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New Double Salt $[PCl_4]_3[TiCl_6][PCl_6]$ and Related Compounds in the PCl_5–$TiCl_4$ System. Synthesis and Structural Determination by Raman Spectra and X-ray Analysis

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Abstract

The preparation of the newly identified double salt $[PCl_4]_3[TiCl_6][PCl_6]$ is described herein. Its structure is elucidated by both X-ray analysis and Raman spectrum. This compound is tetragonal, space group $P4_2/mbc$ with a = 14.648(1) Å, c = 13.922(1) Å, V = 2987(1) Å^3 and Z = 4, and is isostructural with the related tin compound. The structure was refined by least-squares to R = 4.3%, using 668 observed reflections. Raman spectra of $[PCl_4]_2[Ti_2Cl_{10}]$ and $[PCl_4][Ti_2Cl_9]$ were also reinvestigated and, as a result, some reassignments are proposed.

Introduction

The system PCl_5–$TiCl_4$ has been studied thoroughly and the structures of the various isolated compounds were determined by vibrational spectra [1–3] and X-ray analysis [4]. Ionic compounds are obtained while PCl_5 behaves as a Lewis base transferring a chloride anion to $TiCl_4$, acting as a Lewis acid. The reaction is in accordance with:

$$PCl_5 + TiCl_4 \longrightarrow PCl_4^+ + TiCl_5^-$$

It is quite common that hexacoordinated species are more stable than pentacoordinated ones. As a result a $TiCl_5^-$ reacts with a second anion to form a dimer, of an edge-bridged bioctahedral structure with two bridging chlorines, according to:

$$2TiCl_5^- \longrightarrow Ti_2Cl_{10}^{2-}$$

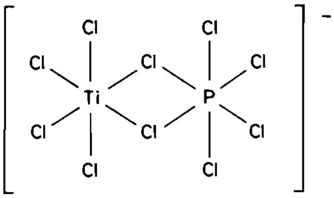
Another possibility is the reaction of a neutral $TiCl_4$, with a $TiCl_5^-$ anion forming a different dimer, of a face shared bioctahedral structure with three bridging chlorines, according to:

$$TiCl_4 + TiCl_5^- \longrightarrow Ti_2Cl_9^-$$

In both dimers, each titanium is then hexacoordinated to terminal and bridging chlorines. Indeed, two such complexes $[PCl_4]_2[Ti_2Cl_{10}]$, **1**, and $[PCl_4][Ti_2Cl_9]$, **2** have been isolated and identified [1–4].

On the other hand it has been stated that no monomeric hexacoordinated species $TiCl_6^{2-}$ could be obtained in the PCl_5–$TiCl_9$ system, even in the presence of an excess of PCl_5 [2]. This is rather surprising, since the $TiCl_6^{2-}$ anion has been isolated and identified in various salts with cations differing from PCl_4^+. Their Raman spectra [5–9] and structure [10] have been reported.

Based on ^{31}P NMR, it has been assumed that a dimeric anion $TiPCl_{10}^-$, is present in a compound obtained by direct reaction of PCl_5 with $TiCl_4$ [11]. This uninegative anion was supposed to be a dimeric one with two different central atoms of titanium and phosphorus, such as:



In a former study, the existence of a double salt $[PCl_4]_3[SnCl_6][PCl_6]$ has been reported [12]. It seemed to us that the assumed dimeric anion with two different central atoms [11], consists actually of two different anions $[PCl_4]_3[TiCl_6]$ $[PCl_6]$, **3**. This would be similar to the double salt in the PCl_5–$SnCl_4$ system. In such a case, the experimental observation of the two ^{31}P NMR signals at −81 ppm and +306 ppm is as expected and clearly understood to be related to the signals of the monomeric ions of PCl_4^+ and PCl_6^-, respectively [11].

The attempted synthesis of such a double salt, consisting of three different ions, was, indeed, successful and has been achieved by reacting an excess

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of PCl_5 with $TiCl_4$ in nitromethane or $POCl_3$. The structure was elucidated by both X-ray analysis and its Raman spectrum.

However, attempts to prepare the simple salt, consisting only of two different ions $[PCl_4]_2[TiCl_6]$, have not succeeded.

