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Gas-phase, liquid and solid complexes in the $POCl_3$–$FeCl_3$ system †

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Raman and UV/VIS spectra were obtained at temperatures up to 625 K for the gas-phase complex formed over $POCl_3$–$FeCl_3$ molten mixtures under static equilibrium conditions. Raman spectra were also measured for molten $POCl_3$–$FeCl_3$ salt mixtures. A comparison of the spectral features of the $POCl_3$–$FeCl_3$ vapours with those of the $POCl_3$–$FeCl_3$ molten mixtures at 525 K indicates that the gas-phase complex has a 1 : 1 stoichiometry ($POCl_3 \cdot FeCl_3$) with characteristic vibrational bands at 95, 362, 530, 1218 and 1268 cm^{-1}. The data indicate a C_{3v} symmetry for the $POCl_3 \cdot FeCl_3$ complex. The energies of the $M \leftarrow L$ charge-transfer transitions in the electronic absorption spectra of the $POCl_3 \cdot FeCl_3$ gas-phase complex suggest, in agreement with the Raman data, that complexing occurs through oxygen bridging. The 1 : 1 $POCl_3 \cdot FeCl_3$ molecular liquid complex is the predominant species in equilibrium with $POCl_3$ and iron chloride at temperatures around 500 K. At temperatures below 450 K and in $POCl_3$-rich mixtures the '3 : 2' ionic liquid compound $[Fe(POCl_3)_6][FeCl_4]_3$ was formed at the expense of $POCl_3 \cdot FeCl_3(l)$. Two solids were identified at room temperature, yellow $POCl_3 \cdot FeCl_3$ and red $[Fe(POCl_3)_6][FeCl_4]_3$, and their Raman spectra have been recorded.

The action of phosphoryl chloride as donor molecule towards inorganic metal halides leading to low-melting complex compounds is well known and a detailed summary of the chemistry of these complexes is available.[1] Formation of gas-phase complexes between $POCl_3$ and metal halides has attracted significant interest for removal of aluminium chloride from Friedel–Crafts mixtures, while such complexes with $ZrCl_4$ and $HfCl_4$ have been investigated due to their potential use for separation of zirconium from hafnium in nuclear reactor materials by distillation.[1] However, not much work has been directed towards the determination of the structural characteristics of these complexes in the gas phase. On the contrary, the vibrational and structural properties of a large number of liquid- and gas-phase metal halide complexes where $AlCl_3$, $GaCl_3$, $InCl_3$ and $FeCl_3$ act as complexing agents have been established.[2,3] Owing to the high reactivity of these complexes and complexing agents with moisture their handling for spectroscopic and thermodynamic measurements is rather difficult. However, with the use of sealed fused-silica containers and glove-box techniques, Raman spectroscopy has been used for determining the thermodynamic and/or structural properties of the gas-phase complexes $POCl_3 \cdot ZrCl_4$,[4] $POCl_3 \cdot HfCl_4$,[4,5] $POCl_3 \cdot GaCl_3$[6] and $POCl_3 \cdot AlCl_3$.[6,7]

Complex formation of phosphoryl chloride with the 'acidic' iron(III) chloride has been the subject of a few early investigations. Treatment of $FeCl_3$ with an excess of $POCl_3$ at 95 °C and subsequent cooling gave water-soluble red crystals of the 2 : 3 complex ($2FeCl_3 \cdot 3POCl_3$, m.p. 98 °C) which lost $POCl_3$ at 50 °C *in vacuo* giving yellow-brown crystals of the 1 : 1 adduct.[8] A high percentage of the 1 : 1 adduct in the vapour phase from sublimation of the $POCl_3 \cdot FeCl_3$ compound was reported.[9] Ultraviolet absorption spectra of a dilute solution of $FeCl_3$ in $POCl_3$ suggested the presence of $FeCl_4^-$ and provided evidence for self-ionization of the solvent.[10] However, electrolysis of a radioactive $^{59}FeCl_3$ complex with $POCl_3$ indicated that iron was present in both cationic and anionic species and that $POCl_2^+$ ions were not present.[11]

The aim of the present work is the spectroscopic characterization of a yellow-green gas-phase complex formed in the iron(III) chloride–phosphoryl chloride system (Fe–O–P–Cl) under static equilibrium conditions according to equation (1).

$$m\mathrm{POCl_3(g)} + n\mathrm{Fe_2Cl_6(g)} \rightleftharpoons \mathrm{(POCl_3)}_m\mathrm{(FeCl_3)}_{2n}\mathrm{(g)} \quad (1)$$

Raman and electronic absorption spectroscopy are used at temperatures up to 625 K to determine the vibrational properties of the complex formed as well as the type of bonding and Fe–Cl interaction. The vibrational frequencies of the complex(es) formed in the vapour as well as in the liquid state were determined. The electronic absorption spectra and molar absorption coefficients of the gas-phase complex were measured. The data are discussed in terms of possible structures in the vapour and/or the liquid phase. Finally, liquid and solid complexes in both molecular and ionic form were found to occur in the temperature range 300–450 K and at liquid-nitrogen temperature.

Experimental

High-purity anhydrous $FeCl_3$ was prepared from the corresponding Cerac/Pure Inc. reagent by repeated slow sublimations in fused-silica tubes under vacuum. It was handled in a nitrogen-filled glove-box having a water vapour content of less than 2 ppm. Liquid $POCl_3$ was obtained from Fluka.

