ABSTRACT

Raman spectroscopy is used for studying the structural properties of POCl$_3$MCl$_5$ (M=Nb, Ta) molecular complexes in the solid, liquid and gaseous state at temperatures up to 800 K. It is shown that complexing occurs through the formation of P-O-M bridges. The spectra are interpreted in terms of a Cs configuration consisting of a "MC\textsuperscript{O}" octahedron sharing a corner with a "OPCl\textsubscript{3}" tetrahedron for the POCl$_3$-NbCl$_5$ and POCl$_3$-TaCl$_5$ liquid and vapor complexes. The structural and vibrational properties of a series of POCl$_3$MCl$_x$ (M=Al, Ga, Fe, Zr and Hf) vapor complexes with C\textsubscript{3v} (involving straight P-O-M bridges) or C\textsubscript{1} (involving bent P-O-M bridges) symmetries are discussed. The energies of the M$\leftarrow$L charge-transfer transitions in the electronic absorption spectra of the POCl$_3$FeCl$_3$ vapor complex indicate that bonding occurs with the formation of a P-O-Fe bridge. Partial ionization in the liquid and solid phases of the POCl$_3$-FeCl$_3$ and in the solid phase of the POCl$_3$-AlCl$_3$ systems is shown to occur below 450 K.

INTRODUCTION

Phosphoryl chloride is known to act as donor molecule towards other inorganic metal halides by forming a wide range of liquid complex compounds with low melting points. However, although a detailed summary of the chemistry of such compounds is available (1), not much work has been directed towards the determination of structural characteristics in the liquid and vapor state. In contrary, the vibrational and structural properties of a large number of liquid and vapor complexes where AlCl$_3$, GaCl$_3$, InCl$_3$ and FeCl$_3$ act as complex forming agents have been established (2,3).

The aim of the present work is the characterization by Raman spectroscopy of the liquid and vapor complexes formed between POCl$_3$ and i) The pentachlorides of Nb and Ta and ii) The "acidic" trichloride of Fe. The complexes are investigated also in the solid state in order to clarify in which form they occur (molecular, glassy or ionic).
Furthermore, the nature of the known complexes formed in the POCl\textsubscript{3}-AlCl\textsubscript{3} system (4) is examined in the solid state for comparison with the P-O-Fe system and a summary of certain structural and vibrational properties of POCl\textsubscript{3}-MCl\textsubscript{4} (M= Al (4), Ga (4), Fe, Zr (5), Hf (5), Nb and Ta) vapor complexes is presented.

**EXPERIMENTAL**

High purity anhydrous NbCl\textsubscript{5}, TaCl\textsubscript{5}, FeCl\textsubscript{4} and AlCl\textsubscript{3} were prepared from the corresponding Cerac/Pure Inc. reagents by repeated slow sublimations in fused silica tubes under vacuum. All handling of chemicals took place in a nitrogen-filled glove-box with a water vapor content of less than 1 ppm. Liquid POCl\textsubscript{3} was purchased from Fluka.

The Raman (optical) cells containing the melt mixtures consisted of fused silica tubing (4±0.1 mm o.d. and 2±0.1 mm i.d., ~3 cm long). In case of cells containing vapor mixtures, silica tubing with 20±0.2 mm o.d, 18±0.2 mm i.d. was used. Preweighed amounts of salts were transferred into clean, dry, flamed and degassed optical cells of known volume. The cells were afterwards attached to an all-glass vacuum line where a container with POCl\textsubscript{3} was also connected. Phosphoryl chloride was then allowed to vaporize and occupy a confined bulb of known volume and it was afterwards 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 salt mixtures were reacted inside a side tube (6±0.1 mm o.d., 4±0.1 mm i.d.), vapor transported into the main cell compartment and finally the side tube was sealed off. In this way a high degree of sample purity could be achieved. The ideal gas pressure, \(P^0\), of each undissociated and unreacted compound could be calculated from the number of moles added to the cell.

Raman spectra were excited with the 514.5 and 488.0 nm lines of a 4W Spectra Physics Ar\textsuperscript{+} laser and the 647.1 and 676.4 nm lines of a Spectra Physics Kr\textsuperscript{+} laser. The scattered light was collected at an angle of 90° (vertical scattering plane) and analyzed 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 for obtaining the high-temperature Raman spectra was similar to that described in detail elsewhere (6).

