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

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The system $POCl_3$–$AlCl_3$ was investigated by measuring the Raman and NMR spectra (^{27}Al, ^{31}P) as a function of the mole fraction of $AlCl_3$ in $POCl_3$. In the liquid state at temperatures below 200°C the observed Raman bands could be assigned to species $POCl_3$ and $POCl_3 \cdot AlCl_3$ in the $POCl_3$-rich region, and to $POCl_3 \cdot AlCl_3$, $(POCl_3)(AlCl_3)_2$ and Al_2Cl_6 in the $AlCl_3$-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 $POCl_3 \cdot AlCl_3$ adduct is stable in the gas phase. In the solid state at room temperature, the compounds '$(POCl_3)_2(AlCl_3)$' and '$(POCl_3)_3(AlCl_3)_2$' were identified spectroscopically as $[Al(POCl_3)_6][AlCl_4]_3$. The solid $(POCl_3) \cdot (AlCl_3)$ compound seems, from an interpretation of the Raman and NMR spectra, to exist as $[Al(POCl_3)_4][AlCl_4]_3$.
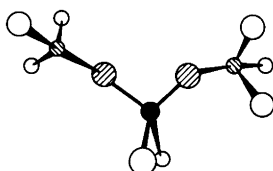
Aluminium chloride, $AlCl_3$ or Al_2Cl_6 (**I**), being a Lewis acid, undergoes complex formation with $POCl_3$ (**II**). The
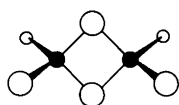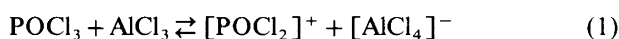

Al_2Cl_6
(**I**)
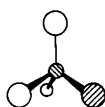
$POCl_3$
(**II**)

$[(POCl_3)_2 \ AlCl_2]^+$

(**III**)

system $POCl_3$–$AlCl_3$ is complicated and has been the subject of only a few investigations. Gutmann *et al.*[1–4] measured the conductivity of $POCl_3$ solutions containing $AlCl_3$ in various amounts and discussed several equations describing the dissociation of this compound in the solvent. $POCl_3$ has a very small self-dissociation,[3] and also the chloride ion-exchange reaction (1) in $POCl_3$ is weak
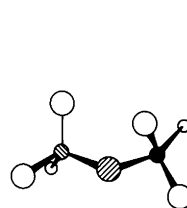
$$POCl_3 + AlCl_3 \rightleftarrows [POCl_2]^+ + [AlCl_4]^- \qquad (1)$$

($\alpha \approx 0.04$ at 25°C).[2] Solutions of $AlCl_3$ in $POCl_3$ solutions exhibit high conductivity, perhaps due to ions such as $[AlCl_2(POCl_3)_2]^+$ (**III**) and $[AlCl_4]^-$.[4] The $POCl_3$–$AlCl_3$ phase diagram indicates two compounds, melting at ca. 187 and 165°C, at compositions corresponding to $POCl_3 \cdot AlCl_3$ and $(POCl_3)_2(AlCl_3)$ or perhaps $(POCl_3)_3(AlCl_3)_2$.[4–7] X-Ray powder diagrams demonstrated that $POCl_3 \cdot AlCl_3$ and $(POCl_3)_3(AlCl_3)_2$ are the only distinct chemical compounds occurring in the system.[8] Analogous compounds are formed in the binary $POCl_3$–$GaCl_3$ system.[9] The densities and liquid–vapor equilibria of $POCl_3$–$AlCl_3$ mixtures have been studied with emphasis on the stability in the vapor phase of the $POCl_3 \cdot AlCl_3$ (**IV**) molecules,[10] formed by reaction (2).

$$POCl_3 + AlCl_3 \rightarrow POCl_3 \cdot AlCl_3 \qquad (2)$$

Brockner et al. investigated vapor pressures in Al_2Cl_6-rich mixtures and found evidence for the formation of complexes [most notably Al_2Cl_6, $POCl_3 \cdot AlCl_3$ and $(POCl_3)(AlCl_3)_2$ (**V**)] in the liquid state.[11] For the


$POCl_3 \ AlCl_3$

(**IV**)

$(AlCl_3)_2 OPCl_3$

(**V**)

* To whom correspondence should be addressed.
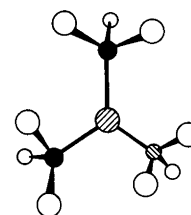
POCl$_3$·AlCl$_3$ addition compound in the molten state, some structural information is available: the complex cannot consist of ions [POCl$_2$]$^+$ and [AlCl$_4$]$^-$; instead it might have a bent oxygen-bridged structure (IV). This conclusion was reached by Gerding et al.[12] from the Raman spectrum 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[7] 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,[13] as also pointed out by Suvorov.[14] Heat evolution associated with compound formation in dilute solutions of AlCl$_3$ in POCl$_3$ at room temperature was studied by calorimetry.[15] Interestingly, non-radioactive POCl$_3$ could be drawn from a solution of ^{36}Cl-substituted AlCl$_3$ in non-radioactive POCl$_3$, proving the absence of radiochloride exchange in the solution.[16] This important observation eliminates the formation of [POCl$_2$]$^+$[AlCl$_4$]$^-$ via reaction (1). Finally, ^{27}Al NMR measurements provided proof of the existence of [AlCl$_4$]$^-$ and [Al(POCl$_3$)$_6$]$^{3+}$ ions, (VII), in a dilute solution.[17] Also, jelly-like or crystalline samples of composition AlCl$_3$·6(POCl$_3$) have been prepared.[5,18]

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$_3$)$_3$(AlCl$_3$)$_2$, (POCl$_3$)$_2$(AlCl$_3$) and (POCl$_3$)(AlCl$_3$)$_2$ (V), as well as the entities [AlCl$_4$]$^-$, [AlCl$_2$(POCl$_3$)$_2$]$^+$ (III), [Al(POCl$_3$)$_4$]$^{3+}$ (VI) and [Al(POCl$_3$)$_6$]$^{3+}$ (VII) 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.
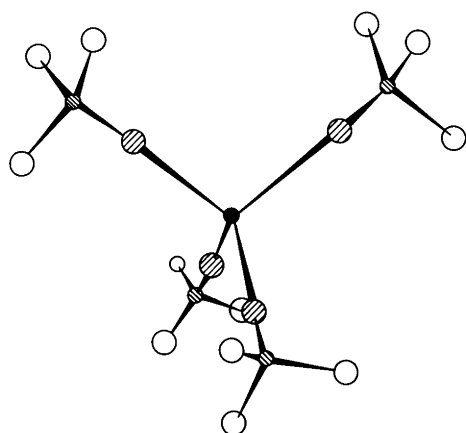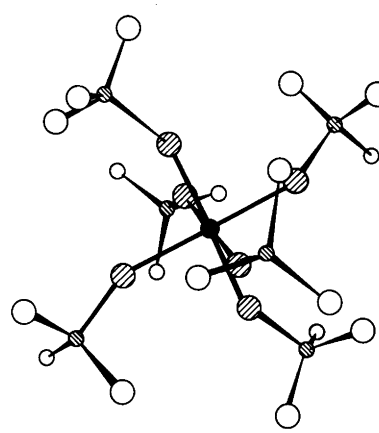
Experimental

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[19] 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.[20] 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 (|⊥) and averaged to obtain better signal-to-noise ratios.

