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(17) Because of the nonbonding electron pair on the nitrogen atom, one of the NR_2 groups would be expected to deviate from planar geometry at any one instant. A dynamic structure is visualized in which both NR_2 groups are equivalent.

(18) Simple applications of Hückel MO theory to the cation give a bonding orbital, $\alpha + [(\lambda^2 + 8)^{1/2}/2]\beta$, the nonbonding orbital on the nitrogen atom, and the antibonding orbital, $\alpha - [\lambda^2 + 8)^{1/2}/2]\beta$. In these expressions α is the Coulomb integral on the nitrogen atom and β is the resonance integral involving the 2p orbitals of nitrogen and the 3p orbitals of P^+. $(\alpha - \lambda\beta)$ is the Coulomb integral of the phosphorus ion.

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(23) The P–N bond in R_2NPCl^+ should have a high degree of double-bond character because of electron withdrawal by the chlorine and the lack of competition between NR_2 and Cl for the p orbital on the phosphorus atom.

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Characterization of Mixed Oxidation State Poly(chlorotitanium) Anions

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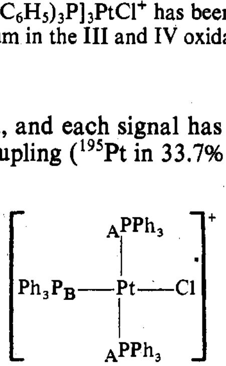
Treatment of tris(triphenylphosphine)platinum(0), $[(C_6H_5)_3P]_3Pt$, with titanium tetrachloride, $TiCl_4$, affords species with the composition $[(C_6H_5)_3P]_3Pt[TiCl_4]_{3,5}$. The latter have been examined by ^{31}P NMR, photoelectron, and ESR spectroscopy, and their magnetic susceptibilities have been measured. For both species the cation $[(C_6H_5)_3P]_3PtCl^+$ has been identified. The anions are suggested to consist of poly(titanium chloride) species containing titanium in the III and IV oxidation states, Ti_3Cl_{11}- and $Ti_5Cl_{19}^-$.

Introduction

We have recently reported the preparations, conductivities, infrared spectra, and several chemical reactions for $[(C_6H_5)_3P]_3Pt(TiCl_4)_n$, where n = 3 and 5, I and II, respectively.[2] The suggested geometries for I and II involved insertion of $TiCl_4$ into the Pt–P bond affording formally Pt(0) complexes. Development of the chemistry of I included treatment with acetonitrile, CH_3CN, and unexpectedly afforded $TiCl_3{\cdot}(CH_3CN)_3$.[3,4] The isolation of a Ti(III) derivative from I, under reaction conditions where $TiCl_4$ is not reduced by CH_3CN, prompted further studies of I and II with regard to specifying the oxidation state for Ti and Pt. These studies have included ^{31}P NMR, ESCA (Pt, Cl, Ti), and hydrolysis of various mixtures of α-$TiCl_3$ with Pt(II) and Pt(0) complexes and $(C_6H_5)_3P$. The latter were carried out because base hydrolysis of I and II did not afford H_2 which was interpreted to indicate the absence of Ti(III) associated with either I or II. It has now been established that both I and II contain Ti(III) and Pt(II) and that, during basic hydrolysis, oxidation of Ti(III) takes place but without quantitative H_2 evolution.[3,4]

Results and Discussion

^{31}P Studies. The ^{31}P NMR spectrum of I in CH_2Cl_2 is shown in Figure 1 and the data are summarized in Table I utilizing both CH_2Cl_2 and *o*-dichlorobenzene (ODCB) as solvents. The spectrum of I consists of two main signals, a triplet and doublet, and each signal has its satellite doublet due to ^{195}Pt–^{31}P coupling (^{195}Pt in 33.7% natural abundance, $I = {}^1/_2$).

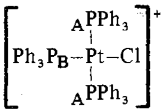


$$\left[\begin{array}{ccc} & {}_{A}PPh_3 & \\ & | & \\ Ph_3P_B\text{—} & Pt & \text{—}Cl \\ & | & \\ & {}_{A}PPh_3 & \end{array}\right]^+$$

I

For this geometry there are two sets of phosphorus atoms, one consisting of two chemically and magnetically equivalent phosphorus atoms designated as A while the other set is a single phosphorus designated as B. The resonance signal of P_B is split by two P_A's into a triplet of 1:2:1 intensities with $^2J_{P_A\text{-}P_B}$ = 19 Hz. This triplet is flanked by a pair of small triplets due to coupling with ^{195}Pt, $^1J_{^{195}Pt\text{-}P_B}$ = 3628 ± 4 Hz. The resonance signal of P_A is split by a single P_B into a doublet with $^2J_{P_A\text{-}P_B}$ = 19 Hz and also flanked by a pair of small doublets due to coupling with ^{195}Pt, $^1J_{^{195}Pt\text{-}P_A}$ = 2486 ± 4 Hz. The relative area of resonance signals of P_A to that of P_B is in good agreement with the calculated value, 2:1. The assignment of the oxidation state of platinum, in I, as Pt(II) is supported by the data in Table II where $^1J_{Pt\text{-}P}$ values are shown to be strongly dependent on the oxidation state of Pt. The

