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Reactions of Phosphorus Pentachloride with Tin Tetrachloride. Tetrachlorophosphonium Salts with $SnCl_6^{2-}$, $Sn_2Cl_{10}^{2-}$, and $SnCl_5^-$ Anions: Preparation and Structure by Vibrational Spectra and X-ray Crystallography

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In the PCl_5–$SnCl_4$ system, four different crystalline compounds were obtained by varying the preparative conditions such as the solvents, relative concentrations of reactants, and temperatures. Their structures were elucidated by both Raman and IR vibrational spectroscopy. Three of these were also identified by using X-ray crystallography. The four compounds are $(PCl_4)_2(SnCl_6)$ (**1**), $(PCl_4)_3(SnCl_6)(PCl_6)$ (**2**), $(PCl_4)_2(Sn_2Cl_{10})$ (**3**), and $(PCl_4)(SnCl_5)$ (**4**). Compound **2** is tetragonal, space group $P4_2/mbc$, with a = 14.754 (2) Å, c = 13.950 (1) Å, V = 3037 (1) Å^3, and Z = 4. Compound **3** is triclinic, space group $P\bar{1}$, with a = 9.013 (1) Å, b = 9.607 (1) Å, c = 7.066(1) Å, α = 95.67 (2)°, β = 95.81 (2)°, γ = 100.62 (3)°, V = 594 (1) Å^3, and Z = 1. Compound **4** is orthorhombic, space group $Cmma$, with a = 12.018 (1) Å, b = 16.469 (3) Å, c = 6.488 (1) Å, V = 1284 (1) Å^3, and Z = 4. All four compounds are of ionic structure with a tetrahedral PCl_4^+ cation and appropriate anions.

Introduction

Phosphorus pentachloride can react as a Lewis base, donating a chloride anion to various covalent chlorides that behave as Lewis acids, by accepting the released chloride anion. Ionic salts containing a PCl_4^+ cation are thus formed. In a recent study,[1] complete vibrational spectra of a series of PCl_4^+ compounds were reported. All those products were obtained by reaction of various trichlorides with phosphorus pentachloride. All the observed molecular spectra were interpreted on the basis of the ionic structure of the general formula PCl_4^+ MCl_4^- in which M = Al, Ga, In, and Fe. In this study, reactions between PCl_5 and $SnCl_4$ were reported and structures of the products were elucidated. Several compounds have been isolated and identified. These were obtained by varying the conditions of the reactions, such as the solvents, relative concentrations of the reactants, and temperatures. The solid products were studied by two different physical methods, namely single-crystal X-ray analysis and vibrational spectroscopy, in both the infrared and the Raman techniques.

Altogether four compounds were isolated and their structures verified. These are $(PCl_4)_2(SnCl_6)$ (**1**), $(PCl_4)_3(SnCl_6)(PCl_6)$ (**2**) $(PCl_4)_2(Sn_2Cl_{10})$ (**3**), and $(PCl_4)(SnCl_5)$ (**4**).

Earlier studies[2-4] reported the existence of only two compounds, which were formulated as $2PCl_5{\cdot}SnCl_4$ and $PCl_5{\cdot}SnCl_4$. The first one was shown by ^{31}P NMR[3] and vibrational spectroscopy[4] to have structure **1**, in agreement with our results. However, no clear evidence was provided for the structure of the second compound. Indeed both structures **3** and **4** were considered,[3] and structure **4** was preferred[4] but without sufficient proof. It is shown herein that both **3** and **4** exist.

From our studies it is shown that all four of these compounds are ionic, with the common cation PCl_4^+. Compounds **1** and **2** contain the monomeric anion $SnCl_6^{2-}$ of octahedral symmetry. Compound **3** contains a dimeric anion, $Sn_2Cl_{10}^{2-}$, with an edge-bridged bioctahedral structure, and compound **4** contains a monomeric $SnCl_5^-$ anion with trigonal-bipyramid structure.

The dimeric $Sn_2Cl_{10}^{2-}$ species is herein experimentally characterized for the first time, as is the double salt, **2**, Full Raman spectra of **3** and **4** are presented and assigned for the first time.

Experimental Section

Preparation. All of the compounds, including the reactants, were extremely hydrolyzable and therefore had to be handled under the exclusion of moisture. All operations, such as the preparation of solutions, mixing them, filtering the solid products, and the sampling for the spectroscopical studies, were performed in a drybox. 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 ones and were used without further purification. Solutions were prepared in different nonaqueous solvents such as dichloromethane, $POCl_3$, and $SOCl_2$. CH_2Cl_2 was dried prior to use, with molecular sieves (3A). Solutions of appropriate concentrations of the reactants were mixed and in some cases refluxed, allowing the solid products to precipitate. These products were washed with the pure solvent and then stored for sampling.

Single crystals of **2** and **3** were obtained from solutions of $POCl_3$ or $SOCl_2$. These solvents provide a larger liquid range between their boiling points and room temperture than CH_2Cl_2. The $POCl_3$ solutions of the reacting materials were refluxed, and clear solutions formed, from which the single crystals precipitated upon cooling to room temperature. Single crystals of **4** were obtained from a solution of $SOCl_2$, which also served as a chlorinating agent, to form PCl_5, from PCl_3, in situ. It seems that this chlorination is a slow reaction, thus allowing the crystallization of single crystals in the reaction with $SnCl_4$.

$(PCl_4)_2(SnCl_6)$ (1). PCl_5 (0.88 g) and $SnCl_4$ (0.1 mL), at a molar ratio of 5:1, were dissolved in 30 mL of CH_2Cl_2. The solution was refluxed for 15 min, and the white precipitate, which formed upon cooling, was filtered and dried under vacuum.

$$PCl_5\ (\text{excess}) + SnCl_4 \xrightarrow[\text{in } CH_2Cl_2]{\text{reflux}} (PCl_4)_2(SnCl_6) \qquad (1)$$

$(PCl_4)_3(SnCl_6)(PCl_6)$ (2). PCl_5 (0.88 g) and $SnCl_4$ (0.1 mL) were dissolved in 30 mL of $POCl_3$. The solution was refluxed for 15 min and allowed to cool. The white product was filtered and dried under vacuum.

$$PCl_5\ (\text{excess}) + SnCl_4 \xrightarrow[\text{in } POCl_3]{\text{reflux}} (PCl_4)_3(SnCl_6)(PCl_6) \qquad (2)$$

$(PCl_4)_2(Sn_2Cl_{10})$ (3). PCl_5 (0.7 g) and $SnCl_4$ (0.4 mL) were dissolved in 30 mL of CH_2Cl_2 (or $POCl_3$). The solution was refluxed for 15 min. The resulting white solid was filtered and dried under vacuum.

$$2PCl_5 + 2SnCl_4 \xrightarrow[\text{in } CH_2Cl_2 \text{ or } POCl_3]{\text{reflux}} (PCl_4)_2(Sn_2Cl_{10}) \qquad (3)$$

$(PCl_4)(SnCl_5)$ (4). This compound was prepared by two different methods:

(a) PCl_5 (0.7 g) and $SnCl_4$ (0.4 mL) were dissolved in CH_2Cl_2, and the solution was kept at room temperature. After ca. 2 h the white crystalline product was filtered and dried under vacuum. Dimerization of compound **4** to yield compound **3** takes place if the solution is warmed.

$$PCl_5 + SnCl_4 \xrightarrow[\text{in } CH_2Cl_2]{\text{room temp}} (PCl_4)(SnCl_5) \qquad (4)$$

(b) PCl_3 (4.8 mL) and $SnCl_4$ (2.1 mL) were dissolved in 40 mL of $SOCl_2$, and the solution was kept at room temperature. A mixture of well-developed crystals of **3** and **4** formed after several hours.

$$\begin{gathered} PCl_3 + SnCl_4 \xrightarrow[\text{in } SOCl_2]{\text{room temp}} \mathbf{3} + \mathbf{4} \\ (3PCl_3 + SOCl_2 \rightarrow PCl_5 + PSCl_3 + POCl_3) \end{gathered} \qquad (5)$$

X-ray Crystallography. The single crystals were transferred in the drybox, from their mother liquor into a petri dish; the crystals were

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[1] Shamir, J.; Van der Veken, B. J.; Herman, M. A.; Rafaeloff, R. *J. Raman Spectrosc.* **1981**, *11*, 215.