**RESULTS AND DISCUSSION**

**Raman Spectra of POCl\textsubscript{3}-MCl\textsubscript{4} (M=Nb, Ta) Vapors and Liquids**

Figure 1 shows representative vapor Raman spectra obtained for POCl\textsubscript{3}(g) and TaCl\textsubscript{5}(g) at 600 K and for a POCl\textsubscript{3}-TaCl\textsubscript{5} vapor mixture at 600 and 700 K. The spectra of the vapor mixtures consist of superpositions of bands due to the pure gaseous components plus five new polarized bands at wavenumbers listed in Table I, which are attributed to a vapor complex. Complex band intensities are decreasing with increasing
temperature, probably due to thermal decomposition. Several bands due to the vapor complex might have been obscured by POCl$_3$(g) and TaCl$_5$(g) bands, which dominate the spectra. The vapor Raman spectra obtained for the POCl$_3$(g)-NbCl$_5$(g) system exhibited similar general features. Three weak polarized bands were assigned to a vapor complex (see Table I for wavenumbers). It is noteworthy that in the course of the experiments when the blue to green Ar$^+$ laser lines were used to excite the spectra, a photodissociation of the colored vapors occurred due to light absorption. Therefore, the use of the rotating cell technique (7) was necessary for preventing this phenomenon.

More information about the number of bands due to the complexes can be obtained by considering the spectra of the liquids. Figure 2 shows Raman spectra obtained from POCl$_3$(l), Ta$_2$Cl$_{10}$(l) and three different TaCl$_5$-POCl$_3$(l) mixtures at 220°C. The spectral data clearly indicate that the complex species is the 1:1 POCl$_3$-TaCl$_5$ (m.p. ~190°C). All 12 bands observed in the spectrum of the 1:1 mixture are assigned to the POCl$_3$-TaCl$_5$(l) complex (see Table I for wavenumbers and polarization characteristics). Similar spectra were recorded for the NbCl$_5$-POCl$_3$(l) system, where again no bands due to POCl$_3$(l) or NbCl$_5$(l)/Nb$_2$Cl$_{10}$(l) were observed in the spectra of the 1:1 mixture. The wavenumbers and polarization characteristics of 13 bands due to the POCl$_3$-NbCl$_5$ complex (m.p. ~170°C) are listed in Table I. Formation of ionic POCl$_3$-MCl$_x$ liquid compounds can be excluded because of the absence of the characteristic NbCl$_5^-$ and TaCl$_5^-$ bands (3).

Table I. Raman spectral data (cm$^{-1}$) of POCl$_3$-NbCl$_5$ and POCl$_3$-TaCl$_5$ liquid and vapor complexes.

| POCl$_3$-NbCl$_5$(l)  | POCl$_3$-NbCl$_5$(g)  | POCl$_3$-TaCl$_5$(l)  | POCl$_3$-TaCl$_5$(g)  |
|----------------------|----------------------|----------------------|----------------------|
| 500 K                | 600 K                | 500 K                | 600 K                |
| 90 vw,dp             | 88 w,dp              |                      |                      |
| 144 s,dp             |                      | 142 w,p              |                      |
| 155 s,p              | 144 s,p              |                      |                      |
| 169 m,dp             | 160 m,dp             |                      |                      |
| 189 w,dp             | 185 m,dp             |                      |                      |
| 211 w,dp             | 210 w,dp             |                      |                      |
| 298 m,dp             | 304 m,dp             |                      |                      |
| 358 s,p              | 360 vw,p             | 360 s,p              | 362 w,p              |
| 399 vs,p             |                      | 402 vs,p             | (ν$_{M-Cl}$)$_{br}$  |
| 524 s,p              | 520 vw,p             | 529 s,p              | 515 w,p              |
| 636 vw,dp            | 642 vw,dp            |                      | ν$_{p-Cl}$           |
| 1210 vw, p           | 1200 w, p            | 1225 vw,p(?)         |                      |
| 1256 vw,p            | 1260 vw,p            | 1268 vw,p            | ν$_{p-o}$            |