Table I. ${}^{31}P$ NMR Data for I



$$\left[\begin{array}{c} {}_{A}PPh_3 \\ | \\ Ph_3P_B\text{–}Pt\text{–}Cl \\ | \\ {}_{A}PPh_3 \end{array}\right]^+$$

Solvent	Chem shift, ppm[b,c]		${}^iJ_{^{195}Pt\text{-}P_A}$, Hz	${}^iJ_{^{195}Pt\text{-}P_B}$, Hz	${}^2J_{P_A\text{-}P_B}$, Hz	Rel area of P_A:P_B
	δ_A	δ_B				
CH_2Cl_2 (CD_2Cl_2)[a]	−22.8	−12.3	2486	3628	19	1.74:1
ODCB[a]	−23.2	−12.5	2488	3632	19	1.97:1

[a] Added in small amount for signal lock. [b] Relative to 85% H_3PO_4; negative sign indicates low field from H_3PO_4. [c] Chemical shift of the free ligand, PPh_3, is +6.0 ppm from H_3PO_4.

Table II. ${}^1J_{Pt\text{-}P}$ vs. Oxidation State of Pt

Compd	Oxidn state of Pt	${}^1J_{Pt\text{-}P}$, Hz	Ref
cis-$PtCl_4[P(n\text{-}Bu)_3]_2$	IV	2065	5
trans-$PtCl_4[P(n\text{-}Bu)_3]_2$	IV	1474	5
cis-$PtCl_2[P(n\text{-}Bu)_3]_2$	II	3504	5
cis-$PtCl_2[PPh(n\text{-}Bu)_2]_2$	II	3551	5
cis-$PtCl_2[PPh_2(n\text{-}Bu)]_2$	II	3641	5
cis-$PtCl_2(PPh_3)_2$	II	3684[a]	5
trans-$PtCl_2[P(n\text{-}Bu)_3]_2$	II	2386	5
trans-$PtCl_2[PPh(n\text{-}Bu)_2]_2$	II	2462	5
trans-$PtCl_2[PPh_2(n\text{-}Bu)]_2$	II	2531	5
$Pt(PPh_3)_3$	0	4370	6
$Pt[P(C_2H_5)_3]_3$	0	4220	7
$Pt[P(PC_7H_7)_3]_3$	0	4340	7
$Pt[P(C_2H_5)_3]_4$	0	3740	7
$Pt[P(PC_2H_7)_3]_4$	0	3780	7

[a] 3680 Hz in this work.

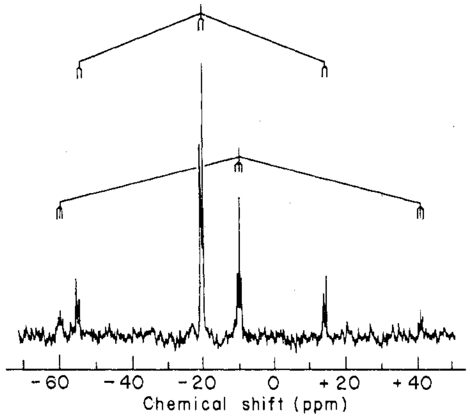
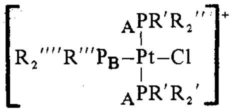


Figure 1. FT ${}^{31}P$ NMR spectrum of I in CH_2Cl_2.

range of *J*'s for each oxidation state, in complexes of similar geometry, is nonoverlapping with respect to other oxidation states thereby allowing unambiguous oxidation state assignment.

Chlorine is suggested to occupy the fourth ligand position in the Pt coordination sphere based on the data contained in Table III. It is apparent that ${}^1J_{Pt\text{-}P}$ is large when the group trans to the phosphine under consideration has a low trans influence such as Cl; otherwise a relatively low ${}^1P_{Pt\text{-}P}$ results for the trans group of high trans influence, such as phosphine. The values are ca. 3500–3700 Hz for the former and ca. 2300–2600 Hz for the latter, for Pt(II) complexes. With regard to the cation complex $PtCl(PBu_3)_3^+$, Table III, ${}^1J_{Pt\text{-}P_A}$ and ${}^1J_{Pt\text{-}P_B}$ are comparable to those in *trans*-$PtCl_2(PBu_3)_2$ and *cis*-$PtCl_2(PBu_3)_2$, Table II, respectively. In addition to the similarity of ${}^1J_{Pt\text{-}P}$ values, the chemical shifts of phosphorus atoms in the three complexes also behave in the same manner. In the cationic complex, the chemical shifts of P_A and P_B are at −10.2 and −0.7 ppm, respectively, as compared to −4.3 ppm in *trans*-$PtCl_2(PBu_3)_2$ and −0.9 ppm in the cis isomer[5] (negative sign indicating low field relative to 85% H_3PO_4). Even though their absolute values are not identical, the relative values are important and indicate that the chemical shift of phosphorus trans to Cl, such P_B in the cation or P's in the cis isomer, is at a higher field compared to a trans phosphine group such as P_A in the cation or P's in the trans isomer. While the development in the σ-bonding hypothesis is insufficient to offer a satisfactory explanation to this trend,[5,10] Grim et al.[8] rationalized the difference in terms of stronger d_π–d_π back-bonding in the Pt–P_B moiety of the cation and in the cis isomer which results in higher electron density at the P atom, hence, higher chemical shift, and weaker d_π–d_π bonding, due to mutual competition, in the Pt–P_A moiety and the trans isomer thereby resulting in lower electron density at P and a resulting lower chemical shift. The similarity between the cation $PtCl(PPh_3)_3^+$ of I and *cis*-$PtCl_2(PPh_3)_2$ also follows this same trend. (Data on *trans*-$PtCl_2(PPh_3)_2$ are not available, probably due to difficulty associated with its syn-

