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Characterization of Tantalum Pentachloride Containing Melts by Raman Spectroscopy

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Raman spectroscopy has been used to obtain information on various $TaCl_5$ containing melts. In molten $TaCl_5$, studied between 220 and 350 °C, a gradual dissociation of molecular Ta_2Cl_{10} (D_{2h}) to monomeric $TaCl_5$ (D_{3h}) appears to take place. Evidence for a stable octahedral $TaCl_6^-$ ion in molten $KTaCl_6$ at 420 °C is presented. The binary $TaCl_5$–$AlCl_3$ system at ~200 °C contains noninteracting Ta_2Cl_{10} and Al_2Cl_6 molecules. The complexes formed when $TaCl_5$ is dissolved in $AlCl_3$–NaCl and $AlCl_3$–KCl melts depend on acidity and temperature: $TaCl_6^-$ (O_h) is present only in basic to slightly acidic melts; $TaCl_5$ (D_{3h}) is mainly stable in neutral and acidic melts at high temperature; Ta_2Cl_{10} is found only in acidic melts at lower temperatures.

Introduction

The electrochemistry and coordination chemistry of tantalum(V) dissolved in $AlCl_3$–NaCl melts[2,3] is complex and highly dependent upon temperature and the acidity (pCl⁻) of the melts.[4] This Raman spectral study was undertaken primarily to obtain information on the nature of pentavalent tantalum species in various chloroaluminate melts. Lower valent tantalum compounds are either strongly colored or only sparingly soluble in chloroaluminate melts, making such solutions unsuitable for normal Raman spectroscopy.

Several Ta(V) species may be expected to occur in chloroaluminate melts of varying acidities. Molecular Ta_2Cl_{10} forms the fundamental unit in the solid pentachloride.[5] $TaCl_5$ molecules of D_{3h} symmetry exist in the gas phase at elevated temperatures.[6] Many hexachlorotantalate salts containing the octahedral $TaCl_6^-$ ion are well characterized.[7-9] A $TaCl_4^+$-type complex has not been reported, a fact that is in agreement with the generally accepted strong Lewis acid character of tantalum pentachloride. Neither have chloride-bridged polymeric ions similar to the niobium complex[10] in $SeF_3^+Nb_2F_{11}^-$ been reported.

Experimental Section

The preparation and purification of $AlCl_3$ and NaCl have been described previously.[11] $TaCl_5$ (Alfa) was purified by subliming it five times at 200 °C through a fine Pyrex frit. $KTaCl_6$ was synthesized by melting an equimolar mixture of KCl and $TaCl_5$ at 500 °C. Optical cells were made from square Pyrex tubing (5 × 5 mm). The salts were transferred to the optical cells in an argon-filled drybox (normal H_2O and O_2 content <2 ppm); the cells were evacuated to ~4 μm and sealed. The samples were melted in a furnace made by winding nichrome wire around the square Pyrex tube placed in an insulating block with proper holes for the laser and Raman light. The Raman apparatus has been described previously.[12] Laser lines at 488.0 or 514.5 nm from a Spectra-Physics Model 164 argon-ion laser were used to illuminate the sample. Scattered light was observed at right angles to the exciting beam and polarization measurements were made by rotating the plane of polarization of the illuminating laser light 90°. A modified Cary-81 spectrometer equipped with a cooled EMI 9568 phototube and photon-counting electronics was used to record the spectra. The spectra of molten $KTaCl_6$ and of pure $TaCl_5$ were obtained with 647.1 nm excitation from a Coherent Radiation Model CR 500K krypton ion laser using a JEOL JRS-400D spectrometer.