[Al(OPCl$_3$)$_4$]$^{3+}$

(VI)

[Al(OPCl$_3$)$_6$]$^{3+}$

(VII)

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 $[Al(H_2O)_6]Cl_3$ and 85 wt% H_3PO_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, $(CD_3)_2SO$ (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
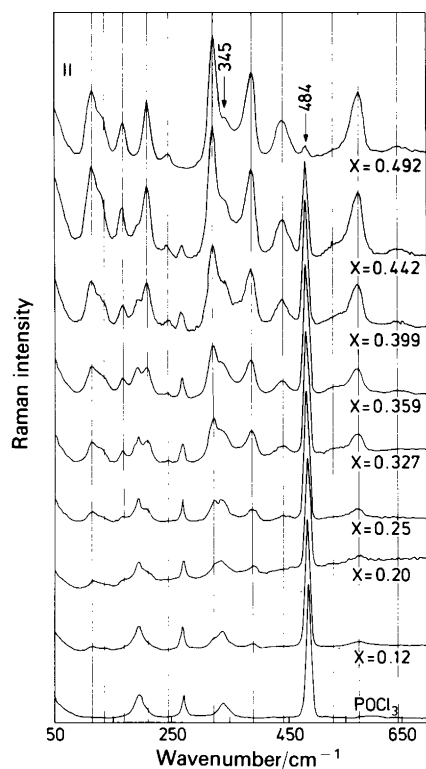

Fig. 1. Polarized Raman spectra for $POCl_3$–$AlCl_3$ mixtures with $x(AlCl_3) \leqslant \sim0.5$ at 195°C. (Solid vertical lines indicate bands not due to $POCl_3$ or Al_2Cl_6).

$POCl_3$ (**I**) takes on C_{3v} 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_2Cl_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.[7,12] 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.

POCl₃-rich concentration range. Raman spectra of $POCl_3$–$AlCl_3$ mixtures with molar ratio $x(AlCl_3) \leqslant \sim0.5$ are shown in Fig. 1. New bands (due neither to $POCl_3$ nor Al_2Cl_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 $x(AlCl_3) \approx 0.5$. 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}.[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 $POCl_3 \cdot AlCl_3$ 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
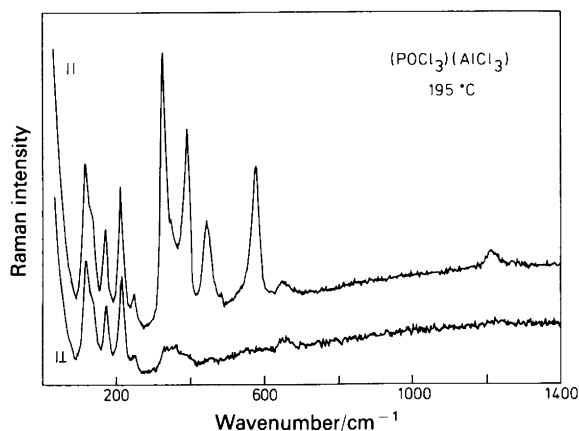

Fig. 2. Polarized and depolarized Raman spectra of pure $POCl_3 \cdot AlCl_3$ at 195°C, calculated from spectra of $x = 0.492$ and $x = 0.0$.

Table 1. Raman frequencies (in cm^{-1}) and assignments of bands in the system POCl$_3$–AlCl$_3$.[a]

| 1:0 POCl$_3$ Liquid 195°C (Fig. 1)	2:1 or 3:2 '(POCl$_3$)$_2$(AlCl$_3$)' [Al(POCl$_3$)$_6$][AlCl$_4$]$_3$ Solid 22°C (Fig. 9)	2:1 or 3:2 22°C (Ref. 9)	1:1 [Al(POCl$_3$)$_4$][AlCl$_4$]$_3$ Solid 22°C (Fig. 9)	POCl$_3$·AlCl$_3$ x=0.492 Liquid 195°C (Fig. 1)	POCl$_3$·AlCl$_3$ Liquid 210°C (Ref. 12)	POCl$_3$·AlCl$_3$ Gas 400°C (Fig. 8)	1:2 (POCl$_3$)(AlCl$_3$)$_2$·AlCl$_3$ Melt 195°C (Figs. 5 and 6)	0:1 AlCl$_3$ Melt 210°C (Fig. 5)	Assignment
1300 (w,p)	1300 (w)	1298 (w)	1225 (w)	1209 (w,p)		[1324 (m,p)]	1216 (w,p)		ν(P=O) sym. str.
	1208 (w)					1235 (w,dp?)			ν(P–O–Al) str.
					830 (1)	800 (w,p)			ν(P–O–Al) asym. str.
					701 (4)				ν(P–O–Al) sym. str.
	662 (w)		662 (w) 651 (w)				660 (w,dp)		ν(PCl$_3$) str.
	638 (w)	640 (m)	638 (m)	645 (w,dp)	~637 (3,br)	617 (w,p?)	603 (m,p)		ν(PCl$_3$) asym. str.
								610 (w,dp)	ν(AlCl$_3$) asym. str.
585 (w,dp)	590 (w)	545 (s)	591 (s) 540 (w)	575 (s,p)	576 (5,br)	546 (m,p)			ν(PCl$_3$) asym. str.
	550 (s) 535 (m) 500 (w)								ν(AlO$_6$)
484 (s,p)	[486 (w)]	495 (m)	521 (w)	~525* (w) [484 (w,p)]	497 (1)	[482 (s,p)]	480 (m,p)	512 (w,p)	ν(AlCl$_3$) sym. str. / {ν(PCl$_3$) sym. str. / ν(AlCl$_4^-$) asym. str.
	450 (w)	460 (m)	452 (s) 438 (m)	442 (m,p)	449 (4)	436 (w,p)	438 (m,p)		ν(P–O–Al) sym. str.
	395 (m) 378 (wbr)	393 (m)	380 (mbr)	392 (s,p)	389 (5) 365 (1)	392 (m,p) 356 (wbr,dp)	396 (w) 368 (w)		ν(AlCl$_3$) sym. str.
	351 (s) 340 (s)	355 (s)	350 (s)	345 (w,dp?)				342 (s,p)	ν(AlCl$_4^-$) sym. str.
337 (m,dp)									ν(PCl$_3$) asym. bend. ν(Al$\langle_{Cl}^{Cl}\rangle$Al) sym. str.
	311 (s)	320 (s)		324 (s,p)	323 (9)	320 (m,p)	314 (s,p)		ν(Al–O)
269 (m,p)	[268 (w)]	260 (w)	251 (m)	245 (w,dp)	260 (4)	[271 (m,p)]		286 (w,p)	ν(Cl–P–Cl) sym. bend.
	240 (w) 210 (s)	214 (s)	239 (w) 210 (s)	209 (m,dp)	236 (4) 208 (6)	212 (w,dp)	241 (w) 211 (m,dp)	219 (s,p)	ν(Al$_2$Cl$_6$) sym. bend.
194 (m,dp)	182 (m)					[185 (w,?)]			{ν(O–PCl$_3$) asym. bend. / ν(AlCl$_4^-$) bend.
		170 (m) 128	168 (s) 142 (m)	169 (s,dp) 133 (w,dp)	171 (3)		160 (w,dp) 128 (w,dp)	166 (w,dp)	ν(AlCl$_2^-$) term. bend. ν(AlCl$_4^-$) bend.
	142 (w) 130 (s)		118 (s)	116 (s,dp)	~105 (10,br)	118 (m,dp)		120 (s,dp)	{ν(AlCl$_2^-$) term. bend. / ν(AlCl$_4^-$) bend.
					95 (5)		94 (m,dp)	102 (s,dp)	ν(Al$_2$Cl$_6$) sym. bend.