[2] Groenveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 1152.

[3] Wieker, W.; Grimmer, A. R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1967**, *22B*, 1220.

[4] Reich, P.; Wieker, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1968**, *23B*, 739.

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Table I. Crystallographic Data

compd	2	3	4
formula	$Cl_{24}P_4Sn$	$Cl_{18}PSn_2$	Cl_9PSn
fw	1093.46	937.48	468.74
space group	$P4_2/mbc$	$P\bar{1}$	*Cmma*
a, Å	14.754 (2)	9.013 (1)	12.018 (1)
b, Å		9.607 (1)	16.469 (3)
c, Å	13.950 (1)	7.066 (1)	6.488 (1)
α, deg		95.67 (2)	
β, deg		95.81 (2)	
γ, deg		100.62 (3)	
V, Å^3	3037 (1)	594 (1)	1284 (1)
Z	4	1	4
d(calcd), g cm^{-3}	2.392	2.621	2.424
cryst size, mm	0.2 × 0.2 × 0.4	0.2 × 0.3 × 0.3	0.1 × 0.1 × 0.2
μ, cm^{-1}	29.58	39.72	36.74
cryst color	colorless	colorless	colorless
range of 2θ, deg	3→50	3→45	3→60
obsrvns	$+h,+k,+l$; $k \geq h$	$\pm h,\pm k,l$	$+h,+k,+l$
scan width, deg	1.20	1.20	1.00
scan time, s	30	20	20
no. of unique data	1389	2087	1000
no. of data with $F_o^2 > 3\sigma(F_o^2)$	794	1938	829
R_1	0.061	0.034	0.030
R_w	0.080	0.063	0.042
wt	σ_F^{-2}	$(\sigma_F^2 - 0.00316F^2)^{-1}$	$(\sigma_F^2 + 0.000236F^2)^{-1}$

covered with an inert silicone oil, Dow Corning 704, to prevent contact with atmospheric moisture. Afterward, a proper crystal was selected in the open, as usual, while being checked under a microscope, and pushed into a thin-walled glass capillary with the aid of a glass fiber, and the capillary was sealed off with epoxy glue.

Data were collected 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 was 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. For each crystal, Lorentz and polarization corrections were applied. Intensity data for **2**–**4** were corrected for absorption by the empirical ψ-scan method.[5a] For **2** a survey of the complete data set showed systematic absences for reflections ($0kl$), k = odd, and (hhl), l = odd, consistent with the assignment of either $P4_2/mbc$ or $P4_2bc$. The correctness of the centrosymmetric space group assignment was indicated by the subsequent successful refinement of the structure. Structure **2** was solved by using the results of MULTAN direct-method analysis. The heaviest atom was located on the 8-fold crystallographic mirror plane at 0.374, 0.757, 0. Refinement of this atom as tin yielded unreasonably high thermal parameters and a high value for the R factor when all other atoms were included in the refinement (R = 12%). This, together with the fact that the unit cell contains the sum of 12 PCl_4^+ cations and presumably 8 $SnCl_6^{2-}$ anions with a total of 16 negative charges, has led us to the conclusion that a disorder exists in the crystal. Further refinement of the structure using half-site occupancies of phosphorus and tin for the central atom in the anion caused a dramatic decrease in the R factor. The structure was refined[5b] in space group $P4_2/mbc$ to convergence by using anisotropic thermal parameters for all atoms. The positions of all atoms of structure **3** were taken from $(PCl_4)_2(Ti_2Cl_{10})$,[6] and the structure was refined in space group $P\bar{1}$ to convergence by using anisotropic thermal parameters for all atoms. For **4**, the systematic absences for reflections (hkl), $h + k$ = odd, and ($hk0$), h = odd, suggested the two space groups *Cmma* and *Abm*2. The correctness of the centrosymmetric space group assignment was indicated by the subsequent successful refinement of the structure. Structure **4** was solved by using the results of MULTAN diret-method analysis. The structure was refined in space group *Cmma* by using anisotropic thermal parameters for all atoms. Values of the atomic scattering factors and anomalous terms were taken from the conventional sources.[5c,d]

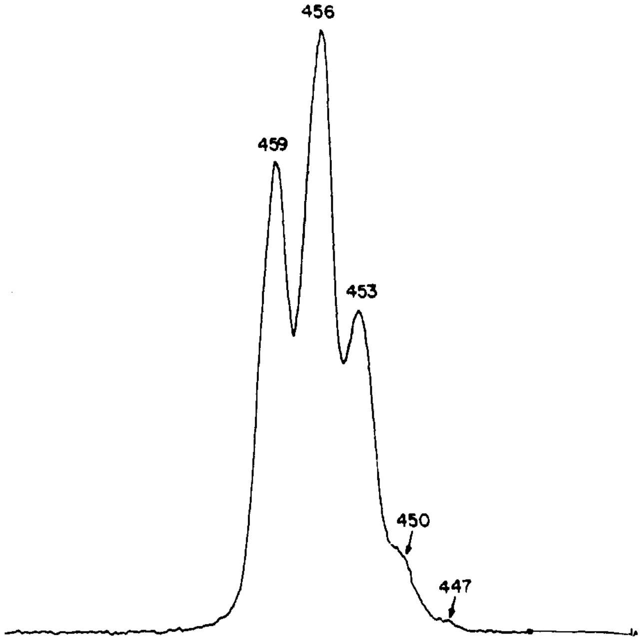

Figure 1. Raman spectrum of $(PCl_4)_2(Sn_2Cl_{10})$ showing the isotope splitting of ν_1 of PCl_4.

The discrepancy indices $R_1 = \sum|F_o| - |F_c|/||F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ are listed in Table I. Lists of all observed and calculated structure factors are available as supplementary material.

Raman Spectra. The Raman spectra were recorded on a Spex double monochromator, Model 1401, fitted with a Spectra-Physics argon ion laser, Model 164, using the 514.5-nm line for excitation, as described elsewhere.[7] The spectra were also rechecked by using the 488.0-nm line for excitation, which resulted in exactly the same spectra.

The spectral slits were equal to 2 cm^{-1}, and when isotope splitting was recorded, spectral slits were reduced to 1 cm^{-1}.

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

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer instrument, Model 180. Polyethylene disks were pressed for the far-IR region, where most fundamentals were observed. Silver chloride disks were used for the higher frequency region in the mid-IR range, where mostly overtones and combination bands were observed.

Results and Discussion

All the observed data support the ionic nature of all four compounds studied. All of these contain the PCl_4^+ cation with various tin chloride anions.

The various observed data, X-ray analyses, and vibrational spectra will be discussed separately for each compound. However, a close look at the spectral data for the PCl_4^+ cation, in common to all these compounds, will be presented first.

PCl_4^+. This tetrahedral cation with T_d symmetry is expected to show four Raman-active vibrations, two of them also being infrared active. In fact all these have indeed been observed, and their frequencies, as listed in Table II, are in good agreement with those in an earlier report.[1]

The expected isotope splittings of the Raman-active totally symmetric vibration ν_1 (A_1), resulting from the natural abundance of isotopes of atomic mass 35 and 37 of chlorine, have also been observed in all these compounds, and a typical recording is presented in Figure 1.

Although we have observed such isotope splittings in our former studies of PCl_4^+ compounds,[1] they are here reported again and given in particular for compounds **1** and **3**, since all five theoretically expected lines have indeed been observed, including that of $P^{37}Cl_4$. This is the weakest line, with an intensity of less than 1% compared to the most intense one. Both the separations of

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(5) (a) The program used was CAMEL JOCKEY WITH THREE HUMPS: Flak, H. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1977**, *A33*, 890. (b) All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package. The function used in the least-squares minimization was $\sum w(|F_o| - |F_c|)^2$. (c) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. (d) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(6) Kistenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* **1971**, *10*, 122.

(7) Loewenschuss, A.; Shamir, J.; Ardon, M. *Inorg. Chem.* **1976**, *15*, 238.

Table II. Frequencies (cm^{-1}) of PCl_4^+ Fundamentals in Various Compounds[a]

	$SnCl_6^{2-}$			double salt		$Sn_2Cl_{10}^{2-}$			$SnCl_5^-$	
assignts	Raman	*I*	IR	Raman	*I*	Raman	*I*	IR	Raman	*I*
ν_2 (E)	180	59	180 sh	176 178	25	176	50		178	34 sh
ν_4 (F_2)	249	56	246 s	246	75	248	76	246 s	244 250	54 59
ν_1 (A_1)	455	100	440 vw	450	100	453	100	452 vw	453	100
ν_3 (F_2)	640 659	1 13	650 m	645 659	5 5	639 654 666	8 6 5	630 m 650 m	648 652 657	8 sh 10

[a] Abbreviations: s, strong; m, medium; vw, very weak; sh, shoulder.

