ (g) \rightarrow Co(Al_2Cl_7)_2\ (g).$$

Figure 4. The temperature dependence of the equilibrium constants of the
$$MCl_2(s) +\ 3AlCl_3(g) = MAl_3Cl_{11}(g)$$
reactions [35]

12
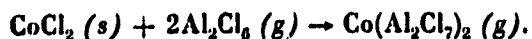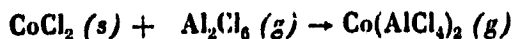
Figure 5. The tetrahedral configuration of the $Co(AlCl_4)_2$ molecules in the gas phase, according to Dell'Anna and Emmenegger [37].

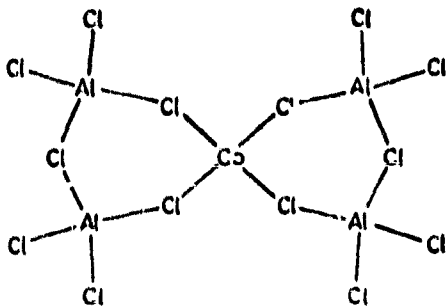Figure 6. The structure of the gas-phase complexes $Co(Al_2Cl_7)_2$ according to Dell'Anna and Emmenegger.

These data were not found to be compatible with the assumption of Dewing [35] that in addition to the $CoAl_2Cl_8$ complexes, molecules having the composition of $CoAl_3Cl_{11}$, i.e. $CoCl_2 \cdot 1.5Al_2Cl_6$ molecules containing one and one-half Al_2Cl_6 are present. Therefore, under consideration of the above-indicated two reactions, they repeated Dewing's calculations concerning the thermodynamic data of the complex formation.

Dell'Anna and Emmenegger proposed a structure containing a cobalt atom with a tetrahedral coordination, in contrast with the results of the investigations of Øye and Gruen concerning melts [20] and of Papatheodorou concerning the gas phase [36]. According to that proposal, in the gaseous $Co(AlCl_4)_2$ complex, the $AlCl_4$ groups surround the cobalt atom with the edge of their tetrahedra, while, in the $Co(Al_2Cl_7)_2$ complex, the Al_2Cl_7 groups are connected to the cobalt atom with the peak of each in their two tetrahedra. This is illustrated in Figures 5 and 6.

Aluminum chloride as the carrier gas of transport phenomena

Schäfer and collaborators [38] reported on the transportation of the following metal chlorides within a certain temperature gradient, using aluminum chloride as the carrier gas [38]:

$FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $PdCl_2$, $PtCl_2$
$MoCl_3$, YCl_3, $LaCl_3$
$ThCl_4$, UCl_4.
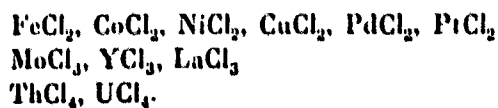
The reactions which take place between the metal chlorides and
aluminum chloride are endothermic, and the complex formation is
reversible; therefore, the transported metal chlorides crystallize
out by themselves at the colder portion of the experimental installation,
and the complex is present only in the gas phase. They characterized
the transport phenomena which take place by the data presented in
Table 3. Thus, these transport phenomena may be used, for example,
to prepare high-purity, oxide-free metal halide crystals.

It should be noted that in contrast with the above-mentioned
reversible transport phenomena, many of the reactions of metal halides
with aluminum chloride are irreversible, and therefore the produced
complex compounds are present in the condensed phase also. Of course,
in such cases, the aluminum chloride cannot be used as a carrier gas.

On the basis of the studies of Schäfer and Trenkel [39], the chemical
transportation by means of aluminum chloride (eventually with Fe-III
chloride or with aluminum iodide) may be realized also by initiating   /500
the reaction directly from the metals. In that case, in the presence
of the halogenating agent (for example, Cl_2, HCl, I_2), first metal
halides are formed, and then these halides form volatile complexes
with aluminum chloride. Schäfer and Trenkel carried out this experiment
with the following metals:

        Cu, Ag, Au, Ru, Rh, Pd, Ir and Pt.
The detailed conditions of the transport experiments are presented in
our report [39].

The aluminum-chloride complexes of chromium chlorides

Study of the complexes of chromium with aluminum chloride again
proved the ability of aluminum chloride to stabilize the lower
oxidation state. Lascelles et al. [40] proved the existence of the
$CrCl_2 \cdot 2AlCl_3$ complex, in addition to the previously known gaseous

14

Table 3.

Characteristic data of transport phenomena according to Shäfer et al. [38].

Starting material (mg)	Pressure of the carrier gas (atm.)	Temperature °C		Period of heating (hours)	Transported product (mg)
600 FeCl₂	1,96	350	250	25	complete transportation
2000 CoCl₂	kb. 1	400	300	20	804 CoCl₂
500 NiCl₂	kb. 1	350	300	65	243 NiCl₂
400 CuCl₂	0,93	300	250	24	complete transportation
1150 CuCl₂	4,18	400	350	1	863 CuCl₂
1000 γ - PdCl₂	2,05	350	300	24	870 α - PdCl₂
500 α - PtCl₂	2,05	350	300	24	470 β - PtCl₂ (Pt₆Cl₁₂)
1000 MoCl₃	1,13	400	350	24	136 MoCl₃
1000 YCl₃	2,84	600	510	24	270 YCl₃
410 LaCl₃	2,62	550	450	24	122 LaCl₃
1000 LuC:₃	6,93	750	650	24	520 LuCl₃
470 ThCl₄	2,47	500	400	24	complete transportation
1500 UCl₄	5,5	350	250	14	complete transportation

$CrCl_3 \cdot 2AlCl_3$ complex, and at the same time, they developed a new method for the preparation of $CrCl_2$. On the basis of the electron spectrum of the gaseous complex, $CrAl_2Cl_8$ containing bivalent chromium, Aits and Schäfer found that the chromium has a distorted octahedral chloride coordination [41].