The Raman cells containing the melt mixtures consisted of fused-silica tubing (outside diameter 4 ± 0.1 mm, inside diameter 2 ± 0.1 mm, ≈3 cm long). Those containing vapour mixtures comprised silica tubing of outside diameter 20 ± 0.2 mm, and inside diameter 18 ± 0.2 mm. Preweighed amounts of $FeCl_3$ were transferred into clean, dry, flamed and degassed optical cells of known volume. The cells were then attached to an all-glass vacuum line to which a container with liquid $POCl_3$ was also connected. Phosphoryl chloride was then allowed to vaporize and occupy a confined bulb of known volume and was transferred by distillation and condensed in the bottom of the optical cell which was immersed in liquid nitrogen. The optical cell was then sealed under vacuum, the chemicals were allowed to react inside a side tube (outside diameter 6 ± 0.1 mm, inside diameter 4 ± 0.1 mm), vapour transported into the main cell

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† *Supplementary data available* (No. SUP 57153, 2 pp.): molar absorption coefficients of the gas-phase complex $POCl_3 \cdot FeCl_3$. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.
Non-SI unit employed: atm = 101 325 Pa.

compartment and finally the side tube was sealed off. In this way high-purity samples were obtained.

Raman spectra were excited with the 514.5 and 488.0 nm lines of a Spectra Physics 164 argon-ion laser and the 647.1 and 676.4 nm lines of a Spectra Physics 2020 krypton-ion laser. The scattered light was collected at an angle of 90° (horizontal scattering plane) and analysed with a Spex 1403, 0.85 m double monochromator equipped with a −20 °C cooled RCA photomultiplier and EG&G/ORTEC rate meter and photon-counting electronics. The optical furnace used and the procedures for obtaining Raman spectra at high temperatures have been described in detail elsewhere.[12,13] It should be pointed out that use of the blue to green argon-ion laser lines for exciting gas-phase Raman spectra resulted in the formation of a yellow-brown deposit at the focusing point of the laser beam in the optical cell. As explained in detail elsewhere[14] this is due to absorption of the laser by the Fe-containing coloured vapours and the photodissociation (2), and thus the 'rotating cell technique'[14] was used for obtaining spectra with the argon-ion excitation lines.

$$FeCl_3(g) \rightleftharpoons FeCl_2(s) + \tfrac{1}{2}Cl_2(g) \qquad (2)$$

Rectangular fused-silica cells of 1 or 0.5 cm path length (Hellma, Mullheim, Baden, Germany) were used for the UV/VIS measurements of the vapours. The cells were degassed and filled with preweighed amounts of $FeCl_3$ in the glove-box. Gaseous $POCl_3$ was added to the cells using the vacuum-gas-addition line system and trapped with liquid nitrogen as described above. The absorption measurements were performed with a Hitachi U-3000 spectrophotometer equipped with a high-temperature optical furnace.[15] During the experiments the portion of the cell interrupting the optical path was at a temperature 2–3 °C higher than the rest of the cell. This prevented condensation of solids or liquids in the optical path and permitted absorption measurements of vapours in equilibrium with condensed phases. Spectroscopic methods for investigating gaseous equilibria involving complexes have been described previously.[16]

Results and Discussion

Raman spectra of $POCl_3$–$FeCl_3$ gas- and liquid-phase mixtures

Fig. 1 shows representative Raman spectra of $POCl_3$–Fe_2Cl_6 vapours in equilibrium with a 1:1 $POCl_3$–$FeCl_3$ molten mixture at 550 and 625 K. The Raman spectra of gaseous phosphoryl chloride[5] and iron chloride vapours[14] are well known. At *ca.* 500 K iron chloride vapours consist of dimeric Fe_2Cl_6, while at *ca.* 625 K traces of monomeric $FeCl_3$ can be detected in the Raman spectra because of the dimer dissociation.[14] The spectra in Fig. 1 consist of a superposition of bands due to $POCl_3(g)$ and $Fe_2Cl_6(g)$ plus some extra bands C attributed to a new gas-phase complex. The data indicate that the complex vaporizes dissociatively. Five bands are assigned to it and their wavenumbers and polarization characteristics are summarized in Table 1. Several other bands due to the complex might have been obscured by those of the component gases. It is noteworthy that when using the 514.5 and/or 488.0 nm excitation lines of the argon-ion laser no bands due to the complex could be observed. Absorption of the laser line by coloured vapours, the electronic absorption bands of which overlap with the energy range of the excitation lines used, is known to lead to increased local spectroscopic temperatures or photodissociation of gas-phase complexes.[2,3,14] As will be demonstrated in the next section, such an overlap occurs for the Fe–O–P–Cl gas-phase complex. Absorption of the argon-ion laser lines by the complex molecules resulted in higher sample temperatures along the beam than indicated by the furnace controller and thermal dissociation of the complex to its components occurs. Furthermore the 647.1 nm krypton-ion laser line used for exciting the Raman spectra of vapours (Fig. 1) overlaps with the tail of the electronic absorption bands of the gas-phase complex, leading to a probable preresonance enhancement of the complex band intensities. Thus, as pointed out in ref. 13, the relative Raman intensities of vapours cannot be used for determining the stoichiometry and thermodynamics of reaction (1).

