Raman and NMR Studies in the System Phosphoryl Chloride – Aluminium Chloride

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The system POCl₃–AlCl₃ was investigated by measuring the Raman and NMR spectra (²⁷Al, ³¹P) as a function of the mole fraction of AlCl₃ in POCl₃. In the liquid state at temperatures below 200°C the observed Raman bands could be assigned to species POCl₃ and POCl₃·AlCl₃ in the POCl₃-rich region, and to POCl₃·AlCl₃, (POCl₃)₂(AlCl₃)₂ and Al₃Cl₆ in the AlCl₃-rich region. Raman and NMR spectra gave no evidence of the existence of any other kind of species in the molten binary system at ca. 160–195°C. The POCl₃·AlCl₃ adduct is stable in the gas phase. In the solid state at room temperature, the compounds (POCl₃)₂(AlCl₃)₂ and (POCl₃)₃(AlCl₃)₃ were identified spectroscopically as [Al(POCl₃)₂][AlCl₄]. The solid (POCl₃)·(AlCl₃) compound seems, from an interpretation of the Raman and NMR spectra, to exist as [Al(POCl₃)₂][AlCl₄].

Aluminium chloride, AlCl₃ or Al₂Cl₆ (I), being a Lewis acid, undergoes complex formation with POCl₃ (II). The system POCl₃–AlCl₃ is complicated and has been the subject of only a few investigations. Gutmann et al. measured the conductivity of POCl₃ solutions containing AlCl₃ in various amounts and discussed several equations describing the dissociation of this compound in the solvent. POCl₃ has a very small self-dissociation, and also the chloride ion-exchange reaction (1) in POCl₃ is weak

POCl₃ + AlCl₃ ⇌ [POCl₂]⁺ + [AlCl₄]⁻  

(1)

(α = 0.04 at 25°C). Solutions of AlCl₃ in POCl₃ solutions exhibit high conductivity, perhaps due to ions such as [AlCl₄(POCl₃)₂]⁺ (III) and [AlCl₄]⁻. The POCl₃–AlCl₃ phase diagram indicates two compounds, melting at ca. 187 and 165°C, at compositions corresponding to POCl₃·AlCl₃ and (POCl₃)₂(AlCl₃) or perhaps (POCl₃)₃(AlCl₃)₂. X-Ray powder diagrams demonstrated that POCl₃·AlCl₃ and (POCl₃)₂(AlCl₃)₂ are the only distinct chemical compounds occurring in the system. Analogous compounds are formed in the binary POCl₃–GaCl₃ system. The densities and liquid–vapor equilibria of POCl₃–AlCl₃ mixtures have been studied with emphasis on the stability in the vapor phase of the POCl₃·AlCl₃ (IV) molecules, formed by reaction (2).

POCl₃ + AlCl₃ → POCl₃·AlCl₃

(2)

Brockner et al. investigated vapor pressures in Al₂Cl₆–rich mixtures and found evidence for the formation of complexes [most notably Al₂Cl₆·POCl₃·AlCl₃ and (POCl₃)(AlCl₃)₂ (V)] in the liquid state. For the

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POCl$_3$·AlCl$_3$ addition compound in the molten state, some structural information is available: the complex cannot consist of ions [POCl$_3$]$_2$$^+$ and [AlCl$_4$]$^-$; instead it might have a bent oxygen-bridged structure (IV). This conclusion was reached by Gerdig et al. from the Raman spectrum of the 1:1 liquid mixture at 210°C and the IR spectrum of the solid in KBr. However, the POCl$_3$·AlCl$_3$ structure does not explain the high conductivity. Wartenberg and Goubeau arrived at the same structure (IV), interpreting IR and Raman spectra of several analogous addition compounds in the solid state. A mass-spectrometric investigation on the vapor above AlCl$_3$·POCl$_3$ melts indicated a high thermodynamic stability of the 1:1 compound in the gas phase, as also pointed out by Suvorov. Heat evolution associated with compound formation in dilute solutions of AlCl$_3$ in POCl$_3$ at room temperature was studied by calorimetry. Interestingly, non-radioactive POCl$_3$ could be drawn from a solution of $^{35}$Cl-substituted AlCl$_3$ in non-radioactive POCl$_3$, proving the absence of radiochloride exchange in the solution. This important observation eliminates the formation of [POCl$_3$]$^+$ [AlCl$_4$]$^-$ via reaction (1). Finally, $^{27}$Al NMR measurements provided proof of the existence of [AlCl$_4$]$^-$ and [Al(POCl$_3$)$_2$]$^+$ ions, (VII), in a dilute solution. Also, jelly-like or crystalline samples of composition AlCl$_3$·6(POCl$_3$) have been prepared.

In total, many structural suggestions have been given for compound formation in the system POCl$_3$·AlCl$_3$, most of them derived by indirect methods: The solid or molten compounds POCl$_3$·AlCl$_3$: (IV); (POCl$_3$)$_2$AlCl$_3$ (V); (POCl$_3$)$_2$AlCl$_4$ (VI); [Al(POCl$_3$)$_2$]$_3^+$ (VIII); [Al(POCl$_3$)$_4$]$_3^+$ (IX); [Al(POCl$_3$)$_6$]$_3^+$ (X) in solution. However, there has been no systematic structural investigation in the solid or liquid state covering the whole composition range. Such a study is attempted here, based on the direct methods of Raman and NMR spectroscopy. In this way, a more detailed view of the structures of the binary system is obtained.

**Experimental**

**Preparation of samples.** Owing to the moisture sensitivity of the reagents, dry-box and vacuum-line techniques were employed. POCl$_3$ was purified as described in Ref. 18. AlCl$_3$ of the highest attainable purity was used. All samples were prepared by weighing the salt (accuracy ±1 mg) as well as POCl$_3$ (accuracy ±10 mg) in the Raman and NMR tubes. After sealing the tubes under vacuum they were heated to 200°C. This resulted in the formation of a homogeneous melt in the tubes. The gas/liquid volume ratios in experimental cells were such that less than 2% of the POCl$_3$ evaporated (in the worst case, except for gas-phase cells). All samples were colourless. The composition of samples is specified by mole fractions $x$(AlCl$_3$), based on the molar amounts of AlCl$_3$ and POCl$_3$.