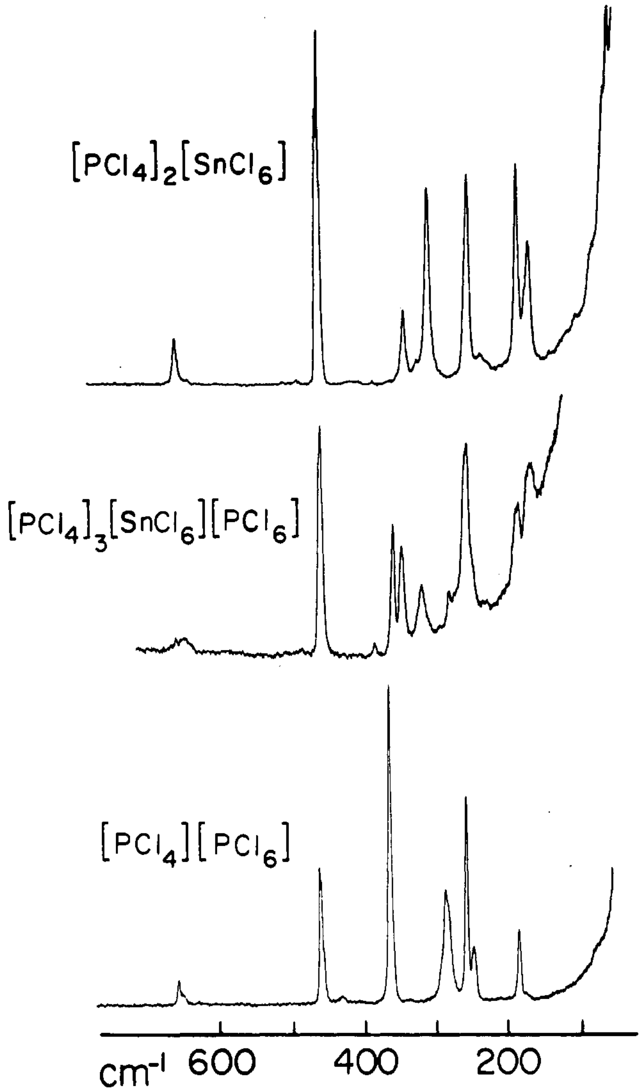

Figure 2. Raman spectra of $(PCl_4)_2(SnCl_6)$, $(PCl_4)_3(SnCl_6)(PCl_6)$, and $(PCl_5)(PCl_6)$.

Table III. Relative Intensities of Isotopic Splittings in the ν_1 of PCl_4^+ in Various Compounds

species	ν_1, cm^{-1}	*I*($SnCl_6^{2-}$)	*I*($Sn_2Cl_{10}^{2-}$)	*I*($SnCl_5^-$)	*I*(calcd)
$P^{35}Cl_4$	459	83	83	83	81
$P^{35}Cl_3{}^{37}Cl$	456	108	108	108	108
$P^{35}Cl_2{}^{37}Cl_2$	453	59	57	55	54
$P^{35}Cl^{35}Cl_3$	450	13	13	14	12
$P^{37}Cl_4$	447	2	2		1

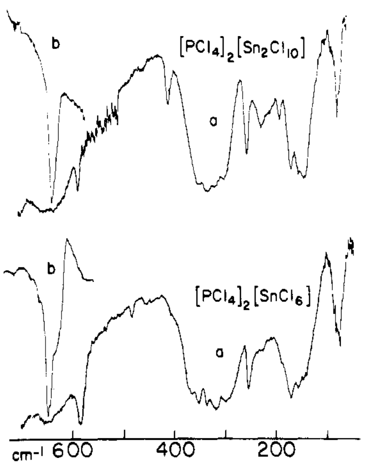

Figure 3. Infrared spectra of $(PCl_4)_2(Sn_2Cl_{10})$ and $(PCl_4)_2(SnCl_6)$: (a) polyethylene disks; (b) silver chloride disks. The latter recordings (b) are 2.5 times smaller, to scale.

3 cm^{-1} and the relative intensities of the various lines, as listed in Table III, are in good agreement with the calculated values, which are based on the natural abundance of the chlorine isotopes in a tetracoordinated species. All this provides additional proof for the presence of the PCl_4^+ cation.

$(PCl_4)_2(SnCl_6)$ (1). The Raman and infrared spectra of this salt are presented in Figures 2 and 3, respectively. Table IV summarizes the numerical frequencies and their assignments, which agree with the ones reported previously.[4]

In addition to the four observed Raman frequencies attributed to the PCl_4^+ cation, four other lines are observed, all attributed to the octahedral $SnCl_6^{2-}$ anion. In an octahedral species of O_h symmetry, three Raman-active vibrations are expected, mutually exclusive with two infrared-active ones. Three of the observed frequencies are assigned as ν_1 (A_{1g}), ν_2 (E_g), and ν_5 (F_{2g}) of the octahedral $SnCl_6^{2-}$ anion, displaying the characteristic strong–weak–medium intensity pattern for an MX_6 species.

An additional Raman line is observed at 337 cm^{-1} of medium intensity with two weak shoulders at 320 and 354 cm^{-1}. Two of these lines have been reported before,[8] as observed in solid $2PCl_5 \cdot SnCl_4$ at 341 and 356 cm^{-1}. The assumption that these stem from the presence of $SnCl_5^-$ in equilibrium with $SnCl_6^{2-}$ is not convincing. This line has also been observed in the double salt **2** at 336 cm^{-1}. This compound has been shown by X-ray analysis, as will be discussed in the next section, to consist soley of tetrahedral and octahedral species but no pentacoordinated ones. It seems that this line could possibly be assigned to the IR-active asymmetric stretching vibration ν_3 (F_{1u}) of the $SnCl_6^{2-}$ ion. Although, in the case of an O_h symmetry, this vibration is expected to be Raman inactive, it may nevertheless become Raman active, in the case where site symmetry differs from point symmetry. In such a case the mutually exclusive selection rules would break down, and this F_{1u} vibration would also show up in the Raman spectrum. As expected, the Raman-forbidden asymmetric stretch ν_3 vibration would be of weaker intensity than the related Ra-

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(8) Brockner, W.; Demiray, A. F. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1979**, *34A*, 976.

Table IV. Vibrational Frequencies (cm^{-1}) of $(PCl_4)_2(SnCl_6)$, $(PCl_4)_3(SnCl_6)(PCl_6)$, and PCl_5[a]

	$(PCl_4)_2(SnCl_6)$									
	this work			ref 4			double salt		$(PCl_4)(PCl_6)$	
assignts	Raman	*I*	IR	Raman	*I*	IR	Raman	*I*	Raman	*I*
ν_3 (F_2) PCl_4^+	659	13	650	656	20	657 vs	659	5	655	8
	640	1				648 vs	645	5	650	2
			582							
			476							
ν_1 (A_1) PCl_4^+	455	100	440 vw	456	100		450	100	454	43
$\nu_2 + \nu_4$ PCl_4^+									424	2
$\nu_3 - \nu_4$ PCl_4^+							375	5		
ν_1 (A_{1g}) PCl_6^-							350	60	360	100
ν_3 (F_{1u}) $SnCl_6^{2-}$	354	sh	358							
	337	20	344				336	48		
	320	sh	328							
$\nu_4 + \nu_5$ (?) $SnCl_6^{2-}$			312			314 s, br				
ν_1 (A_{1g}) $SnCl_6^{2-}$	302	54	292 sh	303	70	287 s, br	308	23		
ν_2 (E_g) PCl_6^-							270	15	278	35
ν_4 (F_2) PCl_4^+	249	56	246 s	248	60	252 s	246	75	250	64
ν_5 (F_{2g}) PCl_6^-							240	sh	238	17
ν_2 (E_g) $SnCl_6^{2-}$	230	5	220 vw				225	5		
ν_2 (E) PCl_4^+	180	59	180 sh	178	30		178	25	175	22
							176		167	2 sh
ν_4 (F_{1u}) $SnCl_6^{2-}$			162							
			148 vs							
			138							
ν_5 (F_{2g}) $SnCl_6^{2-}$	165	sh								
	161	36		161	30		156	24		

[a] Abbreviations: vw, very weak; s, strong; br, broad; sh, shoulder.