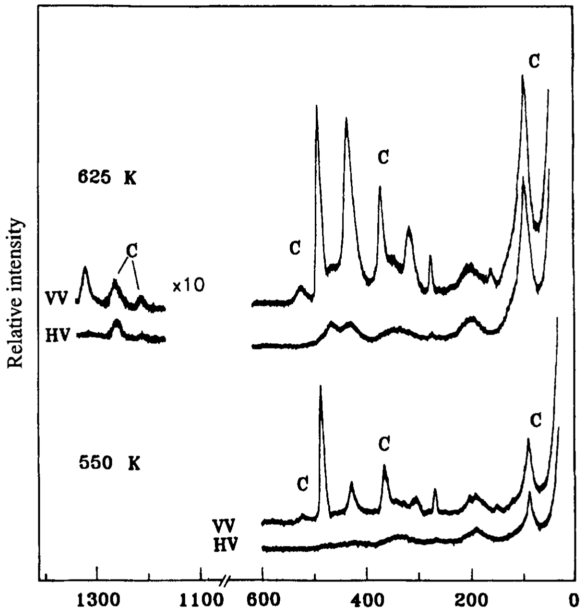

Fig. 1 Raman spectra of vapours over a 1:1 $POCl_3$–$FeCl_3$ mixture at 550 and 625 K. Bands due to the gas-phase complex are marked C. λ_0 = 647.1 nm; laser power, *w* = 200 mW; spectral slit width, s.s.w. = 6 cm^{-1}; time constant, τ = 1 s; scan speed, s.s. = 30 cm^{-1} min^{-1}. VV and HV denote the vertical–vertical and horizontal–vertical spectra polarizations, respectively

The 1:1 mixture could be sublimed across a temperature gradient giving yellow needle-shaped crystals, which were transformed into a dark brown-red liquid melting at *ca.* 160 °C. The gas-phase complex is presumably $POCl_3 \cdot FeCl_3(g)$ in agreement with what has been established for other $POCl_3$–MCl_3 (M = Al or Ga) systems[6] and according to a proposal of Suvorov,[9] who reported a high percentage of $POCl_3 \cdot FeCl_3(g)$ in the gas phase over $POCl_3$–$FeCl_3$ mixtures. More information about the number of bands due to the complex can be obtained by considering the spectra from liquid-state samples.

Several $POCl_3$–$FeCl_3$ molten mixtures with P:Fe ratios of 5:1, 2:1, 3:2, 1:1 and 1:2 were placed in cells. A careful study of the concentration dependence of the spectral features at 525 K indicates that complexation occurs and that the compound formed most probably has a 1:1 stoichiometry, $POCl_3 \cdot FeCl_3$. This can be deduced by comparing the relative intensities of the Raman spectra of $POCl_3$–$FeCl_3$ molten mixtures with 2:1, 1:1 and 1:2 compositions (Fig. 2). The assignment of the observed bands and their polarization characteristics are given in Table 1. In $POCl_3$-rich melts (P:Fe = 2:1) three bands can be assigned as due to the ν_1, ν_2 and ν_3 $POCl_3(l)$ modes,[17] while in $FeCl_3$-rich melts (P:Fe = 1:2) the spectra are dominated by the liquid iron chloride modes.[18] Absence of bands due to ionic species such as $FeCl_4^-$ from the spectra of Fig. 2 points to a molecular nature for the $POCl_3 \cdot FeCl_3$ liquid compound at 525 K. The relative band positions and the polarization properties for $POCl_3 \cdot FeCl_3$ are similar to those of the previously studied $POCl_3 \cdot GaCl_3$[6] and $POCl_3 \cdot AlCl_3$[6,7] gas-phase and molecular liquid complexes.

Bonding in the gas-phase and liquid $POCl_3 \cdot FeCl_3$ adduct presumably occurs *via* a P–O–Fe bridge, as in a series of known

Table 1 Observed vibrational Raman wavenumbers (cm^{-1}) for $POCl_3$–$FeCl_3$ molten mixtures (Figs. 2, 4 and 5) and gaseous $POCl_3{\cdot}FeCl_3$ (Fig. 1)[a]

$POCl_3$–$FeCl_3$ liquid mixtures						
	P:Fe = 2:1					
P:Fe = 5:1 300 K	360 K[c]	525 K	P:Fe = 1:1 525 K	P:Fe = 1:2 525 K	Assignments[b]	$POCl_3{\cdot}FeCl_3$(g) 625 K
				≈70w (dp)	'$FeCl_3$'	95m (dp)
	97s (dp)	97s (dp)	97m (dp)	97vw (br) dp	$POCl_3{\cdot}FeCl_3$ (E)	
114s (dp)	114m (dp)				$\nu_2(FeCl_4^-)$, $[Fe(POCl_3)_6][FeCl_4]_3$	
		127w (sh) dp	127w (dp)	126w (br) dp	$POCl_3{\cdot}FeCl_3$ (E)	
	132 (sh)				$POCl_3{\cdot}FeCl_3$ + $[Fe(POCl_3)_6][FeCl_4]_3$[d]	
134w (dp)					$\nu_4(FeCl_4^-)$, $[Fe(POCl_3)_6][FeCl_4]_3$	
		179w (p)	179vw (br)		$POCl_3{\cdot}FeCl_3$ (A_1)	
191s (dp)					$\nu_6(POCl_3)$, E	
	202m (dp)	202m (dp)	201w (dp)		$POCl_3{\cdot}FeCl_3$ (E)	
≈210 (sh) dp					$\nu_5(FeO_6)$, $[Fe(POCl_3)_6][FeCl_4]_3$	
268m (p)	268vw (p)	268vw (p)	268vw (p)		$\nu_3(POCl_3)$, A_1	
297m (p)					$[Fe(POCl_3)_6][FeCl_4]_3$	
	305m (p)	305m (p)	305m (p)	304w (p)	$POCl_3{\cdot}FeCl_3$ (A_1)	
332s(p)	332m (p)				$\nu_1(FeCl_4^-)$, $[Fe(POCl_3)_6][FeCl_4]_3$	
356m (p)					$\nu_1(FeO_6)$, $[Fe(POCl_3)_6][FeCl_4]_3$	
	362s (p)	362s (p)	362s (p)	362m (p)	ν(Fe–Cl), $POCl_3{\cdot}FeCl_3$ (A_1)	362s (p) [ν(Fe–Cl)]
385w					$[Fe(POCl_3)_6][FeCl_4]_3$	
		≈404w (p)	403m (p)	405s (p)	'$FeCl_3$'	
	≈420 (br) p	420w (dp)				
				453vw (br) dp	'$FeCl_3$'	
486vs (p)	486w (p)	486m (p)	486w (p)		$\nu_2(POCl_3)$, A_1	
521m (p)	521m (p)				ν(P–Cl), $[Fe(POCl_3)_6][FeCl_4]_3$	
	537m (p)	537m (p)	537m (p)	537w (p)	ν(P–Cl), $POCl_3{\cdot}FeCl_3$ (A_1)	530m (p) [ν(P–Cl)]
583w (br) dp			583vw (p)		$\nu_4(POCl_3)$, E	
	≈625vw (br)	≈625vw (br)	618vw (br)	≈615vw (br)	$POCl_3{\cdot}FeCl_3$ (E)	
	1199w (p)	1199w (p)	1194w (br) (p?)	1192vw (br) (p?)	$POCl_3{\cdot}FeCl_3$ (A_1)	1218w (p) [ν(P–O)]
1268w (dp)	1268w (dp)	1267vw (dp)	1269vw (dp)	1269vw (dp)	$POCl_3{\cdot}FeCl_3$ (E) + $[Fe(POCl_3)_6][FeCl_4]_3$[d]	1268vw
1298m (p)	1298w (p)	1298 w			$\nu_1(POCl_3)$, A_1	