**The Raman spectra** of samples in sealed square Pyrex cells were measured by using filtered 514.5 nm argon-ion laser radiation and a JEOL-JRS-400D spectrometer. An accurately regulated four-window furnace was used for heating the samples to 195°C. Signals were detected with a cooled extended S-20 PM-tube and a photon-counting system. The spectra were digitized every 1 or 2 cm$^{-1}$, and the data were stored in a personal computer for further treatment. The excitation power was below 500 mW and the resolution was ca. 2 cm$^{-1}$ in all measurements. In the laser beam the samples tended to emit a strong fluorescence if not prepared with the highest cleanliness. The fluorescence could be reduced by repeated recrystallization of the samples, but some fluorescence background was inevitably present. Raman spectra of solid samples were obtained from several different sampling spots. The polycrystalline nature of the solids precluded polarization measurements, and the spectra were recorded in the depolarized mode ($\parallel$) and averaged to obtain better signal-to-noise ratios.
High-resolution NMR measurements were carried out on a multinuclei Bruker AM 250 spectrometer, operating at 5.875 T with the pulse Fourier-transform technique. The following resonance frequencies apply: $^{27}$Al = 65.17 MHz and $^{31}$P = 101.26 MHz. Chemical shifts are reported relative to external capillary references (standards) consisting of aqueous $\text{[Al(H}_2\text{O)}_6]\text{Cl}_3$ and 85 wt% $\text{H}_3\text{PO}_4$ aqueous solutions, respectively. Positive shifts indicate signals on the low-field side of the references. Samples were filled and sealed into NMR tubes of 10 mm diameter also containing, as a lock, deuterodimethyl sulfoxide, (CD$_3$)$_2$SO (in a closed capillary).

NMR spectra were recorded at 27 and 160°C, the high-temperature limit being caused by the NMR equipment. Because not all samples were liquid at 27 or 160°C, the linewidths of the different NMR spectra should be compared only with caution (footnotes in Table 2 indicate the state of the samples).

Because an external standard was used, line positions will be sensitive to variations in the magnetic susceptibility of the samples. We did not correct the line positions for this effect, which would influence $^{27}$Al and $^{31}$P identically.

Results and discussion

High-temperature Raman spectra of liquids (195°C).

Raman spectra of the compounds POCl$_3$,$^{21-23}$ and AlCl$_3$,$^{24-26}$ are known and well understood. The molecule POCl$_3$ (I) takes on $C_3$ symmetry in the gas phase according to electron diffraction studies$^{27}$ and gas-phase Raman spectra.$^{28}$ The vibrational spectra of POCl$_3$ have been obtained for all phases and assigned several times, see e.g. Refs. 7, 21-23 and 29 (although Ref. 29 should not have been published). The molecule Al$_2$Cl$_6$ (II) has $D_{2h}$ symmetry in the fluid phases; its spectra have also been measured many times, and their interpretation is clear.$^{24-26}$ Appropriate assignments are included in Table 1.

For POCl$_3$–AlCl$_3$ mixtures, however, less information has been reported.$^{2,12}$ Although our Raman spectroscopic results comprise bands at frequencies agreeing well with the previous results, new bands were clearly detectable. The results are summarized in Table 1.

POCl$_3$-rich concentration range. Raman spectra of POCl$_3$–AlCl$_3$ mixtures with molar ratio $x$(AlCl$_3$) ≤ 0.5 are shown in Fig. 1. New bands (due neither to POCl$_3$ nor Al$_2$Cl$_6$) can be observed with the following wavenumbers: 116, 133, 169, 209, 245, 324, 392, 442, 525, 575 and 645 cm$^{-1}$ (indicated by solid vertical lines in Fig. 1). Starting from pure POCl$_3$, the relative intensities of these bands increase with increasing AlCl$_3$ content and achieve their maximum values at $x$(AlCl$_3$) ≈ 0.5. At the same time, bands due to POCl$_3$ become progressively smaller and finally disappear. In the range of P = O bond-stretching vibrations a new band is observed at 1209 cm$^{-1}$; the original band at 1300 cm$^{-1}$ for the pure POCl$_3$ molecular liquid disappears totally in the spectrum of the equimolar mixture. In general, it has been found that the P = O stretching frequency in POCl$_3$ adducts drops as a result of coordination, in some cases by nearly 100 cm$^{-1}$.7,30-32 Apart from the weak band at 484 cm$^{-1}$ [probably due to a small excess of free POCl$_3$ in the spectrum for $x$(AlCl$_3$) = 0.492], the upper spectrum in Fig. 1 seems to show only vibrational bands due to the presence of the presumed POCl$_3$–AlCl$_3$ complex (IV) in the melt. By subtraction of the POCl$_3$ spectrum, scaled in such a way that the band at 484 cm$^{-1}$ just disappears from the upper

Fig. 1. Polarized Raman spectra for POCl$_3$–AlCl$_3$ mixtures with $x$(AlCl$_3$) ≤ 0.5 at 195°C. (Solid vertical lines indicate bands not due to POCl$_3$ or Al$_2$Cl$_6$).

Fig. 2. Polarized and depolarized Raman spectra of pure POCl$_3$–AlCl$_3$ at 195°C, calculated from spectra of $x = 0.492$ and $x = 0.0$. 

346
<table>
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<tr>
<th>'1 : 0'</th>
<th>'2 : 1' or '3 : 2'</th>
<th>'1 : 1'</th>
<th>'1 : 2'</th>
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<td>(\text{POCl}_3) Liquid</td>
<td>(\text{[Al(POCl}_3\text{)]}_3\text{[AlCl}_4\text{]}_3)</td>
<td>(\text{POCl}_3\cdot\text{AlCl}_3) (x = 0.492) Liquid</td>
<td>(\text{POCl}_3\cdot\text{AlCl}_3) Gas</td>
<td>(\text{POCl}_3\cdot\text{AlCl}_3) Melt</td>
<td>(\text{POCl}_3\cdot\text{AlCl}_3\cdot\text{AlCl}_4) Melt</td>
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<td>195°C, Ref. 9</td>
<td>210°C, Ref. 12</td>
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<td>Fig. 1</td>
<td>Fig. 9</td>
<td>Fig. 1</td>
<td>Fig. 8</td>
<td>Figs. 5 and 6</td>
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<td>1300 (w,p)</td>
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<td>(~637) (3,br)</td>
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* Intensity codes: s = strong, m = medium, w = weak, br = broad, p = polarized, dp = depolarized. Average frequency precision is ±3 cm⁻¹. * More prominent at e.g. 150°C. [ ] Band probably due to \(\text{POCl}_3\).
spectrum in Fig. 1, a spectrum of the POCl₃·AlCl₃ complex can be artificially obtained (Fig. 2). This spectrum still contains a weak shoulder at 345 cm⁻¹, which accordingly cannot be due to POCl₃. It is probably due to minute traces of the [AlCl₄]⁻ ion, which has a strong polarized band at ca. 345 cm⁻¹ and which might be formed in small quantities by virtue of reaction (3) being slightly shifted from the left. It cannot be due to chloride exchange, reaction (4), because of the lack of radioclimate exchange.¹⁰ The weakness of the 345 cm⁻¹ band,