Table III. ${}^{31}P$ NMR Data for $PtClL_3^+$ Ions



$$\left[\begin{array}{c} {}_{A}PR'R_2'' \\ | \\ R_2''''R'''P_B\text{–}Pt\text{–}Cl \\ | \\ {}_{A}PR'R_2' \end{array}\right]^+$$

Complex	Chem shift, ppm[a]			${}^1J_{Pt\text{-}P_A}$, Hz	${}^1J_{Pt\text{-}P_B}$, Hz	${}^2J_{P_A\text{-}P_B}$, Hz
	Free ligand δ	δ_A	δ_B			
(A) R′ = R″ = R‴ = R⁗ = *n*-Bu[b]	+32.3	−10.2	−0.7	2270	3454	19.2
(B) R′ = R‴ = Ph[c]	+26.2	−6.2	+5.7	2305	3490	
R″ = R⁗ = *n*-Bu						
(C) R′ = R‴ = C_6H_5[c]	+27.7	−6.0	+5.6	2326	3500	
R″ = R⁗ = Pr						
(D) R′ = R″ = *n*-Bu[d]	+32.3					
R‴ = Ph	+46.9	−8.5	+14.3	2214	3526	19.9
R⁗ = Me						
(E) R′ = R‴ = Me[c]	+28.1	−9.4	+5	2374	3673	
R″ = R⁗ = Ph						

[a] Relative to 85% H_3PO_4; negative sign indicates low field from H_3PO_4. [b] Reference 5. [c] Reference 8. [d] Reference 9.

Table IV. ^{31}P NMR Data for II in ODCB

Chem shift, ppm[a]					
δ_A	δ_B	$^1J_{Pt-P_A}$, Hz	$^1J_{Pt-P_B}$, Hz	$^2J_{P_A-P_B}$, Hz	Rel intens (P_A:P_B)
−23.0	−12.4	2489	3630	19	2.4

[a] Relative to 85% H_3PO_4; negative sign indicates low field from 85% H_3PO_4. Chemical shift of free PPh_3 is +6.0 ppm.

Table V. Binding Energies for C, Pt, Cl, and Ti in I and II

	BE, eV	
Core level	I	II
C(1s)	285.0	285.0
$Pt(4f_{7/2})$	73.4	73.6
$Cl(2p_{3/2})$	198.7	~199.0
$Ti(2p_{3/2})$	459.0	459.3

thesis.) For example, $^1J_{Pt-P_B}$ and the chemical shift of P_B, 3628 ± 4 Hz and −12.3 ppm, respectively, for the cation are comparable to 3680 Hz and −13.8 ppm for *cis*-$PtCl_2(PPh_3)_2$, obtained from this work. While comparison of $^1J_{Pt-P_A}$ and the chemical shift of P_A cannot be made with a trans isomer, the trans assignment is reasonable when the data are compared to data associated with *trans*-(alkyl–alkyl)phosphine complexes of Pt(0), -(II), and -(IV), Table II. The observed coupling constant, $^2J_{P_A-P_B}$, Table I, is also consistent with the reported values in Table III. A value of ca. 20 Hz is typical for a coupling between two nonequivalent P's in a cis position, for square-planar Pt(II) complexes. (For the trans position the value is much larger, usually >500 Hz.)[5]

Two additional geometries which could give rise to similar ^{31}P NMR results are (1) square-planar Pt but with Ti or a chlorotitanium species occupying the fourth coordination site rather than Cl^- and (2) trigonal-bipyramidal Pt, $(PPh_3)_3PtCl_2$ with Cl^- in the equatorial position. These geometries were considered unlikely based on the observed $^1J_{Pt-P}$ values. For example, $TiCl_3$ as a ligand, is expected to have high trans influence which should result in a low $^1J_{Pt-P_B}$ value rather than that observed, 3628 ± 4Hz. This is the case for *cis*-$[Pt(SiPh_2Me)_2(PPhMe_2)_2]$[11] where the observed $^1J_{Pt-P}$ is extraordinarily low, 1559 Hz, as compared to 3549 Hz in *cis*-$PtCl_2(PPhMe_2)_2$.[8] Low $^1J_{Pt-P}$ values would be expected for five-coordinate Pt because, to the first approximation, the amount of s character distributed in the bonds would be smaller than that in a four-coordinate square-planar complex. As has been indicated, the observed $^1J_{Pt-P}$ values are all "normal" for a four-coordinate square-planar geometry.