[a] 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 POCl$_3$.

spectrum in Fig. 1, a spectrum of the $POCl_3 \cdot AlCl_3$ complex can be artificially obtained (Fig. 2). This spectrum still contains a weak shoulder at $345 \, cm^{-1}$, which accordingly cannot be due to $POCl_3$. It is probably due to minute traces of the $[AlCl_4]^-$ 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

$$4 \, POCl_3 \cdot AlCl_3 \rightleftarrows [Al(POCl_3)_4]^{3+} + 3 \, [AlCl_4]^- \qquad (3)$$
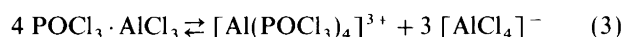
exchange, reaction (4), because of the lack of radio-chloride exchange.[16] The weakness of the $345 \, cm^{-1}$ band,

$$POCl_3 \cdot AlCl_3 \rightleftarrows [POCl_2]^+ + [AlCl_4]^- \qquad (4)$$
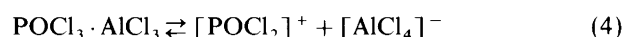
if it is due to $[AlCl_4]^-$ at all, clearly disproves that the 1 : 1 melt should contain major quantities of $[POCl_2][AlCl_4]$, $[AlCl_2(POCl_3)_2][AlCl_4]$, $[AlCl(POCl_3)_3][AlCl_4]_2$ or $[Al(POCl_3)][AlCl_4]_3$ (all of which are formally '1 : 1' compounds). In addition to this, the 484 and $345 \, cm^{-1}$ bands might arise from small amounts of the $(POCl_3)(AlCl_3)_2$ 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 $POCl_3 \cdot AlCl_3$ compound **IV** is the predominant complex formed in the $POCl_3$-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 $POCl_3$ and $POCl_3 \cdot AlCl_3$ to calculate artificial spectra of intermediate composition which are very similar to the experimental ones (three examples are given in Fig. 3).
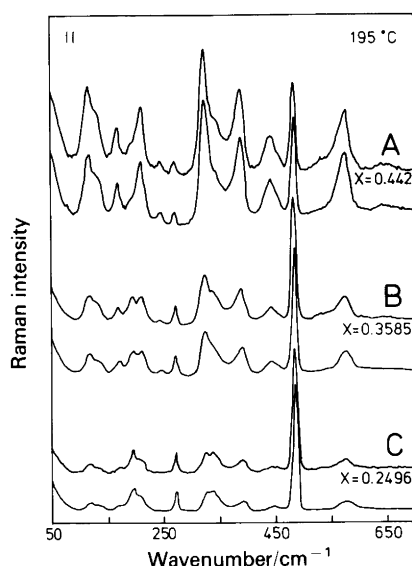
For the equimolar $POCl_3$–$AlCl_3$ melt, temperature-dependent Raman spectra were obtained in the range from 195 to 500°C, Fig. 4. Small changes with temperature were observed (the band at $442 \, cm^{-1}$ shifted to $450 \, cm^{-1}$ and the relative intensity of the shoulder at $130 \, cm^{-1}$ decreased), but not more than to prove a high thermal stability of the $POCl_3 \cdot AlCl_3$ adduct compound.[11,13] It should be noted that evidence for the compound '$(POCl_3)_2(AlCl_3)$' was not found in the $POCl_3$-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 '$(POCl_3)_2(AlCl_3)$' solid compound may be increased by the existence of analogous solids, e.g. '$(POCl_3)_2(GaCl_3)$'[9] and '$(POCl_3)_2(AlI_3)$'.[1] On the other hand, only the $(POCl_3)_3(FeCl_3)_2$ and $(POCl_3) \cdot (FeCl_3)$ compounds exist in the $POCl_3$–$FeCl_3$ system.[4,33] The Raman spectrum of solid '$(POCl_3)_2(AlCl_3)$' should have a characteristic strong Raman band at $545 \, cm^{-1}$ at room temperature.[7] In practice we found a strong doublet band exactly at $545 \, cm^{-1}$ for our solid '3 : 2' compound, $[Al(POCl_3)_6][AlCl_4]_3$ (**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).

$$[Al(POCl_3)_6][AlCl_4]_3 \, (s)$$
$$\rightarrow 2 \, POCl_3 \, (l) + 4 \, (POCl_3) \cdot (AlCl_3) \, (l) \qquad (5)$$
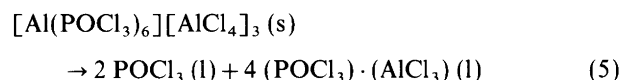
AlCl₃-rich concentration range. In Raman spectra of molten samples with $x(AlCl_3) \geqslant \sim 0.5$, new bands appear (Fig. 5): With diminishing $POCl_3$ content, seven Raman bands become increasingly visible on top of the decreasing bands of the $POCl_3 \cdot AlCl_3$ complex, as indicated by solid lines in Fig. 5 (at ca. 95, 314, 368, 438, 480, 603

Fig. 3. Verification of linear combination of $POCl_3$ and $POCl_3 \cdot AlCl_3$ spectra as a calculational method: experimental (upper) and calculated (lower) spectra in the system $POCl_3$–$AlCl_3$. (A) $x(AlCl_3) = 0.442$; (B) $x(AlCl_3) = 0.359$; (C) $x(AlCl_3) = 0.250$.

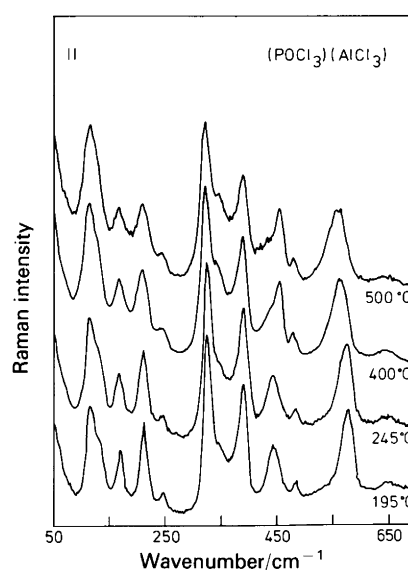*Fig. 4.* Polarized Raman spectra of a mixture with $x(AlCl_3) = 0.492$ at 195, 245, 400 and 500°C.
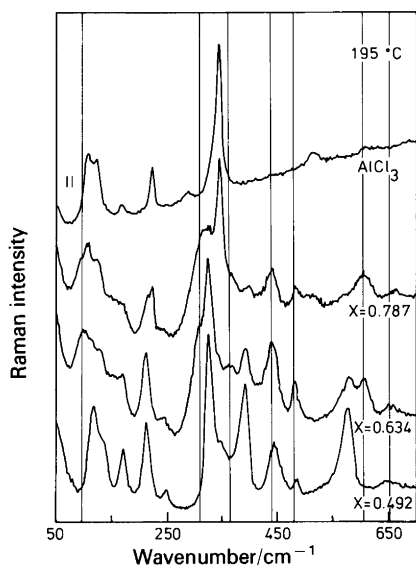
Fig. 5. Polarized Raman spectra for POCl$_3$–AlCl$_3$ mixtures with x(AlCl$_3$) $\geqslant$ ~0.5 at 195°C. (Solid vertical lines indicate bands not due to POCl$_3$·AlCl$_3$ or Al$_2$Cl$_6$).

and 660 cm^{-1}). When the composition of the liquid approached AlCl$_3$, these bands disappeared again. Hence, they belong neither to the '1 : 1' adduct nor to Al$_2$Cl$_6$; instead they are interpreted as coming from the vibrations in the (POCl$_3$)(AlCl$_3$)$_2$ 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(AlCl$_3$) = 0.634. This is considered an experimental proof of the existence of the (POCl$_3$)(AlCl$_3$)$_2$ complex **V** in the melt. Furthermore, by use of a computer program, suitably scaled spectra of POCl$_3$·AlCl$_3$ and Al$_2$Cl$_6$ were subtracted from the spectra [obtained for the mixtures with x(AlCl$_3$) = 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 (POCl$_3$)(AlCl$_3$)$_2$