\[ 4 \text{POCl}_3 \cdot \text{AlCl}_3 \rightleftharpoons [\text{POCl}_3]^{+} + 3 [\text{AlCl}_4]^- \quad (3) \]

if it is due to [AlCl₄]⁻ at all, clearly disproves that the 1:1 melt should contain major quantities of [POCl₃][AlCl₄]. [AlCl₄(POCl₃)₂][AlCl₄], [AlCl₄(POCl₃)], [AlCl₄(POCl₃)₂][AlCl₄], or [Al(POCl₃)][AlCl₄]₂ (all of which are formally ‘1:1’ compounds). In addition to this, the 484 and 345 cm⁻¹ bands might arise from small amounts of the (POCl₃)₄[AlCl₄] compound V, see below. A distinction between these cases is not possible based on our data. By comparing the upper spectrum in Fig. 1 with the other spectra, it seems that the POCl₃·AlCl₃ compound IV is the predominant complex formed in the POCl₃-rich range, at ca. 195°C. This conclusion is supported by the ratios of the relative intensities for the new bands which remain the same (within experimental accuracy) for all measured spectra. Thus it is possible by linear combination of the spectra of POCl₃ and POCl₃·AlCl₃ to calculate artificial spectra of intermediate composition which are very similar to the experimental ones (three examples are given in Fig. 3).

For the equimolar POCl₃·AlCl₃ melt, temperature-dependent Raman spectra were obtained in the range from 195 to 500°C, Fig. 4. Small changes with temperature were observed (the band at 442 cm⁻¹ shifted to 450 cm⁻¹ and the relative intensity of the shoulder at 130 cm⁻¹ decreased), but not more than to prove a high thermal stability of the POCl₃·AlCl₃ adduct compound.¹¹,¹² It should be noted that evidence for the compound ‘(POCl₃)₄(AlCl₄)’ was not found in the POCl₃-rich melt at 195°C, even though such a compound has been reported in the solid state.⁵,⁷ Although questioned,⁶ confidence in the existence of a ‘(POCl₃)₃(AlCl₄)’ solid compound may be increased by the existence of analogous solids, e.g. ‘(POCl₃)₂(GaCl₄)’⁹ and ‘(POCl₃)₃(AlCl₄)’.¹ On the other hand, only the (POCl₃)₃(FeCl₄) and (POCl₃)₃(FeCl₄) compounds exist in the POCl₃–FeCl₃ system.⁴,³,³ The Raman spectrum of solid ‘(POCl₃)₃(AlCl₄)’ should have a characteristic strong Raman band at 545 cm⁻¹ at room temperature.¹ In practice we found a strong doublet band exactly at 545 cm⁻¹ for our solid ‘3:2’ compound. [Al(POCl₃)₃][AlCl₄], (VII), see below. Furthermore, we have observed that the Raman doublet band at ca. 545 cm⁻¹ disappears from the solid sample when it melts. It thus seems that the solid (2:1 or 3:2) compounds are unstable in the melt at 195°C, probably reacting according to reaction (5).

\[ \text{[Al(POCl}_3)_3][\text{AlCl}_4], \quad (s) \]

\[ \rightarrow 2 \text{POCl}_3 + 4 (\text{POCl}_3 \cdot \text{AlCl}_3), \quad (l) \quad (5) \]

AlCl₄-rich concentration range. In Raman spectra of molten samples with x(AlCl₄) ≥ ~0.5, new bands appear (Fig. 5): With diminishing POCl₃ content, seven Raman bands become increasingly visible on top of the decreasing bands of the POCl₃·AlCl₃ complex, as indicated by solid lines in Fig. 5 (at ca. 95, 314, 368, 438, 480, 603...

![Fig. 3. Verification of linear combination of POCl₃ and POCl₃·AlCl₃ spectra as a calculational method: experimental (upper) and calculated (lower) spectra in the system POCl₃·AlCl₃. (A) x(AlCl₄) = 0.442; (B) x(AlCl₄) = 0.359; (C) x(AlCl₄) = 0.250.](image)

![Fig. 4. Polarized Raman spectra of a mixture with x(AlCl₄) = 0.492 at 195, 245, 400 and 500°C.](image)
and 660 cm⁻¹). When the composition of the liquid approached AlCl₃, these bands disappeared again. Hence, they belong neither to the '1:1' adduct nor to Al₂Cl₆; instead they are interpreted as coming from the vibrations in the (POCl₃)(AlCl₃)₂ complex V; a molecule with that formula has been proposed by Brockner et al.,¹¹ based on vapor pressure measurements. The new bands occur with the highest relative intensity in the sample with x(AlCl₃) = 0.634. This is considered an experimental proof of the existence of the (POCl₃)(AlCl₃)₂ complex V in the melt. Furthermore, by use of a computer program, suitably scaled spectra of POCl₃·AlCl₃ and Al₂Cl₆ were subtracted from the spectra [obtained for the mixtures with x(AlCl₃) = 0.634 and 0.787], letting the most intense bands of both of these compounds disappear. In this way, the Raman bands of the presumed (POCl₃)(AlCl₃)₂ complex V appeared more clearly, being otherwise partly hidden under those of the POCl₃·AlCl₃ adduct IV (Fig. 6). The following wavenumbers can be assigned to the (POCl₃)(AlCl₃)₂ complex V: 94, 128, 160, 211, 241, 314, 368, 396, 438, 480, 603, 660 and 1216 cm⁻¹.