The ^{31}P NMR spectrum of II, in ODCB, as summarized in Table IV, is essentially that of I consisting of two main signals—a doublet at lower field and a triplet. Each signal has its own ^{195}Pt satellite with the splittings very similar to those obtained for I. It is apparent that the same cation is present in I and II with the difference between I and II in their respective anions, or formally $Ti_3Cl_{11}^-$ and $Ti_5Cl_{19}^-$. II is stable in ODCB only under static vacuum affording a dark green, opaque solution. Under dynamic vacuum it decomposes with loss of $TiCl_4$ and a brown tint becomes observable in the green solution.[2] The brown color is probably due to the presence of I or an intermediate between I and II. In this ^{31}P NMR study the solution remained dark green throughout the experiment.

X-Ray Photoelectron Spectroscopy. The ESCA data associated with I and II are summarized in Table V. One may convincingly establish the oxidation state of Pt associated with I and II by comparison of $Pt(4f_{7/2})$ binding energies in Table V with those of various oxidation state Pt complexes summarized in Table VI. The conclusion from this comparison is consistent with interpretation of ^{31}P NMR data in that both I and II contain Pt(II).

Table VI. Binding Energies of $Pt(4f_{7/2})$ vs. Formal Oxidation State of Pt

Compd	Oxidn state of Pt	BE of $Pt(4f_{7/2})$, eV
K_2PtCl_6	IV	76.0[a]
cis-$PtCl_2(PPh_3)_2$	II	72.3,[b] 73.3[c]
cis-$PtCl_2[P(n\text{-}Bu)_3]_2$	II	72.1[b]
trans-$PtCl_2[P(n\text{-}Bu_3)_3]_2$	II	72.1[b]
K_2PtCl_4	II	73.6[a]
$Pt(PPh_3)_4$	0	71.7[c]
Pt metal	0	71.2[c]

[a] Reference 12. These values are obtained by subtracting 0.8 eV from the original values because the reported $Pt(4f_{7/2})$ BE of platinum metal is 72.0 eV. The correction factor of −0.8 eV is relative to 71.2 eV for Pt metal. [b] Reference 13. These values are obtained by adding 0.1 eV to the original values because of the reported values of $Pt(4f_{7/2})$ (metallic) at 71.1 eV. [c] Reference 14.

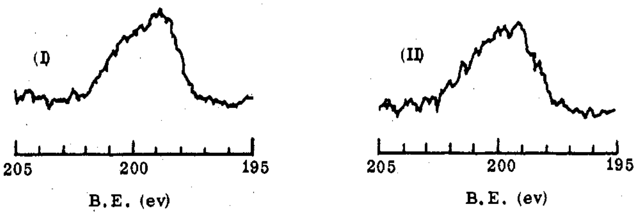


Figure 2. Chlorine (2p) ESCA spectra for I and II.

The value for C(1s) binding energy, 285.0 eV, is typical for transition metal–phosphine complexes and slightly higher than that of graphite, 284.0 eV.[15] It has been observed that in a large polyatomic ligand like PPh_3, charge migration to or from the ligand has little effect on any individual carbon atom because it is spread over so many centers; hence, within experimental error, the C(1s) binding energies for the phenyl carbons are almost identical for all phosphine complexes.[13]

The spectrum of the Cl(2p) level is unsymmetrical, broad and unresolved for both I and II, Figure 2. The maximum on the low side at 198.7 eV is assigned to the $Cl(2p_{3/2})$ component in I while the shoulder of the spectrum centers at 199.6 eV. The complex appearance of this spectrum is very likely to be due to the presence of more than one type of Cl environment, i.e., bridging and terminal Cl's. Terminal chlorines in a given compound usually exhibit the characteristic 2p spectra as a doublet, ca. 1.8 eV apart, due to the spin–orbit coupling.[14] The weaker absorption at higher energy is assigned to the $Cl(2p_{1/2})$ level while the other absorption is assigned to the $Cl(2p_{3/2})$ level. The intensity of each absorption is proportional to $2J + 1$; hence the relative area of the two peaks is 1:2. Because the spectrometric resolution is better than 1.8 eV, the doublet is usually well defined. However, in the presence of mixed terminal and bridging chlorines the spectrum is more complicated, being a broad, unresolved absorption which, when applicable, can be deconvoluted to four components corresponding to two types of chlorines, for example, in a dinuclear complex of $(R_3P)_2Pt_2Cl_4$, with the BE's of the two types of chlorines differing by ca. 1.0 eV.[13] The same situation occurs in polymeric compounds such as $(CoCl_2 \cdot NC_{13}H_9)_n$ where all Cl's are bridging chlorines forming a polymeric chain. In this compound the $Cl(2p_{1/2})$ component was not resolved from the more intense $Cl(2p_{3/2})$ component.

Table VII. Binding Energies of $Cl(2p_{3/2})$ in Covalent and Ionic Compounds

Covalent Cl compd	BE of $Cl(2p_{3/2})$, eV	Ionic Cl compd	BE of $Cl(2p_{3/2})$, eV
cis-$PtCl_2(PPh_3)_2$	198.3[a] 198.1[b]	cysteine·HCl	196.6[c]
cis-$PtCl_2[P(n\text{-}Bu)_3]_2$	198.4[a]	histidine·HCl	196.6[c]
trans-$PtCl_2[P(n\text{-}Bu)_3]_2$	199.6[a]	Cl^- in $[RhCl_2L_4]^+Cl^-$	~196.6–196.5[d]
Ph_3SiCl	199.9[c]		

[a] Reference 13. These values are corrected by adding 0.3 eV to the original values to correct for the difference, by the same amount, in the C(1s) in PPh_3.[8] [b] Reference 14. [c] Reference 19. [d] Reference 17.