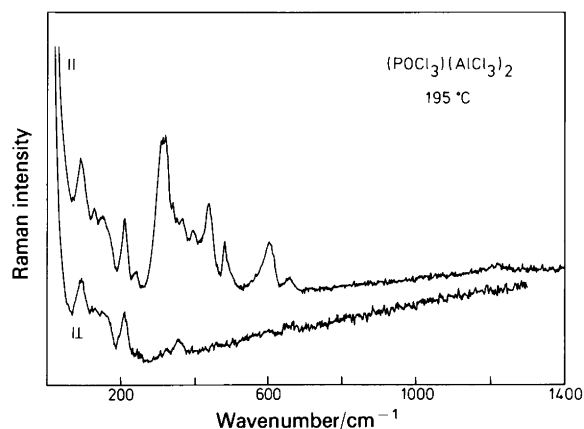*Fig. 6.* Polarized and depolarized Raman spectra of hypothetical, pure (POCl$_3$)(AlCl$_3$)$_2$ at 195°C, calculated from spectra of x(AlCl$_3$) = 0.492, 0.634, 0.787 and 1.0.
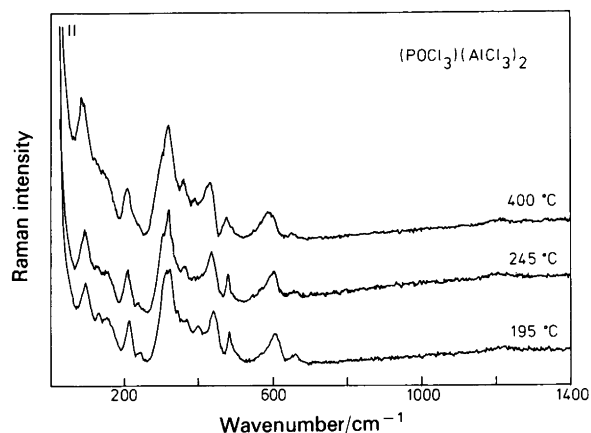
Fig. 7. Polarized Raman spectra of hypothetical, pure (POCl$_3$)(AlCl$_3$)$_2$ versus temperature, calculated from spectra obtained at 195, 245 and 400°C.

complex **V** appeared more clearly, being otherwise partly hidden under those of the POCl$_3$·AlCl$_3$ adduct **IV** (Fig. 6). The following wavenumbers can be assigned to the (POCl$_3$)(AlCl$_3$)$_2$ 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 POCl$_3$·AlCl$_3$ compound **IV**, only small changes could be observed by heating. Accordingly, the (POCl$_3$)(AlCl$_3$)$_2$ complex **V** in the melt must show considerable stability.

Raman spectra of vapor over POCl$_3$·AlCl$_3$ melt (400°C). The gas phase over the 1 : 1 melt was examined for the presence of the POCl$_3$·AlCl$_3$ complex **IV**. The procedure was similar to that applied in our study of vapor complexation in, e.g., the ZrCl$_4$–POCl$_3$ system.[34] Indeed, bands due to the '1 : 1' complex were found (Fig. 8A). POCl$_3$ vapor was also present (compare with the spec-

Fig. 8. Polarized and depolarized Raman gas-phase spectra of the vapor above a melt of x(AlCl$_3$) = 0.492, obtained at 400°C (A). For comparison are shown Raman spectra of POCl$_3$ in the gas phase (saturated vapor) in a closed wide ampoule at 200°C (B).

trum of the pure gas, Fig. 8B) and the spectrum in Ref. 34. Gaseous Al_2Cl_6 cannot be present, because it has its most intense Raman bands at ca. 97, 218 and 336 cm^{-1},[25] where no band occurs in Fig. 8A. $AlCl_3$ is not formed in ap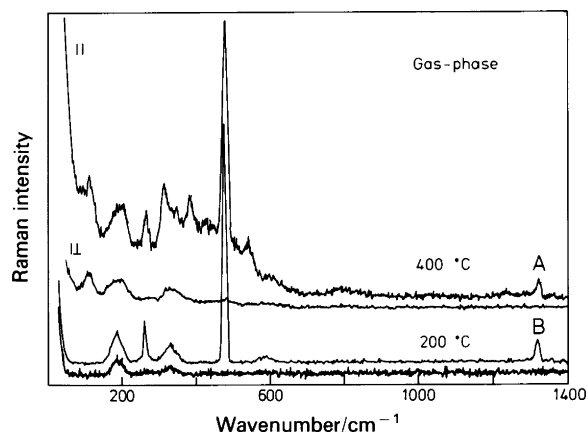preciable amounts at 400°C, and will therefore not be seen.[26] The most prominent complex bands were seen at 118, 320, 392, 546 and 1235 cm^{-1}. The similarity of the Raman spectra of $POCl_3 \cdot AlCl_3$ in the melt and gas phases should be noted (*cf.* Figs. 2 and 8), thus confirming on one hand 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 $POCl_3 \cdot AlCl_3$ and $POCl_3 \cdot GaCl_3$ mixtures.[35]

Room-temperature Raman spectra of solids (22°C). When the $POCl_3$–$AlCl_3$ molten mixtures considered above were cooled to room temperature, polycrystalline solids formed. For samples with $x(AlCl_3) \leqslant$ ca. 0.40 an excess of $POCl_3$ 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 $x(AlCl_3) \leqslant$ ca. 0.40 the precipitates always had similar spectra, reminiscent of solid '$(POCl_3)_2(AlCl_3)$,' (Fig. 9). There have been contradictory statements on the composition of the solid compounds. Groeneveld and Zuur[5] identified a melting-point maximum at $x(AlCl_3) = 0.33$ in the $POCl_3$–$AlCl_3$ phase diagram. Wartenberg and Goubeau[7] 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 Baaz[4] and Barabanova and Voitovich[6] claimed the compound to have the formula $(POCl_3)_3(AlCl_3)_2$, 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 '$(POCl_3)_2(AlCl_3)$' compound has previously been isolated[5] 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, $[Al(POCl_3)_6][AlCl_4]_3$, see below.
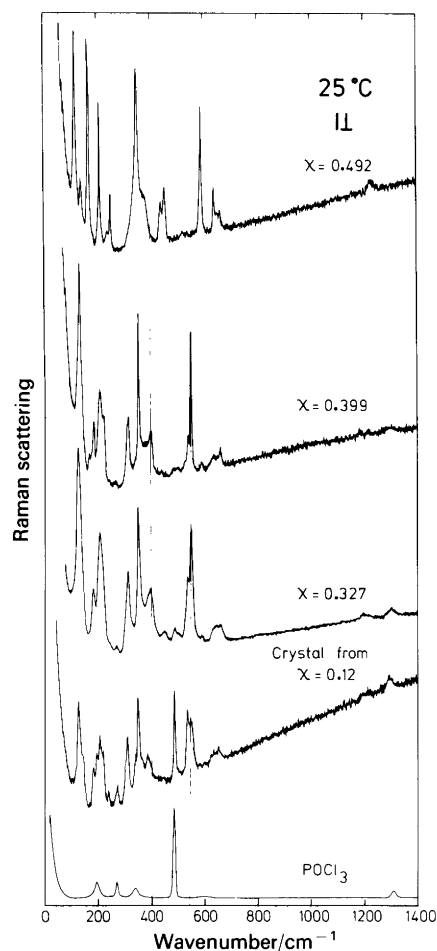

Fig. 9. Raman spectra of solid samples from $POCl_3$-rich melts of $POCl_3$–$AlCl_3$, and for comparison $POCl_3$, at 22°C. Overall composition before eventual decantation is indicated [for $x(AlCl_3) \leqslant 0.33$].