[a] Abbreviations: s = strong; m = medium; w = weak; br = broad; sh = shoulder; p = polarized; dp = depolarized. [b] Assignments of $POCl_3{\cdot}FeCl_3$ are based on assumed C_{3v} symmetry Group-theory classification of vibrational modes: linear P–O–Fe bridge (C_{3v} symmetry), Γ_{vib} = 6 A_1(Raman, IR) + A_2 + 7E(Raman, IR); bent P–O–Fe bridge (C_s symmetry); Γ_{vib} = 13 A′(Raman, IR) + 8A″(Raman, IR). [c] Supercooled. [d] Overlapping bands.

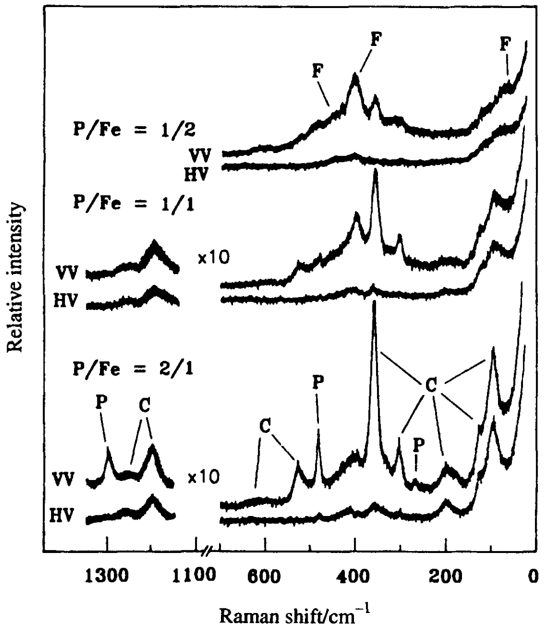

Fig. 2 Raman spectra of molten $POCl_3$–$FeCl_3$ mixtures at 525 K. Bands due to iron chloride, phosphoryl chloride and to the complex are marked by F, P and C respectively. λ_0 = 647.1 nm, w = 35 mW, s.s.w. = 4 cm^{-1}, τ = 0.3 s, s.s. = 60 cm^{-1} min^{-1}

$POCl_3$ addition compounds.[4,7,19] From a structural point of view a C_{3v} symmetry involving a linear P–O–Fe bridge or an alternative C_s configuration with a bent P–O–Fe bridge can be considered. Assignment of five polarized and five depolarized bands as due to the complex (see Table 1) points to C_{3v} rather than to C_s as the most plausible structure. Furthermore, it is noteworthy that the ν(P–Cl) stretching frequency of the complex is blue-shifted relative to the corresponding band of $POCl_3$(g), while ν(P–O) and ν(Fe–Cl) are red-shifted relative to the respective modes of $POCl_3$(g) and $FeCl_3$(g). These shifts are compatible with the proposed type of bonding, indicating that, as expected, the formation of the P–O–Fe bridge weakens the P–O and Fe–Cl and strengthens the P–Cl bond.

Electronic absorption spectra of $POCl_3$–$FeCl_3$ vapours

Molar absorption coefficient of the Fe–O–P–Cl gas-phase complex. The absorption spectra of vapours obtained from cells containing $POCl_3$–Fe_2Cl_6 mixtures show UV bands with maxima near 350 and 260 nm. Owing to overlapping bands of pure $POCl_3$(g), Fe_2Cl_6(g) and the Fe–O–P–Cl gas-phase complex, careful measurements are needed in order to determine and assign the molar absorption coefficients of the species.