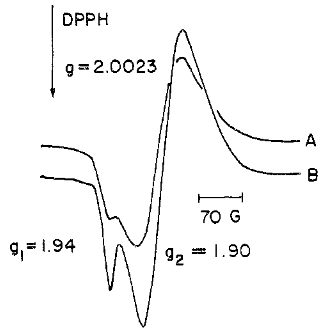


Figure 3. ESR spectra of I at 77 K: A, solid powder; B, frozen CH_2Cl_2 solution.

This broadening effect was rationalized as probably arising from the polymeric nature of the Cl's.[17] The anion $(Re_3Cl_8{}^{2-})_n$ is also believed to be a polymeric anion based on the broad, unresolved spectrum of the Cl(2p) level.[17]

The broadened and unresolved spectra of Cl(2p) levels in the anions $Ti_3Cl_{11}{}^-$ in I and $Ti_5Cl_{19}{}^-$ in II are probably due to the same effect as above, i.e., the bridging nature of chlorines. The possibility of the presence of chloride ion, in addition to chlorines covalently bonded to titanium, is eliminated by the absence of any peaks, in the Cl(2p) spectrum, at ca. 196–197 eV, Table VII.

Because the ^{31}P NMR were interpreted to indicate one Cl coordinated to Pt, the remaining 11 Cl's, associated with I, must reside with the anion. However, the BE's of the Cl in the cation and those in the anion would be very similar such that the former would be masked completely by the latter.

Interpretation of the Ti ESCA data has not been possible because of the lack of suitable literature ESCA data for various Ti complexes of different oxidation states.

Magnetic Properties of I. The anion $Ti_3Cl_{11}{}^-$ has been shown to contain two Ti in the formal 3+ oxidation state.[3,4] The ESR spectra of I obtained in the solid state and as a glass are shown in Figure 3 with g values of 1.94 and 1.90. The signals are broad with the line width of the main absorption ca. 70 G. These observed g values are in excellent agreement with those of Ti(III) complexes; e.g., Ti(III) in a host lattice $Al(acac)_3$ has $g = 2.00, 1.92$;[20] Ti(III) in $AlCl_3{\cdot}6H_2O$, $g_{iso} = 1.93$;[21] Ti(III) in $RbAl(SO_4)_2{\cdot}12H_2O$, $g_z = 1.89$, $g_x = 1.72$, $g_y = 1.77$.[22]

The presence of two g values and the fact that only broad signals could be obtained at low temperature, 77 K, are typical of a Ti(III) complex with moderately distorted octahedral symmetry. In an octahedral field the atomic ^2D ground state (of a d^1 ion) is split into a lower orbital triplet and an excited-state doublet which is usually higher in energy by more than 10^4 cm^{-1}. A distortion, either trigonal (D_3) or tetragonal (D_{4h}), further splits the threefold level into orbitally twofold degenerate and nondegenerate levels. Finally, the spin–orbit interaction leaves three Kramers doublets in the ground manifold and two in the upper manifold. The low-lying excited-state levels, within the ground manifold, in both D_3 and D_{4h} symmetries, can interact with the ground level with the effect of shortening the spin–lattice relaxation time; hence, the signals can only be detected at low temperatures.

Table VIII. Magnetic Susceptibility and μ_{eff} for I

Temp, K	$10^6\,\chi'_m$-(solid),[a] cgsu	μ_{eff}-(solid),[b] μ_B	$10^6\,\chi'_m$-(soln),[a] cgsu	μ_{eff}-(soln),[b] μ_B	μ_{eff}/Ti, μ_B
303			1129.8	1.65	1.17
298	1609.4	1.96			1.39
238			1270.9	1.55	1.10
203			1449.3	1.53	1.09

[a] χ'_m is the molar susceptibility after correcting for diamagnetic susceptibility ($\chi_{diamag} = -842.85 \times 10^{-6}$ cgsu). [b] Magnetic moment per formula weight which contains 2 equiv of Ti(III).