Results and Discussion

I. Solid and Molten $TaCl_5$. The Raman spectrum of solid $TaCl_5$ at 25 °C (Figure 1a and Table I) was found to be in good agreement with published data,[9] except for additional weak bands at 343, 232, and 146 cm⁻¹ which probably stem from factor-group splittings not resolved previously. Spectral changes on going from solid $TaCl_5$ to the melt at 220 °C (see Figure 1b and Table I) can be attributed to band broadening caused by the higher temperatures. Evidently the structural Ta_2Cl_{10} unit of D_{2h} symmetry shown by X-ray methods to be predominant in the solid state[5] is also the dominating species in low-temperature melts. In the spectra recorded at 300 and 350 °C (Figure 1c,d and Table I) a gradual loss of detail and some minor frequency shifts are observed. The position of the Ta–Cl stretching frequency at 411–414 cm⁻¹ remains, however, virtually the same. The spectrum at 350 °C resembles the spectrum reported by Beattie and Ozin[6] for gaseous $TaCl_5$ which is generally assumed to be a monomeric gas composed of trigonal-bipyramidal D_{3h} molecules. In a similar study by Bues et al.[13] on the endothermic dissociation of molten Nb_2Cl_{10} to liquid $NbCl_5$ considerably larger changes in the Raman spectra were observed in the temperature range 220–320 °C. At least two reasons for this difference between the behavior of molten $NbCl_5$ and $TaCl_5$ can be given: (1) the accidental frequency overlap of the characteristic vibrations of Ta_2Cl_{10} and $TaCl_5$ precludes an estimate of the dimer-to-monomer ratio at a given temperature; (2) it has been shown[14] that $TaCl_5$ is a stronger chloride acceptor than $NbCl_5$ under identical conditions, suggesting that the Ta_2Cl_{10} dimer is more stable than the Nb_2Cl_{10} dimer. We conclude that an endothermic monomerization reaction

$$Ta_2Cl_{10} \rightleftharpoons 2TaCl_5 \qquad (1)$$

takes place in molten $TaCl_5$, and that higher temperatures (t > 300 °C) are needed to dissociate molten Ta_2Cl_{10} than to dissociate Nb_2Cl_{10}.

II. Solid and Molten $KTaCl_6$. $KTaCl_6$ is reported to melt congruently at 410 °C.[15] Evidence for three crystalline modifications has been obtained; the $\gamma \rightarrow \beta$ transition occurs

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Table I. Raman Spectral Data (cm^{-1}) for $TaCl_5$[a]

		melt				
solid at 25 °C	solid[b]	220 °C	? °C[b]	300 °C	350 °C	gas[c]
419 vs	418 (10)	414 vs, p	411 (8.8), p	414 vs, p	411 vs, p	406 s, p; ν_1 (A_1')
388 m	390 (0.7)	389 w, sh, dp				
379 m	381 (0.7)					
362 s	363 (2.5)	363 w, p	362 (0.8), p	360 w, p		
343 vw		330 w, dp?		330 w, p?	326 vw, p	324 w, p; ν_2 (A_1')
269 m, br	274 (0.4)	271 w, dp?	282 (0.3)	264 w, dp?		
232 w	241 (0.1)		240 (0.2)			
196 s	197 (3.2)	193 m, dp	191 (1.6)	195 m, dp	186 m, dp	181 w, br; ν_6 (E')
168 s	171 (4.1)	172 m, dp	172 (1.1)	173 w, dp		
161 w, sh	163 sh					
146 w, sh		143 vw, dp	143 (0.4)	146 w, dp?	144 w, p?	
134 m	136 (2.5)					
125 m	126 (3.5)	127 w, dp	126 (0.3)			127 w; ν_8 (E'')
103 w, sh	103 sh	115 w, dp		~90 vw, dp	~90 vw, dp	
	97 (0.9)					
71 w, br	76 (0.1)	83 w, p				
	60 (2.0)					54 w; ν_7 (E')
35 s	37 (2.2)					

[a] Key: w, weak; m, medium; s, strong; br, broad; sh, shoulder; v, very; p, polarized; dp, highly depolarized. [b] Reference 9. [c] Reference 6.