The aluminum chloride complexes of copper chlorides

The study of gaseous complexes produced by the reaction of copper chlorides of various oxidation states and of aluminum chloride presents great interest. Using the mass spectrometric method, the presence of the following types of complexes was proven in a system containing Cu(I) [4]:

CuAlCl$_4$	CuCl · AlCl$_3$	1 : 1
Cu$_2$AlCl$_5$	2CuCl · AlCl$_3$	2 : 1
Cu$_3$AlCl$_6$	3CuCl · AlCl$_3$	3 : 1
CuAl$_2$Cl$_7$	CuCl · 2AlCl$_3$	1 : 2
Cu$_2$Al$_2$Cl$_8$	2CuCl · 2AlCl$_3$	2 : 2 .

Recently, Emmenegger and collaborators [43] succeeded in identifying, in addition to the dimeric aluminum chloride molecule, also the CuAl$_2$Cl$_8$ molecule among the gas-phase products of the reaction of copper-(II) chloride and aluminum chloride. According to the interpretation of the spectrum, this complex possesses no center of symmetry, and the copper atom possesses a coordination of three or less. These findings are not compatible with the structure of any similar complexes encountered up to now. The authors propose the two structures presented on Figure 7. On the basis of various considerations (for example, the visible spectrum of CuCl$_3^-$ is very similar to the spectrum of the CuAl$_2$Cl$_8$) they indicate a preference for the ring structure. However, the exact determination of the structure requires additional information and the joint application of several methods.
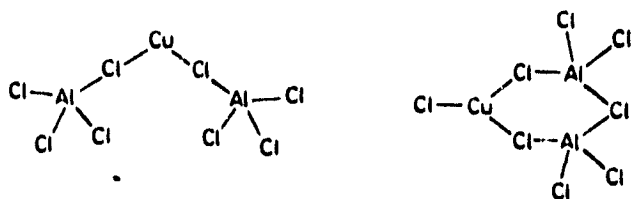

Figure 7. The possible structures of the gas-phase complexes of CuAl$_2$Cl$_8$ according to Emmenegger et al. [43].

## The HgCl$_2$-Al$_2$Cl$_6$ system

On the basis of vapor pressure measurements, Novikov and Kotova [44] found that complex molecules with the composition of AlHgCl$_5$ are present in the vapor phase of the HgCl$_2$-Al$_2$Cl$_6$ system, in addition to AlCl$_3$, Al$_2$Cl$_6$ and HgCl$_2$. They determined the partial pressures and the equilibrium coefficient as a function of the temperature.

The MCl_3-Al_2Cl_6 systems (M = Sb, Bi)

Kotova et al. determined the vapor pressure of the Al_2Cl_6-$BiCl_3$ system [45], and concluded, that in the gas phase, in addition to $AlCl_3$, $BiCl_3$ and Al_2Cl_6, complex molecules with a composition of $AlBiCl_6$ are also present. They determined the partial pressure of all four components of the gas, and the thermodynamic indicators of state of the:

$$AlBiCl_6 \rightarrow AlCl_3 + BiCl_3$$
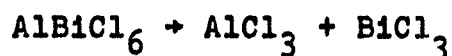
equilibrium.

Malkova found that the complex present in the vapor phase of the antimony-trichloride-aluminum trichloride system has a similar composition ($AlSbCl_6$) [46].

The iron chloride-aluminum chloride system

Szemenenko et al [47] used a mass-spectrometric method to study the vapor phase over the common melt of aluminum chloride and iron-(III) chloride. Other authors also studied this system, using analytical infrared spectroscopic and mass-spectroscopic methods [48]. In all of these studies it was found that complex chlorides, with a composition consisting predominantly of $FeAlCl_6$, are present in the vapor phase. The structure very probably is a bridged structure, similar to that of iron and aluminum chloride dimers as shown in Figure 8.

Figure 8. The assumed structure of $FeAlCl_6$ in the vapor phase [47].
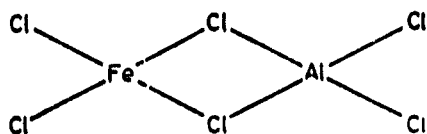
The substitution can easily be accepted, because the two metals have similar coordination properties, and in the crystal, their dichlorides have a similar laminar lattice structure, and it was proven experimentally that they can substitute each other. Their ionic radii are close to each other (r_{Al3+} = 0.57Å and

17

r_{Fe3+} = 0.67Å). The mass-spectroscopic examination of the mixed chlorides and of the individual pure chlorides (thus of Al_2Cl_6 and Fe_2Cl_6) revealed the production of very similar fragments; at the same time, to a slight extent, the presence of $FeAl_2Cl_9$, corresponding to the trimeric form was proven in the gas phase of mixed chlorides, just as with pure chlorides.

On the basis of the findings that in other systems the iron chloride acted as a stronger chlorine acceptor than aluminum chloride, Szemenenko et al. [47] assumed that in the mixed $FeAlCl_6$ chloride, the Fe-Cl bonds are shorter and the Al-Cl bonds are longer than in the pure dimeric molecules.

The mixed chloride created in the reaction of iron chloride and aluminum chloride is a very volatile compound, transporting the iron from the reaction zone already at 50°C. Identification of the production of these complexes is very important for many industrial processes.