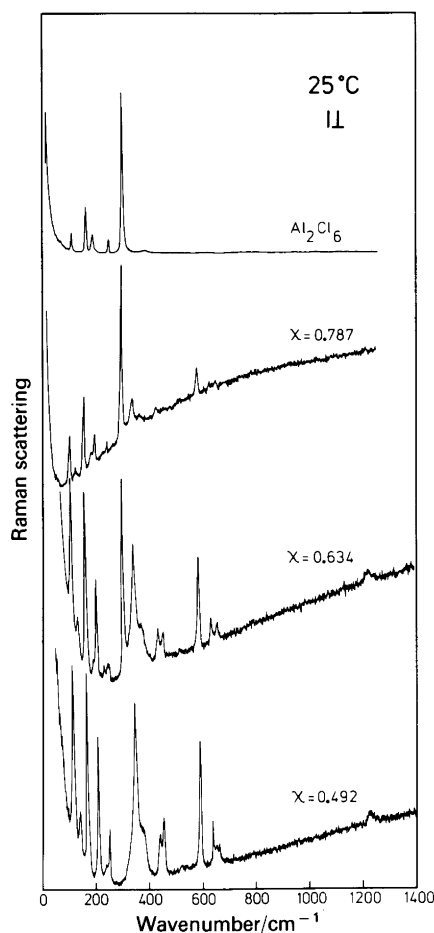*Fig. 10.* Raman spectra of solid samples from $AlCl_3$-rich melts of $POCl_3$–$AlCl_3$ at 22°C.

The compound seems to be rather insoluble in $POCl_3$. Even at 125°C the Raman spectrum of the solution over solid '$(POCl_3)_2(AlCl_3)$' is dominated by bands from $POCl_3$ and $POCl_3 \cdot AlCl_3$. A single polarized band at ca. 535 cm^{-1} may be attributed to the dissolved species, $v(AlO_6)$ (Fig. 11). The solid '$(POCl_3)_2(AlCl_3)$' compound itself dissociates, we think, into $POCl_3$ and $POCl_3 \cdot AlCl_3$ when heated to its melting point (ca. 164°C) [reaction(5)].

For the solid '1 : 1' compound, $x(AlCl_3) = 0.50$, 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 $POCl_3 \cdot AlCl_3$ complex IV in the melt and the '1 : 1' compound in the solid state must mean that the molecular structure IV of $POCl_3 \cdot AlCl_3$ 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 $[Al(POCl_3)_4][AlCl_4]_3$ (VI), formed according to reaction (6).

$$4 \, POCl_3 \cdot AlCl_3 \, (l) \rightarrow [Al(POCl_3)_4][AlCl_4]_3 \, (s) \qquad (6)$$

Raman spectra obtained on solid samples with $x(AlCl_3) \geqslant 0.5$ 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. $[Al(POCl_3)_4][AlCl_4]_3$ (VI) and $AlCl_3$ (I). X-Ray powder diagrams also could be interpreted in that range of $x(AlCl_3)$ assuming the mixtures to consist of '1 : 1' and $AlCl_3$ solids.[8] It thus seems that the $(POCl_3)(AlCl_3)_2$ complex V, existing with considerable stability in the melt and in the vapor,[11] decomposes upon solidification according to reaction (7).
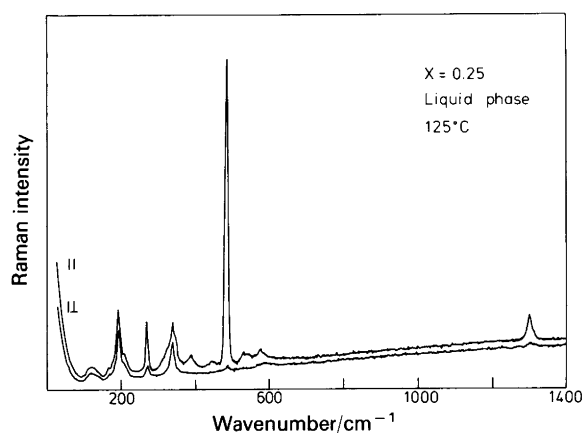
$$4 \, (POCl_3)(AlCl_3)_2 \, (l)$$
$$\rightarrow [Al(POCl_3)_4][AlCl_4]_3 \, (s) + 4 \, AlCl_3 \, (s) \qquad (7)$$

High-temperature NMR Spectra (160°C).

³¹P measurements. ³¹P NMR spectra at 160°C are shown in Fig. 12 as a function of $x(AlCl_3)$. 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 $x(AlCl_3)$. This might have been interpreted as due to the existence of only one kind of $POCl_3$ 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 $POCl_3$ complexes at room temperature are known: Protonation of $POCl_3$ oxygen in acids gives rise to a low-field shift of the ³¹P signal (from 2.2 ppm in pure $POCl_3$ 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 $POCl_3$ to Na⁺.[18] For the solid complexes of $POCl_3$ with, e.g., $SbCl_5$, $SnCl_4$ and BCl_3 (oxygen coordination), higher values, up to ~60 ppm, were found.[38] Similar trends have been found for other $R_3PO \cdot AlCl_3$ 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 $POCl_3 \cdot AlCl_3$ complex. For lower $AlCl_3$ concentrations, the observed signal at ca. 20–30 ppm probably results from an average of ³¹P in $POCl_3$ and $POCl_3 \cdot AlCl_3$ species, whereas for higher $AlCl_3$ contents, ³¹P in the compounds $(POCl_3)(AlCl_3)$ and $(POCl_3)(AlCl_3)_2$ produces via fast exchange processes, a single (i.e. averaged) signal near 40 ppm. Thus, the increasing low-field shift

Fig. 11. Polarized and depolarized Raman spectra of the supernatant liquid in a cell of $x(AlCl_3) = 0.25$ at 125°C, showing bands due to $POCl_3$ and $POCl_3 \cdot AlCl_3$ and perhaps at ca. 535 cm^{-1} a dissolved '$(POCl_3)_2(AlCl_3)$' complex.
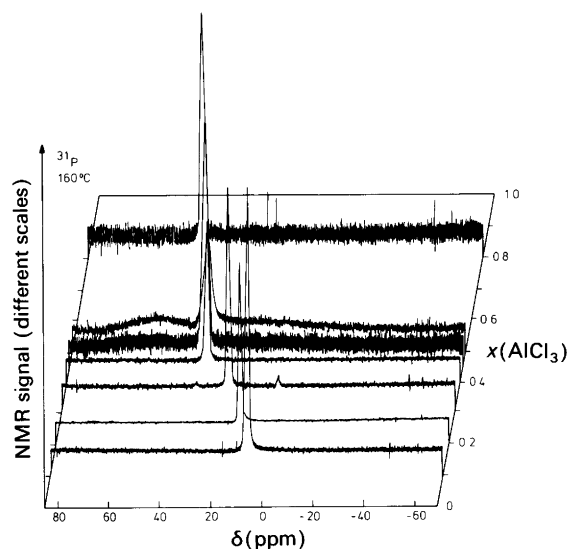

Fig. 12. ³¹P NMR spectra versus composition in the $POCl_3-AlCl_3$ system at 160°C, exhibiting a single NMR resonance at a chemical shift depending strongly on $x(AlCl_3)$.

is explainable by an increasing Lewis acidity ($AlCl_3$ content) in connection with the changing concentration of individual species.