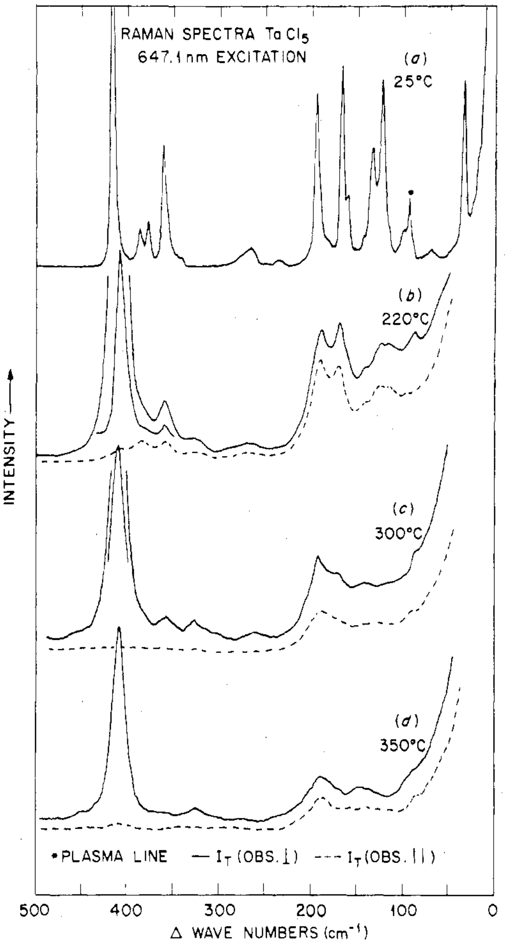

Figure 1. Raman spectra of $TaCl_5$: (a) polycrystalline $TaCl_5$ at 25 °C; (b, c, and d) molten $TaCl_5$ at 220, 300, and 350 °C, respectively.

at 185 °C and the $\beta \rightarrow \alpha$ transition proceeds at 314 °C. We have recorded spectra of (a) the γ form of annealed crystals at 25 °C, (b) the α form at 350 °C obtained by cooling the melt, and (c) the melt at 420 °C. Results are given in Figure 2 and Table II. The room-temperature spectrum is almost identical with the spectrum of $CsTaCl_6$ reported by van Bronswyk et al.[8] The ν_5 (F_{2g}) of $TaCl_6^-$ (assuming a free ion and O_h symmetry) is split into at least two components at 184 and 187 cm^{-1} and the ν_2 (E_g) of $TaCl_6^-$ at 302 cm^{-1} is of very low intensity as in other salts[7,8] containing $TaCl_6^-$. In the spectrum of α-$KTaCl_6$ at 350 °C no splitting is observable due to band broadening. No changes in the spectrum are found upon melting of α-$KTaCl_6$. Thus the $TaCl_6^-$ complex is quite stable in the melt. The invariance of the $TaCl_6^-$ spectrum furthermore reveals that anion–cation interactions of very similar magnitudes are present in molten and solid α-$KTaCl_6$. Compatible with this idea is the report that solid α-$KTaCl_6$ is a solid electrolyte.[15]

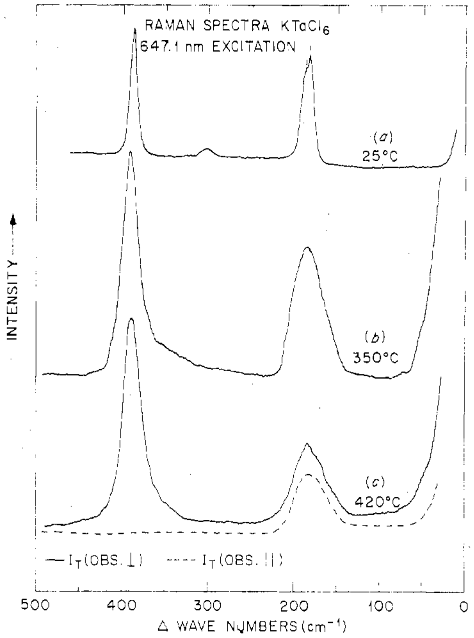

Figure 2. Raman spectra of $KTaCl_6$: (a) polycrystalline γ-$KTaCl_6$ at 25 °C; (b) polycrystalline α-$KTaCl_6$ at 350 °C; (c) molten $KTaCl_6$ at 420 °C.

Table II. Raman Spectral Data (cm^{-1}) for $KTaCl_6$ and $CsTaCl_6$[a]

γ-$KTaCl_6$ at 25 °C	α-$KTaCl_6$ at 350 °C	$KTaCl_6$ (melt) at 420 °C	$CsTaCl_6$[b,c] at 25 °C
386 vs	389 s	390 s, p	382 s; ν_1 (A_{1g})
302 vw, br			299 w; ν_2 (E_g)
187 m 184 m	183 s	183 m	180 s 188 s $\}\nu_5$ (F_{2g})

[a] Key: w, weak; m, medium; s, strong; v, very; p, polarized. [b] Reference 8. [c] Symmetry species derived for $TaCl_6^-$ by using O_h point group symmetry.