The thermal stability of the compound in the melt was investigated by measurements in the temperature range from 195 to 400°C (Fig. 7). As in the case of the POCl₃·AlCl₃ compound IV, only small changes could be observed by heating. Accordingly, the (POCl₃)(AlCl₃)₂ complex V in the melt must show considerable stability.

**Raman spectra of vapor over POCl₃·AlCl₃ melt (400°C)**

The gas phase over the 1:1 melt was examined for the presence of the POCl₃·AlCl₃ complex IV. The procedure was similar to that applied in our study of vapor complexation in, e.g., the ZrCl₄·POCl₃ system.¹⁴ Indeed, bands due to the '1:1' complex were found (Fig. 8A). POCl₃ vapor was also present (compare with the spec-
trum of the pure gas, Fig. 8B) and the spectrum in Ref. 34. Gaseous AlCl₃ cannot be present, because it has its most intense Raman bands at ca. 97, 218 and 336 cm⁻¹, where no band occurs in Fig. 8A. AlCl₃ is not formed in appreciable amounts at 400°C, and will therefore not be seen.²⁶ The most prominent complex bands were seen at 118, 320, 392, 546 and 1235 cm⁻¹. The similarity of the Raman spectra of POCl₃-AlCl₃ in the melt and gas phases should be noted (cf. Figs. 2 and 8), thus confirming on one hand the stability of the ‘1 : 1’ adduct in the gas phase at elevated temperatures and on the other hand the presence of the ‘1 : 1’ adduct in the melt. The first conclusion has recently been reached independently in a Raman investigation on vapors over molten POCl₃-AlCl₃ and POCl₃-GaCl₃ mixtures.³⁵

Room-temperature Raman spectra of solids (22°C). When the POCl₃-AlCl₃ molten mixtures considered above were cooled to room temperature, polycrystalline solids formed. For samples with χ(AlCl₃) ≤ ca. 0.40 an excess of POCl₃ solvent was present, and sometimes a jelly was formed. Typical Raman spectra of the solids, eventually separated by decantation, are shown in Figs. 9 and 10.

For χ(AlCl₃) ≤ ca. 0.40 the precipitates always had similar spectra, reminiscent of solid ‘(POCl₃)₂(AlCl₃),’ (Fig. 9). There have been contradictory statements on the composition of the solid compounds. Groeneveld and Zuur² identified a melting-point maximum at χ(AlCl₃) = 0.33 in the POCl₃-AlCl₃ phase diagram. Wartenberg and Goubeau⁶ isolated and analysed a white precipitate (found: P = 14.04% and Cl = 72.04%; calculated for ‘2 : 1’: P = 14.08% and Cl = 72.46%; calculated for ‘3 : 2’: P = 2.79% and Cl = 73.34%) and considered it to be ‘2 : 1’. On the other hand, Gutmann and Baaž⁴ and Barabanova and Voitovich⁶ claimed the compound to have the formula (POCl₃)₂(AlCl₃)₂, and the X-ray powder diagram was published.⁸ The Raman spectra obtained here show that the identity of the solid depends little on the composition of the mother melt, in agreement with the X-ray powder results.⁸ As already mentioned, a ‘(POCl₃)₂(AlCl₃)’ compound has previously been isolated³ and found to have a strong Raman band at 545 cm⁻¹ at room temperature.⁷ We conclude that among the ‘2 : 1’ and ‘3 : 2’ solids there exists only one compound, [Al(POCl₃)₆][AlCl₆], see below.
The compound seems to be rather insoluble in POCl₃. Even at 125°C the Raman spectrum of the solution over solid (POCl₃)₂(AlCl₃) is dominated by bands from POCl₃ and POCl₃·AlCl₃. A single polarized band at ca. 535 cm⁻¹ may be attributed to the dissolved species, ν(AlO₄) (Fig. 11). The solid (POCl₃)₂(AlCl₃) compound itself dissociates, we think, into POCl₃ and POCl₃·AlCl₃ when heated to its melting point (ca. 164°C) [reaction (5)].

For the solid ‘1:1’ compound, x(AlCl₃) = 0.50, a different Raman spectrum was obtained [Fig. 9 (top) or Fig. 10 (bottom)]. Characteristic bands for that solid are seen at 118, 168, 210, 251, 350, 452, 591, 638 and 1225 cm⁻¹. The lack of identity among the spectra of the POCl₃·AlCl₃ complex IV in the melt and the ‘1:1’ compound in the solid state must mean that the molecular structure IV of POCl₃/AlCl₃ in the molten state is not retained in the solid phase [cf. Fig. 2 and Fig. 9 (top)]. Instead, Raman and NMR spectra indicate that the ‘1:1’ solid compound probably consists of [Al(POCl₃),][AlCl₃]₃ (VI), formed according to reaction (6).

4 POCl₃·AlCl₃ (l) → [Al(POCl₃)₉][AlCl₃]₃ (s) (6)

Raman spectra obtained on solid samples with x(AlCl₃) > 0.5 are shown in Fig. 10. The spectra can be well interpreted by assuming the samples to consist of physical mixtures of the ‘1:1’ compound, i.e. [Al(POCl₃)₉][AlCl₃]₃ (VI) and AlCl₃ (I). X-Ray powder diagrams also could be interpreted in that range of x(AlCl₃) assuming the mixtures to consist of ‘1:1’ and AlCl₃ solids.5 It thus seems that the (POCl₃)₃(AlCl₃)₂ complex V, existing with considerable stability in the melt and in the vapor,11 decomposes upon solidification according to reaction (7).

4 (POCl₃)(AlCl₃)₂ (I)
→ [Al(POCl₃)₉][AlCl₃]₃ (s) + 4 AlCl₃ (s) (7)

**High-temperature NMR Spectra (160°C).**

**31P measurements.** 31P NMR spectra at 160°C are shown in Fig. 12 as a function of x(AlCl₃). Chemical shifts and linewidths of the observed bands are given in Table 2. Linewidths of the bands cannot be used for detailed conclusions because some samples were partly solid, partly liquid at 160°C. Each spectrum exhibits a single NMR resonance. No splitting is seen. The chemical shift of the single line depends strongly on x(AlCl₃). This might have been interpreted as due to the existence of only one kind of POCl₃ species, but in view of the Raman results it more probably means that exchange processes at 160°C are so fast that only an averaged NMR signal can be observed.