The number of iron(III) participating in the gas-phase complex [*i.e.* the value of n in equation (1)] is not known and only apparent values of the molar absorption coefficient, ε, per mole of Fe^{III} in the gas phase can be calculated. However, as discussed in the previous section, the gas-phase complex most probably has a 1 : 1 stoichiometry, and is formed according to the equilibrium (3). For determining the apparent molar

$$POCl_3(g) + \tfrac{1}{2}Fe_2Cl_6(g) \rightleftharpoons POCl_3{\cdot}FeCl_3(g) \quad (3)$$

absorption coefficient of the complex a sufficiently large excess of phosphoryl chloride (P_{POCl_3} = 2.5–6.75 atm) had to be present in the cell, in order to assure that the contribution of the iron chloride sample (which was small enough to vaporize completely) to the absorbance in the homogeneous gas-phase region was negligible. In such a case it could be assumed that all the iron in the cell was in the form of $POCl_3{\cdot}FeCl_3(g)$ and the molar absorption coefficient of this species could be determined. Three different spectrophotometric cells were used to determine the apparent molar absorption coefficients of the gas-phase complex at 346 and 257 nm (ε_{346} and ε_{257}) (see SUP 57153). Fig. 3 shows the overall spectrum from cell E-2 at 550 K [spectrum (*a*)] and $Fe_2Cl_6(g)$ at 500 K [spectrum (*b*)]. The molar absorption coefficients of the $Fe_2Cl_6(g)$ UV bands at 360 and 245 nm were found to be in agreement with the data reported in ref. 20. The temperature dependence (550–635 K) of ε_{346} and ε_{257} of the complex was found from the measurements in the three cells and can be represented by the relations (4) and (5).

$$\varepsilon_{346} = 11\,067.4 - 11.7T \quad \mathrm{dm^3\,mol^{-1}\,cm^{-1}}, \mathrm{s.d.} = 29.9 \quad (4)$$

$$\varepsilon_{257} = 7605 - 9.7T \quad \mathrm{dm^3\,mol^{-1}\,cm^{-1}}, \mathrm{s.d.} = 26 \quad (5)$$

The data (see SUP 57153) indicate that within experimental error the apparent molar absorption coefficients are independent of $POCl_3$ pressure (varied in the range 2.5–6.75 atm). As for other gas-phase complexes,[16] this indicates that either one gaseous species is present or that two or more species with equal 'atomic' (in terms of Fe^{III}) absorptivities are formed.

Attempts to use spectrophotometry in order to determine the thermodynamics of the reaction $FeCl_3(s) + POCl_3(g) \rightleftharpoons POCl_3{\cdot}FeCl_3(g)$ in cells containing an excess of iron chloride and small amounts of $POCl_3$ (*i.e.* corresponding to pressures of ≈0.2 atm) were unsuccessful. This was due to the formation of a stable liquid even at temperatures around 400 K (the melting point of $FeCl_3$ is 581 K).

Charge-transfer spectra. The type of bonding and M–Cl interaction in the $POCl_3{\cdot}FeCl_3$ gas-phase complex can be studied by measuring the energies of the ligand-to-metal (M←L) charge-transfer transitions. A comparison of spectra (*a*) and (*b*) in Fig. 3 shows the differences between the charge-transfer transition energies of $POCl_3{\cdot}FeCl_3(g)$ (at 346 and 257 nm) and $Fe_2Cl_6(g)$ (at 360, ≈282 and 245 nm). However, a third charge-transfer band of the $POCl_3{\cdot}FeCl_3$ gas-phase complex at ≈210 nm is obscured by the strong $POCl_3(g)$ band in the far UV [see band tail in Fig. 3(*a*)]. The $POCl_3(g)$ band is due to a forbidden ($n \longrightarrow \pi^*$) transition from a non-bonding oxygen orbital to the antibonding molecular orbital of the P–O bond.[21] The occurrence of the band at 210 nm is illustrated in spectrum (*c*), Fig. 3, which was obtained from the vapours in equilibrium with a condensed phase [$POCl_3{\cdot}FeCl_3(l)$ + '$FeCl_3(l)$'?] in a cell with no excess of $POCl_3$ at 475 K. The contribution of gaseous Fe_2Cl_6 was subtracted from spectrum (*c*), which can thus be assigned to $POCl_3{\cdot}FeCl_3(g)$. Table 2 summarizes the M←L charge-transfer transition energies for iron(III) chloride compounds. The positions of the charge-transfer band maxima move to higher energies on going from $Fe_2Cl_6(g)$ to $POCl_3{\cdot}FeCl_3(g)$ (see Fig. 3 and Table 2). This is expected from the alteration of the chloride ligand environment caused by the formation of a P–O–Fe bridge.[2]

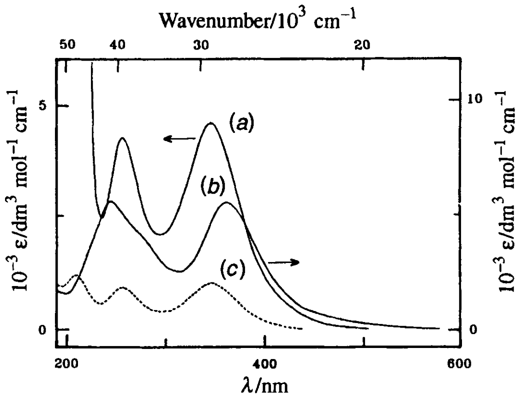

Fig. 3 Molar absorption coefficients of (*a*) $POCl_3{\cdot}FeCl_3(g)$ in equilibrium with $POCl_3(g)$ ($P^0_{POCl_3,\ 600\ K} = 4.5$ atm) at 550 K and (*b*) $Fe_2Cl_6(g)$ at 500 K. The spectrum of $POCl_3{\cdot}FeCl_3(g)$ at 475 K is shown in arbitrary intensity units, (*c*)