The gallium chloride-aluminum chloride system

In the mass spectrometric examination of the vapor of the common melt of gallium chloride and aluminum chloride, Agafonov et al. found, in addition to the individual dimeric chlorides, significant amounts of mixed $GaAlCl_6$ chlorides [49]. The authors determined the heat of sublimation and of dissociation of both, the dimers and the mixed chloride.

The aluminum chloride complexes of beryllium

Szemenenko et al. have shown [50] that in the melt of beryllium chloride and aluminum chloride, a complex compound is formed, the properties of which differ only slightly from those of the Al_2Cl_6 melt. This is not surprising, because the two compounds behave very similarly in other respects, also. The composition of the vapor phase of the melt was determined by chemical [50] and mass spectrometric

methods [50, 51] yieldieng the conclusion that a complex with the composition of $BeAlCl_5$ is present; the two structures shown in Figure 9 were believed to be possible.
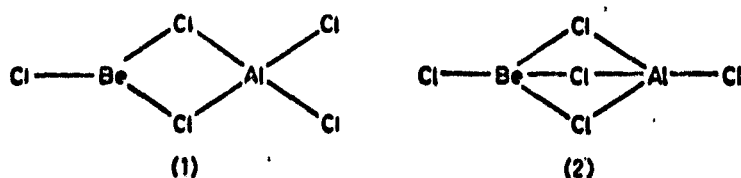

Figure 9. The possible structures of the $BeAlCl_5$ complex in the gas phase according to Szemenenko et al. [50].

According to the authors, the configuration containing three bridged chlorine atoms appears to be more probable, because it has a higher symmetry and the two metal atoms have an identical coordination, and on the other hand, the two tetrahedra forming the structure have a common plane, because of which the metal-metal distance may be expected to be very small. The authors believed that the structure containing two bridged chlorine atoms presents the advantage that in it, both of the metal atoms retain their original coordination, and the connection of the groups is favorable. Szemenenko et al. believed that this latter configuration is the more probable one [50].
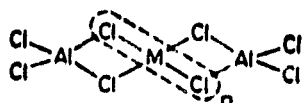

Figure 10. The possible structure of the more polymerized complexes encountered in the vapor phase of the $BeCl_2-Al_2Cl_6$ system, according to Szemenenko et al. [50] (n is the number of $BeCl_2$ units found in a single molecule of the complex)

The other complexes found in the system are: $BeAl_2Cl_8$, $Be_2Al_2Cl_{10}$ and $Be_3Al_2Cl_{12}$. The possible structure of these compounds is shown in Figure 10. The authors believe that this structure is more favorable, because the beryllium is not saturated coordinatively (in contrast to the beryllium atom in the first model of Figure 9), and at the same time, a close Be-Al bond, as in the second model of Figure 9, should not be taken into account.

The MCl_2-Al_2Cl_6 complexes (M = Pd, Ni and Pt)

In this study [52], Papatheodorou reports on the formation of
a dark-red colored gaseous complex, resulting from the reaction of
solid α-$PdCl_2$ and Al_2Cl_6 gas. On the basis of the visible and UV
absorption spectra and thermodynamic calculations, it was found that
the complex formed according to the reaction

$$PdCl_2(s) + Al_2Cl_6(g) . PdAl_2Cl_8(g)$$
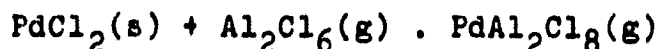
is present in the largest amount. On the basis of absorption spectra,
the structure shown in Figure 11, in which the palladium and chlorine
atoms have a tetragonal plane lattice, and the $PdCl_4$ square is
connected with two $AlCl_4$ tetrahedra along a joint edge each, was
proposed.

In view of his study of the aluminum-chloride complexes of metal
dichlorides, Dewing assumed that it can be concluded from the similar-
ity of the stability of MAl_2Cl_8 complexes, that the bivalent metal
bonds in the complex are very similar to the bonds in the solid metal
chloride. In the opinion of Papatheodorou, this observation applies
also to the complexes of palladium [52]. At the same time, in his
study of $NiAl_2Cl_8$, he concluded that in this complex, by connecting
the nickel atom with two $AlCl_4$ tetrahedral planes, an octahedral
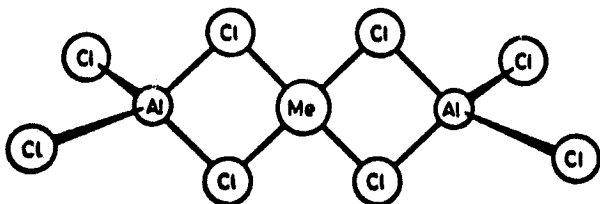arrangement is created [52].

Figure 11. The structure of the
$MeAl_2Cl_8$-type gaseous complexes
according to Papatheodorou [52]

On the basis of the
spectrophotometric investigation
of the volatile complex,
produced as a result of the
reaction of solid platinum(II)
chloride and aluminum chloride,
Papatheodorou [53] attributed
the composition of $PtAl_2Cl_8$,
with the structure shown in
Figure 11, to the complex.

According to the calculations of this author, based on the available
geometric data, the $AlCl_4$ tetrahedra and the $PtCl_4$ tetragonal plane

(the geometry) must be changed to an extent of less than 3%,
in order to enable the formation of the complex with the above-
mentioned structure from the solid halide Pt_6Cl_{12} and the gaseous
Al_2Cl_6. The stability of the complex is similar to that of the
corresponding palladium complex, which implies that the type of bond
and the local coordination around the transition metal atom is not
substantially affected during the transformation into the gaseous
complex from the solid state.