From the literature, 31P chemical shifts of various POCl₃ complexes at room temperature are known: Protonation of POCl₃ oxygen in acids gives rise to a low-field shift of the 31P signal (from 2.2 ppm in pure POCl₃ to 6.9 ppm in liquid HCl and 33.1 ppm in oleum).36,37 Chemical shifts of up to 8.3 ppm have been reported for 31P upon coordination of POCl₃ to Na⁺.18 For the solid complexes of POCl₃ with, e.g., ShCl₃, SnCl₄ and BCl₃ (oxygen coordination), higher values, up to ~60 ppm, were found.18 Similar trends have been found for other R₂PO·AlCl₃ adducts, R being, e.g., phenyl.32,39

Thus, in view of the results reported in the literature, it seems reasonable to assign the observed chemical shift of 31.3 ppm at equimolar composition to 31P in the POCl₃·AlCl₃ complex. For lower AlCl₃ concentrations, the observed signal at ca. 20–30 ppm probably results from an average of 31P in POCl₃ and POCl₃·AlCl₃ species, whereas for higher AlCl₃ contents, 31P in the compounds (POCl₃)(AlCl₃) and (POCl₃)₃(AlCl₃) produces via fast exchange processes, a single (i.e. averaged) signal near 40 ppm. Thus, the increasing low-field shift.
is explainable by an increasing Lewis acidity (AlCl₃ content) in connection with the changing concentration of individual species.

²⁷Al measurements. The results of high-temperature ²⁷Al NMR experiments are shown in Fig. 13 and in Table 2. Only one rather sharp peak at about 92.5 ppm was observed in the range x(AlCl₃) ≤ 0.4. This chemical shift is due to ²⁷Al in the POCl₃·AlCl₃ adduct, which according to the Raman results seems to be the only species existing in the melt (or at least the dominating aluminium compound) in this concentration range. The sharpness of the line and the magnitude of the shift (about 92.5 ppm) indicate that aluminium is tetrahedrally coordinated in POCl₃·AlCl₃. The reasons for this are the following: The quadrupolar ²⁷Al nucleus generally gives broad lines; however, in cubic environments (octahedral or tetrahedral) the electric field gradient is zero, and sharp lines are therefore observed.²² Furthermore, dissolved R₂O·AlCl₃ adducts, in different R₂O solvents such as (CH₃)₂O and (C₂H₅)₂O, show rather sharp bands with chemical shifts between 87 and 104 ppm, at room temperature.⁴⁰ Finally, narrow ²⁷Al signals have been observed at 88-90 ppm for (R)₁PO·AlCl₃, with R = C₆H₄Cl, C₆H₄O and (CH₃)₂N, in ca. 0.02 M solutions in CH₃Cl.³⁹ These compounds, with known crystal structures, have tetrahedrally coordinated aluminium, and the sharpness of the signal has been correlated with the occurrence of linear Al–O–P bonding and an approximate C₃ symmetry.²²³⁹

In the range x(AlCl₃) ≥ 0.5 a significant shift of the ²⁷Al signal to 99 ppm can be seen. The shifted signal probably arises from an averaged superposition of signals from POCl₃·AlCl₃, AlCl₃ and (POCl₃)₂(AlCl₃)₂ species, unresolved owing to ‘fast’ exchange processes (for example a δ difference of ~20 ppm corresponds to ~1300 Hz; therefore collapse occurs when exchange is fast compared to 1/1300 s). The assignment of a very broad and weak band at ~20 ppm is not clear, but it might indicate that another kind of Al species with low symmetry exists in this range. The spectrum of AlCl₃ is discussed below.

No observation from the high-temperature ³¹P and ²⁷Al NMR spectra (of melts or partly solid samples) seems to contradict the existence of the two adducts, POCl₃·AlCl₃ and (POCl₃)₂(AlCl₃)₂, derived from the Raman spectra of the melts.

Room-temperature NMR spectra (27°C).

³¹P measurements. Results of room temperature ³¹P NMR measurements are shown in Fig. 14 and summarized in Table 2. Generally, the room temperature spectra have more bands than (and are very different from) the spectra recorded at high temperature (cf. Figs. 12 and 14, and the corresponding columns in Table 2). This is probably due to structural changes, in combination with less averaging by slower exchange processes at room temperature. With increasing AlCl₃ content, the relative intensity of the peak at ~4 ppm decreases, disappearing completely at around x(AlCl₃) = 0.4. Considering the ³¹P shift of pure POCl₃ (δ = 2.2 ppm), the peak probably arises from ³¹P in ‘free’ POCl₃ molecules. According to this interpretation, a vanishing quantity of ‘free’ POCl₃ exists at x(AlCl₃) = ~0.4. The broad peak of medium intensity at about 16 ppm observed for samples with 0.3 ≤ x(AlCl₃) ≤ 0.5 (Fig. 14) most probably is due to ³¹P in the (POCl₃)₂(AlCl₃) or (POCl₃)₂(AlCl₃)₂ solid compound. In our opinion it is [Al(POCl₃)₃][AlCl₄]₂. For x(AlCl₃) ≤ 0.3 the spectra correspond to dilute solutions in which the concentration of the compounds named above is too low to let ³¹P NMR bands of them be
Table 2. Results of NMR measurements on POCl₃-AlCl₃ mixtures at 27 and 160°C. Samples were solid unless indicated otherwise in a footnote. (δ = chemical shift in ppm, LW = linewidth in Hz).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Resonance signals</th>
<th>³¹P</th>
<th>²⁷Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>27°C</td>
<td>160°C</td>
<td>27°C</td>
</tr>
<tr>
<td></td>
<td>δ</td>
<td>LW</td>
<td>δ</td>
</tr>
<tr>
<td>0, pure POCl₃</td>
<td></td>
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<tr>
<td>0.07²</td>
<td></td>
<td>2.2²</td>
<td></td>
</tr>
<tr>
<td></td>
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<tr>
<td>0.08²</td>
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<tr>
<td>0.12</td>
<td>3.7²</td>
<td>95²</td>
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<td>29²</td>
<td>500²</td>
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<td></td>
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<tr>
<td>0.20</td>
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<td>119²</td>
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<tr>
<td>29²</td>
<td>480²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.327</td>
<td>4.5²</td>
<td>140²</td>
<td>12.0²</td>
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<td>16²</td>
<td>1000²</td>
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<td></td>
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<tr>
<td>29²</td>
<td>145²</td>
<td>19.8²</td>
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<td>33²</td>
<td>80²</td>
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<td>~60</td>
</tr>
<tr>
<td>~60²</td>
<td>~60²</td>
<td>~2000²</td>
<td>~102</td>
</tr>
</tbody>
</table>