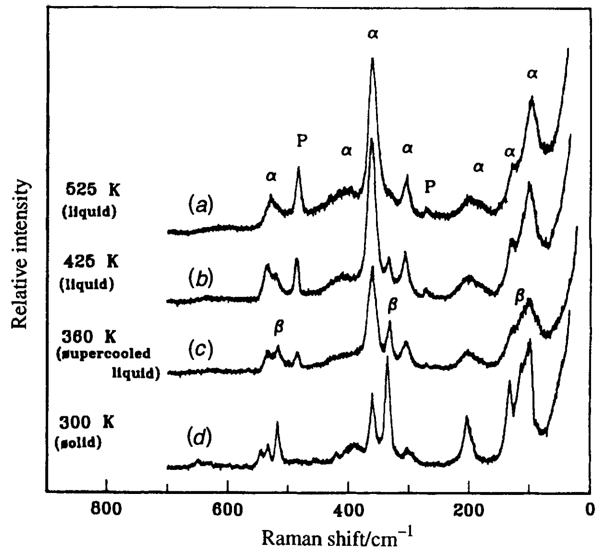

Fig. 4 Raman spectra of $POCl_3$–$FeCl_3$ molten mixtures (P : Fe = 2 : 1) at (*a*) 525, (*b*) 425 and (*c*) 360 K and of the solids at 300 K (*d*). Bands due to $POCl_3(l)$ are marked by P, while those due to $POCl_3{\cdot}FeCl_3(l)$ and $[Fe(POCl_3)_6][FeCl_4]_3(l)$ are marked by α and β, respectively. Spectrum (*d*) was obtained from a mixture of the '1 : 1 yellow' and '3 : 2 red' solid compounds (see text). Parameters as in Fig. 2

Molecular and ionic complexes in $POCl_3$-rich mixtures. From the above discussion of the Raman spectra of liquids obtained at 525 K it follows that the molecular nature of the $POCl_3$–$FeCl_3$ molten mixtures can be considered established at $T > 500$ K. However, a study of the temperature dependence of the Raman spectra of $POCl_3$-rich mixtures indicates that below 450 K bands due to a new species appear. This is illustrated in Fig. 4, where the temperature dependence of the spectra is shown for the 2 : 1 $POCl_3$–$FeCl_3$ mixture. The measured vibrational band wavenumbers are listed in Table 1, where a tentative assignment is also given. By lowering the temperature from 525 to 425 K new bands appear at 114, 332 and 521 cm^{-1} and become progressively stronger by further lowering the temperature to 360 K, attaining their maximum intensities in the solid state at 25 °C and/or at liquid-nitrogen temperature. The bands at 332 and 114 cm^{-1} are assigned as due to the ν_1 and ν_2 modes of $FeCl_4^-$ [18] and point to an ionic nature for the 'low'-temperature liquid species, which, judged from the spectra in Fig. 4, is formed at the expense of $POCl_3(l)$ and $POCl_3{\cdot}FeCl_3(l)$, most probably according to the equilibrium (6).

$$POCl_3(l) + 2(POCl_3{\cdot}FeCl_3)(l) \rightleftharpoons (3POCl_3{\cdot}2FeCl_3)(l) \quad (6)$$

Equilibrium (6) is shifted to the right by increasing the $POCl_3$ content. Indeed the spectrum of the 5 : 1 liquid mixture at room temperature (Fig. 5) exhibits bands due to $POCl_3(l)$ and to the $3POCl_3{\cdot}2FeCl_3$ liquid complex and the observed band wavenumbers are listed and assigned in Table 1 (first column). The spectrum of the 2 : 1 liquid mixture at 525 K which consists of $POCl_3{\cdot}FeCl_3(l)$ and $POCl_3(l)$ is included in Fig. 5 for comparison. The '3 : 2' ionic liquid could be formulated as $[Fe(POCl_3)_6][FeCl_4]_3$ and contain the $[FeCl_4]^-$ anion and the $[Fe(POCl_3)_6]^{3+}$ cation as a result of interactions between the lone electron pair of the oxygen of the $POCl_3$ solvent molecules

Table 2 Ligand-to-metal (M←L) charge-transfer transitions in iron(III) chloride compounds [$10^{-3}\tilde{\nu}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})]

$[NEt_4][FeCl_4]$[a] 2.9 × 10^{-4} mol dm^{-3} in MeOH	Fe_2Cl_6(g) (500 K)	$FeCl_3$(g) (875 K)	$FeAlCl_6$(g) (500 K)[b]	$POCl_3{\cdot}FeCl_3$(g) (550 K)
27.2	27.8[c] (5545)[b,d]	27.8[c] (4250)	27.8 (5500)	28.9 (4650)
	35.5[e] (1800)[d,f]	39.2[c] (3230)[f]		38.9 (2300)
40.3	40.8[c] (5400)[b,d]	46.5[e] (1600)[f]	40.8 (7200)	47.6[g]

[a] Ref. 22. [b] Ref. 20. [c] Also observed in ref. 20. [d] $\frac{1}{2}\,\varepsilon_{max}$ [e] Observed in this work by resolving into Gaussians. [f] Value determined by resolving into Gaussians. [g] Band observed at 475 K from gaseous sample in equilibrium with condensed phase; obscured at higher temperatures (see text).

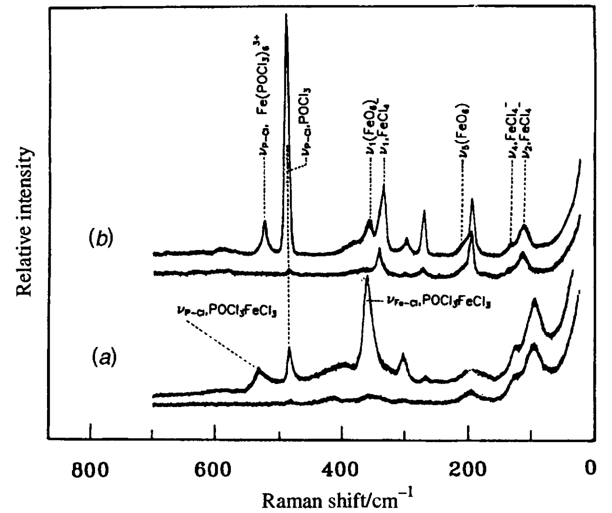

Fig. 5 Raman spectra of $POCl_3$–$FeCl_3$ molten mixtures; (*a*) P:Fe = 2:1 at 525 K consisting of $POCl_3{\cdot}FeCl_3$(l) and $POCl_3$(l); (*b*) P:Fe = 5:1 at 300 K consisting of $[Fe(POCl_3)_6][FeCl_4]_3$(l) and $POCl_3$(l). Parameters as in Fig. 2