In addition, Raman spectra of the related compounds **1** and **2** have been reinvestigated. Our results are in good agreement with earlier reports [1–3] but seem to be of better resolution and include a wider spectral range in the low frequency region. As a result, some different vibrational assignments seem appropriate.

Experimental

Preparation

All the compounds, including the reactants, are extremely hydrolysable and had, therefore, to be handled under conditions guaranteeing the exclusion of moisture. All operations, such as the preparation of solutions, mixing, filtering the solid products and the sampling for the spectroscopical studies were performed in a dry box. Only the refluxing of the solutions was done in the open, with a drying tube connected to the top of the condenser.

The anhydrous reacting materials were commercial products and were used without further purification. Solutions were prepared in different non-aqueous solvents such as nitromethane, $POCl_3$ and $SOCl_2$. Solutions of appropriate concentrations of the reactions were mixed and, in some cases refluxed, thus allowing the solid products to precipitate out. These were washed with the pure solvent and then stored for sampling.

$[PCl_4]_2[Ti_2Cl_{10}]$, 1

This compound was prepared as described in the literature [4] by reacting equimolar amounts of PCl_5 and $TiCl_4$ in $POCl_3$. The reaction mixture was refluxed and then allowed to cool to room temperature. The yellow product was filtered and dried under vacuum. The reaction is in accordance with:

$$2PCl_5 + 2TiCl_4 \xrightarrow[\text{in } POCl_3]{\text{reflux}} [PCl_4]_2[Ti_2Cl_{10}]$$

$[PCl_4][Ti_2Cl_9]$, 2

This compound was also prepared as described in the literature [4], by allowing a mixture solution of PCl_3, $TiCl_4$ and $SOCl_2$ to stand overnight. The $SOCl_2$ behaves as a solvent and as a chlorinating agent to form PCl_5 which reacts *in situ* with the $TiCl_4$ to precipitate out compound **2**. The yellow product was filtered and dried under vacuum. The reaction is in accordance with:

$$\text{(a)}\quad 3PCl_3 + SOCl_2 \longrightarrow PCl_5 + PSCl_3 + POCl_3$$

$$\text{(b)}\quad PCl_5 + 2TiCl_4 \xrightarrow[\text{in } SOCl_2]{\text{room temp.}} [PCl_4][Ti_2Cl_9]$$

$[PCl_4]_3[TiCl_6][PCl_6]$, 3

This newly reported material was obtained by reacting an excess of PCl_5 with $TiCl_4$ under reflux, in nitromethane or $POCl_3$.

PCl_5 (1.9 g) and $TiCl_4$ (0.2 ml), at molar ratio of 5:1, were dissolved in 30 ml of CH_3NO_2. The solution was refluxed for 15 min and allowed to cool to room temperature. The yellow needle shaped product was filtered and dried under vacuum. The product was suitable for Raman studies, but not for X-ray crystallography. In another reaction, PCl_5 (1.54 g) and $TiCl_4$ (0.2 ml), at molar ratio of 4:1, were dissolved in 30 ml of $POCl_3$, refluxed for 15 min and allowed to cool to room temperature. The yellow product was filtered and dried under vacuum. Well defined single crystals were obtained for both X-ray crystallography as well as Raman studies.

The reaction is in accordance with:

$$PCl_5(\text{excess}) + TiCl_4 \xrightarrow[\text{in } POCl_3 \text{ or } CH_3NO_2]{\text{reflux}} [PCl_4]_3[TiCl_6][PCl_6]$$

X-ray Crystallography

Single crystals of **3** were transferred in the dry box, from their mother liquor, into a Petri dish and were covered with an inert silicone oil (Dow Corning 704) to prevent contact with the air. Afterwards, a proper crystal was selected in the open, as usual, while being checked under a microscope, pushed into a thin-walled glass capillary with the aid of a glass fiber and sealed off with epoxy glue.

