

Infrared Spectroscopic Study of the Cryogenic Thin Film and Matrix-Isolated Complexes of TiCl_4 with NH_3 and $(\text{CH}_3)_3\text{N}$

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The matrix isolation technique and infrared spectroscopy have been used to isolate and characterize for the first time the 1:1 complex of TiCl_4 with NH_3 . Intense spectral features at 440 and 457 cm^{-1} were assigned to the Ti–Cl antisymmetric stretching modes in this complex; the NH_3 symmetric deformation was observed above 1200 cm^{-1} , shifted over 200 cm^{-1} from the parent band position. The spectra suggest a trigonal bipyramidal arrangement about the central titanium with the NH_3 ligand in an axial position. A similar set of product bands was observed for the 1:1 complex of TiCl_4 with $(\text{CH}_3)_3\text{N}$, a species which had been observed previously but not fully characterized. Cryogenic thin film experiments with subsequent warming led to the formation of the 1:1 complex and further reaction products, including the 1:2 complex and two or more amido and/or imido complexes.

Introduction

Chemical vapor deposition (CVD) is used extensively for the production of thin films for the semiconductor and other industries. In CVD, a solid thin film is deposited on a heated substrate from the reaction of gaseous precursors in the vapor phase or on the surface of the substrate.¹ Several deposition parameters, including substrate temperature, reactant partial pressures, and gaseous flow rates can affect the structure, purity, and electrical properties of the thin films. For most systems, a knowledge of the kinetics and reaction mechanism is important to guide the selection of the deposition parameters. Unfortunately, in many cases little is known about the reaction intermediates and kinetic parameters.

TiCl_4 and NH_3 have been used^{2,3} as precursors in the CVD of TiN thin films in the temperature range 400–750 °C. The formation of the 1:2 complex $\text{TiCl}_4 \cdot 2\text{NH}_3$ has been postulated to be a likely intermediate in this reaction.^{3,4} Recently, Winter et al. reported the formation of TiN thin films following decomposition of the 1:2 complex as a single source precursor.⁴ Previous condensed state studies of this reaction system have reported complexes of higher stoichiometry, up to $\text{TiCl}_4 \cdot 8\text{NH}_3$ (although these may not have been pure materials in every case) as well as reaction to form (amidochloro)titanium species.^{5–8} While a 1:1 complex might well be the initial intermediate for this pair of reactants en route to either higher complexes or amidochloro compounds, the 1:1 complex has never been reported.

The matrix isolation technique^{9–11} was developed for the isolation and characterization of reactive intermediates, including

free radicals, acid–base complexes, and molecular ions. Recently, this technique has been applied to study intermediates formed in the room temperature and elevated temperature reactions of several sets of precursors used in CVD.^{12–14} In view of the importance of the $\text{TiCl}_4/\text{NH}_3$ reaction in CVD and the lack of knowledge about reaction intermediates in this system, a study was undertaken to examine the initial reaction products during deposition into inert matrices and cryogenic thin films. A similar set of experiments on the $\text{TiCl}_4/(\text{CH}_3)_3\text{N}$ system were carried out for comparison.

Experimental Section

The experiments conducted in this study were carried out on conventional matrix isolation equipment that has been described.¹⁵ NH_3 (Matheson), $^{15}\text{NH}_3$ (Cambridge Isotopes, 98% ^{15}N), $(\text{CH}_3)_3\text{N}$ (Matheson), and $(\text{CD}_3)_3\text{N}$ (MSD Isotopes, 99% D) were introduced into the vacuum system as gases and were purified by repeated freeze–thaw cycles at 77 K. TiCl_4 (MCB) was introduced by means of a glass finger and distilled using a dry ice/acetone bath at –77 °C to partially remove impurity HCl. Some residual HCl was noted in the matrix spectra. On the basis of band intensities, the estimated Ar/HCl ratio was approximately 2000. Argon and nitrogen were used as the matrix gases without further purification.

In a typical matrix experiment the gaseous samples were prepared in separate vacuum manifolds, with dilutions between matrix/reactant (M/R) ratios = 250/1 and 1000/1. Samples were then deposited on the cold window employing twin jet, modified twin jet, or merged jet deposition for 20–24 h at a flow rate of 1–2 mmol/h before the final spectrum was recorded. In the twin jet mode, the two deposition lines were each pointed at 45° to the cold window, so that sample mixing occurred directly in front of or on the cold surface. In the merged jet mode, the two deposition lines were joined with an Ultratorr tee 15 or 35 cm from the cold window, and the samples flowed together for this distance before depositing onto the cold window. In the modified twin jet mode, the two deposition lines used in the twin jet mode were altered so that each deposition line nearly faced the other and were oriented at approximately 90° to the cold window. This arrangement provided an intermediate mixing period compared to the reaction zones available in the twin jet and merged jet modes. Final spectra were recorded by

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averaging 500 interferograms at 1 cm^{-1} resolution on a Nicolet IR42 Fourier transform infrared spectrometer.