^{27}Al measurements. The results of high-temperature ^{27}Al 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 $x(AlCl_3) \leqslant 0.4$. This chemical shift is due to ^{27}Al in the $POCl_3 \cdot AlCl_3$ 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 $POCl_3 \cdot AlCl_3$. The reasons for this are the following: The quadrupolar ^{27}Al nucleus generally gives broad lines; however, in cubic environments (octahedral or tetrahedral) the electric field gradient is zero, and sharp lines are therefore observed.[32] Furthermore, dissolved $R_2O \cdot AlCl_3$ adducts, in different R_2O solvents such as $(CH_3)_2O$ and $(C_2H_5)_2O$, show rather sharp bands with chemical shifts between 87 and 104 ppm, at room temperature.[40] Finally, narrow ^{27}Al signals have been observed at 88–90 ppm for $(R)_3PO \cdot AlCl_3$ with $R = C_6H_5, C_6H_5O$ and $(CH_3)_2N$, in ca. 0.02 M solutions in CH_2Cl_2.[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 C_3 symmetry.[32,39]

In the range $x(AlCl_3) \geqslant 0.5$ a significant shift of the ^{27}Al signal to 99 ppm can be seen. The shifted signal probably arises from an averaged superposition of signals from $POCl_3 \cdot AlCl_3$, $AlCl_3$ and $(POCl_3)(AlCl_3)_2$ species, unresolved owing to 'fast' exchange processes (for exam-

ple 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 $AlCl_3$ is discussed below.

No observation from the high-temperature ^{31}P and ^{27}Al NMR spectra (of melts or partly solid samples) seems to contradict the existence of the two adducts, $POCl_3 \cdot AlCl_3$ and $(POCl_3)(AlCl_3)_2$, derived from the Raman spectra of the melts.

Room-temperature NMR spectra (27°C).

^{31}P measurements. Results of room temperature ^{31}P 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 $AlCl_3$ content, the relative intensity of the peak at ~ 4 ppm decreases, disappearing completely at around $x(AlCl_3) = 0.4$. Considering the ^{31}P shift of pure $POCl_3$ ($\delta = 2.2$ ppm), the peak probably arises from ^{31}P in 'free' $POCl_3$ molecules. According to this interpretation, a vanishing quantity of 'free' $POCl_3$ exists at $x(AlCl_3) = \sim 0.4$. The broad peak of medium intensity at about 16 ppm observed for samples with $0.3 \leqslant x(AlCl_3) \leqslant 0.5$ (Fig. 14) most probably is due to ^{31}P in '$(POCl_3)_2(AlCl_3)$'' or '$(POCl_3)_3(AlCl_3)_2$' solid compound. In our opinion it is $[Al(POCl_3)_6][AlCl_4]_3$. For $x(AlCl_3) \leqslant 0.3$ the spectra correspond to dilute solutions in which the concentration of the compounds named above is too low to let ^{31}P NMR bands of them be
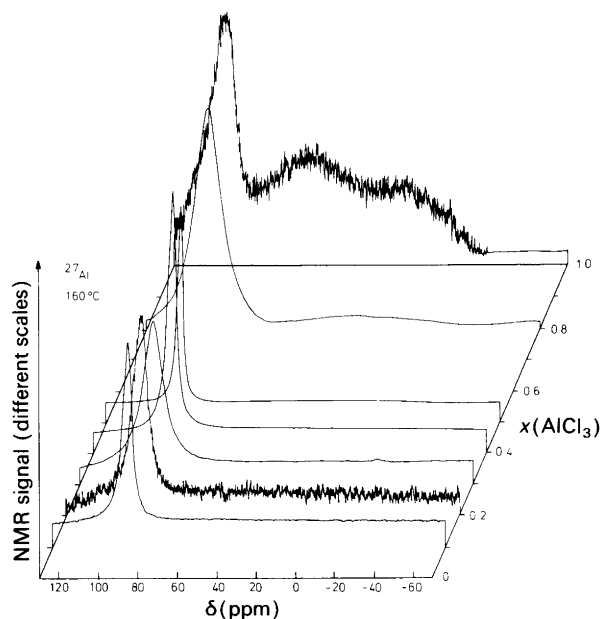

Fig. 13. ^{27}Al NMR spectra in the $POCl_3$–$AlCl_3$ system at 160°C, as a function of $x(AlCl_3)$.
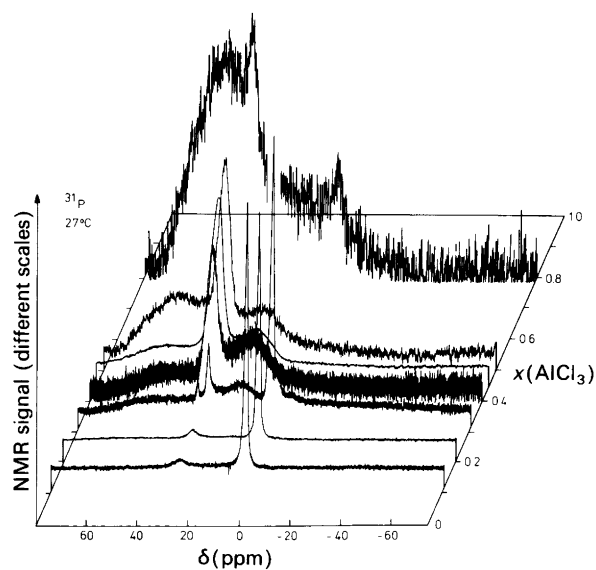

Fig. 14. ^{31}P NMR spectra in the $POCl_3$–$AlCl_3$ system at room temperature (27°C), as a function of $x(AlCl_3)$.
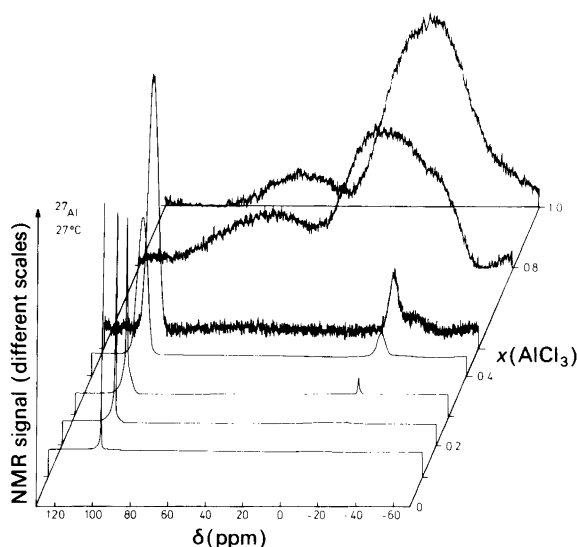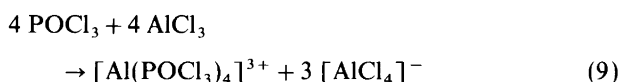
Table 2. Results of NMR measurements on POCl$_3$-AlCl$_3$ mixtures at 27 and 160°C. Samples were solid unless indicated otherwise in a footnote. (δ = chemical shift in ppm, LW = linewidth in Hz).