With regard to the local symmetries, D_3 and D_{4h}, of Ti(III) which may give rise to the signals, the former is preferred. Considering that the anion $Ti_3Cl_{11}{}^-$ contains both terminal and bridging chlorines, it is likely that the structure of this anion resembles other multinuclear titanium–chloride complexes, such as $Ti_2Cl_9{}^{3-}$ and the four forms of polymeric $TiCl_3$.[23,24]

Magnetic susceptibility measurements on I were carried out in the solid state and solution and are summarized in Table VIII. The observed μ_{eff} values of 1.96 and 1.65 μ_B at ca. 300 K in solid and solution, respectively, are very close to the μ_{eff}'s of many mononuclear Ti(III) complexes which have been reported, e.g., 1.77 μ_B for $(C_6H_5N)_3TiCl_6$, 1.78 μ_B for $[Ti(H_2O)_4Cl_2]Cl{\cdot}2H_2O$, and 1.80 μ_B for $CsTi(SO_4)_2{\cdot}12H_2O$, all at 298 K.[25] However, when taking into consideration that there are two atoms of Ti(III) in each molecule of I, μ_{eff} per one Ti(III) is 1.39 μ_B in the solid state. This value is considerably lower than the expected value of 1.73 μ_B for the "spin-only" μ_{eff} of a d^1 ion and indicates spin–spin interaction between two Ti(III)'s associated with the anion. This spin–spin interaction is judged to be weak by comparison to $(Et_2NH_2)_3(Ti_2Cl_9)$ and β-$TiCl_3$ complexes; μ_{eff}'s (per one Ti(III)) are 0.88 μ_B at 293 K and <0.7 μ_B at 300 K, respectively.[26] Another observation which is consistent with the weak spin–spin interaction in the anion $Ti_3Cl_{11}{}^-$ is the increase of the molar susceptibility, χ'_m, with decreasing temperature, Table VIII, which indicates the Neel point has yet to be attained and is located below 203 K. Several Ti(III) complexes have been found to behave in a similar manner, for example, polymeric α-$TiCl_3$ and α-$TiBr_3$ complexes, whose slightly "low" μ_{eff}'s, 1.31 and 1.38 μ_B at 300 K, have Neel points at 217 and ca. 180 K, respectively.

Electronic Spectroscopy. The electronic spectrum of I, in the solid state, from 1.0 to 2.7 μm^{-1} shows no absorptions other than a broad charge-transfer band at >27 μm^{-1}. The solution spectrum in CH_2Cl_2 has a weak shoulder on the intense charge-transfer band centered at 1.59 μm^{-1}. It is unlikely that this latter absorption is due to a d–d transition based on its intensity and absorption maximum when compared to other Ti(III) complexes: e.g., $(C_5H_6N)_3TiCl_6$, 1.28 μm^{-1};[28] α-$TiCl_3$, 1.38,[29] 1.43 μm^{-1};[30] β-$TiCl_3$, no d–d transitions;[31] and γ-$TiCl_3$, 1.43 μm^{-1}.[31] Both I and β-$TiCl_3$ are brown, exhibit low magnetic moments, and lack d–d transitions in their electronic spectra. The electronic spectrum of II also contains a shoulder at ca. 1.6 μm^{-1} on an intense charge-transfer band. As in the case for I, II does not contain typical d–d transitions and also exhibits a low magnetic moment.

Infrared Spectroscopy. The IR spectra of I and II have previously been reported and discussed.[2] Several reassignments are now necessary based on the fact that both I and II involve Pt(II) and two Ti(III)'s as opposed to the original suggestion involving Pt(0) and Ti(IV). Originally a case was made for PPh_3 coordination to a strong-acid center, Ti(IV), rather than Pt(0) based on the frequency of the x-sensitive IR absorptions.[2] With the present knowledge that I and II involve Pt(II) (^{31}P NMR and ESCA data), it is now clear that PPh_3 is bonded to Pt(II) rather than Ti. The lesson learned is that when interpreting x-sensitive vibration frequencies, one must correlate these absorption frequencies keeping in mind similar effective Lewis acid character of the metal coordination center, i.e., its oxidation state.

With regard to the IR spectrum of I, the absorptions in the range 4000–450 cm^{-1} are associated with the vibrational modes of PPh_3 ligands while the rest of the spectrum, between 450 and 250 cm^{-1}, belongs to the vibrational modes of the anion $Ti_3Cl_{11}^-$. The band at 460 cm^{-1} was tentatively assigned as ν(Ti–P); however, it is clear that PPh_3 ligands are not bonded to Ti's, but rather to Pt, i.e., $PtCl(PPh_3)_3^+$. Infrared spectra of $Pt(PR_3)_2XY$ species, both cis and trans, always show a group of weak-to-medium absorption bands in the region 450–400 cm^{-1}. These bands are usually sharp and well defined; for example, in *cis*-$PtCl_2(PPh_3)_2$, there are absorptions at 465, 440, and 420 cm^{-1}. It has been suggested that these bands are likely to be internal ligand modes split or activated on complexation.[32–35] This suggestion is reasonable because in the studies of the far-infrared and Raman spectra of complexes containing PPh_3 ligands, most of the bands can be correlated very well with vibrations of free ligand, both in position and in relative intensity.[34] Furthermore, in complexes of the type $Pt(PR_3)_2XY$, the other vibrational modes that involve platinum ligands always appear at much lower cm^{-1}; e.g., in *cis*-$PtCl_2(PPh_3)_2$, the two ν(Pt–Cl) modes are at 321 and 297 cm^{-1} and ν(Pt–P) modes are at 195 and 177 cm^{-1}.[36] Therefore, it appears that the band at 460 cm^{-1} arises from the PPh_3 ligands of the cation $PtCl(PPh_3)_3^+$, with the other bands at lower energy being masked completely by the broad, intense band at 395 cm^{-1}.