Data were collected for compound **3** at 22 ± 2 °C on a PW 1100 Philips four-circle computer-controlled diffractometer, Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam being used. The unit cell dimensions were obtained by a least-squares fit of 20 reflections in the range $12° < \theta < 16°$. Data were measured by using a ω–2θ motion. Crystallographic data and other pertinent information are given in Table I. Lorentz and polarization corrections were applied. Intensity data were corrected for absorption by the empirical ψ-scan method. The structure was solved using positional parameters of $[PCl_4]_3[SnCl_6][PCl_6]$ [12] and refined* [13] in space group $P4_2/mbc$ to convergence using anisotropic thermal parameters for all

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*All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE I. Crystallographic Data for $[PCl_4]_3[TiCl_6][PCl_6]$

Formula	$Cl_{24}P_4Ti$
Formula weight	1022.67
Space group	$P4_2/mbc$
a, Å	14.648(1)
c, Å	14.922(1)
V, Å^3	2987(1)
Z	4
Crystal size, mm	0.33 × 0.33 × 0.16
d(calcd), g cm^{-3}	2.274
μ, cm^{-1}	24.83
2θ range, (°)	3 → 50
Number of unique data	1336
Data with $F_o^2 > 3\sigma(F_o^2)$	668
Number of variables	74
R	0.043
R_w	0.045

atoms. The central atom in the anion (Ti,P) was refined using half-site occupancies of phosphorous and titanium. The discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [(\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table I.

Raman Spectra

The Raman spectra were recorded on a Spex double monochromator, model 1401, fitted with Spectra Physics, Krypton and Argon ion lasers, model 164 using the 647.1 nm and 514.5 nm lines for excitation, as described elsewhere [14]. The spectra obtained with these two different excitation lines were identical.

The spectral slits were equal to 2 cm^{-1} and in recording the isotope splitting, spectral slits were reduced to 1 cm^{-1}.

The samples were kept in glass capillaries, sealed off in a flame.

Results and Discussion

PCl_4^+

All the observed data support a structure of ionic nature for the three compounds studied. All of these, contain the PCl_4^+ cation. This tetrahedral cation with T_d symmetry is expected to show four Raman active vibrations. In fact all these have been observed. Their frequencies, as listed in Table II, are in good agreement with earlier reported ones, as discussed thoroughly in the literature [15].

The expected isotope splitting of the totally symmetric stretching vibration $\nu_1(A_1)$, resulting from the natural abundance of the chlorine isotopes of masses 35 and 37, have also been observed in compounds **1** and **2** but not in the double salt **3**. Similar observations have also been noticed in the PCl_5–$SnCl_4$ system, where the isotopic splittings have been observed in all simple salts, except in the double salt $[PCl_4]_3[SnCl_6][PCl_6]$ [12].

TABLE II. Raman Frequencies in cm^{-1} of PCl_4^+ Fundamentals and their Relative Intensities

Compound Assignments	1		2		3	
	R	I	R	I	R	I
	672	3			669	3
$\nu_3(F_1)$	658	9	663	12	658	sh
	638	9	648	6	645	6
$\nu_1(A_1)$	455	100	456	100	455	100
$\nu_4(F_2)$	250	80	250	94	251	85
	244	sh				
$\nu_2(E)$	179	58	180	31	176	62

TABLE III. Relative Intensities of Isotopic Splittings in ν_1 of PCl_4^+

Species	Compound				I_{calc}
	1		2		
	cm^{-1}	I_{obs}	cm^{-1}	I_{obs}	
$P^{35}Cl_4$	459	86	459	19	81
$P^{35}Cl_3{}^{37}Cl$	456	108	456	108	108
$P^{35}Cl_2{}^{37}Cl_2$	453	60	453	103	54
$P^{35}Cl^{37}Cl_3$	451	8	451	28	12
$P^{37}Cl_4$	448	1			1

The separations in the observed splittings are, as expected, of 3 cm^{-1}. However, relative intensities, as listed in Table III, agree with the calculated values only for compound **1**, but differ in compound **2**. We can offer no explanation for these observations.