* Liquid sample. ² 35°C. ³ 137°C. ⁴ Partly solid sample. ⁵ [Al(OH₂)₆]Cl₃ solution standard. ⁶ Ref. 18. ⁷ Ref. 17. ⁸ Ref. 36.

observed in the spectra. If the solid compound contains the [Al(POCl₃)₆]³⁺ ion VII, a comparison can be made with [Na(POCl₃)₆]⁺, which has a ³¹P chemical shift of ≤ 8.3 ppm.¹⁸ The larger shift for the Al complex (16 ppm) in comparison with the Na complex is explainable by the higher charge density of Al³⁺, meaning a larger influence on the POCl₃ molecule. The signal strength at 32 ppm increases with the AlCl₃ concentration and achieves a maximum relative intensity at around x(AlCl₃) = 0.5. Therefore, it seems reasonable that this peak belongs to ³¹P in the solid ‘1: 1’ compound, i.e. [Al(POCl₃)₆][AlCl₃]₂. The even larger chemical shift of the signal of [Al(POCl₃)₆][Cl]_₃ VI, than of [Al(POCl₃)₆][AlCl₃]²⁺ (VII) is in accord with Al³⁺ being able to exert a stronger influence on four than on six POCl₃ ligands. In addition to the [Al(POCl₃)₆]³⁺ peak at 32 ppm, two others can be observed for samples of x(AlCl₃) > 0.5: (i) The peak of low intensity at ~16 ppm, assigned to [Al(POCl₃)₆][AlCl₃]₂, and (ii) an unexplained one at 52 ppm, which dominates the spectrum of the x(AlCl₃) = 0.787 sample. In contrast to this, the room-temperature Raman spectra of the solids show only a mixture of [Al(POCl₃)₆][AlCl₃]₂ and AlCl₃ (Fig. 10).

²⁷Al measurements. In all ²⁷Al NMR spectra at room temperature up to x(AlCl₃) = 0.5 (Fig. 15 and Table 2), the sharp peak at 102 ppm is dominant. In the literature it has been found that tetrahedral [AlCl₄]⁻ gives a single very narrow line with a chemical shift of about 102–103 ppm, being rather independent of temperature and with different linewidths in the solid and liquid states (obtained in various solutions,¹⁷ in NaAlCl₄–POCl₃ samples¹⁸ and in salts or melts of MAICl₄ with M = Li, Na or K).³¹–⁴³ On the other hand, dissolved R₃PO·AlCl₃ adducts with R = Me₂O and Et₂O, and, e.g., the solid C₄H₄O·AlCl₃ adduct, show ²⁷Al chemical shifts between 87 and 104 ppm.³⁰,⁴⁴ By observing (in Fig. 15) the 102 ppm ²⁷Al NMR
signal for the solid compounds \( \gamma(\text{POCl}_1)_3\text{AlCl}_4 \), \( \gamma(\text{POCl}_1)_3\text{AlCl}_3 \), and \( \gamma(\text{POCl}_1)_3\text{AlCl}_3 \) in the POCl\(_1\) rich part of the AlCl\(_1\)–POCl\(_1\) system at room temperature, the question naturally arises: Are these compounds simply salts of [AlCl\(_4\)]\(^-\), formed according to eqns. (8) and (9)?

\[
\begin{align*}
6 \text{POCl}_1 + 4 \text{AlCl}_3 & \rightarrow [\text{Al}(\text{POCl}_1)_3\text{AlCl}_3]^{3+} + 3 [\text{AlCl}_4]^- \\
4 \text{POCl}_1 + 4 \text{AlCl}_3 & \rightarrow [\text{Al}(\text{POCl}_1)_3\text{AlCl}_3]^{3+} + 3 [\text{AlCl}_4]^- 
\end{align*}
\]

The answer seems to be yes. The \(^{27}\text{Al}\) NMR peaks at about \(-23\) and \(102\) ppm from solutions of aluminium chloride in phosphoryl chloride have previously been assigned by Kidd and Truax\(^{17}\) to \([\text{Al}(\text{POCl}_1)_3\text{AlCl}_3]^{3+}\) (VII) and \([\text{AlCl}_4]^-\), respectively, formed by eqn. (8). A minor problem with the assignment of the \(-23\) ppm band to \([\text{Al}(\text{POCl}_1)_3\text{AlCl}_3]^{3+}\) is that the band should have its maximum intensity for \(x(\text{AlCl}_3) = 0.4\). On the other hand, the small magnitude of the chemical shift, being near \([\text{Al}(\text{OH}_2)_3\text{Al}]^{3+}\) (the zero-point of the \(\delta\)-scale), indicates hexacoordination. Within this interpretation, no signal due to \([\text{Al}(\text{POCl}_1)_3\text{AlCl}_3]^{3+}\) ion (VI) is observed, expected on the low-field side of the signal at \(-23\) ppm. Another interpretation would be that the \(-23\) ppm signal is due to the \([\text{Al}(\text{POCl}_1)_3\text{AlCl}_3]^{3+}\) signal, but this seems unlikely from the magnitude of the chemical shift.