*Abbreviations: s=strong, m=medium, w=weak, v=very, p=polarized, dp=depolarized

It appears that the positions of bands assigned as due to the vapor complexes in the spectra of POCl$_3$-MCl$_x$(M= Ta, Nb) vapors are very close to the positions of the most
prominent bands of the POCl$_3$MCl$_x$ complexes, a fact indicating that the predominant vapor complex species are the 1:1 POCl$_3$MCl$_x$ (M=Ta, Nb) molecules. This is in agreement with what has been established for the case of POCl$_3$MCl$_x$ [M= Al, Ga (4), Fe (8)] and POCl$_3$MCl$_y$ [M= Zr, Hf (5)] gaseous compounds. The stability of the vapor complexes is decreasing in the order: Al > Ga, Fe > Zr, Hf > Nb, Ta.

Table II lists the principal stretching frequencies for the studied POCl$_3$MCl$_x$ (x=3, 4 and 5) vapor complexes. It is noteworthy that in all cases studied, the $v_{P-O}$ and $v_{M-Cl}$ stretching frequencies were red-shifted relative to the corresponding bands of the free POCl$_3$(g) and the free metal chlorides, while on the other hand the $v_{P-Cl}$ stretching frequencies were blue-shifted relative to the corresponding band of POCl$_3$(g). These shifts are compatible with the formation of P-O-M bridging bonds, which are expected to weaken the P-O and M-Cl bonds and strengthen the P-Cl bonds.

Table II. Principal stretching frequencies (in cm$^{-1}$) in POCl$_3$MCl$_x$ vapor complexes

| Compound          | $v_{M-Cl}$ cm$^{-1}$ | $v_{P-O}$ cm$^{-1}$ | $v_{P-Cl}$ cm$^{-1}$ | Ref. |
|-------------------|----------------------|---------------------|----------------------|------|
| POCl$_3$(g)       | 478.5                |                     | 1319                 |      |
| AlCl$_3$(g)       | 377                  |                     |                       |      |
| POCl$_3$AlCl$_3$(g) | 313                 | 537                 | 1231                 | 4    |
| GaCl$_3$(g)       | 381                  |                     |                       |      |
| POCl$_3$GaCl$_3$(g) | 366                 | 513                 | 1220                 | 4    |
| FeCl$_3$(g)       | 370                  |                     |                       |      |
| POCl$_3$FeCl$_3$(g) | 362                 | 530                 | 1200                 | 8    |
| ZrCl$_4$(g)       | 377                  |                     |                       |      |
| POCl$_3$ZrCl$_4$(g) | -                   | 508                 | -                    | 5    |
| HfCl$_4$(g)       | 381                  |                     |                       |      |
| POCl$_3$HfCl$_4$(g) | 347                 | 512                 | 1263                 | 5    |
| NbCl$_5$(g)       | 393                  |                     |                       |      |
| POCl$_3$NbCl$_5$(g) | 360                 | 520                 | 1265                 | this work |
| TaCl$_5$(g)       | 406                  | 515                 | 1268                 | this work |

The bonding in the vapor and liquid adduct POCl$_3$MCl$_x$ complexes occurs by coordination of the oxygen with the metal atom, leading presumably to a Cl$_3$POMCl$_y$ configuration with $C_3$ symmetry (Cl$_3$PO tetrahedron sharing corner with OMCl$_x$ octahedron) giving rise to coordination numbers of 6 and 4 for M(Nb,Ta) and P, respectively (3).

Electronic Absorption Spectra of POCl$_3$-FeCl$_3$ Vapors

The type of bonding and M-Cl interaction in the POCl$_3$FeCl$_3$ vapor complex can be studied exclusively by means of UV/VIS spectrophotometry by measuring the energies of the ligand-to-metal (M$\rightarrow$L) charge transfer transitions. However, considering the
gaseous equilibrium:

$$\text{POCl}_3(g) + \frac{1}{2}\text{FeCl}_3(g) \rightleftharpoons \text{POCl}_3\cdot\text{FeCl}_3(g)$$