Table V. Positional Parameters for **2**[a]

atom	*x*	*y*	*z*
Sn,P	0.3745 (1)	0.7569 (1)	0.00000
Cl(1)	0.2821 (4)	0.6328 (4)	0.00000
Cl(2)	0.4684 (4)	0.8818 (4)	0.00000
Cl(3)	0.2539 (4)	0.8520 (4)	0.00000
Cl(4)	0.4973 (4)	0.6637 (3)	0.00000
Cl(5)	0.3750 (3)	0.7574 (3)	0.1617 (2)
P(1)	0.1273 (2)	0.6273	0.25000
Cl(11)	0.2323 (2)	0.6273 (2)	0.3313 (2)
Cl(12)	0.1277 (3)	0.5196 (2)	0.1710 (3)
P(2)	0.00000	0.00000	0.25000
Cl(21)	0.1049 (2)	−0.0070 (3)	0.1684 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

man-active totally symmetric stretch ν_1. Indeed, the observed intensities are $I_{\nu_3} = 0.37I_{\nu_1}$. Due to the same effect, the degeneracy of this triply degenerate ν_3 (F_{1u}) vibration would be lifted, thus also explaining the observance of the two weak shoulders of this triplet.

The weak shoulder observed on the high-frequency side of ν_5 (F_{2g}) is most likely a result of the lifting of the double degeneracy of this vibration, or else it may be assigned to the Raman-forbidden but IR-active bending mode ν_4, which appears in the Raman spectrum as discussed above for the case of ν_3.

In the IR spectrum, all expected fundamentals are indeed observed, two for the tetrahedral PCl_4^+ cation and two for the octahedral $SnCl_6^{2-}$ anion. The observed frequencies of all four vibrations are in good agreement with previously reported data.[1,9,10] Wharf and Shriver[10] have already mentioned in their thorough study of the vibrational frequencies in anionic tin–halogen species that although no disagreement exists over the assignment of the various fundamentals, the agreement among the exact band positions is only fair.

Indeed, in many compounds, the observed frequencies of $SnCl_6^{2-}$ are such that $\nu_3 < \nu_1$. However in some others, such as K_2SnCl_6, $\nu_3 > \nu_1$, and this is also observed in **1**, which is the more general case for O_h species.

Table VI. Bond Lengths (Å) and Angles (deg) for **2**[a]

Sn,P–Cl(1)	2.283 (6)	Sn,P–Cl(5)	2.255 (3)
Sn,P–Cl(2)	2.305 (5)	P(1)–Cl(11)	1.919 (4)
Sn,P–Cl(3)	2.266 (6)	P(1)–Cl(12)	1.934 (4)
Sn,P–Cl(4)	2.274 (6)	P(2)–Cl(21)	1.924 (3)
Cl(1)–Sn,P–Cl(2)	179.7 (2)	Cl(3)–Sn,P–Cl(4)	179.0 (2)
Cl(1)–Sn,P–Cl(3)	91.6 (2)	Cl(3)–Sn,P–Cl(5)	90.0 (1)
Cl(1)–Sn,P–Cl(4)	89.4 (2)	Cl(4)–Sn,P–Cl(5)	90.0 (1)
Cl(1)–Sn,P–Cl(5)	90.2 (1)	Cl(11)–P(1)–Cl(11)′	110.5 (2)
Cl(2)–Sn,P–Cl(3)	88.7 (2)	Cl(11)–P(1)–Cl(12)	109.5 (2)
Cl(2)–Sn,P–Cl(4)	90.3 (2)	Cl(11)–P(1)–Cl(12)′	109.0 (1)
Cl(2)–Sn,P–Cl(5)	89.8 (1)	Cl(12)–P(1)–Cl(12)′	109.3 (2)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

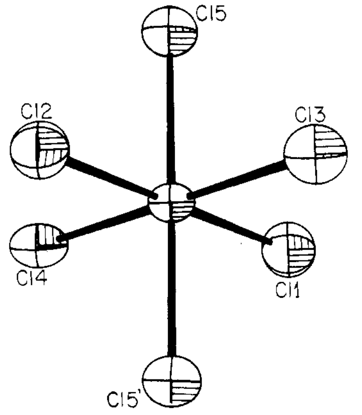

Figure 4. ORTEP view of ACl_6 in $(PCl_4)_3(SnCl_6)(PCl_6)$.

The observed IR bands, ν_3 and ν_4, of $SnCl_6^{2-}$ are very intense but also very broad, showing several peaks that are rather poorly resolved, particularly when compared to the excellent resolution in the Raman spectrum. Since both of these vibrations are triply degenerate (F_{1u}), these degeneracies may be lifted in the solid, as already discussed above, as a result of the difference between site and point symmetries. In this case, one would expect three separated peaks. Although the observed resolution is rather poor, it seems that actually more than the three expected peaks are observed. It is therefore possible to assume that some of these

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Table VII. Positional Parameters for 3[a]

atom	x	y	z
Sn	0.36019 (8)	0.31804 (7)	0.3881 (1)
Cl(1)	0.5810 (3)	0.2159 (3)	0.3782 (4)
Cl(2)	0.1575 (3)	0.4421 (3)	0.4205 (5)
Cl(3)	0.2803 (3)	0.2422 (3)	0.0574 (4)
Cl(4)	0.2288 (4)	0.1198 (3)	0.5224 (5)
Cl(5)	0.5182 (3)	0.5511 (3)	0.2845 (4)
P	0.1930 (3)	0.7781 (3)	0.0482 (4)
Cl(6)	0.2019 (4)	0.5875 (3)	−0.0579 (5)
Cl(7)	0.0622 (4)	0.7692 (4)	0.2486 (5)
Cl(8)	0.1110 (4)	0.8762 (3)	−0.1521 (5)
Cl(9)	0.3937 (3)	0.8808 (3)	0.1518 (5)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

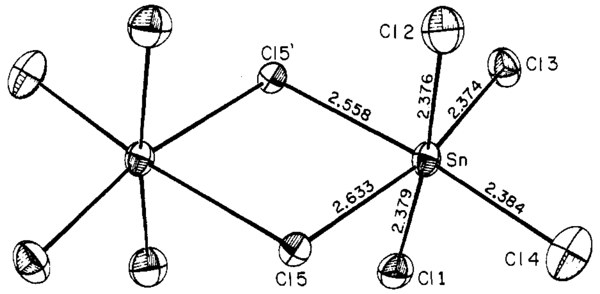

Figure 5. ORTEP view of $Sn_2Cl_{10}^{2-}$ in $(PCl_4)_2(SnCl_{10})$.

extra peaks result from originally IR-forbidden and Raman-active vibrations; which appear in the IR spectrum as a result of the breakdown of the selection rules, as discussed above for the Raman spectrum. One of the extra peaks at 314 cm^{-1} can possibly also be assigned to an IR-active combination band $\nu_4 + \nu_5$.[10]

$(PCl_4)_3(SnCl_6)(PCl_6)$ (2). Structural Results. The atomic positional parameters are listed in Table V, while Table VI gives the bond lengths and angles. Figure 4 shows the numbering scheme in the ACl_6 (A = Sn,P) unit. This unit resides on the 8-fold crystallographic mirror at x, y, 0 and, as mentioned in the Experimental Section, is the superposition of $SnCl_6^{2-}$ and PCl_6^- in a 1:1 ratio. The average A–Cl bond length (2.277 Å) is the average between a typical Sn–Cl ($SnCl_6^{2-}$) distance (2.427 Å)[11] and a typical P–Cl (PCl_6^-) distance (2.13 Å).[12] There are 12 PCl_4^+ ions in the cell, eight of which reside on the eight crystallographic 2-fold axes at x, $x + {}^1/_2$, 1/4. The other four PCl_4^+ ions reside on a $\bar{4}$ site at 0, 0, 1/4. The 12+ charge of these cations is balanced by four $SnCl_6^{2-}$ ions and four PCl_6^- ions.