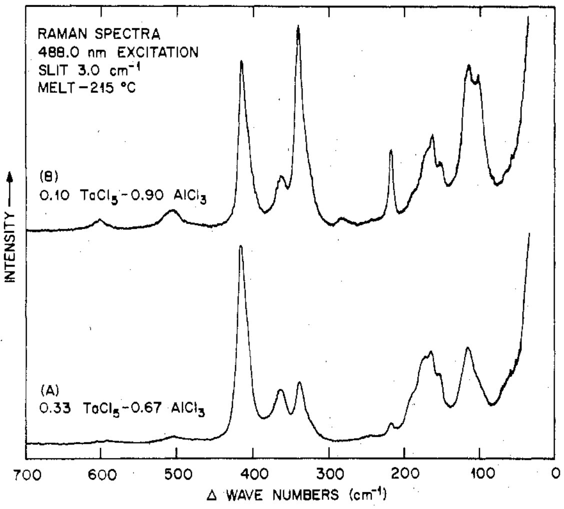

Figure 3. Raman spectra of (A) 0.33 $TaCl_5$–0.67 $AlCl_3$ and (B) 0.10 $TaCl_5$–0.90 $AlCl_3$ at 215 °C.

Table III. Raman Spectral Data (cm^{-1}) for Molten Mixtures of $TaCl_5$ and Al_2Cl_6[a]

$TaCl_5$[b] at 220 °C	$TaCl_5$-$AlCl_3$ at 33-67 mol %, 215 °C	Al_2Cl_6[c] at 225 °C	$TaCl_5$-$AlCl_3$ at 10-90 mol %, 215 °C
		608 m, p?	608 vs, dp
		512 m, p	509 w, p
414 vs, p	418 vs, p	440 w	417 s, p
389 w, sh, dp			
363 w, p	367 m		365 w/m
330 w, dp?	340 m, p	341 vs, dp	341 s, p
271 w, dp?		290 m, p	284 w
	219 vw, p	218.5 vs, p	219 m, p
193 m, dp	191 w, sh, dp		187 vw, sh, dp
172 m, dp	176 m, dp		173 w, sh, dp
143 vw, dp	167 m, dp	166 w, dp	164 m, dp
127 w, dp	155 w, dp		153 w, dp
115 w, dp	117 m, dp	119 s, dp	120 s, sh, dp
			116 s, dp
83 w, p	99 vw, dp?	104 s, p	104 s, dp

[a] Key: w, weak; m, medium; s, strong, v, very; sh, shoulder; p, polarized; dp, highly depolarized. [b] From Table I. [c] Reference 17.

III. $TaCl_5$–$AlCl_3$ Melts. Phase diagram studies and vapor pressure measurements[16] indicate that the $TaCl_5$–$AlCl_3$ binary system is a simple eutectic melt system in equilibrium with an approximately ideal vapor phase. The simplicity of the system was confirmed by this Raman study. Spectra of melts containing 0.5 and 0.1 mole fraction of $TaCl_5$, respectively, (Figure 3 and Table III) are simple superpositions of the known spectra of molecular Ta_2Cl_{10}[9] and Al_2Cl_6,[17] both of D_{2h} symmetry. The system may, thus, be described as a molecular liquid over the entire composition range. This is to be expected in view of the strong Lewis acidic nature of both Ta_2Cl_{10} and Al_2Cl_6. Dilution of molten $TaCl_5$ with Al_2Cl_6 would be expected to shift eq 1 to the right in favor of the monomer. This effect was not detectable, however, since the temperature apparently has a much larger influence on the dissociation than the mole fraction of tantalum pentachloride. The excessively high vapor pressure of $AlCl_3$-rich melts did not allow studies much above 215 °C.