Composition x(AlCl$_3$)	^{31}P 27°C δ	^{31}P 27°C LW	^{31}P 160°C δ	^{31}P 160°C LW	^{27}Al 27°C δ	^{27}Al 27°C LW	^{27}Al 160°C δ	^{27}Al 160°C LW
0, pure POCl$_3$	2.2[a,h]							
0.07[f]					−9.5[b,a]	~500[b,a]		
					93.5[b,a]	~300[b,a]		
					103.0[b,a]	70[b,a]		
0.08[g]					−21.2[a]	55[a]		
					102.5[a]	10[a]		
0.12	3.7[d]	95[d]	7.7[a,c]	145[a,c]				
	29[d]	500[d]			102.7[d]	20[d]	93.4[a]	335[a]
0.20	3.5[d]	119			−21[d]	broad[d]		
	29[d]	480	12.0[a]	120[a]	102.5[d]	40[d]	92.7[a]	535[a]
0.327	4.5	140			−21.4	80		
	16	~1000			102.4	40	92.7[d]	790[d]
	29	145	19.8[d]	145[d]				
	33	~80						
0.399	16	~2000			−24.8	340		
	32.3	570	29	167	102.8	415		
	~52							
0.422	16.5	~1400	31.3	260	~−35	~600		
	32.8	550			−24.9	317		
	53	broad			102.7	396	91.1	320
0.492	16	broad			~−35	broad		
	32.5	620	31.3	360	−24.9	335		
	52	broad			102.5	396	92.6	220
0.787	~4				~−30	~3500		
	~38		40.6	190	~0		~20	~3200
	48	~3000			~60	>2500	99.2	1030
1, pure AlCl$_3$					~−11	3000	~10	~3000
					~60	2100	~60	~2000
							~102	~1500
1, pure AlCl$_3$					−2[e,i]			

[a] Liquid sample. [b] 35°C. [c] 137°C. [d] Partly solid sample. [e] [Al(OH$_2$)$_6$]Cl$_3$ solution standard. [f] Ref. 18. [g] Ref. 17. [h] Ref. 36. [i] Ref. 43.

observed in the spectra. If the solid compound contains the $[Al(POCl_3)_6]^{3+}$ ion **VII**, a comparison can be made with $[Na(POCl_3)_4]^+$, which has a ^{31}P 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 Al^{3+}, meaning a larger influence on the POCl$_3$ molecule. The signal strength at 32 ppm increases with the AlCl$_3$ concentration and achieves a maximum relative intensity at around x(AlCl$_3$) = 0.5. Therefore, it seems reasonable that this peak belongs to ^{31}P in the solid '1 : 1' compound, i.e. $[Al(POCl_3)_4][AlCl_4]_3$. The even larger chemical shift of the signal of $[Al(POCl_3)_4]^{3+}$ **(VI)**, than of $[Al(POCl_3)_6]^{3+}$ **(VII)** is in accord with Al^{3+} being able to exert a stronger influence on four than on six POCl$_3$ ligands. In addition to the $[Al(POCl_3)_4]^{3+}$ peak at 32 ppm, two others can be observed for samples of x(AlCl$_3$) ⩾ 0.5: (i) The peak of low intensity at ~ 16 ppm, assigned to $[Al(POCl_3)_6][AlCl_4]_3$, and (ii) an un-

explained one at 52 ppm, which dominates the spectrum of the x(AlCl$_3$) = 0.787 sample. In contrast to this, the room-temperature Raman spectra of the solids show only a mixture of $[Al(POCl_3)_4][AlCl_4]_3$ and AlCl$_3$ (Fig. 10).

^{27}Al *measurements.* In all ^{27}Al NMR spectra at room temperature up to x(AlCl$_3$) = 0.5 (Fig. 15 and Table 2), the sharp peak at 102 ppm is dominant. In the literature it has been found that tetrahedral $[AlCl_4]^-$ 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 NaAlCl$_4$-POCl$_3$ samples[18] and in salts or melts of MAlCl$_4$ with M = Li, Na or K).[41–43] On the other hand, dissolved $R_3PO \cdot AlCl_3$ adducts with R = Me$_2$O and Et$_2$O, and, e.g., the solid $C_4H_8O \cdot AlCl_3$ adduct, show ^{27}Al chemical shifts between 87 and 104 ppm.[40,44] By observing (in Fig. 15) the 102 ppm ^{27}Al NMR

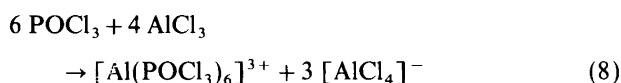*Fig. 15.* ^{27}Al NMR spectra in the POCl$_3$–AlCl$_3$ system at room temperature (27°C), as a function of x(AlCl$_3$).

signal for the solid compounds '(POCl$_3$)$_2$(AlCl$_3$)', '(POCl$_3$)$_3$(AlCl$_3$)$_2$' and '(POCl$_3$)(AlCl$_3$)' in the POCl$_3$-rich part of the AlCl$_3$–POCl$_3$ system at room temperature, the question naturally arises: Are these compounds simply salts of [AlCl$_4$]$^-$, formed according to eqns. (8) and (9)?

$$6 \text{ POCl}_3 + 4 \text{ AlCl}_3$$

$$\rightarrow [\text{Al(POCl}_3)_6]^{3+} + 3 [\text{AlCl}_4]^- \qquad (8)$$

$$4 \text{ POCl}_3 + 4 \text{ AlCl}_3$$

$$\rightarrow [\text{Al(POCl}_3)_4]^{3+} + 3 [\text{AlCl}_4]^- \qquad (9)$$

The answer seems to be yes. The ^{27}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 [Al(POCl$_3$)$_6$]$^{3+}$ (**VII**) and [AlCl$_4$]$^-$, respectively, formed by eqn. (8). A minor problem with the assignment of the -23 ppm band to [Al(POCl$_3$)$_6$]$^{3+}$ is that the band should have its maximum intensity for x(AlCl$_3$) = 0.4. On the other hand, the small magnitude of the chemical shift, being near [Al(OH$_2$)$_6$]$^{3+}$ (the zero-point of the δ-scale), indicates hexacoordination. Within this interpretation, no signal due to the [Al(POCl$_3$)$_4$]$^{3+}$ 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 [Al(POCl$_3$)$_4$]$^{3+}$ signal, but this seems unlikely from the magnitude of the chemical shift.

According to eqns. (8) and (9), the ratio of the [Al(POCl$_3$)$_n$]$^{3+}$ and [AlCl$_4$]$^-$ signals ($n = 4$ or 6) should be equal to the molar ratio 1 : 3. In our ^{27}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(AlCl$_3$). This deviation in the ratio can be

explained by the formation of small quantities of [AlCl(POCl$_3$)$_3$][AlCl$_4$]$_2$ or [AlCl$_2$(POCl$_3$)$_2$][AlCl$_4$] (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 [AlCl(POCl$_3$)$_3$]$^{2+}$ or [AlCl$_2$(POCl$_3$)$_2$]$^+$ ions may cause extreme quadrupolar broadening of the ^{27}Al NMR signal. For the composition 2 : 1 or 3 : 2 similar considerations apply (formation of certain amounts of [AlCl(POCl$_3$)$_5$][AlCl$_4$]$_2$ or [AlCl$_2$(POCl$_3$)$_4$][AlCl$_4$], representing POCl$_3$-richer compositions), and also five-coordinated Al cations may occur.