Vibrational Spectra. The Raman spectrum of this double salt, as verified by X-ray analysis, is presented in Figure 2, and the numerical frequencies and their assignments are listed in Table IV. The observed spectrum of this double salt seems to be a superposition of the spectra of **1** and of PCl_5, whose structure is formulated as $(PCl_4)(PCl_6)$: these spectra are also presented in Figure 2. Since both compounds consist of the very same cation, the spectrum of the double salt is expected to be similar to that of **1** and, in addition, is expected to include those lines attributed to the PCl_6^- anion. Indeed, the three Raman-active vibrations of the PCl_6^- anion are observed as follows: ν_1 at 350 cm^{-1}, ν_2 at 271 cm^{-1} and the weakest line ν_5 only as a shoulder at 240 cm^{-1}, instead of at 360, 278, and 238 cm^{-1}. These slight shifts toward lower frequencies may be attributed to the anion's being part of a different crystal structure. Similar slight shifts in the same direction are also observed in the $SnCl_6^{2-}$ vibrations, except for ν_1, which is slightly shifted toward higher frequency. Thus the Raman spectrum of this double salt is in agreement with the single-crystal analysis.

$(PCl_4)_2(Sn_2Cl_{10})$ (3). Structural Results. The atomic postional parameters are listed in Table VII. Table VIII gives the bond lengths and angles. Figure 5 shows the numbering scheme in $Sn_2Cl_{10}^{2-}$. With $Z = 1$ in space group $P\bar{1}$ there is only half of a $Sn_2Cl_{10}^{2-}$ ion in the asymmetric unit, with the other half related to it by a crystallographic inversion center at 1/2, 1/2, 1/2. The overall symmetry of the dinuclear anion is very nearly D_{2h}. The molecular geometry of $Sn_2Cl_{10}^{2-}$ is very similar to that exhibited by $Ti_2Cl_{10}^{2-}$ as previously found in the isostructural compound $(PCl_4)_2(Ti_2Cl_{10})$.[6] The distances Sn–Cl(5) and Sn–Cl(5)' in the bridge system are 2.633 (2) and 2.558 (2) Å, respectively, indicating that the Cl atoms are not equally shared by the two tin atoms; a similar phenomenon is found in $Ti_2Cl_{10}^{2-}$ (Ti–Cl$_b$) =

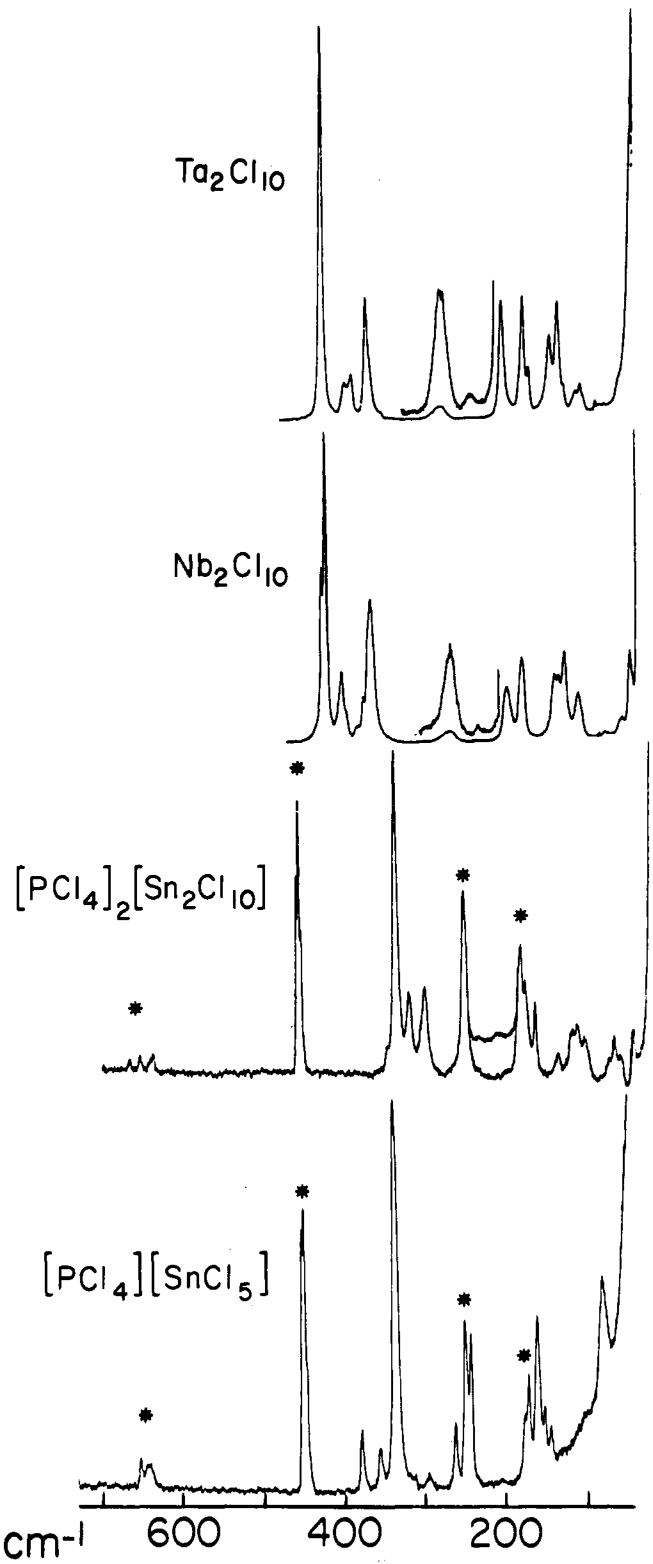

Figure 6. Raman spectra of $(PCl_4)(SnCl_5)$, $(PCl_4)_2(SnCl_{10})$, Nb_2Cl_{10}, and Ta_2Cl_{10}. Asterisks denote lines of the PCl_4^+ cation.

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Table VIII. Bond Lengths (Å) and Angles (deg) for **3**[a]

Sn–Cl(1)	2.379 (3)	Sn–Cl(5)′	2.558 (2)
Sn–Cl(2)	2.376 (3)	P–Cl(6)	1.928 (4)
Sn–Cl(3)	2.374 (2)	P–Cl(7)	1.931 (4)
Sn–Cl(4)	2.384 (3)	P–Cl(8)	1.935 (4)
Sn–Cl(5)	2.633 (2)	P–Cl(9)	1.927 (3)
Cl(1)–Sn–Cl(2)	173.5 (1)	Cl(3)–Sn–Cl(5)′	166.8 (1)
Cl(1)–Sn–Cl(3)	91.9 (1)	Cl(4)–Sn–Cl(5)	172.8 (1)
Cl(1)–Sn–Cl(4)	91.9 (1)	Cl(4)–Sn–Cl(5)′	93.3 (1)
Cl(1)–Sn–Cl(5)	87.93 (9)	Cl(5)–Sn–Cl(5)′	79.50 (9)
Cl(1)–Sn–Cl(5)′	87.19 (1)	Sn–Cl(5)–Sn′	100.50 (9)
Cl(2)–Sn–Cl(3)	93.0 (1)	Cl(6)–P–Cl(7)	109.6 (2)
Cl(2)–Sn–Cl(4)	91.4 (1)	Cl(6)–P–Cl(8)	109.1 (2)
Cl(2)–Sn–Cl(5)	88.11 (1)	Cl(6)–P–Cl(9)	110.1 (2)
Cl(2)–Sn–Cl(5)′	87.1 (1)	Cl(7)–P–Cl(8)	109.2 (2)
Cl(3)–Sn–Cl(4)	99.9 (1)	Cl(7)–P–Cl(9)	109.5 (2)
Cl(3)–Sn–Cl(5)	87.3 (1)	Cl(8)–P–Cl(9)	109.4 (2)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

2.506 and 2.481 Å). On the other hand, in contrast to those of titanium species, there is no difference between the planar and axial terminal Sn–Cl distances.

Vibrational Spectra. The recorded Raman and infrared spectra of this salt are presented in Figures 6 and 3, respectively. The frequencies attributed to the $Sn_2Cl_{10}^{2-}$ anion are listed in Table IX along with those of some related species. Figure 6 also includes our recorded spectra of Nb_2Cl_{10} and Ta_2Cl_{10}, the closely related neutral compounds, which are in good agreement with literature data.[13]

The similar patterns of all of these spectra are easily noticed, although the observed frequencies are different, and this will be discussed later in detail.