Thin film experiments were carried out by depositing the reactant gases from separate manifolds without added matrix gas. The pure reagents were generally deposited for 20–40 min at 2 mmol/h onto the 14 K cold surface and a spectrum at 1 cm^{-1} resolution recorded. In order to explore further reaction products, the refrigeration system was turned off and the thin film allowed to warm slowly. As the temperature of the film increased, spectra were recorded at periodic intervals up to as high as room temperature.

Results

Prior to the study of the reactions of TiCl_4 with NH_3 and $(\text{CH}_3)_3\text{N}$, blank experiments were conducted on each reactant in solid argon and nitrogen. The blank spectra were in good agreement with literature spectra.^{16–21} Bands observed in the 2800–2900 cm^{-1} region correspond to those reported in literature matrix spectra^{22,23} of HCl which was present as an impurity in all experiments involving TiCl_4 . Blank spectra were also recorded of the pure reactants at cryogenic temperatures. Thin film spectra were not found in the literature, but the band positions agreed well with those observed in matrices (with increased band width).

$\text{TiCl}_4 + \text{NH}_3$. When a sample of $\text{Ar}/\text{TiCl}_4 = 500$ was codeposited with a sample of $\text{Ar}/\text{NH}_3 = 500$ in a twin jet experiment, a number of new weak infrared absorptions were noted. These were located at 440, 446, 456, 730, 733, 1070, 1089, 1195, 1202, 1289, 1373, 1408, 1463, and 3407 cm^{-1} . The band at 440 cm^{-1} was the most intense, with an absorbance of approximately 0.2 unit. In several subsequent twin jet experiments at differing sample concentrations, these bands were consistently observed. In the highest yield twin jet experiments, the 440 cm^{-1} band was seen with intensities as high as 0.8 absorbance unit.

In an attempt to increase band intensity and product yield, merged jet experiments were conducted with the Ultratorr tee 35 cm from the cold window. No product or parent absorptions were seen in the resultant spectrum. The final spectrum of a merged jet experiment with a 15 cm mixing region showed strong bands due to excess parent TiCl_4 , but no product or NH_3 bands were present.

Modified twin jet deposition was devised to increase slightly the mixing and reaction time compared to normal twin jet deposition. The codeposition of a sample of $\text{Ar}/\text{TiCl}_4 = 500$ with a sample of $\text{Ar}/\text{NH}_3 = 500$ in the modified twin jet mode produced a spectrum in which all of the above product bands were observed with increased intensity; the intensity of the 440 cm^{-1} band was nearly 1.0 absorbance unit. In addition, distinct new product bands were observed at 611, 637, 3296, 3298, 3301, 3412, and 3423 cm^{-1} with additional weak product bands at 1169, 1252, and 1326 cm^{-1} . A number of experiments were then carried out in which the concentration ratio of $\text{TiCl}_4/\text{NH}_3$ was changed to 2/1 and 1/2 and the total concentration was also altered. Under these conditions, the same set of product bands was observed. However, they did not all maintain a constant intensity ratio with respect to one another indicating the formation of more than one product. Since HCl was an impurity in all Ar/TiCl_4 samples, an experiment was conducted

Table 1. Band Positions^a and Assignments for the Reaction Products of NH_3 and HCl in Argon and Nitrogen Matrices

Ar matrix ^b	Ar matrix ^c	N_2 matrix ^b	N_2 matrix ^c	assignt
730,733	733	620	620	$\text{NH}_3\cdot\text{HCl}$
1070	1072	1247	1245	$\text{NH}_3\cdot\text{HCl}$
1088	1089			$\text{N}_2\text{H}_7^+\text{Cl}^-$
1290	1289	1108, 1115	1110	$\text{NH}_3\cdot\text{HCl}$
1373	1371	720	720	$\text{NH}_3\cdot\text{HCl}$
1407	1408	1413, 1422	1415	NH_4^+Cl^-
		1437, 1445	1442	$\text{NH}_3\cdot\text{HCl}$
1467	1464			$\text{N}_2\text{H}_7^+\text{Cl}^-$
3423	3420	3414	3417	$\text{NH}_3\cdot\text{HCl}$

^a Band positions in cm^{-1} . ^b This work. ^c References 24 and 25.