$[PCl_4]_3[TiCl_6][PCl_6]$, 3

Structure results

The atomic positional parameters are listed in Table IV and Table V gives the bond lengths and angles. As previously found in the isostructural double salt $[PCl_4]_3[SnCl_6][PCl_6]$, the ACl_6 unit (A = Ti, P), resides on the eight-fold crystallographic mirror at x, y, 0. The unit is the superposition of $TiCl_6^{2-}$ and PCl_6^- in 1:1 ratio. The average A–Cl bond length, 2.22 Å is the average between a typical Ti–Cl ($TiCl_6^{2-}$) distance, 2.34 Å [10] and a typical P–Cl (PCl_6^-) distance of 2.13 Å [16]. There are twelve PCl_4^+ ions in the cell, eight of which reside on the eight-fold crystallographic two-fold axis at x, $x + ½$, ¼. The other four PCl_4^+ ions reside on a $\bar{4}$ site at 0, 0, ¼. The 12+ charge of these cations is balanced by four $TiCl_6^{2-}$ ions and four PCl_6^- ions.

TABLE IV. Positional Parameters and e.s.d.s for 3 [a]

Atom	x	y	z
Ti, P	0.3749(2)	0.7585(2)	0.00000
Cl(1)	0.2827(2)	0.6383(3)	0.00000
Cl(2)	0.4678(3)	0.8784(3)	0.00000
Cl(3)	0.2551(3)	0.8541(2)	0.00000
Cl(4)	0.4950(3)	0.6649(3)	0.00000
Cl(5)	0.3752(2)	0.7594(2)	0.1578(1)
P(1)	0.1279(2)	0.6279	0.25000
Cl(11)	0.2343(2)	0.6278(2)	0.3311(2)
Cl(12)	0.1277(2)	0.5201(2)	0.1691(3)
P(2)	0.00000	0.00000	0.25000
Cl(21)	0.1064(2)	−0.0073(2)	0.1695(3)

[a] E.s.d.s. in the least significant digits are shown in parentheses.

Raman spectrum

The observed spectrum of compound 3 is presented in Fig. 1. The numerical frequencies of the double salt and those of related species, with their assignments, are listed in Table VI. The Raman spectrum of 3, is fully assigned on the basis of the tetrahedral PCl_4^+ cation and of the two octahedral anions, $TiCl_6^{2-}$ and PCl_6^-. Four Raman active vibrations are expected for the PCl_4^+ cation with T_d symmetry and three Raman active vibrations are expected for each of the two $TiCl_6^{2-}$ and PCl_6^- anions with an O_h symmetry. All these expected vibrations have, indeed, been observed and assigned in good agreement with earlier reported frequencies [5–9, 12].

TABLE V. Bond Lengths (Å) and Angles (°) for 3

Ti,P–Cl(1)	2.219(4)
Ti P–Cl(2)	2.222(4)
Ti,P–Cl(3)	2.244(5)
Ti,P–Cl(4)	2.230(5)
Ti,P–Cl(5)	2.196(1)
P(1)–Cl(11)	1.924(2)
P(1)–Cl(12)	1.940(3)
P(2)–Cl(21)	1.923(3)
Cl(1)–Ti,P–Cl(2)	179.7(2)
Cl(1)–Ti,P–Cl(3)	91.1(2)
Cl(1)–Ti,P–Cl(4)	89.6(2)
Cl(1)–Ti,P–Cl(5)	90.3(1)
Cl(2)–Ti,P–Cl(3)	89.2(2)
Cl(2)–Ti,P–Cl(4)	90.1(2)
Cl(2)–Ti,P–Cl(5)	89.7(1)
Cl(3)–Ti,P–Cl(4)	179.3(2)
Cl(3)–Ti,P–Cl(5)	89.9(1)
Cl(4)–Ti,P–Cl(5)	90.1(1)
Cl(11)–P(1)–Cl(11)′	110.2(2)
Cl(11)–P(1)–Cl(12)	110.0(2)
Cl(11)–P(1)–Cl(12)′	108.5(1)
Cl(12)–P(1)–Cl(12)′	109.6(2)

The extreme weakness [9] of ν_2 of the $TiCl_6^{2-}$ has brought about different reported values for this vibration, as listed in Table VI. It seems that, in our spectrum, ν_2 can be identified as a weak shoulder at 264 cm^{-1}, in close agreement with Clark's assignment [6].