It is easy to eliminate the four Raman-active vibrations of the PCl_4^+ cation and their observed frequencies, as listed in Table II, leaving the rest to be attributed to the anion.

The $Sn_2Cl_{10}^{2-}$ anion is, as has been first verified by our X-ray analysis, a dimer of an edge-bridged bioctahedral structure with a D_{2h} symmetry. A total of 30 vibrations are expected and have been fully described.[13,14] The 15 Raman-active vibrations are mutually exclusive with the 13 IR-active ones and the 2 inactive vibrations. In the well-resolved Raman spectrum, altogether 17 observed features can be attributed to the $Sn_2Cl_{10}^{2-}$ anion, in which the lowest vibrations may be mixed with lattice vibrations. When this spectrum is compared to those of Nb_2Cl_{10}, Ta_2Cl_{10},[13] $Ti_2Cl_{10}^{2-}$,[14-16] and Sb_2Cl_{10},[17,18] several similar regions can be noticed. In the high-frequency region assigned to the stretching vibrations of the terminal metal–chlorine bonds, a set of four lines is observed. Two additional very weak features are observed in the 200-cm^{-1} region, which agree well with the expected frequencies of the stretchings of bridging metal–chlorine bonds. These frequencies are equal to about 0.6 of the terminal halogen stretchings, in good agreement with similar reported values.[19] Finally, in the lower frequency region, deformation bands are observed.

The highest expected frequency for an M_2X_{10} species has been calculated[13,16] to be a B_{2g} vibration and is expected to be of very low intensity.[14] Yet seemingly it has not been observed in any of the related species. The most intense line, in all of these related species, is most probably an A_g vibration. However, in $Sn_2Cl_{10}^{2-}$, it seems that the observed terminal stretching frequencies are as anticipated. This expected B_{2g} vibration is indeed observed as a weak line but nevertheless as a pronounced shoulder at 343 cm^{-1}. Actually in our recorded Raman spectrum of Nb_2Cl_{10} a similar line is observed at 419 cm^{-1}, as a well-resolved shoulder on the very intense A_g vibration at 413 cm^{-1}, in good agreement with the calculated value;[13] this line was never reported before. Indeed if one correlates the frequency ratios of the various observed intense lines, assigned as ν_1 (A_g) vibrations, in all the reported spectra, then all the terminal stretching frequencies are of consistent ratio. The missing B_{2g} vibrations, in the related species, can then be calculated from the multiplication of this ratio of the ν_1 frequencies by the B_{2g} vibration at 343 cm^{-1} in $Sn_2Cl_{10}^{2-}$. These calculated values are also in good agreement with the value obtained from theoretical calculations for $Ti_2Cl_{10}^{2-}$ [16] and with our observed frequency in Nb_2Cl_{10}. On the basis of these same ratios, and similar multiplications of $Sn_2Cl_{10}^{2-}$ frequencies, other observed lines in the different spectra seem also to be quite consistent and correlated. These values are listed in Table IX (under the columns "calcd").

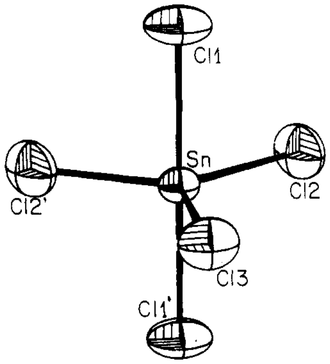

Figure 7. ORTEP view of $SnCl_5^-$ in $(PCl_4)(SnCl_5)$.

Since many vibrations are expected in a rather narrow spectral range, of about 300 cm^{-1}, accurate assignments can hardly be expected for the various numerous lines. However, in assigning them, we followed ref 16.

The infrared spectrum is poorly resolved when compared to the Raman spectrum. Thus the accuracy of the observed IR frequencies is less so. Both Raman and IR vibrations occur at closely similar frequencies, without true coincidences.[13]

Various factors influence the observed frequencies of similar vibrations of related species with the same symmetry.[19,20] Higher frequencies are observed if (a) the oxidation state of the central atom is higher, (b) the total net charge on the species is more positive, and (c) the central atom is lighter in mass.

All of these factors are noticed in comparing the observed frequencies of various related M_2Cl_{10} species. The highest frequencies are observed in the transition-metal compounds Nb_2Cl_{10} and Ta_2Cl_{10}, in which the central atom is in the pentavalent oxidation state and the net charge is zero.

The observed frequencies in the related main-group-element compound Sb_2Cl_{10}[17,18] with the same oxidation state of the central atom, and similar net charge, are lower due to the fact that antimony is of larger mass than niobium.

The frequencies in both anionic $M_2Cl_{10}^{2-}$ (M = Ti, Sn) are lower, since the oxidation state of the central atom is lower than those in the group 5[27] elements and in antimony and the net charge on the species is also lower, being doubly negative. Since tin is heavier than titanium, the frequencies in $Sn_2Cl_{10}^{2-}$ are lower than in $Ti_2Cl_{10}^{2-}$.

The observed Raman spectra of $SnCl_6^{2-}$ and $Sn_2Cl_{10}^{2-}$ are clearly different and easily distinguishable. The former consists of only a few lines of the degenerate vibrations whereas the latter is complicated and consists of numerous lines. However, the infrared spectra look rather alike and are hardly distinguishable. This probably results from the fact that the degeneracy of the

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Table IX. Vibrational Frequencies (cm^{-1}) of $Sn_2Cl_{10}^{2-}$ and of Related M_2Cl_{10} Species[a]

	$Sn_2Cl_{10}^{2-}$ [b]			Nb_2Cl_{10} [b]			Ta_2Cl_{10} [b]			$Ti_2Cl_{10}^{2-}$ [c]		Sb_2Cl_{10} [d]		
assign	Raman	I	IR	Raman	I	calcd	Raman	I	calcd	Raman	calcd	Raman	I	calcd
ν_9 (B_{2g})	343	9		419	58	425			427	[395][f]	393			393
			340 s											
ν_1 (A_g)	333	100		413	100	413	415	100	415	382 vs	382	382	51	382
			326 s											
			322 m											
ν_2 (A_g)	315	27		395	23	391	388	10	392	361 m	361	378	15	361
			314 s											
	304	sh		376	6	377	379	12	379	342 m	349	340	100	349
ν_{12} (B_{3g})	295	29		367	14	365	360	31	368	309 s	338	334	23	338
				356	46									
			292 s											
ν_3 (A_g)	230	~0.5		260	4	285	267	3	287		264	274		
												267	10	264
			216 m											
			205 sh											
ν_{13} (B_{3g})	204	~1		229	0.3	253	235	0.5	254	243 sh	234	(206)[e]	vw	234
			180 w											
ν_4 (A_g)	170	31		188	17	211	193	29	212	187 s	195	185	30	195
ν_7 (B_{1g})	157	24		170	27	195	166	30	196	180 m	180	171	17	180
			158 s											
			144 sh											
			134 s											
ν_{14} (B_{3g})	129	7		130	21	160	159	12	161	136 m	148	137	3	148
			126 sh											
ν_{10} (B_{2g})	110	18		123	19	136	133	20	137	132 m	126	126	10	126
ν_8 (B_{1g})	103	19		118	27	128	123	28	128	128 sh	118	112	7	118
ν_{11} (B_{2g})	94	15		100	14	117	115	8	117	[126][f]	108	104	17	108
			90 w											
ν_5 (A_g)	63	2		72	1	78	98	5	79	117 s	72			
ν_{15} (B_{3g})	59	6		68	1	73	94	7	74	[108][f]	68	51	4	68
							75	2						
ν_6 (A_g)	50	4		46	2	62	70	1	62	64 s	57	46	2	57
							65							
lattice vib	35	2		38	14	43	33	1	44		40	31	6	40

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. Species assignments are based on ref 16. Columns "calcd" include calculated frequencies of $\nu_x{}^i = \nu_x{}^{Sn}(\nu_1{}^i/\nu_1{}^{Sn})$, where i = one of the species listed, except $Sn_2Cl_{10}^{2-}$ and x = one of the 15 Raman-active fundamentals; $\nu_x{}^{Sn}$ = frequency of $Sn_2Cl_{10}^{2-}$. [b] Experimental; this work. [c] Experimental; ref 15 and 16. [d] Experimental; ref 18. [e] Experimental; ref 17. [f] Calculated; ref 16.