Table 2. Band Positions^a and Assignments for the 1:1 Complex $\text{TiCl}_4\cdot\text{NH}_3$ in Argon and Nitrogen Matrices

$\text{Ar}/\text{TiCl}_4/\text{NH}_3$	$\text{N}_2/\text{TiCl}_4/\text{NH}_3$	$\text{N}_2/\text{TiCl}_4/^{15}\text{NH}_3$	assignt
440	440	439	ax Ti–Cl str
446	449 ^b	449 ^b	$\nu_1 + \nu_4$
456	457	457	eq Ti–Cl str
624 ^b	648	645	NH_3 rock
1198 ^b	1228 ^b	1222 ^b	NH_3 sym def
	1604		NH_3 antisym def
3298 ^b	3299 ^b	3298 ^b	NH_3 sym str
3410 ^b	3400 ^b	3388 ^b	NH_3 antisym str

^a Band positions in cm^{-1} . ^b Multiplet.

in which a sample of Ar/HCl (from the HCl adsorbed to the walls of the TiCl_4 manifold) was codeposited with a sample of $\text{Ar}/\text{NH}_3 = 500$. A series of product absorptions were observed which matched some but not all of the above bands. The bands in this experiment also agreed well with literature reports of the $\text{NH}_3\cdot\text{HCl}$ complex in solid argon.²⁴ The major product bands in the $\text{Ar}/\text{TiCl}_4/\text{NH}_3$ system are listed in Tables 1 and 2 while Figure 1 shows representative spectra of this system.

Previous studies have shown that nitrogen matrices can be used to reduce the complexity of spectral regions near parent NH_3 absorptions since rotation and inversion of the NH_3 molecule are minimized. When a sample of $\text{N}_2/\text{TiCl}_4 = 500$ was codeposited with a sample of $\text{N}_2/\text{NH}_3 = 500$ in the modified twin jet mode, numerous product absorptions were noted. Many of these were similar to those observed above in argon matrices; the 400–500 cm^{-1} region was clearer and sharper in solid N_2 . In addition, a new band was noted at 1604 cm^{-1} ; this region was obscured in the argon matrix experiments by bands of rotating NH_3 and impurity H_2O . Additional experiments were carried out in solid nitrogen. Again, the product bands did not all maintain constant intensity ratios but separated into three distinct sets as a function of deposition conditions. N_2 matrix band positions for the major product bands are also listed in Tables 1 and 2.

Several experiments were conducted employing samples of $\text{N}_2/^{15}\text{NH}_3$ with N_2/TiCl_4 . Exchange of the ^{15}N label with residual $^{14}\text{NH}_3$ in the manifold did occur, even after repeated conditioning of the line. A final $^{15}\text{N}/^{14}\text{N}$ ratio as high as 10/1 was estimated from parent band intensities. Consequently, all of the product bands listed above were observed, some with comparable intensities and others with reduced intensity. Where a band was observed with reduced intensity, a new product band was also observed shifted a few wavenumbers to lower energy. An ^{15}N isotopic counterpart was not clearly identified for the 1604 cm^{-1} band. However, some broadening of the impurity H_2O band at 1598 cm^{-1} was noted. Product bands for the $^{15}\text{NH}_3/\text{TiCl}_4$ system are listed in Table 2; Figure 2 compares the $^{15}\text{NH}_3$ results with normal isotopic NH_3 over selected

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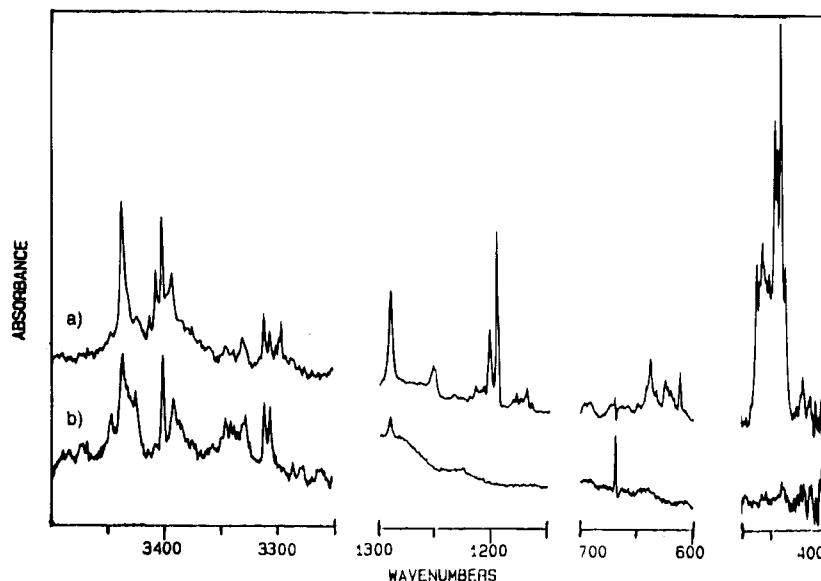


Figure 1. Infrared spectrum of the reaction products arising from the codeposition of TiCl_4 and NH_3 into solid argon (trace a) compared to a spectrum of the reaction products arising from the codeposition of NH_3 and HCl in solid argon (trace b) over selected spectral regions.