TABLE VI. Raman Frequencies in cm^{-1} of $[PCl_4][TiCl_6][PCl_6]$, 3 and their Relative Intensities

Compound Assignment	3		$[PCl_4][PCl_6]$ [12]		$TiCl_6^{2-}$			
	R	I	R	I	R [6, 7]	R [5]	R [8]	R [9]
$\nu_3(F_2)–PCl_4^+$	669 658 645	3 sh 6	665 650	8 1				
$(\nu_3 - \nu_2)–PCl_4^+$ or $(\nu_1 + \nu_5)–TiCl_6^{2-}$	483	5						
$\nu_1(A_1)–PCl_4^+$	455	100	454	43				
$(\nu_2 + \nu_4)–PCl_4^+$			424	2				
$(\nu_3 - \nu_4)–PCl_4^+$	383	2						
$\nu_1(A_{1g})–PCl_6^-$	355	86	360	100				
$\nu_1(A_{1g})–TiCl_6^{2-}$	323	53			320vs	331	321vs	326vs
$\nu_2(E_g)–PCl_6^-$	275	25	278	35				
$\nu_2(E_g)–TiCl_6^{2-}$	264	sh			271vw	284vw	236w	
$\nu_4(F_2)–PCl_4^+$	251	85	250	69				
$\nu_5(F_{2g})–PCl_6^-$	239	sh	238	17				
$\nu_2(E)–PCl_4^+$	181	62	175 167	22				
$\nu_5(F_{2g})–TiCl_6^{2-}$	176	62			173s	194	186m	185vs
$(\nu_1 - \nu_5)–PCl_6^-$	115	2						

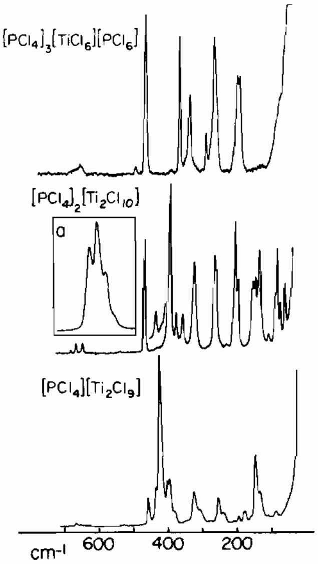

Fig. 1. Raman spectra of $[PCl_4]_3[TiCl_6][[PCl_6]$, $[PCl_4]_2$-$[Ti_2Cl_{10}]$ and $[PCl_4][Ti_2Cl_9]$.

The usual pattern of intensities of an octahedral species namely, that $I_{\nu_1} > I_{\nu_5} > I_{\nu_2}$ is not observed in the vibrations of PCl_6^-. In this anion, the weakest line is that of ν_5 at 238 cm^{-1} and ν_2 is of medium intensity at 278 cm^{-1} [12]. Therefore the ν_5 vibration of PCl_6^-, in the double salt **3**, is hardly observed as a very weak shoulder at 239 cm^{-1}.

The intense lines at 181 and 176 cm^{-1} are assigned as the ν_2 of PCl_4^+ and ν_5 of $TiCl_6^{2-}$, respectively. However, these assignments cannot be made unequivocally and may, possibly, have to be reversed, since the reported frequencies for both vibrations are in the very same spectral region. The ν_2 of PCl_4^+ is reported in the range of 169–192 cm^{-1} [12, 15] and ν_5 of $TiCl_6^{2-}$ in the range of 173–194 cm^{-1} [5–9].

Several weak lines have been assigned to various combination bands.

Raman Spectra of 1 and 2

These two spectra are also displayed in Fig. 1 and are in good agreement with earlier reported ones [2]. However, the resolution of our spectra, is superior to those mentioned and also include spectral features in the low frequency range. As a result, several reassignments of the observed frequencies are proposed. The assignments for both compounds are based on the analysis of formerly reported data [3]. However, it should be born in mind that, in the low frequency region, not only bending modes can show up, but lattice vibrations as well. Therefore some uncertainty prevails in these assignments.