The $NdCl_3$-Al_2Cl_6 gas-phase system

Øye and Gruen [54,55] studied the vapor pressure of the neodymium
chloride and aluminum chloride system at various aluminum chloride
vapor pressures in the 500-900K temperature range. They found that,
under certain conditions, the observed sudden increase in the vapor
pressure was due to the creation of strongly volatile complex
compounds. The following equations give information about the
composition of the complexes:

$$NdCl_3(s) + 1.5 \ Al_2Cl_6(g) = NdAl_3Cl_{12}(g)$$

$$NdCl_3(s) + 2Al_2Cl_6(g) = NdAl_4Cl_{15}(g)$$
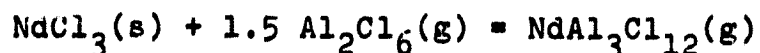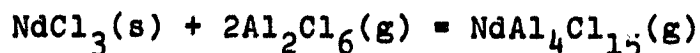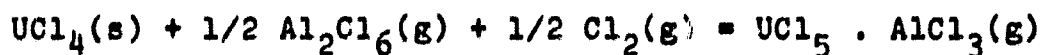
The aluminum-chloride complexes of uranium chloride

Uranium tetrachloride forms a volatile complex with aluminum
chloride, as proven by the spectrophotometric experiments of Gruen
and Mcbeth [56, 57]. On the basis of the calculated partial pressure
data, they found that at 650K, the vapor pressure of the complex
is about 10^4 times larger than that of UCl_4. This ratio is decreased
with increasing temperature, because the heat of sublimation of
$UCl_4(s)$ is higher than the heat of formation of the complex. In the
presence of 1 atm. of Al_2Cl_6 at 600K the vapor pressure of the
complex is 0.4 Hg mm, which means that the UCl_4 may be transported
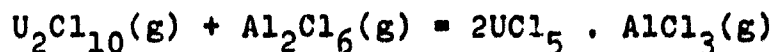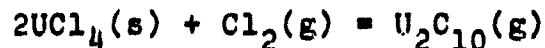at relatively lower temperatures, using aluminum chloride as carrier
gas.

Although the structure of the complex cannot be determined un-
equivocally from the spectra, according to the author's, it may
be assumed that two $AlCl_4$ tetrahedra are connected to the uranium
atom.

Gruenn and Mcbeth also examined the complex of uranium penta-
chloride with aluminum chloride [57]. The formation of the complex
may be described by the following reaction:

$$UCl_4(s) + 1/2\ Al_2Cl_6(g) + 1/2\ Cl_2(g) = UCl_5 \cdot AlCl_3(g)$$

or

$$2UCl_4(s) + Cl_2(g) = U_2C_{10}(g)$$

$$U_2Cl_{10}(g) + Al_2Cl_6(g) = 2UCl_5 \cdot AlCl_3(g)$$

because in the gaseous state the uranium pentachloride is present
in the form of a dimer at the lower temperature. The similarity of
the absorption spectra of U_2Cl_{10} and $CUl_5 \cdot AlCl_3$ allows the conclusion
that in this complex, the uranium atom has an octahedral coordination,
like the dimer. This can be conceived in such a way that the UCl_6
octahedron is connected along an edge with the $AlCl_4$.

The aluminum-chloride complexes of the chlorides of lanthanide elements

Zvarova and Zvara [158] observed that the chlorides of lanthanide
elements form very volatile complexes with aluminum chloride, making
it possible to separate the elements by gas chromatography (gas-solid
chromatography). The authors attributed the great increase in the
volatility of the lanthanide chlorides to the formation of a complex
compound characterized by the summary formula of $LaAlCl_6$.

They investigated the following rare-earth metals:

Ce, Pr, Pm, Gd, Tb, Dy, Tm, Yb, Lu.

At a partial pressure of about 100 mm Hg of Al_2Cl_6, the above-mentioned /506

lanthanides form volatile complexes, which may be transported at
temperatures between 150-500°C. In order to prevent a dissociation
of the complex, they have mixed an inert gas together with aluminum
chloride, using the two together as the carrier gas. Zvarova and
Zvara [58] studied in great detail the correlation between the
characteristics of the gas-chromatographic separation and various
experimental conditions. The method that they developed achieved
a highly efficient separation of adjoining lanthanides.

Summary remarks

On the basis of both parts of the present summary review,
(including the first article)[1] I am summarizing the data concerning
the molecular form and molecular parameters, as follows:

In the molten aluminum chloride complexes, the composition is
greatly dependent on the aluminum chloride concentration, i.e., on
the acidity of the solution. At an aluminum chloride content of
100%, dimeric Al_2Cl_6 molecules are present, consisting of two $AlCl_4$
tetrahedra, connected along a joint edge. As the aluminum chloride
concentration is decreased, primarily $Al_2Cl_7^-$ ions are present.
They consist of two $AlCl_4$ tetrahedra, connected with each other
through a joint peak. The Al-Cl-Al bridge is linear and the two
$AlCl_3$ terminal groups have an open structure. However, the possibility
of free rotation cannot be excluded [26]. At an aluminum chloride
concentration of 50% in the melt, $AlCl_4^-$, the tetrachloro-aluminate
ion is the prevailing ionic form. Depending on the surrounding
ions, its structure is a regular or a slightly distorted tetrahedron.

In the crystalline phase the $AlCl_4^-$ ion has a regular tetrahedral
symmetry (e.g., [2], [59]), which, however, may be slightly distorted
under the influence of its environment.