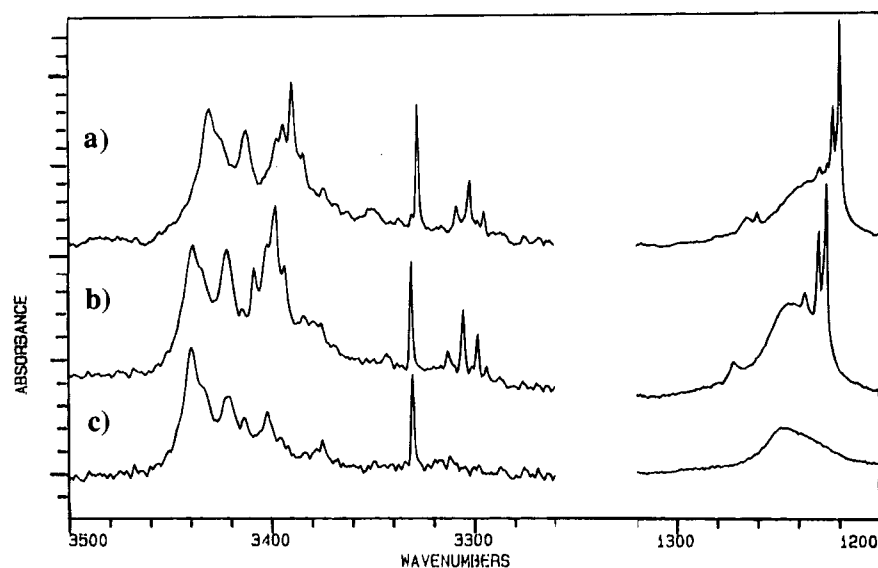


Figure 2. Infrared spectra of the reaction products arising from the codeposition of TiCl_4 with $^{15}\text{NH}_3$ (trace a) and NH_3 (trace b) in solid nitrogen compared to a spectrum of the reaction products of NH_3 and HCl (trace c) in solid nitrogen over selected spectral regions.

spectral regions. Several thin film experiments were conducted in which the pure reactant materials were codeposited in the twin jet mode. The proportions of TiCl_4 deposited in relation to NH_3 were varied extensively, and after deposition was complete, the films were slowly warmed to room temperature. A number of product bands were observed upon initial deposition, as listed in Table 3 for a representative experiment. When the thin film was then warmed, some product bands were seen to increase initially and then decrease, while others grew in at elevated temperatures. The product bands and their intensities were also a strong function of the mole ratio of the two reactants. The variation of band intensity with mole ratio and with temperature permitted the sorting of the product bands into several distinct sets corresponding to different product absorbers. Since TiCl_4 vapor contains some amount of HCl impurity, thin film experiments were also conducted codepositing HCl with NH_3 . Table 3 summarizes the results of the thin film experiments while representative spectra are shown in Figure 3.

$\text{TiCl}_4 + (\text{CH}_3)_3\text{N}$. When a sample of $\text{N}_2/\text{TiCl}_4 = 500$ was codeposited with a sample of $\text{N}_2/(\text{CH}_3)_3\text{N}$ in a twin jet experiment, a number of new infrared absorptions were observed throughout the infrared spectrum. For comparison, a sample

of N_2/HCl was codeposited with a sample of $\text{N}_2/(\text{CH}_3)_3\text{N} = 500$, and some of the product bands seen in the $\text{TiCl}_4/(\text{CH}_3)_3\text{N}$ experiment were observed. These matched bands assigned^{26,27} to the $(\text{CH}_3)_3\text{N}\cdot\text{HCl}$ complex. The remaining product bands are given in Table 4 and shown in Figure 4.

A twin jet codeposition of a sample of $\text{N}_2/\text{TiCl}_4 = 500$ with a sample of $\text{N}_2/(\text{CD}_3)_3\text{N} = 500$ resulted in a series of new product absorptions. A comparison experiment depositing HCl and $(\text{CD}_3)_3\text{N}$ into a nitrogen matrix was then conducted. The product bands in this experiment matched some but not all of the product bands from the $\text{TiCl}_4/(\text{CD}_3)_3\text{N}$ experiments. The product bands not assignable to the $(\text{CD}_3)_3\text{N}\cdot\text{HCl}$ complex are also listed in Table 4.

Discussion

Product Identification. The codeposition of TiCl_4 and NH_3 into either argon or nitrogen matrices led to the observation of

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Table 3. Band Positions (cm^{-1}) for the Thin Film Codeposition Products of TiCl_4 and NH_3

thin film ^a (14 K)	$\text{TiCl}_4 \cdot 2\text{NH}_3^b$		$\text{TiCl}_4 \cdot 4\text{NH}_3^b$ (solid, mull)
	295 K	solid, mull	
423	421		
676	681	678	
	803		799
		851	
	878		874
893			901
980	980		976
			1094
		1238	1233
1253	1253	1255	1255
1420	1410	1400	1399
1595	1597	1591	1593
			1657
			1759
2804	2805		
3019	3020	3046	3040
3152		3144	3137
3247		3231	3239
3315		3318	3308

^a This work, codeposition of approximately equal amounts of NH_3 and TiCl_4 . ^b Reference 4.