According to eqns. (8) and (9), the ratio of the \([\text{Al}(\text{POCl}_1)_3\text{AlCl}_3]^{3+}\) and \([\text{AlCl}_4]^-\) signals \((n=4 \text{ or } 6)\) should be equal to the molar ratio \(1:3\). In our \(^{27}\text{Al}\) NMR spectra, the ratio of the intensities of the peaks at about \(-23\) and \(102\) ppm is rather close to one third, although on the lower side of that number, especially for small \(x(\text{AlCl}_3)\). This deviation in the ratio can be explained by the formation of small quantities of \([\text{AlCl}(\text{POCl}_1)_3\text{AlCl}_3]_{1,3,4}\) or \([\text{AlCl}_3(\text{POCl}_1)_3\text{AlCl}_3]_{1,3,4}\) (also representing the composition \(1:1\)). These components give extra strength to the sharp \(102\) ppm signal because of the tetrahedral symmetry of the [AlCl\(_4\)]\(^-\) ion, but do not contribute to the \(-23\) ppm signal, because the low symmetry of the \([\text{AlCl}(\text{POCl}_1)_3\text{AlCl}_3]^{3+}\) or \([\text{AlCl}_3(\text{POCl}_1)_3\text{AlCl}_3]^{3+}\) ions may cause extreme quadrupolar broadening of the \(^{27}\text{Al}\) NMR signal. For the composition \(2:1\) or \(3:2\) similar considerations apply (formation of certain amounts of \([\text{AlCl}(\text{POCl}_1)_3\text{AlCl}_3]_{1,3,4}\) or \([\text{AlCl}_3(\text{POCl}_1)_3\text{AlCl}_3]_{1,3,4}\), representing POCl\(_1\)-richer compositions), and also five-coordinated Al cations may occur.

For \(x(\text{AlCl}_3) = 0.787\), the peak at \(102\) ppm disappears, and the spectrum becomes noisy and somewhat similar to the spectrum of solid AlCl\(_3\). Broad bands appear at \(-50\), \(-50\) (intense) and \(-30\) ppm. For the strongest band in AlCl\(_3\), at \(-10\) ppm, the assignment must be due to the AlCl\(_4\) unit in the crystal. This is in accordance with an independent observation of a \(^{27}\text{Al}\) signal at \(-2\) ppm in solid AlCl\(_3\) at room temperature, obtained by using static as well as magic angle spinning.\(^{45}\) The \(-60\) ppm signal probably comes from less than octahedrally coordinated Al. The origin of the weak peak at \(-30\) ppm is not clear, the signal being visible only at high AlCl\(_3\) contents \((x(\text{AlCl}_3) > 0.442)\) but not in crystalline AlCl\(_3\). At high temperatures \((160^\circ\text{C})\), the former two signals in AlCl\(_3\) can also be seen (at \(-10\) and \(-60\) ppm, Fig. 13 and Table 2), and there is a prominent strong signal at \(-102\) ppm.

It is difficult to assign the \(^{27}\text{Al}\) NMR signals of solid pure AlCl\(_3\), which exhibits two peaks at \(27^\circ\text{C}\) and three peaks at \(160^\circ\text{C}\). The crystal structure of AlCl\(_3\) shows layers of octahedrally coordinated Al in a close packed Cl lattice.\(^{45}\) A considerable disorder must be postulated in order to allow for an interpretation of the NMR data. Most probably the very intense peak at \(102\) ppm indicates the presence of \([\text{AlCl}_4]^-\) fragments in solid AlCl\(_3\) at high temperatures. Further, it seems reasonable to assign the peak in the neighborhood of \(0\) ppm \((\sim 11\) ppm at \(27^\circ\text{C}\) and \(10\) ppm at \(160^\circ\text{C}\)) to octahedral AlCl\(_4\) units in the crystal lattice. We have no explanation for the signal at \(-60\) ppm.

Assignments of Raman spectra and structure of compounds. The molecules POCl\(_1\) and Al\(_2\)Cl\(_4\) have well interpreted vibrational spectra\(^{21-24,26}\) which formed the basis for assignments given in Table 1. Previous spectroscopic results on the POCl\(_1\)–AlCl\(_3\) mixtures were included,\(^{7,12,18}\) also incorporating assignments of Raman and IR bands of boron- and bromine-substituted compounds,\(^7\) as well as results from POCl\(_1\)–GaCl\(_3\).\(^{12}\)

The molecule POCl\(_1\)–AlCl\(_3\) in the melt and gas phase. Coordination takes place between the electron-deficient aluminium atom of AlCl\(_3\) and the electron-rich oxygen of POCl\(_1\). Depending on the geometry of the Al–O–P bridge formed, three symmetry point groups are
possible: $C_{nv}$ (linear), $C_{s}$, and $C_{1}$ (angled). The first case needs serious consideration because linear Al–O–P bonds have recently been found in crystal structures of compounds such as $(R)_{1}$PO·AlCl₃, $R = C_{6}H_{5}$, $C_{6}H_{5}O$ and $(CH_{3})_{2}N$. Table 3 gives an overview of expected normal vibrations in each symmetry case. Herzberg has analysed the vibrations in the related dimethyl ether molecule of $C_{2v}$ symmetry, and also more closely related molecules such as $HSiOCH_{3}$ and the germanium and deuterium analogues have been studied. By comparing the expectations for POCl₃·AlCl₃ with the experimentally observed Raman bands (ca. six polarized and ca. seven depolarized), it most probably seems that the $1:1$ compound in the melt has a near-$C_{3v}$ (linear) symmetry (IV).

The vibrational motions may be roughly divided into motions belonging to ‘PCl₃’, ‘AlCl₃’ and the P–O–Al bridge, as shown in Table 1. These assignments should be understood as nothing more than qualified guesses.

Raman bands were seen at 830 and 701 cm⁻¹ by Gerding et al., who assigned them to asymmetric and symmetric P–O–Al bridge stretchings, based on comparison to other R–O–R' systems, such as Cl₂OP·POCl₃ (806 dp and 713 p) and ClO₂⁻SO₂Cl (773 dp and 716 p, in cm⁻¹). We were not able to see bands at 830 and 701 cm⁻¹.

The molecule $(POCl₃)/(AlCl₃)₂$ in melt. In this molecule of $C_{s}$ or $C_{1}$ symmetry (V), oxygen is the central atom. A related molecular arrangement has been seen in ions such as $[AlCl₄]⁻$ and $[AlCl₉O₂]²⁻$. No rigorous assignment will be attempted for the 13 frequencies of the $(POCl₃)/(AlCl₃)₂$ molecule in Table 1. It is clear, however, that the general pattern of bands is compatible with the existence of oxygen-bound PCl₃ and AlCl₃ units in the complex. As is often seen, the number of bands is much lower than expected from theory (cf. Table 3). More bands might be observed under better experimental conditions.

The lack of existence of the solid $(POCl₃)/(AlCl₃)₂$ should be noted. In comparison, e.g. crystals of composition $(SOCl₂)(AlCl₃)₂$ have been prepared in the SOCl₂–AlCl₃ system.  