In contrast with the linear bridge assumed in the case of the

---

[1] At this place, I am emphasizing only a few of the most important
references, but in the detailed discussion, all the source works
are indicated.

melts, in both studies on the crystal phase structure of the $Al_2Cl_7^-$ ion, a bent Al-Cl-Al bridge was detected. However, while in the case of the $Te_4(Al_2Cl_7)_2$ complex, the two terminal groups of $AlCl_3$ have an open structure [31], in the $(Pd(Al_2Cl_7C_6H_6))_2$ complex a covered position was found [30]. The appearance of this energetically less favorable conformation must be attributed to the forces acting within the crystal.
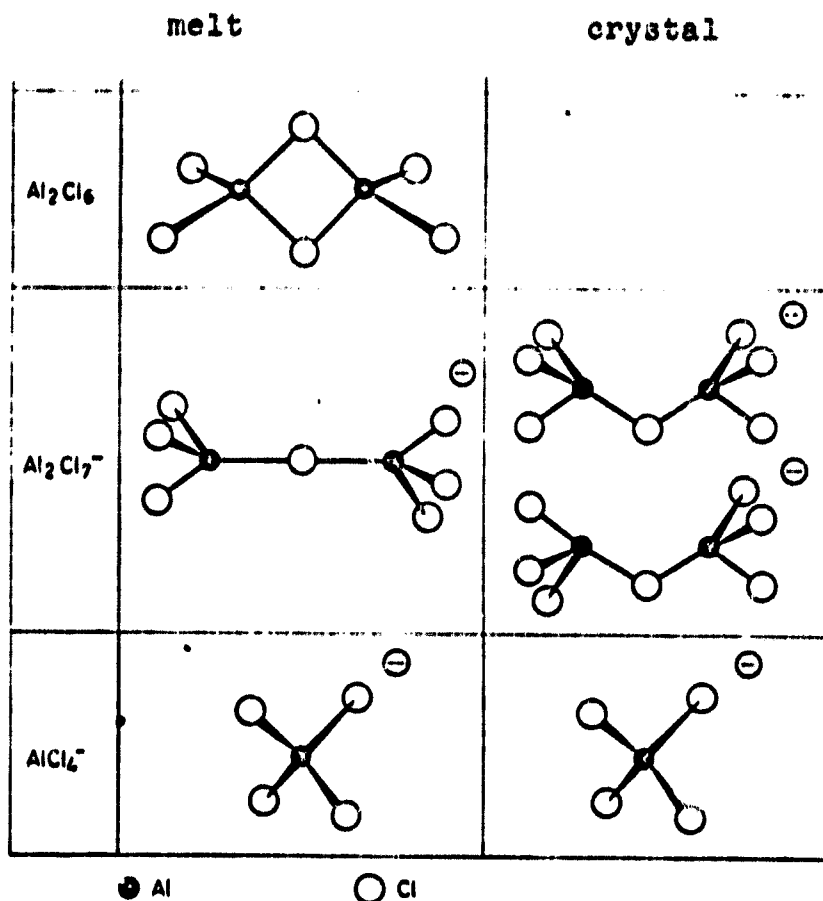
melt   crystal

Figure 12. The anionic structures in the condensed-phase aluminum-chloride complexes (and for the sake of comparison, the structure of the molten Al_2Cl_6).

Figure 12 presents the anionic structure in the condensed phase aluminum chloride complexes. It is of interest to examine the change

in the lengths of the Al-Cl bonds, as we progress from the dimeric molecule containing two-bridge chlorine atoms, through the single chlorine-bridge $Al_2Cl_7^-$ anion,toward the $AlCl_4^-$ ion. Unfortunately, we have only few data available on this subject, I am summarizing them in Table 4, together with some of the results of the gas-phase studies.

Disregarding the phase differences in the studies, we can draw the following conclusions for the Al-Cl bonds on the basis of Table 4 and Figure 12. Basically, there are three different Al-Cl bonds: terminal, tetrahedral and bridged. The monomeric bond length of aluminum chloride and the terminal bond length of the aluminum chloride dimer are practically identical, and we may also include here the terminal bonds of the $AlCl_7^-$ ion (although they represent a transition toward the tetrahedral distances). Their average value is 2.08 Å. In the compounds containing $AlCl_4^-$ tetrahedra, regardless of their state,the average values of the Al-Cl distances are nearly identical, on average 2.14 Å. Finally, the average lengths of dimeric aluminum chloride and of the bridged bonds $Al_2Cl_7^-$ ion are 2.26 Å.

The length of the terminal Al-Cl bonds increases gradually, as we pass from the aluminum chloride dimer containing 2 bridged chlorine atoms, through the 1 chlorine-bridge $Al_2Cl_7^-$ ion to the $AlCl_4^-$ ion (on the average: Al_2Cl_6: 2.06 Å; $Al_2Cl_7^-$: 2.10 Å and $AlCl_4^-$: 2.41 Å).

Thanks to the great interest in the volatile metal chloride-aluminum chloride complexes, practically all metals of the periodic system are known to form strongly volatile complexes with aluminum chloride. This is illustrated in Table 5, based on the summarizing study of Schäfer [64].