a sufficiently large excess of phosphoryl chloride ($P^\phi_{\text{K}} = 2.5 - 6.75$ atm) had to be present in order to consider that the contribution of the iron chloride sample (small enough to vaporize completely) to the absorbance in the homogeneous gas region was negligible. Thus in such a case it can be assumed that all the iron in the cell is in the form of $\text{POCl}_3\cdot\text{FeCl}_3(g)$ and the molar absorptivities of this species can be determined (9). Figure 3 shows that the appearance of the $\text{POCl}_3\cdot\text{FeCl}_3(g)$ spectrum [curve (a)] is different from that of $\text{Fe}_2\text{Cl}_6(g)$ [curve(b)]. The wing of the band at the far UV range is due to a forbidden ($\pi^* \rightarrow \pi$) transition from a non-bonding oxygen orbital to the antibonding molecular orbital of the P-O bond (10). It turned out, however, that a third charge transfer band of the $\text{POCl}_3\cdot\text{FeCl}_3$ vapor complex is obscured from the strong $\text{POCl}_3(g)$ absorption band [spectrum (a)]. This is illustrated in spectrum (c), Fig. 3, which is obtained from a gaseous sample in equilibrium with a condensed phase ($\text{POCl}_3\cdot\text{FeCl}_3(l)$ + $\text{FeCl}_3(l)$) in a cell with no excess $\text{POCl}_3$ at 490 K. The contribution of gaseous $\text{Fe}_2\text{Cl}_6$ is subtracted from spectrum (c), which can thus be assigned to $\text{POCl}_3\cdot\text{FeCl}_3(g)$. It appears from Figure 3 that the positions of the charge transfer bands' maxima move to higher energies on going from $\text{Fe}_2\text{Cl}_6(g)$ to $\text{POCl}_3\cdot\text{FeCl}_3(g)$. This is exactly what it should be expected from the alteration of the chloride ligands' environment caused by the formation of a P-O-Fe bridge. The electron donating ability of the chloride ligands decreases since their electronic density is pulled away and the $M\rightarrow L$ charge transfer is hindered and occurs at higher energies. Thus weak covalent bonding is implied for the Fe-Cl interaction in the $\text{POCl}_3\cdot\text{FeCl}_3(g)$ molecule in agreement with the results of the Raman spectroscopic investigation (see Table II and refs. 8,9).

Partial Ionization of $\text{POCl}_3\cdot\text{FeCl}_3$ and $\text{POCl}_3\cdot\text{AlCl}_3$ solid complexes

It has been established that the $\text{POCl}_3\cdot\text{AlCl}_3$ molten mixtures are molecular liquids consisting of $\text{POCl}_3\cdot\text{AlCl}_3(l)$, $\text{POCl}_3\cdot(\text{AlCl}_3)_2(l)$, $\text{Al}_2\text{Cl}_6(l)$ and $\text{POCl}_3(l)$ at temperatures above their melting points (4, 11). Furthermore, while the molecular nature of the $\text{POCl}_3\cdot\text{FeCl}_3$ molten mixtures can be considered established at $T>500$ K (8), a study of the temperature dependence of their Raman spectra indicates that below 450 K, and as temperature is gradually decreased, a partial self-ionization of the liquid occurs, which is more pronounced in the $\text{POCl}_3$-rich mixtures (e.g. for a P/Fe ratio of 2/1) (8). By lowering the temperature from 525 to 425 K three new bands appeared at 114, 332 and 520 cm$^{-1}$ that became progressively stronger on going from 425 to 360 K and attained their maximum intensities in the solid state at liquid nitrogen temperature (9). The bands at 114 and 332 cm$^{-1}$ are assigned to $\text{FeCl}_4^-$, while the band at 520 cm$^{-1}$ is more difficult to assign. In view of the 525 cm$^{-1}$ value reported for the $v_{\text{FeCl}}$ mode of $\text{PFCl}_2$ (12) one could assign the 520 cm$^{-1}$ band to the $v_{\text{P-Cl}}$ mode of $\text{POCl}_3^+$. The molecular nature of the $\text{POCl}_3\cdot\text{AlCl}_3(l)$ complex (4) is not retained in the solid state. A very prominent band at 352 cm$^{-1}$, which is attributed to $\text{AlCl}_3^+$ appears in the crystal Raman spectra from 2:1 and 1:1 $\text{POCl}_3\cdot\text{AlCl}_3$ mixtures (see Figure 4). However the
strong feature at 549 with a shoulder at 535 cm\(^{-1}\) observed for the crystalline phase from the 2:1 mixture is not observed in the 1:1 solid. The 1:1 ionic compound is probably the \([\text{Al(POCl}_3]\_4][\text{AlCl}_4]\_3\) for which a X-ray powder diagram is reported (13). While freezing a 2:1 mixture, gas bubbles are evolved which are believed to be POCl\(_3\). This is further justified from the close resemblance of the spectra of the solids from the 2:1 and 3:2 mixtures, indicating that the same ionic compound is formed, which is believed to be the \([\text{Al(POCl}_3]\_6][\text{AlCl}_4]\_3\) in agreement with ref.11, with the 535-549 cm\(^{-1}\) band assigned to the Al-O stretching mode of \([\text{Al(POCl}_3]\_6]\)^{2+}, in analogy with the 526 cm\(^{-1}\) \(\nu(\text{Al}-\text{O})\) Al-O band of \([\text{Al(OH}_2]\_6]\) (14).