IV. $TaCl_5$ in $AlCl_3$–NaCl and $AlCl_3$–KCl Melts. Raman spectra of $TaCl_5$ dissolved in chloroaluminate melts have been obtained under conditions which resemble those of the spectrophotometric and voltammetric study.[2,3] Melt compositions studied ranged from $MAlCl_4$ melts saturated with MCl (basic melts) to stoichiometric $MAlCl_4$ melts (neutral melts) to melts containing 53 and 63 mol % $AlCl_3$ (acidic melts). The temperature ranged from 165 to 300 °C. The formality of $TaCl_5$ added to the melts ranged from 0.7 to 0.9 F. This implies that the concentration of the solvent species $AlCl_4$ and $Al_2Cl_7^-$ was up to 10 times higher than the concentration of the Ta species of interest. Fortunately, the Ta–Cl species turn out to be relatively stronger Raman scatterers as compared to the Al–Cl species, increasing the limit of detection of the Ta(V) species.

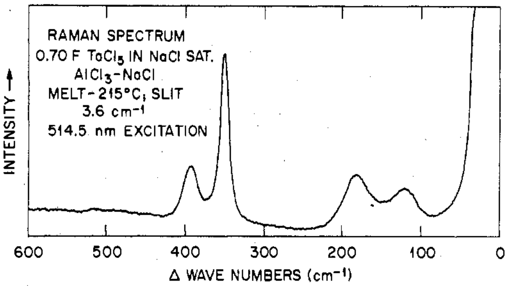

Figure 4. Raman spectrum of 0.7 F $TaCl_5$ in $AlCl_3$–$NaCl_{satd}$ melt at 215 °C.

Table IV. Raman Spectral Data (cm^{-1}) for $TaCl_5$ Dissolved in Chloroaluminate Melts

0.7 F $TaCl_5$ in $AlCl_3$-$NaCl_{sat.}$ at 215 °C	0.7 F $TaCl_5$ in $AlCl_3$-$KCl_{sat.}$ at 260 °C
	482 vw, dp
392 m, p	385 m
350 s, p	347 s
182 m, dp	183 m
120 w, dp	122 w/m

0.8 F $TaCl_5$ in $AlCl_3$-NaCl (50–50 mol %)			0.9 F $TaCl_5$ in $AlCl_3$-NaCl (53–47 mol %)		
300 °C	245 °C	200 °C	290 °C	245 °C	165 °C
410 vw, sh			410 m	412 w	
391 m	393 m	394 m	390 vw, sh		
349 s	350 s	350 s	349 s	349 s	351 s
181 m	182 m	181 m	311 w	312 w	315 w
120 m	121 m	118 m	181 m	180 m	181 m
			119 m	117 m	117 m

0.9 F $TaCl_5$ in $AlCl_3$-NaCl (63–37 mol %)			0.7 F $TaCl_5$ in $AlCl_3$-KCl (63–37 mol %)	
285 °C	230 °C	180 °C	260 °C	205 °C
414 m/s	419 m/s	421 m/s	416 m, p	421 m, p
	409 vw, sh?			
	367 vw	366 vw		
348 s	348 s	349 s	347 s, p	348 s, p
310 m	311 m	311 m	309 s, p	310 s, p
	174 vw, sh	171 vw, sh	176 w, sh, dp	176 w, sh, dp
163 m/s	164 m/s	162 m/s	161 m, dp	162 m, dp
	154 vw, sh	156 vw, sh		151 vw, sh
113 vw, sh	112 w, sh	115 w	116 w, sh, dp	116 w, sh, dp
99 w	97 w	96 w	96 m, dp	97 m, dp

$TaCl_5$ is quite soluble in basic, neutral, and strongly acidic (63 mol % $AlCl_3$) melts. In the intermediate range of compositions (53–55 mol % $AlCl_3$) a minimum in solubility is observed. As expected an increase in temperature results in an increase in solubility and volatility of $TaCl_5$. This minimum in solubility in the intermediate range of composition is in qualitative agreement with the phase diagrams of the ternary systems MCl-$AlCl_3$-$TaCl_5$ (M = Na, K).[16,18] Two liquid phases were found at compositions around the mole ratio $MCl/AlCl_3 \approx 1$.[16,18]

With the results discussed earlier the Ta species found in $AlCl_3$–MCl melts may be easily identified. In *basic melts* one observes (Figure 4 and Table IV), in addition to the known spectrum[17] of tetrahedral $AlCl_4^-$, a strong polarized band at 385–392 cm^{-1} and a strong depolarized band at 182–183 cm^{-1} which overlaps the ν_4 (F_2) vibration of $AlCl_4^-$ at 186 cm^{-1}.