In their study on the thermodynamic indicators of the gas-phase complex halides and of their formation processes, Novikov

Table 4.
The length of the Al-Cl bonds in various compounds.

melt	r(Al-Cl),Å			phase	reference
	terminal	tetra-hedral	bridged		
AlCl₃	2,06±0,01			gas	[60]
Al₂Cl₆	2,065±0,002 2,06		2,252±0,001 2,34	gas liquid	[61] [62]
Al₂Cl₇⁻				solid	
Te₄(Al₂Cl₇)₂ [Pd(Al₂Cl₇C₆H₆)]₂	2,102 2,09		2,242 2,21	solid solid	[31] [30]
AlCl₄⁻				gas	
KAlCl₄ NaAlCl₄ Co(AlCl₄)₂ Te₄(AlCl₄)₂ Se₈(AlCl₄)₂ [Pd(AlCl₄C₄H₆)]₂		2,16 2,13 2,154 2,12 2,13 2,13		solid solid solid solid solid	[4] [2] [59] [31] [63] [30]
Átlagérték	2,08	2,14	2,26		

Table 5.
Listing of the metals which form volatile complexes with aluminum chloride (§) (The asterisk * is used to designate the elements, the condensed-phase aluminum-chloride complexes which are discussed in this study).

Li § *	Be § *											B	C	N	O	F	Ne
Na § *	Mg § *											Al §	Si	P	S	Cl	Ar
K § *	Ca § *	Sc	Ti *	V *	Cr § *	Mn § *	Fe § *	Co § *	Ni § *	Cu § *	Zn §	Ga § *	Ge	As	Se *	Br	Kr
Rb §	Sr *	Y §	Zr	Nb	Mo §	Tc	Ru §	Rh §	Pd § *	Ag §	Cd § *	In *	Sn *	Sb §	Te *	I	Xe
Cs § *	Ba § *	La §	Hf	Ta	W	Re	Os	Ir §	Pt §	Au §	Hg §	Tl *	Pb *	Bi § *	Po	At	Rn

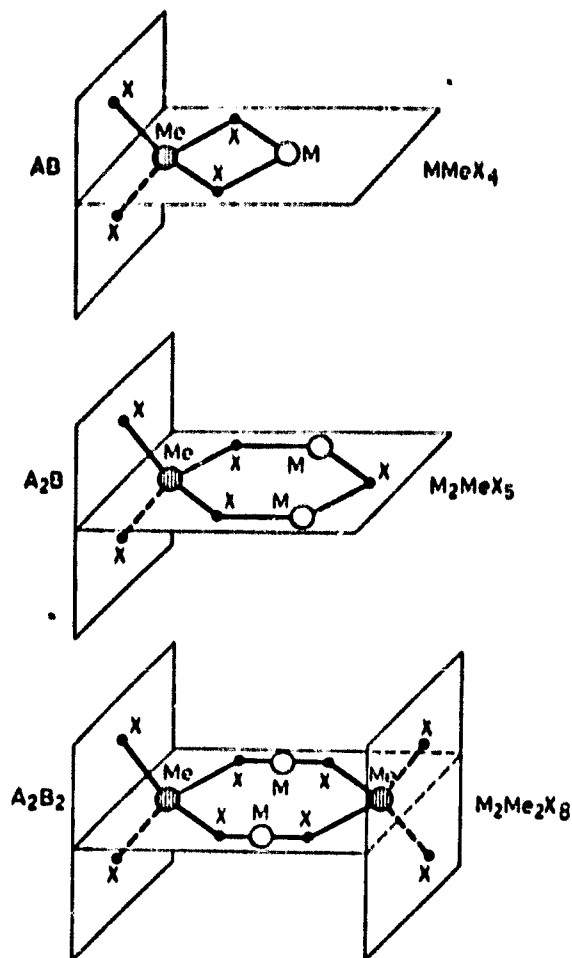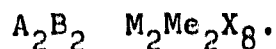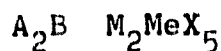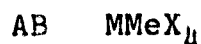| Ce §	Pr §	Nd §	Fm §	Sm	Eu	Gd §	Tb §	Dy §	Ho	Er	Tm §	Yb §	Lu §	
Th §	Pa	U § *	Np	Pu	Am									

Figure 13. The molecular configuration of the mixed complexes of M X and Me^{III}X$_3$-type halides, according to Solc and Sidorov [66].
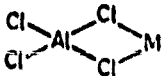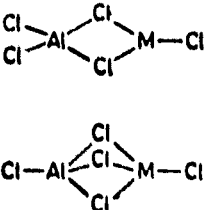
and Gavryuchenkov [65] found that, as a general rule, those halides form gas phase, easily volatilized complexes, which by themselves and in the gas phase tend to dimerize, and the complex compounds of which, with other halides, are more stable with respect to dissociation than their corresponding pure dimers.

Solc and Sidorov examined [66] the structure of mixed-metal fluorides and we believe that their general conclusions are applicable also to the chlorides. According to their detailed mass-spectrometric investigation, the following types of complex halides occur most frequently in the vapor phase (considering only the common complexes of alkali metals and trivalent metals): their designation is:
A = M^{I}X and B = Me^{III}X$_3$

AB   MMeX$_4$

A$_2$B   M$_2$MeX$_5$

A$_2$B$_2$ M$_2$Me$_2$X$_8$.

Up to now, the molecular geometry in the gas phase was determined only in the case of the AB type compounds, including only one chlorine derivative, the potassium (tetrachloroaluminate) [4]. However, on the basis of analogy with the AB type compounds, and of

27

spectroscopic examinations, Solc and Sidorov assume [66] that the configuration presented in Figure 13 prevails in the A_2B and A_2B_2 type compounds.