$[PCl_4]_2[Ti_2Cl_{10}]$, 1

Fifteen Raman active vibrations are expected for an M_2X_{10} dimeric species with a D_{2h} symmetry, namely $6A_g + 2B_{1g} + 3B_{2g} + 4B_{3g}$ [3]. All these have indeed been observed in the Raman spectrum of **1**, as displayed in Fig. 1, in addition to the four Raman active vibrations of the PCl_4^+ cation. The numerical frequencies of $[Ti_2Cl_{10}]^{2-}$ vibrations with their assignments are listed in Table VII.

TABLE VII. Raman Frequencies in cm^{-1} of $[Ti_2Cl_{10}]^{2-}$ in 1 and their Relative Intensities

Assignment	R	I	Calculated [3]
$\nu_9(B_{2g})$	415	2	395
$\nu_1(A_g)$	381	100	382
$\nu_2(Ag)$	362	22	361
$\nu_{12}(B_{3g})$	343	22	342
	309	52	
$\nu_3(A_g)$	243	sh	309
$\nu_{13}(B_{3g})$	215	2	243
$\nu_4(A_g)$	188	sh	187
$\nu_7(B_{1g})$	185	74	180
$\nu_{14}(B_{3g})$	137	37	136
$\nu_{10}(B_{2g})$	129	39	132
$\nu_8(B_{1g})$	119	55	128
$\nu_{11}(B_{2g})$	90	5	126
$\nu_5(A_g)$	70	sh	117
$\nu_{15}(B_{3g})$	64	51	108
$\nu_6(A_g)$	55	18	64
lattice vibration	42	25	

Four terminal and two bridging stretching modes are expected and have been observed. In a recent study of several M_2X_{10} species [12] the missing $\nu_9(B_{2g})$ vibration, expected at the highest frequency, has been observed in the Raman spectra of Nb_2-Cl_{10} and $[PCl_4]_2[Sn_2Cl_{10}]$. Similarly, it has also been observed as a weak line at 415 cm^{-1} in the Raman spectrum of $[Ti_2Cl_{10}]^{2-}$ in compound **1**, instead of at 395 cm^{-1}, as calculated [3].

The line 309 cm^{-1} which was formerly assigned as ν_3, a Ti–Cl bridging stretching vibration [1, 3], seems unjustified. In all the three related dimeric species $[PCl_4]_2[Sn_2Cl_{10}]$, Ta_2Cl_{10} and Nb_2Cl_{10}, the two bridging stretchings ν_3 and ν_{13} are very weak bands [12], whereas the 309 cm^{-1} band in $[Ti_2Cl_{10}]^{2-}$ is a rather intense line. On the other hand the ν_{12} vibration seems quite intense in the above-mentioned related species and, more so, is observed [13] as a split vibration. As a result, it seems more justified to assign the lines at 343 and 309 cm^{-1} as a doublet of the split vibration ν_{12}.

The two Ti–Cl bridging stretchings ν_3 and ν_{13} could, therefore, be assigned as the weak shoulder at 243 cm^{-1} and as the weak feature at 215 cm^{-1}.

Earlier assignments [1, 3] identify the line at 180 cm^{-1} as both the ν_2 of PCl_4^+ and ν_7 of $[Ti_2$-$Cl_{10}]^{2-}$ vibrations. In our spectrum, a definite shoulder is observed at 188 cm^{-1} which may possibly be assigned to ν_4 and thus assign the line at 185 cm^{-1} to ν_7, both of $[Ti_2Cl_{10}]^{2-}$. These two vibrations show similar intensities as observed in the related vibrations in the spectrum of Nb_2Cl_{10} [12], thus allowing the line to be assigned at 179 cm^{-1} as ν_2 of PCl_4^+.

Under the column 'Calculated' in Table VII the frequencies of $[Ti_2Cl_{10}]^{2-}$ are listed, as calculated by normal coordinate analysis [3] which are in good agreement with the observed frequencies. The main difference is in the assignment of ν_3 and ν_{12} and in the very low frequency region, where bending modes mix with vibrational ones.

[PCl$_4$][Ti$_2$Cl$_9$], 2

For an M_2X_9 dimeric species with a D_{3h} symmetry, 13 Raman active vibrations 4A$'_1$, 5E$'$ and 4E$''$ are expected as well as eight infrared ones, 5E$'$ and 3A$''_2$ [3]. Out of these, the five E$'$ mode vibrations are coinciding in both the Raman and IR. As a result, altogether 16 different fundamentals are expected.