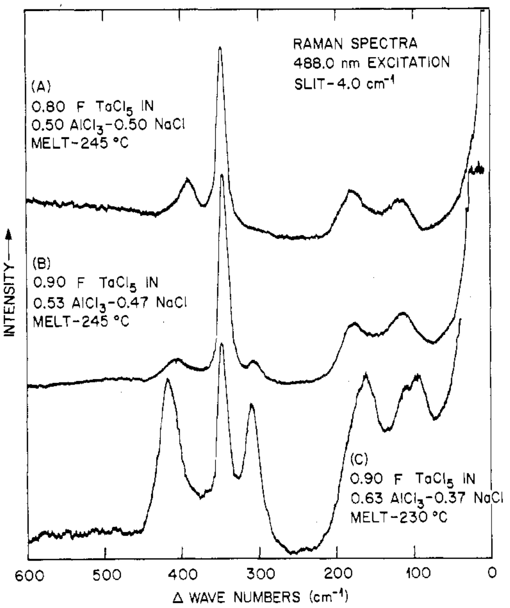

Figure 5. Raman spectra of (A) 0.8 F $TaCl_5$ in 0.50 $AlCl_3$–0.50 NaCl, (B) 0.9 F $TaCl_5$ in 0.53 $AlCl_3$–0.47 NaCl, and (C) 0.9 F $TaCl_5$ in 0.63 $AlCl_3$–0.37 NaCl.

These two bands are the characteristic bands of octahedral $TaCl_6^-$ observed also in pure molten $KTaCl_6$ (see Table II).

Thus as long as excess free chloride ions are present in the melt, $TaCl_5$ will be converted to $TaCl_6^-$ according to

$$TaCl_5 + Cl^- \rightarrow TaCl_6^- \qquad (2)$$

When $TaCl_5$ is added to *neutral or slightly acidic* chloroaluminates (50–53 mol % $AlCl_3$), a competitive acid–base reaction between the Ta and Al complexes must be involved to account for the observations (Figure 5 and Table IV). Upon subtracting bands[17] due to $AlCl_4^-$ and $Al_2Cl_7^-$ one is left with bands which can be assigned to $TaCl_6^-$ and monomeric $TaCl_5$, the latter showing up in detectable concentrations at 290–300 °C. An acid–base reaction of the type

$$TaCl_5 + 2AlCl_4^- = TaCl_6^- + Al_2Cl_7^- \qquad (3)$$

can be used to describe the situation. The stability of $TaCl_6^-$ is favored when the $Al_2Cl_7^-$ concentration is low, i.e., in basic and neutral melts. When the melt is made acidic (going from 50 to 53 mol % $AlCl_3$), eq 3 is gradually shifted to the left.

The high solubility of $TaCl_5$ in *strongly acidic melts* (63 mol % $AlCl_3$) appears to be in contradiction with the arguments given above. However, it is well-known that the solvent properties of $AlCl_3$–MCl melts change considerably when going from basic to strongly acidic compositions. The hard Cl^- and $AlCl_4^-$ anions found in basic melts are gradually replaced by the softer and more molecular-like species $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, and Al_2Cl_6 as the melt gets richer in $AlCl_3$. The presence of such species increases the solubility of covalent solutes. As an illustration of this concept we have previously shown[19] that molecular sulfur, S_8, is quite soluble in acidic melts at 250 °C, whereas its solubility is quite small in basic melts at 250 °C.