a number of new infrared absorptions which could not be attributed to either parent species. As noted above, several of these bands were observed in experiments in which NH_3 was codeposited with HCl and are assigned to products arising from this pair of reactants.^{24,25} These bands and assignments are listed in Table 1. The remaining product bands were quite similar in both argon and nitrogen matrices, with the exception of increased sharpness and clarity in the low energy region and the appearance of one additional band observed at 1604 cm^{-1} only in the nitrogen matrix experiments. Consequently, the following discussion will focus on the results of the N_2 matrix experiments. A series of experiments at differing absolute and relative concentrations of the two reactants indicated that more than one product species was being formed. Specifically, bands at 440 , 457 , 648 , and 1604 cm^{-1} and multiplets near 449 , 1228 , 3299 , and 3400 cm^{-1} maintained a constant intensity ratio with respect to one another and can be assigned to a single absorber (species A). Bands at 679 , 1199 and 1272 cm^{-1} were noted to increase more rapidly than bands due to species A when the NH_3 concentration was increased, and are assigned to a second product, (species B).

The bands due to species A were produced in low yield in twin jet deposition experiments, high yield in modified twin jet experiments yet were absent in merged jet deposition experiments. These observations suggest that they are due to the initial reaction product for this pair of reactants. Further, all but one of the product bands (the band at 648 cm^{-1}) were located near the absorptions of one or the other of the precursor species. This is indicative of the formation of a molecular complex where the two reactants are perturbed in the product complex yet retain their structural identity.²⁸ This is also consistent with the fact that molecular complexes of stoichiometry 1:2 and higher have been reported³⁻⁸ for this pair of reactants so that formation of an initial complex is reasonable. On the basis of the above arguments, the fact that very dilute samples were employed and the fact that this species was observed over a range of $\text{TiCl}_4/\text{NH}_3$ concentration ratios, species A is identified as the 1:1 complex $\text{TiCl}_4 \cdot \text{NH}_3$. While complexes of higher stoichiometry have been reported previously, this represents the first identification and characterization of the initial 1:1 molecular complex for this system. The fact that it

was not observed in the merged jet experiments demonstrates that it is a highly reactive intermediate that is rapidly converted to secondary products.

The remaining few absorptions due to species B were relatively weak and grew more rapidly than species A as the concentration NH_3 in the matrix increased. The infrared spectrum of the 1:2 complex has been reported⁴ with band positions near but somewhat shifted from the bands observed here for the 1:1 complex. In view of the concentration dependence and location of the bands at 679 , 1199 , and 1272 cm^{-1} , they are assigned to the 1:2 complex $\text{TiCl}_4 \cdot 2\text{NH}_3$ isolated in N_2 matrices.

Codeposition of TiCl_4 with trimethylamine into N_2 matrices led to a number of infrared absorptions, some of which are due to reaction of $(\text{CH}_3)_3\text{N}$ with impurity HCl .^{26,27} The remainder, listed in Table 4, are due to a reaction product of TiCl_4 with $(\text{CH}_3)_3\text{N}$. Previous studies^{8,29} have indicated that a 1:1 complex between these two reactants forms readily. Further, the deposition conditions employed for the $(\text{CH}_3)_3\text{N}$ experiments were very similar to those used in the above NH_3 experiments where the 1:1 complex was shown to dominate. Consequently, the product bands listed in Table 4 arising from the codeposition of TiCl_4 with $(\text{CH}_3)_3\text{N}$ and $(\text{CD}_3)_3\text{N}$ are assigned to the 1:1 complex isolated in solid N_2 .

To provide more favorable conditions for the formation of secondary reaction products, TiCl_4 was codeposited with NH_3 in the absence of matrix material to form cryogenic solid thin films. When NH_3 was codeposited with an excess of TiCl_4 or when they were deposited in nearly equal amounts, absorptions were noted near 430 , 670 , 1250 , 1590 , 3250 , and 3325 cm^{-1} . When TiCl_4 was codeposited with an excess of NH_3 , all of these bands were seen except those at 1590 and 3325 cm^{-1} which were obscured by the intense bands of unreacted parent NH_3 . These bands occur in spectral regions similar to the bands observed in the matrix experiments and can be assigned to absorptions of the 1:1 and/or 1:2 complex.