It seems that in the recorded Raman spectrum of compound 2, displayed in Fig. 1, all the 16 fundamentals, both Raman and IR active ones, have been observed, in addition to the four vibrations of the PCl_4^+ cation. The numerical frequencies of the $[Ti_2Cl_9]^-$ vibrations with their assignments are listed in Table VIII.

TABLE VIII. Raman Frequencies in cm^{-1} of $[Ti_2Cl_9]^-$ in 3 and their Relative Intensities

Assignments	R	I	IR [20]	Calculated [3]
ν_{12} (A$''_2$)	431	sh	416 vs	416
ν_1 (A$'_1$)	417	100		419
ν_{15} (E$''$)	399 390	25 26		394
ν_6 (E$'$)	378	sh	379 vs	375
ν_2 (A$'_1$)	321	19		318
ν_{16} (E$''$)	305	sh		300
ν_{13} (A$''_2$)	270	2	268m	268
ν_7 (E$'$)	236	6	230 w	236
ν_3 (A$'_1$)	207	1		210
ν_{14} (A$''_2$)	194	3	188w	188
ν_8 (E$'$)	175	6	171w	171
ν_{17} (E$''$)	158	2		129
ν_4 (A$'_1$)	141	38		146
ν_{18} (E$''$)	130	sh		126
ν_9 (E$'$)	108	2	74w	74
ν_{10} (E$'$)	85	3	57w	57

The observation in the Raman of the A$''_2$ vibrations, which are only IR active stems, most probably, from the fact that the point symmetry D_{3h} of the $[Ti_2Cl_9]^-$ differs from the site symmetry. Thus the selection rules break down and all the fundamentals show up in the Raman. However, as expected in such a case, the asymmetric IR active vibrations are weaker when compared to the intense symmetric ones which are Raman active.

The fact that the IR active, asymmetric stretching ν_{12}(A$''_2$) is observed at higher frequency than the Raman active, symmetric stretch ν_1(A$'_1$), is in agreement with the general trend in vibrational spectroscopy. Indeed, in $[Ti_2Br_9]^-$ this has also been reported to be the case [17] in which the frequencies are 324 and 317 cm^{-1} respectively.

As described in the literature [18, 19] several groupings of frequencies are observed in such a spectrum of M_2X_9 species. The highest frequencies are due to terminal chlorine–metal stretching vibrations, 2 IR active ones (A$''_2$ and E$'$) and 3 Raman active ones (A$'_1$, E$''$ and E$'$), altogether four fundamentals. It seems that ν_{15}(E$''$) appears, as a split one, at 399 and 390 cm^{-1}, their average being 394.5 cm^{-1} in good agreement with the calculated value.

The second grouping, starting at 321 cm^{-1}, is due to bridging chlorine–metal stretching vibrations, consisting of similar modes, 2 IR active ones (A$''_2$ and E$'$) and 3 Raman active ones (A$'_1$, E$''$ and E$'$), altogether four fundamentals. All the rest of the vibrations observed below 207 cm^{-1} are due to bending and deformation modes of terminal chlorine–metal units and bridging chlorine–metal units.

In each grouping, the Raman active A$'_1$ modes are expected to be the most intense lines whereas the IR active A$''_2$ ones are expected to be weak in the Raman spectrum. These have, indeed, been observed as such.

The reported IR frequencies [20, 21] for the IR active, A$''_2$ vibrations, as well as the coinciding Raman and IR active E$'$ modes are, for the majority, in good agreement with the Raman observed frequencies. By elimination, we assigned the remaining lines to E$''$ modes.

The listed frequencies in Table VIII under column 'Calculated' are derived from normal coordinate analysis [3] and seem to be in good agreement with the observed ones. The main difference is in the assignment of ν_{17} and in the low frequency region where the bending modes mix with vibrational modes.

Supplementary Material

Tables of structure factors and thermal parameters for compound 3 (6 pages). Copies are available on request from author A.B.

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