The bands at 421, 366, 171, 156, and 115 cm^{-1} observed for $TaCl_5$ dissolved in $AlCl_3$–NaCl (63–37 mol %) melts at 180 °C must be assigned to one or more Ta(V) species. It can be seen from Table IV that a gradual shift in frequencies and loss of detail occur upon heating the melt from 180 to 285 °C. The strongest peak assignable to a Ta species is shifted from 421 to 414 cm^{-1}. If an acidic complex like $TaCl_4^+$ were present, one would expect the symmetrical Ta–Cl stretching vibration to occur at a frequency >430 cm^{-1}. For comparison the symmetrical P–Cl stretching frequencies in the analogous PCl_5 and PCl_4^+ species are found at 393 and 459 cm^{-1}, respectively.[20] This was not observed. Therefore, we conclude that the temperature-dependent equilibrium involving Ta(V) is the dimer–monomer equilibrium (eq 1). It is noteworthy that the totally symmetric Ta–Cl stretching frequency of Ta_2Cl_{10} in pure molten pentachloride and the corresponding frequency in $TaCl_5$ dissolved in $AlCl_3$–NaCl (63–37 mol %) at 180 °C differ slightly (7 cm^{-1}). This is indicative of solvation or interaction existing in acidic chloroaluminate solutions of Ta_2Cl_{10}. Stated in another way, this interaction between Ta_2Cl_{10} and the molecular-like strongly acidic melt is probably the mechanism that brings about the higher solubility. The possibility that the enhanced solubility of $TaCl_5$ in strongly acidic melts is due to the formation of a mixed Ta(V)–Al(III) chloride-bridged polymer has also been considered. Evidence for mixed dimers such as $FeAlCl_6$ and $SbNbCl_{10}$ has recently[21,22] been obtained. For the above two cases the coordination numbers of the two metal centers in the dimers with respect to chlorine are the same (4 and 6, respectively). This would not be true for a mixed di- or polymeric Al(III)–Ta(V) species. Furthermore, significant spectral changes would be expected. It should also be noted that no intermediates were found in the binary system $TaCl_5$–$AlCl_3$ (see Table III).

The acid–base chemistry of $TaCl_5$ dissolved in chloroaluminates may, thus, be described in terms of three entities: $TaCl_6^-$ (O_h) present only in basic to slightly acidic melts, $TaCl_5$ (D_{3h}) present mainly in neutral to acidic melts at high temperatures, and Ta_2Cl_{10} (D_{2h}) present largely in acidic melts at low temperatures.

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Registry No. $TaCl_5$, 7721-01-9; $KTaCl_6$, 16918-73-3; $AlCl_3$, 7446-70-0; $AlCl_3$–NaCl, 7784-16-9; $AlCl_3$–KCl, 13821-13-1.

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Volumes of Activation for the Substitution Reactions of *cis*- and *trans*-$[PtL_2(Cl)X]$ with Pyridine in Various Solvents

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The pressure dependence of the second-order rate constant for the substitution by pyridine in *trans*-$[Pt(py)_2(Cl)(NO_2)]$ was measured in the solvents nitromethane, methanol, ethanol, and dichloromethane. The respective $\Delta V^{*}_{\text{exptl}}$ values were calculated to be -6.2 ± 0.4 at 10 °C, -8.8 ± 0.6 at 25 °C, -13.1 ± 0.8 at 25 °C, and -19.8 ± 1.7 $cm^3\ mol^{-1}$ at 25 °C. The $\Delta V^{*}_{\text{exptl}}$ values for the corresponding reactions of *cis*-$[Pt(py)_2(Cl)\ (NO_2)]$ and *trans*-$[Pt(PEt_3)_2Cl_2]$ in methanol at 25 °C are -5.5 ± 0.5 and -13.6 ± 0.8 $cm^3\ mol^{-1}$, respectively. These $\Delta V^{*}_{\text{exptl}}$'s were found to be only slightly temperature dependent. The activation parameters ΔH^{*}_2 and ΔS^{*}_2 were also determined for each reaction. The volume change associated with the partial formation of the Pt–py bond was estimated to be -4 ± 1 $cm^3\ mol^{-1}$. A qualitative explanation of the solvent dependence of $\Delta V^{*}_{\text{exptl}}$ is also given.

Introduction

The rate of substitution in d^8 square-planar complexes is known to obey a two-term rate law:[2–6]

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{nucleophile}]$$

The relative importance of the two terms is governed by various factors such as the nucleophilicity of the nucleophile and solvent, the degree of steric crowding within the substrate, the size of the nucleophile and solvent molecules, and the solvation of the reactants and transition states. Naturally some of these properties are interrelated. However, in the title reactions the k_1 term is virtually negligible in the solvents chosen so that only the k_2 path will be discussed here in detail. The mechanism of substitution is generally acknowledged[2–6] as being associative, with both the entering nucleophile and leaving ligand tightly bound in the transition state.

The volume of activation, $\Delta V^{*}_{\text{exptl}}$, provides a very effective criterion for characterizing reaction mechanisms, especially when the possibility exists to extract the volume changes, $\Delta V^{*}_{\text{intr}}$, arising from the variations in bond lengths and angles.[7] In the majority of cases this requires a knowledge of the origin and nature of solute–solvent interactions involved in the development of the transition state and their respective volume contributions to $\Delta V^{*}_{\text{exptl}}$.