Other product bands observed in these thin film experiments near 890 and 980 cm^{-1} were not apparent in the matrix experiments. As the temperature of the thin film was increased, these two bands did *not* maintain a constant intensity ratio. This indicated that at least two additional reaction products were formed. The infrared spectrum of a solid with the composition $\text{TiCl}_4 \cdot 4\text{NH}_3$ has also been reported⁴ and is listed in Table 3. This solid appears to contain absorptions due to the 1:2 complex as well as bands at 799 , 874 , 901 , and 976 cm^{-1} . Also, TiCl_4 and NH_3 have been shown to form amido complexes $\text{TiCl}_x(\text{NH}_2)_y$ ($x + y = 4$) and imido complexes $[\text{TiCl}_2\text{NH}]_x$ readily,^{7,8} and these absorb³⁰ near 1000 cm^{-1} . Consequently, it is likely that the thin solid films in this study contain a mixture of the 1:2 complex, amido complexes, imido complexes and NH_4^+Cl^- . It was also noted that during warming of the thin films containing excess NH_3 , bands due to NH_4Cl grew substantially in intensity. This was confirmed in thin film experiments employing NH_3 and HCl , where the resultant spectrum agreed well with the literature spectrum³⁰ of NH_4^+Cl^- . This suggests the production of HCl during the warming process and supports the formation of one or more additional amido and imido products. The bands between 800 – 1000 cm^{-1} are likely due to two or more amido and imido complexes and the bands in this region in the reported spectrum of $\text{TiCl}_4 \cdot 4\text{NH}_3$ may also be due to such complexes.

Band Assignments. The band assignments for the matrix isolated 1:1 complex are relatively straightforward based on isotopic shifts and proximity to parent absorptions. The singlets

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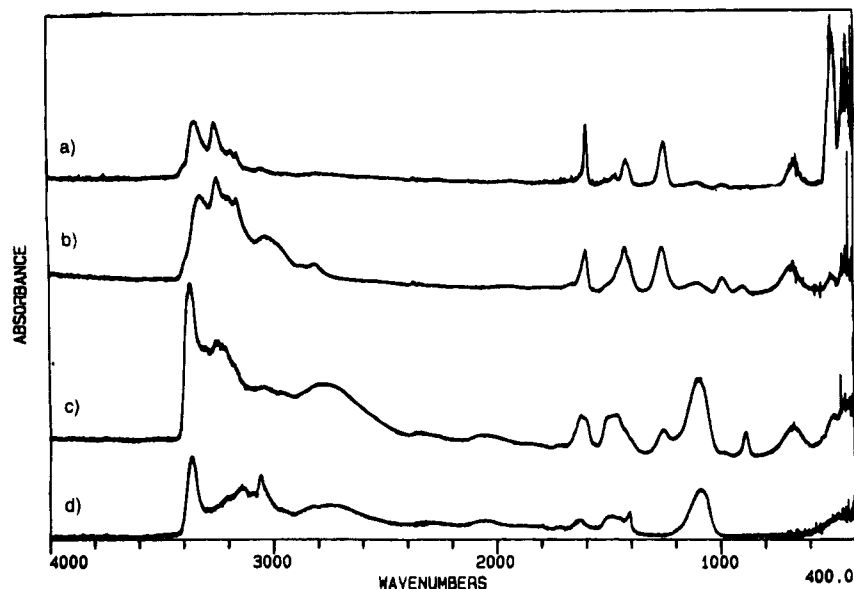


Figure 3. Infrared spectra from 400 to 4000 cm^{-1} of thin films produced by the codeposition of TiCl_4 and NH_3 at 11 K, with TiCl_4 in large excess (trace a), with approximately equal amounts of both reactants (trace b), and with NH_3 in large excess (trace c) compared to the spectrum of a thin film produced by the codeposition of NH_3 and HCl at 11 K (trace d).

Table 4. Band Positions^a and Assignments for the Products of the Codeposition of TiCl_4 with $(\text{CH}_3)_3\text{N}$ and $(\text{CD}_3)_3\text{N}$ in N_2 Matrices

$(\text{CH}_3)_3\text{N}$	$\text{TiCl}_4 + (\text{CH}_3)_3\text{N}$	$(\text{CD}_3)_3\text{N}$	$\text{TiCl}_4 + (\text{CD}_3)_3\text{N}$	assignt
	411		410	ax Ti-Cl str
(421) ^a	434	(409)	420	NC_3 asym def
	465		465	eq Ti-Cl str
824	812	738	727	NC_3 sym str
1038	985,988	(716)		CH_3 rock
1097		(763)		CH_3 rock
1186		872	864	CH_3 rock
1268	1236	1217		NC_3 asym str
1406	1520	1005	1145	CH_3 sym def
1440		(1037)		CH_3 asym def
1455		1050		CH_3 asym def
1469	1485	1064	1080	CH_3 sym def
1473	1466	(1064)		CH_3 asym def
2700-3000	2996			CH_3 str
2700-3000	3042			CH_3 str

^a Band positions in cm^{-1} . ^b Band positions in parentheses were not observed in the blank spectra in this study, but were taken from argon matrix results reported in ref 21.

at 440 and 457 cm^{-1} and the multiplet centered at 449 cm^{-1} showed essentially no shift upon ^{15}N substitution, indicating assignment to vibrations of the TiCl_4 skeleton. Further, these bands are located near the parent TiCl_4 antisymmetric stretching mode and $\nu_1 + \nu_4$ combination mode at 503 cm^{-1} and 516, 519, 523 and 526 cm^{-1} , respectively (the multiplet structure is due to titanium isotopic splitting). With a reduction in symmetry from T_d in the parent (see also below), at least two Ti-Cl antisymmetric stretching modes are anticipated. On the basis of previous studies of molecular complexes, these are expected to shift to lower energy relative to the parent mode. Thus, the bands at 440 and 457 cm^{-1} are so assigned. The multiplet near 449 cm^{-1} matches well the structure of the $\nu_1 + \nu_4$ parent combination mode and is so assigned.