Table X. Positional Parameters for **4**[a]

atom	x	y	z
Sn	0.00000	0.25000	0.10919 (7)
P	0.25000	0.00000	0.50000
Cl(1)	0.00000	0.10340 (9)	0.1108 (3)
Cl(2)	0.1707 (1)	0.25000	0.2759 (3)
Cl(3)	0.00000	0.25000	−0.2492 (3)
Cl(4)	0.3426 (1)	0.06797 (9)	0.3309 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table XI. Bond Lengths (Å) and Angles (deg) for **4**[a]

Sn–Cl(1)	2.414 (1)	Sn–Cl(3)	2.325 (2)
Sn–Cl(2)	2.319 (1)	P–Cl(4)	1.922 (1)
Cl(1)–Sn–Cl(1)′	179.51 (6)	Cl(2)–Sn–Cl(3)	117.80 (5)
Cl(1)–Sn–Cl(2)	89.89 (2)	Cl(4)–P–Cl(4)′	109.25 (7)
Cl(1)–Sn–Cl(3)	90.24 (4)	Cl(4)–P–Cl(4)″	108.77 (7)
Cl(2)–Sn–Cl(2)′	124.40 (7)	Cl(4)–P–Cl(4)‴	110.39 (7)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

triply degenerate IR vibrations in $SnCl_6^{2-}$ is lifted and numerous peaks are observed, presenting a complicated spectrum similar to that of $Sn_2Cl_{10}^{2-}$.

Although the tetravalent tin is present in both negatively charged $SnCl_6^{2-}$ and $Sn_2Cl_{10}^{2-}$ anions, the relative charge per tin atom is different. As a result the Raman stretching frequencies are at 308 cm^{-1} in $SnCl_6^{2-}$ and are higher, at 343–334 cm^{-1}, in $Sn_2Cl_{10}^{2-}$, with the lower net charge per tin atom.

(PCl_4)($SnCl_5$) (4). Structural Results. The atomic positional parameters are listed in Table X, while Table XI gives the bond lengths and angles. Figure 7 shows the numbering scheme in $SnCl_5^-$. Each of the $SnCl_5^-$ ions resides on the 4-fold crystallographic *mm* axis at 0, 1/4, *z* with one mirror plane (0, *y*, *z*) bisecting Sn, Cl(1), Cl(1)′, and Cl(3) and with another plane (0, 1/4, *z*) bisecting Sn, Cl(2), Cl(2)′, and Cl(3). The overall symmetry of the ion is approximately D_{3h}, but the trigonal bipyramid is slightly distorted. The Sn–Cl(2) and Sn–Cl(3) distances are 2.319 (1) and 2.325 (2) Å, and the Cl(2)–Sn–Cl(2)′ and Cl(2)–Sn–Cl(3) angles are 124.40 (7) and 117.80 (5)°, respectively. The $SnCl_5^-$ ion has been previously characterized in the salt 3-chloro-1,2,3,4-tetraphenylcyclobutenuim pentachlorostanate.[21] The reported in-plane Sn–Cl bond lengths are 2.30, 2.40, and 2.38 Å, and the in-plane Cl–Sn–Cl angles are 114, 120, and 126°. The perpendicular Sn–Cl bond lengths are 2.37 and 2.39 Å. The corresponding distance in the $SnCl_5^-$ ion described here is 2.414 (1) Å (Sn–Cl(1)). The 1− charge of the $SnCl_5^-$ ion is balanced by a PCl_4^+ ion residing on the 4-fold 222 site at 1/4, 0, 1/2.

Vibrational Spectra. The Raman spectrum of this salt is presented in Figure 6. The numerical frequencies including their assignments are listed in Table XII. As verified by X-ray analysis, the $SnCl_5^-$ anion has a trigonal-bipyramidal structure of almost D_{3h} symmetry. Very few MX_5 species of this symmetry have been identified. Species of this kind tend easily to dimerize into M_2X_{10} species, enabling a hexacoordinated central atom to be formed, or to act as a Lewis acid, accepting a halide anion to form a MX_6^- anion. As a result, experimental spectral data of MX_5 species are rather scarce and seldom complete.

If the four Raman-active vibrations of the PCl_4^+ cation are eliminated, eight features are observed, which seem to be all the fundamentals of the $SnCl_5^-$ anion. Although only six of these are

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Table XII. Vibrational Frequencies (cm^{-1}) of $SnCl_5^-$ and Related Data[a]

	$(PCl_4^+)(SnCl_5^-)$[b]			$SnCl_5^-$[c]		
assignt	Raman	I	calcd	Raman	IR	$SbCl_5$[d]
ν_5 (E') $SnCl_5^-$	379	16	378	353 m–358 vs	350 vs–360 s	395–399
ν_3 (A$_2''$) $SnCl_5^-$	356	10	354	312 vw	314 vs–321 s	371–372
ν_1 (A$_1'$) $SnCl_5^-$	338	100	338	338 vs–333 vs	336 w, sh–340 sh	353–357
$2\nu_4$ (?) $SnCl_5^-$	296	4				
ν_2 (A$_1'$) $SnCl_5^-$	264	15	290	269 w–265 mw		303–307
ν_6 (E') $SnCl_5^-$	174	24	169	171 w–170 sh	169 vs	175–180
ν_8 (E'') $SnCl_5^-$	162	39	158	161 m	160 vs–163 m	164–167
	153	15				
ν_4 (A$_2''$) $SnCl_5^-$	144	10	148	152 m–147 w, sh	150 vs–154 sh, br	154–156
ν_7 (E') $SnCl_5^-$	78	24	67	70 sh	66 vw–69 w	67–74
				65 w		

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; calcd, values obtained by multiplying the fundamental frequencies of $SbCl_5$ by the ratio of $\nu_1(SnCl_5)/\nu_1(SbCl_5)$. [b] This work. [c] Reference 22. [d] References 17, 18, 24, and 25.

expected to be Raman active, it seems that, in the crystalline solid, the selection rules break down as a result of differing site and point symmetries. Thus the two originally noncoinciding infrared-active vibrations are also observed in the Raman spectrum.

On the whole, our observed frequencies agree very well with those reported in the literature,[22] except for two major differences, namely in the assignments of the ν_5 and ν_3 vibrations. Nakamoto[23] mentions that the majority of MX_5 compounds, having D_{3h} symmetry, show the frequency order $\nu_5 > \nu_3 > \nu_1 > \nu_2$. The assignment of 312 cm^{-1} as ν_3,[22] which is lower than ν_1, is in contradiction to the above statement of Nakamoto. In addition, it has only been observed in one of the two compounds studied[22] and even then only as a very weak feature. In our work, no feature is observed in this region between ν_1 at 338 cm^{-1} and ν_2 at 264 cm^{-1}. Instead, another medium-intensity feature is observed at 379 cm^{-1}, which we assign as ν_5, and we assign 356 cm^{-1} as ν_3. Thus our assignment is in accordance with the order summarized by Nakamoto. Actually, the ratio of the observed frequencies in $SnCl_5^-$ to those of $SbCl_5$[24,25] is consistent for all vibrations, except for ν_2. Calculating this frequency for the $SnCl_5^-$ ion from that of $SbCl_5$ would give a value of ~290 cm. As a matter of fact, a very weak feature was observed at 296 cm^{-1} in some samples but was totally missing in some other samples. No such line has been observed in the reported data,[22] and it seems than, when observed at all, it probably is of an impurity[26] or else can be assigned to $2\nu_4$ of $SnCl_5^-$. In addition, it would also be hard to explain why a symmetric stretch ν_2 of the axial chlorines would be so weak in the Raman spectrum whereas the asymmetric stretchings ν_5 and ν_3 would be even more intense, in contrast to the usual pattern $I_{sym} > I_{asym}$.

In the deformation mode region of $SnCl_5^-$ vibrations, the symmetric bend ν_2 of PCl_4^+ is also expected to appear. Since this is an E type vibration, a split line could be observed and assigned at 178 and 174 cm^{-1}. However, in agreement with the reported frequencies[22] it seems more reasonable to assign these lines for separate vibrations, the 178-cm^{-1} line to the cation and the 174-cm^{-1} line as an $SnCl_5^-$ vibration. This is also a good value when an $SbCl_5$ frequency at 178 cm^{-1} is converted to an $SnCl_5^-$ vibration to yield 169 cm^{-1}. In this case the 162–153-cm^{-1} doublet should be assigned to one doubly degenerate vibration—ν_8 (E''). There seems no problem in assigning the lowest observed frequency of 78 cm^{-1} as ν_7, whereas it is more difficult to assign accurately the other three bending modes, and we followed the assignments of $SbCl_5$.