The molecular shape of the complex halide in the gas phase was determined (in some cases, only assumed), on the basis of the above cited, mostly spectroscopic studies. This is summarized below:

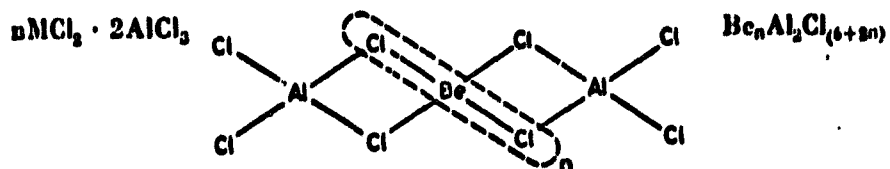| Type of complex	The actually determined, or assumed co-ordination around M	Examples
$MCl \cdot AlCl_3$		$alk.Cl \cdot AlCl_3$ (alk.$=$Li, Na, K, Rb, Cs)
$mMCl \cdot nAlCl_3$	4,6,8-member rings containing the $-Cl-M-Cl-Al-$ chain	$mCuCl \cdot nAlCl_3$ (?) $m = 1-3$, $n = 1-2$
$MCl_2 \cdot AlCl_3$		$BeAlCl_3$ (?) $HgAlCl_3$

Type of complex	The actually determined, or assumed coordination around M	Examples	

$MCl_2 \cdot AlCl_3$ — Arrangement around M

$PdAl_2Cl_8$
$PtAl_2Cl_8$

tetragonal

$BeAl_2Cl_8$
$CoAl_2Cl_8$ (?)

tetrahedral

$NiAl_2Cl_8$
$CrAl_2Cl_8$
$CoAl_2Cl_8$ (?)

octahedral

$CuAl_2Cl_8$ (?)

bent

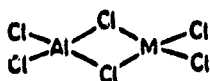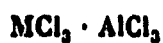$CuAl_2Cl_8$ (?)

trigonal, ring type

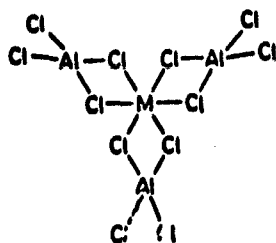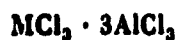| Type of complex	The actually determined or assumed coordination around M	Examples
$nMCl_2 \cdot 2AlCl_3$	tetrahedral	$Be_nAl_2Cl_{(6+2n)}$
$MCl_3 \cdot AlCl_3$	tetrahedral	$FeAlCl_6$ $GaAlCl_6$
$MCl_3 \cdot 3AlCl_3$	octahedral	$CrAl_3Cl_{12}$ $NdAl_3Cl_{12}$
$MCl_4 \cdot 2AlCl_3$	octahedral	UAl_2Cl_{10}
$MCl_5 \cdot AlCl_3$	octahedral	$UAlCl_8$ (?)

Expression of thanks

30
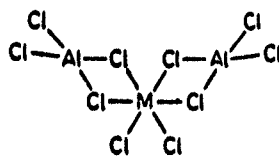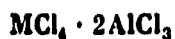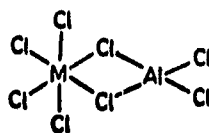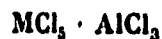
References

1. Hargittai, M., "Condensed phase systems," *Kemiai Kolemenyek 50*, 371 (1978).

2. Baenziger, N.C., *Acta Cryst.* $\underline{4}$, 216 (1951).

3. Pauling, L., *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960.

4. Spiridonov, V. P., Erokhin, E.V., Lutoskin, B.I., *Veszt. MGU Szer. khim.*, 296 (1971).

5. Grothe, H., *Z. electrochem. allg. Chem.*, $\underline{54}$, 216 (1950).

6. Morozov, I. Sz., Toptyigin, D.Ja., *Izv. AN SSSR*, 1920 (1959).

7. Morozov, A.I., Morozov,I.S.,*Zsurn. neorg. khim.* $\underline{18}$,989 (1973).

8. Lide, D.R.Jr., Cahill,P.,Gold, L.P., *J.Chem. Phys.* $\underline{40}$,156 (1964).

9. Spiridonov, V.P.,Erokhim, E.V., *Zsurn. neorg. khim.* $\underline{14}$,636 (1969).

10. Spiridonov, V.P., Brezgin, Ju.A.,Sakhparonov, M.I., *Zsurn. strukt. khim.* $\underline{12}$,1080 (1971).

11. Spiridonov, V.P., Brezgin, Ju.A., Sakhparanov, M.I., *Zsurn. strukt. khim.* $\underline{13}$,320 (1972).

12. Spiridonov, V.P., *Kemiai Kozlemenyek* $\underline{37}$,399 (1972).

13. Gerding, H., Houtgraaf, H., *Rec. trav. chim.* $\underline{72}$,21 (1953).

14. Corbett, J.D., *Inorg. Chem.* $\underline{I}$,700 (1962).

15. Moore, R.H., Morrey, J.R., Voiland, E.E., *J. Phys. Chem.* $\underline{67}$,744 (1963).

16. Morrey, J.R., Moore, R.H., *J. Phys. Chem.* $\underline{67}$,748 (1963).

17. Carlson, G.L., *Spectrochim. Acta.* $\underline{19}$,1291 (1963).

18. Øye, H.A., Gruen, D.M., *Inorg. Chem.* $\underline{3}$,836 (1964).

19. Balasubrahmanyam, K,m Nanis, L., *J.Chem. Phys.* $\underline{42}$,676 (1965).

20. Øye, H.A., Gruen, D.M.,*Inorg. Chem.* $\underline{4}$,1173 (1965).

