clusters by the bis(amino)borane. The bridging in (1) may be eliminated because the distance between chlorine-bridged Ti centers is too large a reach for the bis(amino)borane even when one considers sp^3 boron. Structure (2) is almost as favored as the chelate structure—the latter being favored on the basis that the observed coupled infrared vibrations for $\nu(BN_2)$ and ν(BCl) are a result of strained ring formation. A discussion of this feature of the infrared spectrum of I has been presented.

Experimental Section

The preparation of $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$ has been previously described.[1a] Infrared samples were ground under dry nitrogen in a glove bag, mixed with Nujol (previously dried over sodium) or Flurolube (previously dried over Linde Molecular Sieve Type 4A), and enclosed between KBr plates fitted with Teflon gaskets to inhibit hydrolysis and oxidation. Infrared measurements were carried out with a Perkin-Elmer Model 337 grating spectrophotometer in the range 4000–400 cm^{-1}; the range 500–250 cm^{-1} was recorded with a Perkin-Elmer Model 457 grating spectrophotometer employing polyethylene plates. Electronic spectra were obtained on solids ground with Nujol and enclosed between quartz plates; a Cary Model 14 spectrophotometer was employed.

Reaction of $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$ with $[(CH_3)_2N]_2BCl$.—I (261.8 mg, 0.59 mmol) was treated with $[(CH_3)_2N]_2BCl$ (1.1344 g, 8.44 mmol) at −35°. The heterogeneous reaction mixture was vigorously stirred for 18 hr at 32°. All materials volatile at 25° were distilled from the reaction vessel into a trap maintained at −196°. The contents of this trap were warmed to 25°; a yellow solid (*ca.* 10 mg) precipitated from a pale red solution. A pale yellow liquid was separated from the yellow solid by distillation into an adjoining trap at −196°. This liquid was identified as $[(CH_3)_2N]_2BCl$ (1.0992 g, 8.16 mmol) by its 25.0° vapor tension of 5.0 Torr and vapor phase infrared spectroscopy. The nonvolatile residue in the reaction vessel consisted of a brown solid. Bis(dimethylamino)chloroborane (1.0992 g, 8.16 mmol) was again distilled into the reaction vessel and the reactants vigorously stirred at 32° for 15 days. Bis(dimethylamino)chloroborane (1.0720 g, 7.98 mmol) was separated from the reaction mixture in the manner previously described and identified by its 25.0° vapor tension of 5.0 Torr and vapor phase infrared spectrum. The analytical composition of the nonvolatile brown residue in the reaction vessel is *ca.* $I\cdot 0.8[(CH_3)_2N]_2BCl$.

Acknowledgment.—Support of this work by the National Science Foundation under Grant GP-9308 is most appreciated.

CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORIES,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Low-Spin Binuclear Titanium Complexes. III. The Preparation and Characterization of Heptachlorodititanate(VI) Salts[1a]

BY G. S. KYKER[1b] AND E. P. SCHRAM[1c]

Received June 17, 1969

Treatment of bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$, with HCl affords bis(dimethylamine)dichloroboronium heptachlorodititanate(VI), $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$. Pyrolysis of the latter affords dimethylaminodichloroborane, $(CH_3)_2NBCl_2$, and dimethylammonium heptachlorodititanate(VI), $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$. Both of the heptachlorodititanate anions are low-spin binuclear species.

Introduction

The characterization of bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$, by interpretation of magnetic susceptibility data as well as infrared and electronic spectrophotometry has been reported.[1a,2] Treatment of $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$ (hereafter referred to as I) with HCl was effected to determine the susceptibility of the coordinate NTi bond to protonation.

Results and Discussion

Preparation and Characterization of Bis(dimethylamine)dichloroboronium Heptachlorodititanate(VI), $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$.—Treatment of $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$ (I) with HCl (3 atm) in the temperature interval 50–80° results in the formation of I·2HCl, hereafter referred to as II. A similar protonation of the free ligand, associated with II, takes place to afford $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$. This latter reaction differs from the former in the ease of protonation; $[(CH_3)_2N]_2BCl$ reacts rapidly with 2HCl at 25° to form the indicated salt whereas more severe reaction conditions were necessarily employed with I. Because $[(CH_3)_2N]_2BCl$ reacts rapidly with HCl to afford the boronium salt $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$, the possibility that addition of 2 mol of HCl to I might occur in a similar manner to afford $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$ (II) was investigated. II does not contain unreacted I[2] or $TiCl_3$ on the basis of X-ray powder pattern data; in a similar manner the absence of $[(CH_3)_2N]_2BCl_2{}^+Cl^-$ and $[(CH_3)_2NH_2]^+Cl^-$ is assured (Table I). In an effort to determine if the cation $[(CH_3)_2NH_2]_2BCl_2{}^+$ was present in II, an infrared investigation of the latter species was carried out.

Evidence for $[(CH_3)_2NH]_2BCl_2{}^+$ in II. A Comparison between the Infrared Spectra of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ and II.—The cation associated with $[(CH_3)_2NH]_2$-

---

[1] (a) Part II: G. S. Kyker and E. P. Schram, *Inorg. Chem.*, **8**, 2313 (1969). (b) Completed in partial fulfillment of the Ph.D. degree. (c) To whom correspondence should be addressed.