The intimate reaction mechanism, operating in the present system, implies that only one bond is formed (viz., that between the nucleophile and the platinum center) in the rate-determining step. Thus the basic concept of $\Delta V^{*}_{\text{exptl}}$ dictates that $\Delta V^{*}_{\text{intr}}$ must be negative for this process.[7,8] However, it would be extremely valuable to determine the absolute value associated with bond formation.

The Menschutkin reaction,[9–11] which is perhaps the most studied reaction in the field of high-pressure kinetics, provides a good precedent for investigating the solvent dependence of substitution into transition-metal complexes.

Experimental Section

Materials. *trans*-$[Pt(py)_2(Cl)(NO_2)]$ was prepared by dissolving equimolar quantities (10 mmol) of *trans*-$[Pt(py)_2Cl_2]$[12] and $AgClO_4 \cdot H_2O$ in a minimum amount of Me_2SO. The mixture was stirred for 1 h at 40 °C and then cooled to room temperature and filtered. After *p*-toluenesulfonic acid was dissolved in the filtrate (1 mmol), 10 mmol of $NaNO_2$ was added. Crystallization of the white *trans*-$[Pt(py)_2(Cl)(NO_2)]$ product occurred immediately. The precipitate was washed with water and ethanol and repeatedly recrystallized from boiling chloroform. Anal. Calcd for $C_{10}H_{10}ClN_3O_2Pt$: C, 26.6; H, 2.3; N, 9.7; Cl, 8.8. Found: C, 27.5; H, 2.4; N, 9.7; Cl, 7.7.

cis-$[Pt(py)_2(Cl)(NO_2)]$ was prepared from the *cis*-dichloro-compound by the same procedure. Anal. Found: C, 26.3; H, 2.2; N, 9.5.

$[Pt(py)_3NO_2]ClO_4$ was prepared from *trans*-$[Pt(py)_2(Cl)(NO_2)]$ in methanol by a similar method. After the AgCl was filtered off, an excess of pyridine was added, and the resulting solution was stirred at 30 °C for 2 days. The solution was then evaporated to dryness on a rotary evaporator. The solid residue was dissolved in water and the solution filtered and again evaporated to dryness. The white precipitate was recrystallized twice from methanol. Anal. Calcd for $C_{15}H_{15}ClN_4O_6Pt$: C, 31.7; H, 2.6; N, 9.9. Found: C, 29.9; H, 2.7; N, 9.8.

trans-$[Pt(PEt_3)_2Cl_2]$ was prepared according to the method of Jensen.[13]

Pyridine was distilled a number of times as described previously.[14] All other salts used were of reagent grade.

The solvents (reagent grade or Uvasol product) used in the conductivity measurements were purified and dried according to standard procedures.[14,15] Purification was repeated until a constant, minimum conductivity was reached. The purity of each solvent was also monitored by density measurements.

Kinetic Measurements. Most of the reactions were followed conductometrically with a B-642 Autobalance Universal Bridge. A standard Pyrex-glass cell fitted with platinum electrodes was used for the kinetic runs at normal pressure. For measurements at higher pressures the conductivity cell shown in Figure 1 was constructed. Basically it consists of a Kel-F body, F, into which a flexible Teflon tube, H, is screwed. The cell is sealed at this joint, as well as at the remote end of the Teflon tube—where the cell can be filled by removing the Teflon screw, I— with Viton O-rings, G. The platinum electrodes, E, are fixed to the body of the cell by means of Teflon cones, C, through which tight-fitting platinum wire (0.8 mm) leads, D, pass; the Teflon cones are pressed in place by hollow cylindrical Kel-F screws, B. The cell itself fits into an aluminum holder, J, which in turn can be attached to the "plug", A, of the high-pressure bomb. The electrical leads consist of insulated copper wires which are sealed into the plug by a steel cone, K, seated in an epoxy-resin glue.[16] The plug is also fitted with a Viton O-ring. The bomb is enclosed in a cylindrical copper tubing jacket through which water is pumped from an external thermostat. The temperature inside the bomb can be controlled by

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