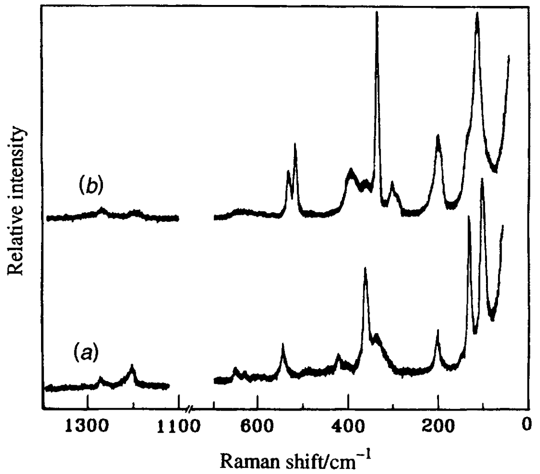

Fig. 6 Raman spectra of polycrystalline '1:1 yellow' $POCl_3{\cdot}FeCl_3$ (*a*) and '3:2 red' $[Fe(POCl_3)_6][FeCl_4]_3$ (*b*) at 300 K. λ_0 = 647.1 nm; *w* = 30 mW; s.s.w. = 4 cm^{-1}; τ = 0.3 s; s.s. = 60 cm^{-1} min^{-1}

and the Fe^{3+} cation. The band at 521 cm^{-1} is then assigned as due to the ν(P–Cl) stretching mode. Within the $[Fe(POCl_3)_6]^{3+}$ complex ion the iron atom is thus surrounded by six oxygen atoms in a near-to-octahedral co-ordination resulting in a $(FeO_6)(PCl_3)_6$ configuration containing six Fe–O–P bridges. It should then be possible to identify the Raman-active modes of the FeO_6 octahedron which span the representation $\nu_1(A_{1g})$ + $\nu_2(E_g)$ + $\nu_5(T_{2g})$. The Fe–O 'stretching' frequency of different compounds containing six-co-ordinated iron bound to ligands through oxygen is not greatly affected by the type of ligand and for certain complexes occurs below 400 cm^{-1}.[23] Thus the polarized band at 356 cm^{-1} observed in our spectra (Fig. 5 and Table 1, first column) could be assigned as due to the ν_1 mode of 'FeO_6' in the cationic complex; ν_2 is usually of very weak intensity and is rarely seen in the Raman spectra. The depolarized shoulder band at ≈210 cm^{-1} (see Fig. 5 and Table 1, first column) is assigned to the ν_5 mode. This assignment is supported by the fact that the $\nu_1:\nu_5$ frequency ratio is close to the value for a series of 'octahedral' XY_6 type molecules and ions for which these two frequencies have been measured.[23] It should be pointed out that a $[Fe(POCl_3)_6][FeCl_4]_3$ configuration is in conformity with earlier indications for self-ionization of the $POCl_3$–$FeCl_3$ liquids, suggesting that iron is present in both cationic and anionic species in solution and that the cationic species is not $POCl_2^+$.[10,11] Previously,[24] the formation of $[M(POCl_3)_4]^+$ complex ions has been deduced from Raman studies of $POCl_3$–$MAlCl_4$ (M = Na or Li) liquids.

As will be discussed below, spectrum (*d*) in Fig. 4 is due to an orange-yellow solid mixture of the compounds $POCl_3{\cdot}FeCl_3$(s) and $3POCl_3{\cdot}2FeCl_3$(s). The existence of the '1:1' and '3:2' solid compounds in the $POCl_3$–$FeCl_3$ system is well known.[1] The behaviour is somewhat analogous to that of the $POCl_3$–$AlCl_3$ system, where cooling of the molecular liquid complexes leads to ionic solids,[6,7,19] which depending on the P:Al ratio of the liquid mixture can be formulated as $[Al(POCl_3)_6][AlCl_4]_3$ and/or $[Al(POCl_3)_4][AlCl_4]_3$.[7]

Heat treatment of cells containing the 3:2 and 5:1 mixtures at 110–120 °C resulted in mixtures of dark orange-red and yellow solids which were indistinguishable by visual inspection. A temperature gradient (110–30 °C) had to be applied along the cell containing the 5:1 mixture in order to condense the large excess of gaseous $POCl_3$ in the cold part of the tube away from the solids. Removal of this cell from the furnace resulted in dissolution of the solid phase (which is presumably a mixture of the '1:1' and '3:2' compounds) in $POCl_3$. By heating the orange-yellow solid mixture at 50 °C under vacuum the $POCl_3$ could be condensed at a cold part of the tube and a pale yellow (with some orange shades) solid was obtained. The yellow solid is $POCl_3{\cdot}FeCl_3$, while the orange-red unstable compound is $[Fe(POCl_3)_6][FeCl_4]_3$.[1] The occurrence of the two solids is demonstrated in Fig. 6. Spectrum (*a*) was obtained from the yellow solid phase containing mainly the molecular $POCl_3{\cdot}FeCl_3$ compound as indicated by the close resemblance with the spectrum of the 1:1 liquid at 525 K [see for example Fig. 4(*a*)]. Spectrum (*b*) was obtained from the red $[Fe(POCl_3)_6][FeCl_4]_3$ solid. This last compound was prepared by treating overnight at 95 °C iron(III) chloride with an eight-fold excess of $POCl_3$ in a vacuum-sealed U-shaped quartz cell, resulting in a bright red solid–liquid mixture. In order to separate the red crystals from the excess of $POCl_3$ the side of the tube containing this mixture was heated gently at 40–45 °C in a tube furnace in such a way that $POCl_3$ distilled into the empty cell side located outside the furnace. Further heating at ≈75 °C resulted after several hours in the yellow solid $POCl_3{\cdot}FeCl_3$. The wavenumbers of vibrational bands of the 1:1 and 3:2 solids are listed in Table 3. It can now be visualized that a superposition of bands due to $POCl_3{\cdot}FeCl_3$(s) and to $[Fe(POCl_3)_6][FeCl_4]_3$(s) would result in a spectrum similar to the one shown in Fig. 4(*d*) previously assigned to a mixture of the two solids (see above).