For x(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 ~ 60, ~ 0 (intense) and ~ -30 ppm. For the strongest band in AlCl$_3$, at ~ -11 ppm, the assignment must be due to the AlCl$_6$ unit in the crystal. This is in accordance with an independent observation of a ^{27}Al signal at ~ -2 ppm in solid AlCl$_3$ at room temperature, obtained by using static as well as magic angle spinning.[43] 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(AlCl$_3$) > 0.442) but not in crystalline AlCl$_3$. At high temperatures (160°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}Al NMR signals of solid pure AlCl$_3$, which exhibits two peaks at 27°C and three peaks at 160°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 [AlCl$_4$]$^-$ fragments in solid AlCl$_3$ at high temperatures. Further, it seems reasonable to assign the peak in the neighborhood of 0 ppm (~ -11 ppm at 27°C and ~ 10 ppm at 160°C) to octahedral AlCl$_6$ 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$_3$ and Al$_2$Cl$_6$ have well interpreted vibrational spectra[21–26,28] which formed the basis for assignments given in Table 1. Previous spectroscopic results on the POCl$_3$–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$_3$ · GaCl$_3$.[12]

The molecule POCl$_3$ · 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$_3$. Depending on the geometry of the Al–O–P bridge formed, three symmetry point groups are

possible: C_{3v} (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 $(R)_3PO \cdot AlCl_3$, $R = C_6H_5$, C_6H_5O and $(CH_3)_2N$.[39] Table 3 gives an overview of expected normal vibrations in each symmetry case. Herzberg[46] has analysed the vibrations in the related dimethyl ether molecule of C_{2v} symmetry, and also more closely related molecules such as H_3SiOCH_3 and the germanium and deuterium analogs have been studied.[47–49] By comparing the expectations for $POCl_3 \cdot AlCl_3$ 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.,[12] who assigned them to asymmetric and symmetric P–O–Al bridge stretchings, based on comparison to other R–O–R' systems, such as Cl_2OP–O–$POCl_2$ (806 dp and 713 p) and ClO_2S–O–SO_2Cl (773 dp and 716 p, in cm⁻¹). We were not able to see bands at 830 and 701 cm⁻¹.

The molecule $(POCl_3)(AlCl_3)_2$ 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 before in ions such as $[Al_3Cl_8O]^-$ and $[Al_4Cl_{10}O_2]^{2-}$.[50] No rigorous assignment will be attempted for the 13 frequencies of the $(POCl_3)(AlCl_3)_2$ 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 $(POCl_3)(AlCl_3)_2$ should be noted. In comparison, e.g. crystals of composition $(SOCl_2)(AlCl_3)_2$ have been prepared in the $SOCl_2$–$AlCl_3$ system.[51–53]

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

Compound	Point group symmetry		
	C_{3v}	C_s	C_1
POCl₃	$3 A_1{}^a$ $3 E^b$		
POCl₃·AlCl₃	$6 A_1{}^a$ $A_2{}^c$ $7 E^b$	$13 A'^a$ $8 A''^b$	$21 A^a$
(POCl₃)(AlCl₃)₂		$18 A'^a$ $15 A''^b$	$33 A^a$

a Polarized Raman active. *b* Depolarized Raman active. *c* Not Raman active.

The compound '3 : 2' (i.e. [Al(POCl₃)₆][AlCl₄]₃) in the solid. The '(POCl₃)₃(AlCl₃)₂' compound has a distinct X-ray powder diagram.[4] The Raman and NMR spectra of solids in the range $x(AlCl_3) \leqslant$ ca. 0.4 can be fully interpreted by the formation of the '(POCl₃)₃(AlCl₃)₂' and '(POCl₃)₂(AlCl₃)' compounds. We think that the solid consists of $[Al(POCl_3)_6][AlCl_4]_3$, formed according to reaction (8).

The octahedral ion $[Al(OH_2)_6]^{3+}$ has its Al–O Raman bands as $v_1(A_{1g}) = 526$ cm⁻¹ strong, polarized, $v_2(E_g) = 450$ cm⁻¹ weak, depolarized, $v_5(F_{2g}) = 336$ cm⁻¹ very weak, depolarized.[54,55] Analogously, the $[Al(POCl_3)_6]^{3+}$ 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 $(C_4H_8O)_2(AlCl_3)$ seem to correspond to the ionic arrangement $([AlCl_2(OC_4H_8)_4]^+, [AlCl_4]^-)$, whereas the $(C_4H_8O)(AlCl_3)$ complex should be a '1 : 1' molecule.[44] The '2 : 1' compound, but not the '1 : 1' one, showed the characteristic Raman band of the $[AlCl_4]^-$ anion. The $[AlCl_2(OC_4H_8)_4]^+$ ion is in the *trans* configuration (D_{4h} symmetry), and the $v_s(A_{1g})$ modes for $AlCl_2$ and AlO_4 stretchings were observed at ca. 280 and 230 cm⁻¹, respectively.[44] Our '2 : 1' compound did not have bands here, instead we have the ca. 345 and 545 cm⁻¹ bands assigned to the $[AlCl_4]^-$ and $[Al(POCl_3)_6]^{3+}$ ions.

Other possibilities for the structure of the '(POCl₃)₂(AlCl₃)' complex might of course be postulated: A second POCl₃ molecule might be attached to the phosphorus atom rather than to the aluminium: $[Cl_2OP$–O–$PCl_3]^+[AlCl_4]^-$. Alternative structures involving five-coordinate aluminium or, e.g. $[POCl_3)_2AlCl_2]Cl$, see **III**, seem less probable.

The 1 : 1 compound (i.e. [Al(POCl₃)₄][AlCl₄]₃) in the solid. In the solid state this compound has a distinct X-ray powder diagram[4] and a distinct Raman spectrum. The most pronounced difference between the '1 : 1' and the $[Al(POCl_3)_6][AlCl_4]_3$ 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 $[Al(POCl_3)_4]^{3+}$ entities **(VI)**. However, the idea that $[AlCl_2(POCl_3)_2][AlCl_4]$ **(III)** may be formed, as suggested by Gutmann and Baaz,[4] cannot be rejected.

Again, it may be of interest to note that in the related $SOCl_2$–$AlCl_3$ system, $AlCl_3$ dissolves completely, forming probably Cl_2SO–$AlCl_3$ adducts and, at higher $AlCl_3$ concentrations, ionic species $[Cl_2Al(OSCl_2)_2]^+$ and $[AlCl_4]^-$, causing increased electrical conductivity.[56,57] Raman bands were assigned to the $[Cl_2Al(OSCl_2)_2]^+$ and $[AlCl_4]^-$ ions in solution.[56]

The '6 : 1' compound (i.e. [Al(POCl₃)₆]Cl₃) in the solid. Such a compound has been claimed[5] 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 aluminium, see VII.

General comment. In closing, it should be noted that vibrational spectra of the $POCl_3$-containing compounds $NbCl_5 \cdot OPCl_3$ and $(NbOCl_3 \cdot OPCl_3)_4$ have been obtained. The crystal structures are known,[31,58] showing $POCl_3$ groups bound to Nb through O bridges. Even though the structures are known, the spectra could not be assigned in detail by empirical methods.[31,59] $NbCl_5 \cdot POCl_3$ has P=O and P–Cl bond-stretching frequencies at 1190 and 610 cm^{-1}, respectively, in its IR spectrum,[59] 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 $POCl_3$–$AlCl_3$ system, of molecules such as $POCl_3$, $POCl_3 \cdot AlCl_3$, $(POCl_3)(AlCl_3)_2$ and Al_2Cl_6 in the melt phase, depending on the composition of the binary system. Similarly, $[Al(POCl_3)_6][AlCl_4]_3$, $[Al(POCl_3)_4][AlCl_4]_3$ and probably $[Al(POCl_3)_6]Cl_3$ seem to exist in the solid state, and eventually also $[AlCl_2(POCl_3)_2][AlCl_4]$.

Room-temperature NMR spectra are quite different from high-temperature NMR spectra, and give evidence of the existence of $[AlCl_4]^-$ and $[Al(POCl_3)_n]^{3+}$ ($n = 4,6$) species.

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