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VIBRATIONAL SPECTRA OF DIMER COMPLEX (TiCl₄·POCl₃)₂

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The Raman and Infrared spectra of solid state (TiCl₄·POCl₃)₂ complex have been measured. The assignment for the observed data have been made on an assumption of the C_{2h} molecular symmetry. The coordination effects have been discussed based on the observed frequencies.

INTRODUCTION

Both 1:1 and 1:2 complexes of titanium tetrachloride with phosphoryl chloride, in the condensed states, have been studied by X-ray structural analysis^{1,2} and the thermochemical technique.^{3,4} The 1:1 complex has been shown to be a dimer with two bridge formation by the chlorine atoms¹ and the 1:2 is a cis-monomer.²

Previously, Sheldon and Tyree^{5,6} have studied the IR spectrum of the dimer complex in the P=O stretching frequency region. However, the IR spectrum below this region and Raman spectrum have not yet been reported.

In this investigation we report the Raman spectrum of the dimer complex (TiCl₄·POCl₃)₂ and the IR spectrum. The fundamental vibrations, except for the torsional and the skeleton modes, have been tentatively assigned assuming a C_{2h} symmetry for the whole molecular structure.

EXPERIMENTAL

The complex (TiCl₄·POCl₃)₂ was prepared by the method described in the literature.³ All preparations and sample handling were carried out in a nitrogen filled dry box.

The Raman spectrum was recorded of a solid state

sample held in a capillary, on a Jarrell-Ash model 25-300 Raman laser spectrometer equipped with an argon ion laser (514.5 and 488.0 nm) as the light source. The IR spectrum was recorded as a Nujol mull between CsI or polyethylene windows, on a Perkin-Elmer IR-180 spectrophotometer. The Raman and IR spectral data of (TiCl₄·POCl₃)₂ are listed in Table I. The Raman spectrum in the region of P=O stretching frequency and the region below 700 cm⁻¹ and the IR spectrum in the region 1500 to 180 cm⁻¹ are shown in Figures 1 and 2, respectively.

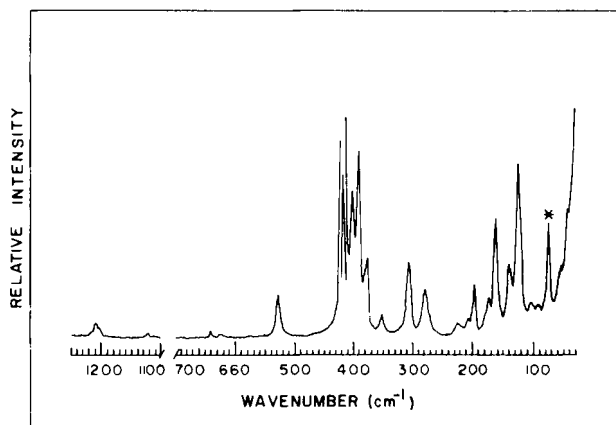


FIGURE 1 The Raman spectrum in the region of P=O stretching frequency and the region below 700 cm⁻¹ for (TiCl₄·POCl₃)₂. *Spurious band.

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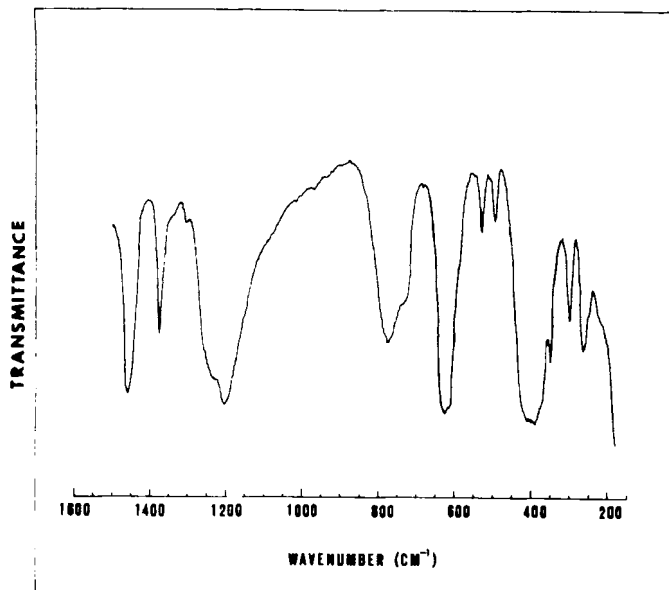


FIGURE 2 The IR spectrum in the region 1500–180 cm^{-1} for $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$.

RESULTS AND DISCUSSION

Remarkable differences between the Raman spectra of dimer and monomer⁷ complexes were observed specially in the frequency region below 450 cm^{-1} .