Table 3 Observed vibrational Raman wavenumbers (cm^{-1}) for $POCl_3{\cdot}FeCl_3$(s) and $[Fe(POCl_3)_6][FeCl_4]_3$(s) (Fig. 5)

$POCl_3{\cdot}FeCl_3$(s)	$[Fe(POCl_3)_6][FeCl_4]_3$(s)
103vs	
	114vs
131s	130 (sh)
203m	200s
	291w
	303w
	335vs
339w (br)	
	≈360w
362vs	
	394m
423w	
≈480w (br)	
	518s
	533m
545m	
631w	≈635w (br)
651w	
1202m	1199w
1272w	1269w

Conclusion

Raman and UV/VIS spectra obtained from $POCl_3$–$FeCl_3$ vapour mixtures at temperatures up to 650 K indicated the existence of the $POCl_3{\cdot}FeCl_3$ gas-phase complex in equilibrium with $POCl_3$(g) and Fe_2Cl_6–$FeCl_3$(g). Above 500 K the $POCl_3$–$FeCl_3$ molten system can be considered as a molecular liquid mixture consisting of $POCl_3$(l), $FeCl_3$(l) and $POCl_3{\cdot}FeCl_3$(l), while below 450 K the 3:2 ionic liquid formulated as $[Fe(POCl_3)_6][FeCl_4]_3$ was formed in mixtures with $x_{POCl_3} > 0.5$ at the expense of $POCl_3$(l) and $POCl_3{\cdot}FeCl_3$(l). Two solids were identified at room temperature: (*i*) '1:1 yellow' $POCl_3{\cdot}FeCl_3$ and (*ii*) '3:2 red' $[Fe(POCl_3)_6][FeCl_4]_3$.

References

1 R. H. Tomlinson, in *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London, 1971, vol. 8, Suppl. 3, pp. 464–517.

2 G. N. Papatheodorou, in *Current Topics in Material Science*, ed. E. Kaldis, North-Holland, New York, 1982, vol. 10, pp. 249–352.

3 M. Brooker and G. N. Papatheodorou, *Adv. Molten Salt Chem.*, 1983, **5**, 27.

4 S. Boghosian, G. N. Papatheodorou, R. W. Berg and N. J. Bjerrum, *Polyhedron*, 1986, **5**, 1393.

5 G. N. Papatheodorou, *ACS Symp. Ser.*, 1982, **179**, 309.

6 S. Boghosian, D. A. Karydis and G. A. Voyiatzis, *Polyhedron*, 1993, **12**, 771.

7 F. Birkeneder, R. W. Berg and N. J. Bjerrum, *Acta Chem. Scand.*, 1993, **47**, 344.

8 V. V. Dadape and M. R. A. Rao, *J. Am. Chem. Soc.*, 1955, **77**, 6192.

9 A. V. Suvorov, *Zh. Koord. Khim.*, 1977, **3**, 1141.

10 V. Gutmann and M. Baaz, *Monatsh. Chem.*, 1960, **91**, 537.

11 J. A. Cade, M. Kasrai and I. R. Ashton, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2375.

12 G. N. Papatheodorou, in *Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases*, ed. J. W. Hastie, NBS Publication 561, National Bureau of Standards, Washington, DC, 1979, pp. 647–678.

13 S. Boghosian and G. N. Papatheodorou, *J. Phys. Chem.*, 1989, **93**, 415.

14 L. Nalbandian and G. N. Papatheodorou, *High Temp. Sci.*, 1990, **28**, 49.

15 L. Nalbandian, Ph.D. Thesis, University of Patras, 1990.

16 G. N. Papatheodorou, *J. Phys. Chem.*, 1973, **77**, 472; G. H. Kucera and G. N. Papatheodorou, *J. Phys. Chem.*, 1979, **83**, 3213.

17 K. Olie and D. J. Stufkens, *Spectrochim. Acta, Part A*, 1976, **32**, 469.

18 G. A. Voyiatzis and G. N. Papatheodorou, unpublished work.

19 S. Boghosian, G. D. Zissi and G. A. Voyiatzis, in *Molten Salts*, eds. C. L. Hussey, D. S. Newman, G. Mamantov and Y. Ito, The Electrochemical Society, Pennington, NJ, 1994, vol. 94–99, p. 276.

20 C.-F. Shieh and N. W. Gregory, *J. Phys. Chem.*, 1975, **79**, 828.

21 M. Halmann, *J. Chem. Soc.*, 1963, 2853.

22 R. S. Drago, R. L. Carlson and K. F. Purcell, *Inorg. Chem.*, 1965, **4**, 15.

23 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley-Interscience, New York, 1986, pp. 150, 229, 245.

24 F. Birkeneder, R. W. Berg, H. A. Hjuler and N. J. Bjerrum, *Z. Anorg. Allg. Chem.*, 1989, **573**, 170.

Received 31*st January* 1996; *Paper* 6/00744I