### Table 3. Symmetry types of normal vibrations in POCl₃, POCl₃·AlCl₃ and $(POCl₃)/(AlCl₃)₂$ compounds depending on the geometry.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Point group symmetry</th>
<th>$C_{nv}$</th>
<th>$C_{s}$</th>
<th>$C_{1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>POCl₃</td>
<td>3 $A_{1}^+$</td>
<td>2 $E$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POCl₃·AlCl₃</td>
<td>6 $A_{1}^+$</td>
<td>13 $A_{1}^+$</td>
<td>21 $A^+$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 $E$</td>
<td>8 $A^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(POCl₃)/(AlCl₃)₂$</td>
<td>18 $A^+$</td>
<td>15 $A^+$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Polarized Raman active. $^b$ Depolarized Raman active. $^c$ Not Raman active.

The compound 3:2 (i.e. [Al(POCl₃)₂]AlCl₃) in the solid. The $(POCl₃)/(AlCl₃)₂$ compound has a distinct X-ray powder diagram. The Raman and NMR spectra of solids in the range x(AlCl₃) ≤ ca. 0.4 can be fully interpreted by the formation of the $(POCl₃)/(AlCl₃)₂$ and $(POCl₃)₂AlCl₃$ compounds. We think that the solid consists of [Al(POCl₃)ₙ][AlCl₄]ₙ, formed according to reaction (8).

The octahedral ion [Al(OH₂)₆]⁴⁺ has its Al–O Raman bands as $ν₁(A_{1g}) = 526$ cm⁻¹ strong, polarized, $ν₂(E_g) = 450$ cm⁻¹ weak, depolarized, $ν₃(F₄g) = 336$ cm⁻¹ very weak, depolarized. Analogously, the [Al(POCl₃)ₙ]⁺⁺ ion, see VII, should have its strong polarized stretching band near 530 cm⁻¹. Such a band is indeed found at ~ 545 cm⁻¹. In this connection it may be noted that the IR and Raman spectra of the tetrahydrofuran complex $(C₂H₅O)₂(AlCl₃)$ seem to correspond to the ionic arrangement $[(AlCl₃)(OC₂H₅)₂]³⁺$, $[AlCl₄]⁻$, whereas the $(CH₂O)₂(AlCl₃)$ complex should be a ’1:1’ molecule. The ’2:1’ compound, but not the ’1:1’ one, showed the characteristic Raman band of the $[AlCl₄]⁻$ anion. The $[AlCl₃(OC₂H₅)₃]⁺$ ion is in the trans configuration ($D₃h$ symmetry), and the $ν₁(A_{1g})$ modes for AlCl₃ and AlO₂ stretchings were observed at ca. 280 and 230 cm⁻¹, respectively. Our ’2:1’ compound did not have bands here, instead we have the ca. 345 and 545 cm⁻¹ bands assigned to the $[AlCl₄]⁻$ and [Al(POCl₃)ₙ]⁺⁺ ions.

Other possibilities for the structure of the $[(POCl₃)/(AlCl₃)]_n$ complex might of course be postulated: A second POCl₃ molecule might be attached to the phosphorus atom rather than to the aluminium: $[Cl₂PO·POCl₃]²⁺[AlCl₄]⁻$. Alternative structures involving five-coordinate aluminium or, e.g. $(POCl₃)_2(AlCl₃)Cl$, see III, seem less probable.

The 1:1 compound (i.e. [Al(POCl₃)₂]AlCl₃) in the solid. In the solid state this compound has a distinct X-ray powder diagram and a distinct Raman spectrum. The most pronounced difference between the ‘1:1’ and the [Al(POCl₃)ₙ][AlCl₄]ₙ Raman spectra is perhaps the lack of the 545 cm⁻¹ band (Fig. 9), in accordance with the interpretation of the structure: the solid $(POCl₃)/(AlCl₃)$ compound contains [Al(POCl₃)ₙ]⁺⁺ entities (VI). However, the idea that $[AlCl₃(POCl₃)₂][AlCl₄]$ (III) may be formed, as suggested by Gutmann and Baay, cannot be rejected.

Again, it may be of interest to note that in the related SCl₂–AlCl₃ system, AlCl₃ dissolves completely, forming probably Cl₂SO–AlCl₃ adducts and, at higher AlCl₃ concentrations, iononic species $[Cl₂Al(OSCl₂)₃]⁺$ and $[AlCl₄]⁻$, causing increased electrical conductivity.  

Raman bands were assigned to the $[Cl₂Al(OSCl₂)₃]⁺$ and $[AlCl₄]⁻$ ions in solution.

The 6:1 compound (i.e. [Al(POCl₃)₂]Cl₃) in the solid. Such a compound has been claimed to exist as a glassy mass, melting at ca. 42°C. We confirm the existence of such a glassy material at high POCl₃ contents. The material indeed crystallizes badly (liquid crystals), and
probably involves octahedrally coordinated aluminum, see VII.

General comment. In closing, it should be noted that vibrational spectra of the POCl₃-containing compounds NbCl₅·OPCl₃ and (NbOCl₃·OPCl₃)₄ have been obtained. The crystal structures are known.¹¹,²⁸ showing POCl₃ groups bound to Nb through O bridges. Even through the structures are known, the spectra could not be assigned in detail by empirical methods.¹¹,⁵⁹ NbCl₅·POCl₃ has P=O and P–Cl bond-stretching frequencies at 1190 and 610 cm⁻¹, respectively, in its IR spectrum,⁷⁰ and normal-coordinate analyses have been attempted.⁶⁰

Conclusions

Raman experiments and the consistent results of NMR measurements at 160°C prove the existence, within the POCl₃·AlCl₃ system, of molecules such as POCl₃:POCl₃:AlCl₃, POCl₃:AlCl₃, (POCl₃):AlCl₃, and AlCl₃ in the melt phase, depending on the composition of the binary system. Similarly, [Al(POCl₃)₃]Cl and [Al(POCl₃)₂]Cl, and probably [Al(POCl₃)Cl]Cl, seem to exist in the solid state, and eventually also [AlCl₃(POCl₃)₂]Cl.

Room-temperature NMR spectra are quite different from high-temperature NMR spectra, and give evidence of the existence of [AlCl₃]⁻ and [Al(POCl₃)₃]⁺ (n = 4,6) species.

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References


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