No coincidence in the Raman and IR bands was observed, particularly in the Ti–Cl stretching frequency region, which indicates the presence of a center of symmetry in the molecular structure. This is consistent with an approximate C_{2h} symmetry given by the X-ray diffraction study.¹ The fifty-four normal vibrations are shared among four symmetry species of the C_{2h} point group as shown in the following:

$$\Gamma = 16a_g + 11a_u + 11b_g + 16b_u.$$

The vibrational frequencies of coordinated POCl_3 are expected to be in the same region of related complexes, and the assignment of these vibrations are made by comparison with those of $\text{TiCl}_4 \cdot 2\text{POCl}_3$, $\text{SnCl}_4 \cdot 2\text{POCl}_3$, $\text{SbCl}_5 \cdot \text{POCl}_3$ and $\text{NbCl}_5 \cdot \text{POCl}_3$.^{7,8} The Raman band at 1210 cm^{-1} and IR band at 1205 cm^{-1} are assigned to the P=O stretching vibrations and the frequency shift of about 115 cm^{-1} from the band of free POCl_3 ^{9,10} is comparable with that for $\text{TiCl}_4 \cdot 2\text{POCl}_3$. Two Raman and two IR bands at about 640 and 625 cm^{-1} are assigned to the asym-

TABLE I
Observed Raman and IR frequencies (cm^{-1}) of
 $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ ^a

Raman	IR	Assignment
	1304 sh*	
	1235 sh*	
1210 w		$\nu \text{PO Ag}$
1205 sh	1205 vs	$\nu \text{PO Bu}$
1124 vw		$2 \times 417 + 305 = 1139$
	775 m	$408 + 377 = 785$
642 w		$\nu_a \text{PCl Ag}$
	634 sh	$\nu_a \text{PCl Bu}$
625 w		$\nu_a \text{PCl Bg}$
	624 s	$\nu_a \text{PCl Au}$
	608 sh†	
528 m		$\nu_s \text{PCl Ag}$
	528 w	$\nu_s \text{PCl Bu}$
	494 w†	
417 vs		$\nu \text{TiCl}_t'' \text{ Ag}$
	408 s	$\nu \text{TiCl}_t'' \text{ Au}, \rho \text{PCl}_3 \text{ Bu}$
401 m		$\nu \text{TiCl}_t'' \text{ Bg}$
390 s		$\rho \text{PCl}_3 \text{ Ag}$
	386 vs	$\nu \text{TiCl}_t'' \text{ Bu}, \nu \text{TiCl}_t'' \text{ Bu}$
377 m		$\nu \text{TiCl}_t'' \text{ Ag}$
352 m		$\rho \text{PCl}_3 \text{ Bg}$
	350 w	$\rho \text{PCl}_3 \text{ Au}$
305 m		$\nu \text{TiCl}_b \text{ Ag}$
	298 m	$\delta_s \text{PCl}_3 \text{ Bu}$
279 m		$\nu \text{TiCl}_b \text{ Bg}, \delta_s \text{PCl}_3 \text{ Ag}$
	264 m	$\nu \text{TiCl}_b \text{ Au}, \nu \text{TiCl}_b \text{ Bu}$
223 w		$\delta_a \text{PCl}_3 \text{ Ag}$
	220 w	$\delta_a \text{PCl}_3 \text{ Bu}$
206 w		$\delta_a \text{PCl}_3 \text{ Bg}$
	206 w	$\delta_a \text{PCl}_3 \text{ Au}$
196 m		} skeleton deformation
175 sh		
171 w		$\nu \text{TiO} ?$
161 m		} skeleton deformation and lattice
139 m		
134 sh		
124 s		
103 w		
90 w		
71 w		
48 sh		
37 w		

^a TiCl_t'' = terminal bond trans to POCl_3 ; TiCl_t' = terminal TiCl_2 bond; TiCl_b = bridging bond.

† Bonds due dissociation of the complex.

metric P–Cl stretching vibrations, which are degenerate in the free ligand, and the symmetric at 528 cm^{-1} in both spectra. Considering the assignment of $\text{TiCl}_4 \cdot 2\text{POCl}_3$,⁷ the bands at about 350 and 400 cm^{-1} are assigned to the POCl_3 rocking vibrations and those at about 220 and 205 cm^{-1} to the asymmetric PCl_3 bending. The symmetric PCl_3 bending vibrations are observed at 298 and 279 cm^{-1} .

The Ti—Cl stretching vibrations of TiCl_4 complexes are expected in the frequency region 450 to 280 cm^{-1} .^{11,12} It is well known that the bridged Ti—Cl bond is considerably weaker than that of the TiCl terminal bond;¹³ this bond distance in $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$, determined by the X-ray study confirms this fact.¹ Therefore, the bridged Ti—Cl stretching frequencies can be expected in a lower frequency region than the terminal stretching frequencies. To assign these vibrations, the vibrational study of $(\text{Ti}_2\text{Cl}_{10})^{2-}$ is considered.¹⁴ The Raman bands at $417 (a_g)$, $401 (b_g)$ and $377 (a_g) \text{ cm}^{-1}$ are assigned to the terminal Ti—Cl stretching vibrations and those at $305 (a_g)$ and $279 (b_g) \text{ cm}^{-1}$ to the bridged ones. In the corresponding IR spectrum, the bands at $408 (a_u)$ and $386 (a_u, b_u) \text{ cm}^{-1}$ are also assigned to the terminal stretching vibrations and that at $264 (a_u, b_u)$ to the bridged ones.

These assignments of the Ti—Cl stretching vibrations also satisfy the frequency ratio between the bridged and terminal stretching frequencies. The value calculated for the average frequencies between bridged and terminal bonds is about 0.69, and this lies within the limits normally found from 0.60 to 0.85.¹³

It is very difficult to determine the characteristic Ti—O stretching band because of the high degree of vibrational coupling, which is given by the potential energy distribution in related complexes. This band is assigned below 200 cm^{-1} .

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