The appearance of a broad absorption at 395 cm^{-1}, in the spectrum of I, is comparable to those observed in $TiCl_4{\cdot}2L$, 370–390 cm^{-1},[37] $TiCl_5^-$, 385 cm^{-1},[37] $TiCl_3{\cdot}2L$, 380–390 cm^{-1},[37] $TiCl_3{\cdot}3L$, 360–370 cm^{-1},[37] $TiCl_6^{2-}$, 320–330 cm^{-1},[37] and $TiCl_6^{3-}$, 290–300 cm^{-1}.[24] It is apparent that the higher the negative charge and coordination number of Ti, the lower the ν(TiCl) frequency. On the basis of these cited data, the absorption at 395 cm^{-1} is tentatively assigned to ν_{as}(TiCl) associated with five-coordinated Ti(IV) in the $Ti_3Cl_{11}^-$ ion. It should be recalled that in the discussion of ESR spectra of I, it was concluded that Ti(III) is located in the octahedral chloride environment slightly distorted toward D_3 symmetry. From this, one infers the coordination number of Ti(III) is 6. Because the ν_{as}(Ti–Cl) absorption band for six-coordinated Ti(III) appears in the range 360–370 cm^{-1}, the absence of this absorption for I is somewhat surprising. Most likely it is masked by the strong, broad band centered at 395 cm^{-1}.

It is almost certain that the $Ti_3Cl_{11}^-$ ion contains bridging chlorines based on the stoichiometry and appearance of the ESCA Cl(2p) core level. The stretching frequencies for Ti–Cl bridges usually appear below 290 cm^{-1}, e.g., for $Ti_2Cl_9^{3-}$, 260 cm^{-1} [24] and for α-$TiCl_3$, 289 cm^{-1}.[37] Three previously unreported absorptions occur at 315 (w), 280 (m), and 257 cm^{-1} (s). The last one, with a shoulder at 260 cm^{-1}, is tentatively assigned to the ν_{as}(TiCl) bridge. The nature of the first two bands is not known; however, they definitely arise from the anion $Ti_3Cl_{11}^-$.

The expected ν(Pt–Cl) from the cation $PtCl(PPh_3)_3^+$ is very likely to be obscured by the strong ν_{as}(Ti–Cl) band at 395 cm^{-1}. In *trans*-$PtCl(CO)(PPh_3)_2^+$ the weak ν(Pt–Cl) band is observed at 335 cm^{-1}.[38] Because CO has a higher trans influence than PPh_3, the Pt–Cl band in $PtCl(PPh_3)_3^+$ should be slightly stronger than the corresponding Pt–Cl band in *trans*-$PtCl(CO)(PPh_3)_2^+$; hence the ν(Pt–Cl) in the former cation should be >335 cm^{-1} which should place it immediately underneath the strong ν_{as}(Ti–Cl) band at 395 cm^{-1}.

Compound II. With regard to lower energy absorptions, II has a strong band at 420 cm^{-1} with a shoulder at 385 cm^{-1} whereas I has a single absorption at 395 cm^{-1}. The absorption at 420 cm^{-1} is assigned to $\nu_{as}(TiCl_2)$, for either five- or six-coordinate Ti(IV), while the band at 388 cm^{-1} is assigned to the $\nu_{as}(TiCl_2)$ for six-coordinate Ti(IV) with reference to $Ti_2Cl_9^-$ with $\nu_{as}(TiCl_2)$ at 416 and 379 cm^{-1}.[39] Assignment of other vibrational bands has been previously discussed.

Geometrical Considerations for I and II. The ^{31}P NMR data obtained for I and II are consistent with the common cation $\{[(C_6H_5)_3P]_3PtCl\}^+$, while conductivity data indicate formation of ion pairs.[2] On the basis of the stoichiometry of I and II and the fact that both I and II contain two Ti(III)'s,[3,4] I is formulated as $[L_3PtCl]^+[Ti_3Cl_{11}]^-$ while II is suggested to be represented by either $[L_3PtCl]^+[Ti_5Cl_{19}]^-$ or $[L_3PtClTi_2Cl_8]^+[Ti_3Cl_{11}]^-$ where L is $(C_6H_5)_3P$. The low conductivities of both I and II are consistent with ion-pair formation possibly involving weak interaction between Cl associated with Pt and the anion. With regard to $Ti_3Cl_{11}^-$, the suggested geometry involves two triple chlorine bridges with three terminal Cl's at one end and two terminal Cl's at the other; the vacant site would allow interion Cl (from Pt) bridging. Treatment of I with HCl affords I·HCl with no change in the IR spectrum of I which is consistent with the suggested geometry, i.e., one assessible Cl site.[3,4]

With regard to the geometry of II, a formulation such as $[L_3PtCl]^+[Ti_5Cl_{19}]^-$ requires nine Cl's in triplet bridges, eight terminal Cl's, and all Ti's six-coordinate. This formulation leaves no vacant sites on Ti for interion Cl bridging the cation. On the other hand, the dramatic difference in color between I and II, brown and green, respectively, is difficult to explain based on coordination of two $TiCl_4$'s with L_3PtCl^+. The presently favored formulation for II is $[L_3PtCl]^+[Ti_5Cl_{19}]^-$, and the green color is associated with electron population of a low-lying excited state which results as a consequence of the presence of a multiple center metal chain.