21. Tremillon, B., Letisse, G, *J. Electroanal. Chem.* $\underline{17}$,371 (1968).

22. Boston, C.R., Grantham, L.F., Yosim, S.J., _J. Electrochem. Soc_. 117, 28 (1970).

23. Torsi, G., Mamantov, G., Begun, G.M., _Inorg. Nucl. Chem. Lett_. 6, 553 (1970).

24. Cyvin, S.J., Klaeboe, P., Rytter, E., Øye, H.A., _J. Chem. Phys_. 52, 2776 (1970).

25. Øye, H.A., Rytter, E., Klaeroe, P., Cyvin, S.J., _Acta Chem. Scand_. 25, 559 (1971).

26. Rytter, E., Øye, H.A., Cyvin, S.J., Cyvin, B.N., Klaeboe, P., _J. Inorg. Nucl. Chem_. 35, 1185 (1973).

27. Persina, E.V., Raszkin, S.S., _Optika i szpektr_. 13, 488 (1962).

28. Bredig, M., "The Experimental Evidence for 'Complex Ions' in Some Molten Salt Mixtures," In Mamantov, G., _Analysis and Characteristics in Molten Salts_, Dekker, New York, 1969.

29. Müller, A., Krebs, B., _J.Mol. Spectr_. 24, 180 (1967).

30. Allegra, G., Casagrande, G.T., Immirzi, A., Porri, L., Vitulli, G., _J. Am. Chem. Soc_. 92, 289 (1970).

31. Couck. T.W., Lokken, D.A., Corbett, J.D., _Inorg. Chem_. II, 357 (1972).

32. Moss, R.H., Thesis, University of Connecticut, 1955, Yamaguti, Y., Sisido, S., _J. Chem. Soc, Japan_ 62, 301 (1941).

33. Dewing, E.W., _J. Am. Chem. Soc_, 77, 2639 (1955).

34. Dewing, E.W., _Nature_ 214, 483 (1967).

35. Dewing, E.W., _Metallurgical Trans_. I, 2169 (1970).

36. Papatheodorou, G.N., _Z. anorg. allg. Chem_. 411, 153 (1975).

37. Dell'Anna, A., Emmenegger, F.P., _Helv. Chim. Acta_ 58, 1145 (1973).

38. Schäfer, H., Binnwies, M., Domke, W., Karbinski, J., _Z anorg. allg. Chem_. 403, 116 (1974).

39. Schäfer, H., Trenkel, M., _Z anorg. allg. Chem_ 414, 137 (1975).

40. Lascelles, K., Shelton, R.A.J., Schäfer, H., _J. Less-Common Metals_ 29, 109 (1972).

41. Aits, M., Schäfer, H., _Z. anorg. allg. Chem._ 408,37 (1974)

42. Binnewies, M.,Schäfer, H., _Z. anorg. allg. Chem._ 407,327 (1974).

43. Emmenegger, F. P., Rohrbasser, C., Schlapfer, C.W., _Inorg. Nucl. Chem. Lett._ 12,127 (1976).

44. Novikov, G.I.,Kotova, E., _Sz. Zsurn. fix. khim._ 47,483 (1973).

45. Kotova, E.S., Kuzmenko, A.L., Novikov, G.I., _Zurn fiz. khim._ 46, 2960 (1972).

46. Malkova, A.S., Candidate's dissertation, Moscow, 1969.

47. Szemenenko, K.N., Naumova, T.N., Gorokhov, L.N., Semenova, G.A., Novoselova, A.F., _Dokl. AN SSSR_ 154, 169 (1964).

48. Fowler, R.M., Melford, S.S., _Inorg. Chem._ 15,473 (1976).

49. Agafonov, I.L., Nyikolaeva, L.G., Agiunov, N.H.,_Zsurn. fiz. khim._ 48, 1065 (1974).

50. Szemenenko, K.N., Naumova, T.N., Gorokhov, L.N., Novoselova, A.V., _Dokl. AN SSSR_ 154, 648 (1964).

51. Rabeneck, H., Schäfer, H., _Z. anorg. allg. Chem._ 395,69 (1973).

52. Papatheodorou, G.N., _J. Phys. Chem._ 77,472 (1973).

53. Papatheodorou, G.N., _Inorg. Chem._ 12,1899 (1973).

54. Gruen, D.M. Øye, H.A., _Inorg. Nucl. Chem. Lett._ 3,453 (1967).

55. Øye, H.A., Gruen, D.M., _J. Am. Chem. Soc._ 91,2229 (1969).

56. Gruen, D.M., Mcbeth, R.L., _Inorg. Nucl. Chem. Lett._ 4,299 (1968).

57. Gruen, D.M., Mcbeth, R.L., _Inorg. Chem._ 8,2625 (1969).

58. Zvarova, T.S. Zvara, I., _J. Cromatogr._ 44,604 (1969).

59. Ibers, J.A., _Acta Cryst._ 15,967 (1962).

60. Zasorin, E.Z., Rambidi, N.G., _Zsurn. sztrukt. khim._ 8,391 (1967).

61. Shen, Q.,Dissertation, Oregon State University, Corvallis, Oregon 1973.

62. Harris, R.L., Wood, R.E., Ritter, H.L., _J. Am. Chem. Soc._ 73, 3151 (1951).

63. McMullan, R.K., Prince, D.J., Corbett, J.D., _Inorg. Chem._ 10, 1749 (1971).

64. Schäfer, H., _Z. anorg. allg. Chem._ 414,151 (1975).

65. Novikov, G.I., Gavryuchenkov, F.G., _Uszpekhi khim._ 36,399 (1967).

66. Solc., V.B., Sidorov, L.N., _Vest.MGU Szer. khim._ 13,371 (1972).