The remaining bands assigned to the 1:1 complex all shifted upon ^{15}N substitution, indicating assignment to vibrations of the coordinated NH_3 group. The symmetric deformation mode of NH_3 has been shown³⁰ to shift to higher energy upon complexation, often 200 cm^{-1} or more from the parent position near 970 cm^{-1} . The site split doublet at 1226, 1230 cm^{-1} appears in this region, and has a ^{15}N shift of 6 cm^{-1} . This compares to a 4 cm^{-1} shift for parent NH_3 and is consistent

with many previous studies.²⁸ Hence, this doublet is readily assigned to the symmetric deformation mode of NH_3 in the complex. The band at 1604 cm^{-1} is shifted slightly from the doubly degenerate deformation mode of parent NH_3 and is assigned to the corresponding vibration of the coordinated NH_3 . The multiplets near 3300 and 3400 cm^{-1} lie slightly lower in energy than the parent NH_3 symmetric and antisymmetric N-H stretching modes, respectively, and are assigned to the analogous modes of the coordinated NH_3 . The ^{15}N shifts of these modes are approximately 1 and 12 cm^{-1} , respectively (with some uncertainty due to site splitting and multiplet structure). This compares to shifts of 3 and 9 cm^{-1} , respectively, for parent NH_3 in solid N_2 .

The final product band was observed at 648 cm^{-1} and showed a 3 cm^{-1} ^{15}N shift. While all of the internal vibrations of the NH_3 group have been observed and assigned above (assuming no reduction in local symmetry), six additional vibrational modes are anticipated upon complex formation arising from the vibrations of one subunit relative to the other. These are due to the loss of 6 rotational and translational degrees of freedom upon complex formation. While most occur at quite low energy (e.g. the Ti-N stretch), one has been observed in the spectral region 590-950 cm^{-1} for a variety of NH_3 complexes.³⁰ This is the NH_3 rocking mode in the complex, which was observed at 704 cm^{-1} for the $\text{SiF}_4\cdot\text{NH}_3$ complex.³¹ This is quite near the 648 cm^{-1} band observed here, and thus assignment of the 648 cm^{-1} band to the NH_3 rock is quite reasonable. The Ti-N stretching mode is also anticipated from the loss of rotational and translational degrees of freedom upon complex formation. However, this mode involves the movement of two relatively heavy atoms in a weak bond, and is expected to lie below 400 cm^{-1} .

The bands at 679, 1199, and 1272 cm^{-1} were attributed above to the 1:2 complex, and are tentatively assigned here to the rocking and symmetric deformation modes of the two NH_3 groups in the complex. These are shifted slightly with respect to the corresponding vibrations of the 1:1 complex, as anticipated. In addition, the infrared spectrum of the 1:2 complex in Nujol reported⁴ band positions of 678, 1238 and 1255 cm^{-1} for the rocking and symmetric deformation modes. The Ti-Cl stretching modes for the 1:2 complex were not observed

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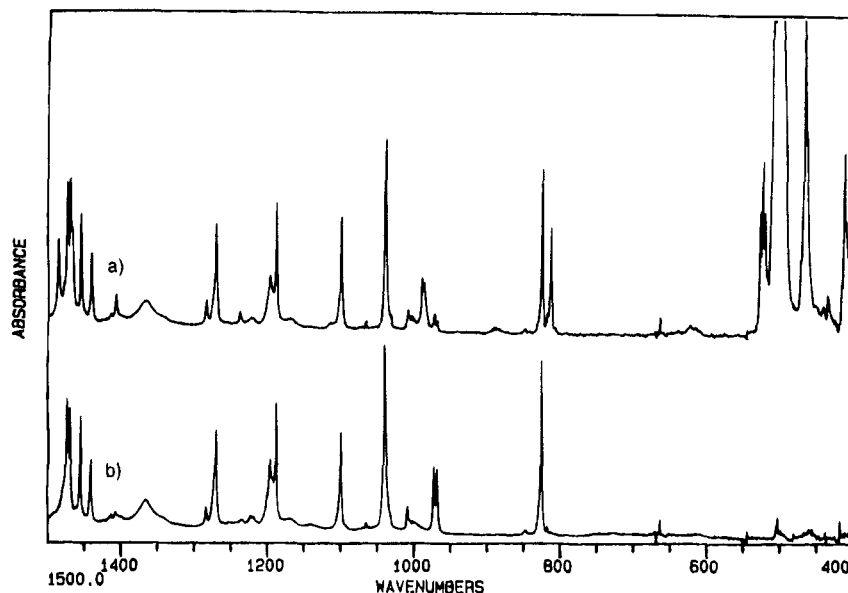