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REFERENCES

1. R. H. Tomlinson, in Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 8, Supplement 3, p. 496. Longmans, London (1971).
2. G. N. Papatheodorou, in Current Topics in Materials Science, E. Kaldis, Editor, Vol. 10, p.251, North Holland Pub. Co., New York (1982).
3. M. Brooker and G. N. Papatheodorou, in Advances in Molten Salt Chemistry, G. Mamantov, Editor, Vol. 5, p. 27. Elsevier, New York (1983). 
4. S. Boghosian, D. A. Karydis and G. A. Voyiatzis, Polyhedron, 12, 771 (1993).
5. S. Boghosian, G. N. Papatheodorou, R.W. Berg and N.J. Bjerrum, Polyhedron, 5, 1393 (1986).
6. G. N. Papatheodorou, in Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, J. W. Hastie, Editor, NBS Publication 561, p.647, National Bureau of Standards, Washington, DC (1979).
7. L. Nalbandian and G. N. Papatheodorou, High Temp. Sci., 28, 49 (1990).
8. G. A. Voyiatzis and S. Boghosian, in Molten salt Chemistry and Technology/1993, M.L. Saboungi and S. Kojima, Editors, PV 93-9, p. 14, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1993).
9. S. Boghosian, G. A. Voyiatzis and G. N. Papatheodorou, to be submitted for publication.
10. M. Halmann, J.Chem.Soc., 2853 (1963).
11. F. Birkeneder, R. W. Berg and N. J. Bjerrum, Acta Chem.Scand., 47, 344 (1993).
12. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, p. 122, Wiley Interscience, New York (1986).
13. V. Gutmann and M. Baaz, Monatsh.Chem., 90, 729 (1959).
14. M. H. Brooker, in The Chemical Physics of Solvation, R. R. Dogodnadze, Editor, Vol. 38 B, p. 119, Elsevier, Amsterdam 1986.
Fig. 1. Raman spectra of POCl₃-TaCl₅ vapors. $P'_{POCl_3}$ = 2 atm, $P'_{TaCl_5} = 0.5$ atm. Bands due to the complex are marked by "C". $\lambda_0 = 488.0$ nm, $w = 320$ mw, $ssw = 6$ cm⁻¹, $\tau = 0.5$ s, $ss = 18$ cm⁻¹ min⁻¹.

Fig. 2. Concentration dependence of Raman spectra of POCl₃-TaCl₅ molten mixtures. $\lambda_0 = 488.0$ nm, $w = 15$ mw, $ssw = 3.5$ cm⁻¹, $\tau = 0.1$ s, $ss = 60$ cm⁻¹ min⁻¹.
Fig. 3. Molar absorptivities of POCl$_3$, FeCl$_3$ (g) in equilibrium with POCl$_3$(g) ($P_{POCl_3}$ = 4.5 atm) at 550 K [curve (a)] and Fe$_2$Cl$_6$(g) at 500 K [curve (b)]. To the bottom [curve (c)] the spectrum of POCl$_3$/FeCl$_3$(g) is shown in arbitrary intensity units.

Fig. 4. Raman spectra of POCl$_3$-AlCl$_3$ at room temperature and solids from 1:1 and 2:1 POCl$_3$-AlCl$_3$ mixtures at room temperature. $\lambda_0$ 4.8.0 nm, $w$ 15 mw, $ssw$ 3.5 cm$^{-1}$, $\tau$ 0.1 s, $ss$ 60 cm$^{-1}$ min$^{-1}$. 