Experimental Section

Equipment and techniques employed were similar to those previously described.[2] X-ray photoelectron spectra were recorded as previously described.[40] Ultraviolet–visible spectra were recorded with a Cary 14 recording spectrometer. Samples of low solubility were examined in the solid state as mulls on filter paper sandwiched between two microscope slides. This technique was adopted from the Kleinberg technique except 25–58 Halocarbon grease, obtained from Halocarbon Products Corp., Hackensack, N.J., was used instead of Nujol.[41] ^{31}PNMR spectra were obtained at 36.4 MHz, with all of the protons decoupled, with a Bruker HX-90 NMR spectrometer equipped with a Bruker Model B-NC 12 data system. Reagents were purified and reactions carried out as previously described.[2]

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Spectrophotometric Study of the Cobalt(II) Bromide–Aluminum Bromide Vapor Complex

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The reaction of solid cobalt(II) bromide with gaseous aluminum bromide to form deep green gaseous complex(es) has been investigated spectrophotometrically in the range 550–900 K and at pressures up to 2 atm. Thermodynamic considerations suggest the reaction $CoBr_2(s) + Al_2Br_6(g) \rightleftarrows CoAl_2Br_8(g)$ [$\Delta H = 9.9$ kcal/mol; $\Delta S = 9.4$ eu]. The electronic absorption spectra are discussed in terms of the possible coordination of Co(II) in the gaseous molecule(s). Spectroscopic and thermodynamic considerations suggest that the predominant absorbing species in the gas phase is $Co(AlBr_4)_2$ molecules having the Co(II) in a close-to-octahedral coordination. The volatility enhancement ratios of cobalt(II) halide in the presence of various "acidic" A_2X_6 gases are calculated and compared. At temperatures below 750 K, aluminum bromide is a better gas-complexing agent than aluminum chloride for the respective cobalt halides.

Introduction

Recent spectrophotometric studies have established the thermodynamics and stoichiometry of the gaseous complexes formed on reacting aluminum chloride with transition metal halides [MCl_x: M = Pd(II),[1] Pt(II),[2] Co(II),[3,4] V(II) and V(III),[5] Cr(II),[6] U(III) and U(IV),[7] Nd(III)[8]]. For the divalent transition metal chlorides the predominant gaseous species were found to be MAl_2Cl_8.[1-4,6] Furthermore, since the absorption spectra of these complexes are ligand field sensitive, some information about the structure of the gaseous molecule has been obtained. The electronic absorption spectra of Pt(II) and Pd(II) complexes were found to be compatible with a square-planar configuration of the "central"[1,2] ion whereas for the Co(II) complex both octahedrally and tetrahedrally coordinated Co(II) atoms were considered.[3] The spectra of V(II)[5] and Cr(II)[6] complexes were interpreted as having the transition metals in distorted octahedral chloride coordination.

In the present work, we report spectroscopic and thermodynamic data for the formation of the deep green gaseous complex(es) of aluminum bromide with cobalt bromide

$$m\mathrm{CoBr_2(s)} + n\mathrm{Al_2Br_6(g)} \rightleftarrows (\mathrm{CoBr_2})_m(\mathrm{Al_2Br_6})_n\mathrm{(g)} \qquad (1)$$

The data are discussed in terms of the stoichiometry and possible structure of the gaseous complex and are compared with the corresponding data of the chloroaluminate complex(es) of Co(II).[3]

The purpose of this study is to examine the ability of aluminum bromide to form gaseous complexes and to compare the thermodynamics, structure, and volatility enhancement ratios of the bromoaluminate complexes with those of the chloroaluminate complexes.

Experimental Section

High-purity anhydrous aluminum bromide and cobalt bromide were prepared from the corresponding Cerac/Pure, Inc., reagents by slow sublimation in silica tubes under vacuum. The anhydrous materials were handled in a helium atmosphere drybox with a water vapor level <20 ppm.

The method for investigating spectrophotometrically equilibria of the type of reaction 1 has been described elsewhere.[1,2] A Cary Model 17H spectrophotometer equipped with a high-temperature cell compartment has been used. The optical cells were fused-silica UV type cylindrical cells (5- or 10-cm path length) purchased from Pyrocell.

The apparent molar absorptivity, ϵ, of the gaseous complex(es) and the partial pressures, P_c, of the complex(es) were determined by two different sets of experiments using Beer's law

$$\epsilon = AV/nl \qquad P_c = ART/l\epsilon \qquad (2)$$

where A is the optical density; V, the cell volume; n, the moles of Co(II) in the gas phase; and l, the path length. The temperature gradient along the optical cell was adjusted so that the cell windows were 2–3 °C hotter than the center of the cell where the excess solid $CoBr_2$ was maintained at temperature T. Measurements of A (or P_c) as a function of time showed that equilibrium was reached in less than 30 min.

The apparent pressures, P', of the Al_2Br_6 dimer were calculated from the amounts of Al_2Br_6 placed in the cell and the relation

$$P' = P_0 - P_D \qquad (3)$$

Here P_0 is the "ideal gas" pressure of Al_2Br_6 calculated from the added