In both $SnCl_5^-$ and $Sn_2Cl_{10}^{2-}$ the most intense ν_1 line is at similar frequencies, 338 and 334 cm^{-1}. However in $SnCl_5^-$ the asymmetric vibrations are observed at even higher frequencies. On the whole, the $SnCl_5^-$ spectrum is, as expected, simpler than that of $Sn_2Cl_{10}^{2-}$.

The infrared spectrum is very similar to that of $Sn_2Cl_{10}^{2-}$, which is to be attributed to the poor resolution, and as a result no clear differences can be observed.

This interpretation overlooks the slight distortion observed by X-ray data in which the $SnCl_5^-$ ion has a C_{2v} structure of XY_4Z (Z = equatorial chlorine). In such a case 11 fundamentals would be expected altogether, all of them Raman and IR active. In fact, fewer lines have been observed, and therefore it seems quite justified to interpret the observed vibrational spectra principally on the basis of a D_{3h} symmetry with the electron rules relaxed, so that all of the fundamentals are observed in the Raman spectrum.

Comparison of PCl_5–$SnCl_4$ and PCl_5–$TiCl_4$ Systems. The present results demonstrate the transformation

$$2(PCl_4^+)(SnCl_5^-) \xrightarrow{\text{heat}} (PCl_4^+)_2(Sn_2Cl_{10}^{2-})$$

in which two monomeric anions form a dimer. This clearly indicates that the dimer is thermodynamically more stable than the monomer and is in accordance with the more general trend that pentacoordinated species, whether neutral molecules or negatively charged ions, form dimeric species. This is observed in neutral compounds, such as Nb_2X_{10} or Ta_2X_{10} (X = Cl or Br),[13] or in negatively charged species, such as $Ti_2Cl_{10}^{2-}$.[14-16] Pentacoordinated species of D_{3h} symmetry tend to convert to an octahedral structure with an O_h symmetry, as a hexacoordinated species. Such a changeover can take place in several different reactions. One route, in which the pentacoordinated species acts as a Lewis acid, is the addition of a halide anion:

$$MX_5^{n-} + X^- \rightarrow MX_6^{(n+1)-} \tag{6}$$

Another route is the formation of dimers with an edge-bridged bioctahedral structure

$$2MX_5^{n-} \rightarrow M_2X_{10}^{2n-} \tag{7}$$

in which each central atom M becomes hexacoordinated. Further, an additional possibility is the formation of a dimer having a face-shared bioctahedral structure with three bridging halogens; instead of two bridging halogens as in the former case. This dimerization proceeds as follows:

$$MX_5^{n-} + MX_4 \rightarrow M_2X_9^{n-} \tag{8}$$

as has been observed in $Ti_2Cl_9^-$. The net charge per central atom decreases in the sequence of these three types of reactions to form hexacoordinated species as follows: (6) > (7) > (8) in which the net charge per central atom is $(n+1)-$, $n-$, and $n-/2$, respectively.

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It is therefore of interest to compare the two systems PCl_5–$SnCl_4$ and PCl_5–$TiCl_4$. Both of these systems have been studied by vibrational spectroscopy[15,16,28] and X-ray analysis.[6,28] In the tin system three types of anions were verified to exist with the PCl_4^+ cation, in the following relative stabilities in which the dimer is more stable at higher temperatures:

$$SnCl_6^{2-}\text{ (stable)};\quad Sn_2Cl_{10}^{2-} \xleftarrow{\text{heat}} SnCl_5^-$$

However, in the titanium system, no $TiCl_6^{2-}$ seems to exist with the PCl_4^+ cation[15] even with an excess of PCl_5. The relative thermodynamic stabilities are in the opposite direction, namely the monomer being more stable at higher temperatures:

$$TiCl_6^{2-}\text{ (nonexistent)};\quad Ti_2Cl_{10}^{2-} \xrightarrow{185\ °C} TiCl_5^-$$

We have no clear explanation for these differences, because the $TiCl_6^{2-}$ anion has been established in other salts with other cations. It is possible that these differences stem from steric effects or possibly from varying relative Lewis acidities and basicities.[15,16] Further work on the PCl_5–$TiCl_4$ system is in progress.

Registry No. **1**, 17731-85-0; **2**, 96211-86-8; **3**, 96211-87-9; **4**, 96211-88-0; PCl_5, 10026-13-8; $SnCl_4$, 7646-78-8; PCl_3, 7719-12-2; $SOCl_2$, 7719-09-7.

Supplementary Material Available: Tables of structure factors and thermal parameters for **2**, **3**, and **4** (24 pages). Ordering information is given on any current masthead page.

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(28) This work.

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Mechanism of Conversion of Iron(III) Tetratolylporphyrin Hydroxide to the Corresponding μ-Oxo-Bridged Dimer

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The rate of conversion of iron(III) tetra-*p*-tolylporphyrin hydroxide to the corresponding μ-oxo-bridged dimer was studied by ^1H NMR at room temperature in carbon tetrachloride solution. The dependence of the rate on the initial concentration of the iron porphyrin and on the concentration of hydroxide ion (OH and OD) was examined. The data are consistent with a two-step mechanism. The first step is dissociation of hydroxide from an iron porphyrin. In the second step that iron porphyrin reacts with a second iron porphyrin hydroxide to form the dimer. The deuterium isotope effect on the second step was about 5.

Introduction

The product that has been isolated after reaction of hydroxide with sterically unhindered iron(III) porphyrin chlorides (Fe(P)Cl[1]) in organic solvents is the μ-oxo-bridged dimer.[2] Recently it has been shown that sterically hindered porphyrins prevent dimer formation and permit isolation of Fe(P)OH.[3-11] It has also been reported that the visible spectrum of the product obtained by reaction of Fe(TPP)Cl with OH^- indicated that Fe(TPP)OH was formed.[3,12,13]

In our studies of metal–nitroxyl interactions in spin-labeled iron(III) porphyrins,[14] we observed that when a solution of Fe(P)Cl was shaken with aqueous OH^-, the initial product was Fe(P)OH and that complete conversion to the dimer required several hours. Similarly when Fe(TTP)Cl or Fe(TPP)Cl was shaken with OH^-, the product was Fe(P)OH which converted to $(Fe(P))_2O$ within several hours. These observations prompted us to examine the process by which Fe(TTP)OH was converted to $(Fe(TTP))_2O$. Fe(TTP)OH was selected for this study because the ^1H NMR spectra of the methyl groups provided a convenient method to follow the course of the reaction.

Experimental Section

Physical Measurements. Electronic spectra were obtained in toluene solution (ca. 0.05 mM) on a Beckman Acta V spectrometer in 1-mm cells for the region 300–470 nm and in 10-mm cells for the region 470–800 nm. Infrared spectra were obtained on benzene solutions (1 mM) in a 1-mm NaCl cell on a Digilab FTS-20B infrared spectrometer. The background spectrum of the cell and solvent was digitally subtracted from the spectrum of the solution of iron porphyrin. NMR spectra were obtained at 21–22 °C in carbon tetrachloride solution in 5-mm tubes on a Magnachem A200 FT NMR. For the kinetic studies 20 ppm spectra were obtained with 8*K* data points and sufficient delay between pulses to give accurate integration of the signals. In a sample containing tetramethylsilane (Me_4Si), the methyl signal in $(Fe(TTP))_2O$ was 2.81 ppm downfield of Me_4Si. In subsequent spectra of samples that did not contain Me_4Si, the shifts were assigned relative to the shift of this methyl signal.

Preparation of Iron Porphyrins. Pyrrole was distilled before use. Reagent grade and spectroscopic grade solvents were used without purification. H_2TPP[15,16] and H_2TTP[15,16] were purified by chromatography in chloroform solution on silica gel. Fe(TPP)Cl[17,18] and Fe(TTP)Cl[17]

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(1) Abbreviations: P = porphyrin dianion; TPP = dianion of 5,10,15,20-*meso*-tetraphenylporphyrin; TTP = dianion of 5,10,15,20-*meso*-tetra-*p*-tolylporphyrin.

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