Figure 4. Infrared spectrum from 400 to 1500 cm^{-1} of the products of the codeposition of a sample of N_2/TiCl_4 and $\text{N}_2/(\text{CH}_3)_3\text{N}$ at 11 K (trace a) compared to the spectrum of the products of the codeposition of a sample of N_2/HCl with a sample of $\text{N}_2/(\text{CH}_3)_3\text{N}$ at 11 K (trace b).

although they would be expected to be more intense than the absorptions of the coordinated NH_3 groups. However, these vibrations would likely be shifted to lower energy than those in the 1:1 complex at 440 and 457 cm^{-1} and may fall below 400 cm^{-1} , the lower spectral limit of the spectrometer.

Band assignments for the $\text{TiCl}_4(\text{CH}_3)_3\text{N}$ complex and its deuterium counterpart are readily made as well. The bands at 411 and 465 cm^{-1} were virtually unshifted with deuterium substitution which requires assignment to vibrations of the TiCl_4 subunit. These bands fall in the region in which the TiCl_4 antisymmetric stretching modes appeared for the $\text{TiCl}_4\cdot\text{NH}_3$ complex and are assigned to the corresponding modes for the $\text{TiCl}_4\cdot\text{N}(\text{CH}_3)_3$ complex. Beattie and Gilson²⁹ reported an antisymmetric Ti-Cl stretching vibration at 456 cm^{-1} in the solid state spectrum of the complex, the location of which agrees relatively well with the present results. The product band at 434 cm^{-1} shifted to 420 cm^{-1} upon deuterium substitution indicating a vibration of the coordinated $(\text{CH}_3)_3\text{N}$ group. While the parent NC_3 antisymmetric deformation modes were too weak to be detected in the present experiments, they have been identified at 421 and 409 cm^{-1} for the normal and deuterated species in an argon matrix.²¹ Beattie and Gilson observed a band at 434 cm^{-1} in the solid state spectrum of the complex which they assigned to the NC_3 antisymmetric deformation. Also, previous studies have shown that this mode shifts to higher energy upon complexation.^{32,33} All of this points strongly to the assignment of the 434 cm^{-1} band in the present study to the NC_3 antisymmetric deformation. A number of additional bands of the $\text{TiCl}_4\cdot\text{N}(\text{CH}_3)_3$ complex were observed and are listed in Table 4. Each of these falls within a few wavenumbers of a parent mode of $(\text{CH}_3)_3\text{N}$ (or $(\text{CD}_3)_3\text{N}$) and are readily assigned to the corresponding mode of the coordinated trimethylamine.

Further Considerations. The geometric structure of these complexes is of interest. Simple bonding theory predicts a trigonal bipyramidal structure about the central Ti for the 1:1 complex, with the NH_3 group in either the equatorial (C_{2v}) or axial (C_{3v}) position. The structure of the similar $\text{SiF}_4\cdot\text{NH}_3$ complex was found³¹ to be C_{3v} , based on matrix infrared spectra. Subsequently this structure was confirmed by several ab initio

calculations³⁴⁻³⁶ and recently by gas phase microwave spectroscopy.³⁷ The matrix infrared determination was based on the number and location of the Si-F stretching modes. Unfortunately, the lower limit of the spectrometer, 400 cm^{-1} , precludes application of this argument here. However, the observation of the $\nu_1 + \nu_4$ combination band of the complex with a very similar isotopic structure and relative intensity to the parent provides some information. In the T_d TiCl_4 parent, these modes are the symmetric stretch and the symmetric bend, where the C_3 axis is maintained. If the NH_3 group is in an axial position in the complex, then the nature of these modes will be largely retained and the combination $\nu_1 + \nu_4$ should have an appearance similar to the parent, as it does. However, if the NH_3 group is in an equatorial position, only two chlorine atoms would be in equatorial positions and the nature of these modes would be expected to be different than the corresponding parent modes. Then, the combination is likely to be different in either isotopic structure or relative intensity. Thus, the similarity of the $\nu_1 + \nu_4$ combination band in the complex to that of the parent suggests that the NH_3 group is in an axial position in an overall trigonal bipyramidal structure.

A similar approach might be applied to the $\text{TiCl}_4\cdot\text{N}(\text{CH}_3)_3$ complex as well. Here a distinct $\nu_1 + \nu_4$ combination band was *not* observed, i.e. a band with the same isotopic structure and intensity as the parent band. The above argument would suggest a different structure for the trimethylamine complex, although such a conclusion must be regarded as tentative. Beattie and Gilson favored a C_{3v} structure for this complex in the solid state, based on the observed spectrum, including the spectral region below 400 cm^{-1} . This region was not accessible in the present study, so that direct comparison to their solid state data cannot be made.

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