[2] G. S. Kyker and E. P. Schram, *Inorg. Chem.*, **8**, 2306 (1969).

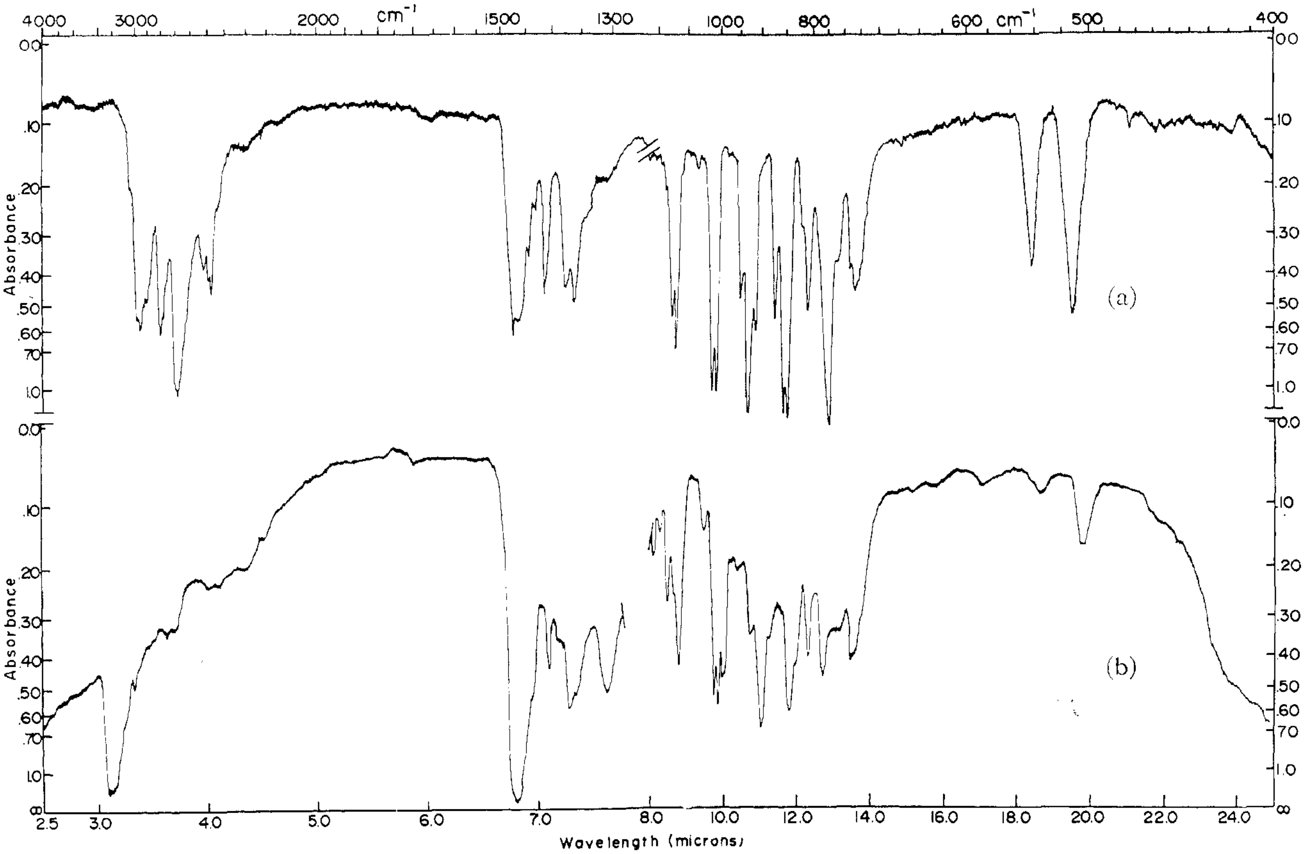

Figure 1.—Infrared spectra of (a) $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ (mull) and (b) $\{[(CH_3)_2NH]_2BCl\}_2{}^+\{Ti_2Cl_7\}^-$ (mull).

Table I

X-Ray Powder Diffraction Data for (1) $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$, (2) $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$, and (3) $(CH_3)_2NH_2{}^+Cl^-$ [a]

d, Å			
(1)	(2)		(3)
9.66 m[b]	12.11 m	2.88 vw	4.98 s
8.71 m	6.08 s	2.80 w	3.64 vs
7.47 s	5.56 vs	2.57 w	3.35 w
6.49 m	5.20 w	2.67 w	3.10 w
5.97 s	4.91 vw	2.49 m	2.94 s
5.66 s	4.67 vvw	2.39 w	2.78 m
5.13 w	4.23 m	2.35 w	2.58 m
4.78 w	3.87 vvw	2.25 w	2.29 w
4.10 vvw	3.73 vw	2.03 vw	2.17 w
3.64 vvw	3.54 m	1.97 vw	1.89 w
3.35 w	3.40 m	1.85 w	
2.93 m	3.30 s	1.78 w	
2.78 vw	3.17 m	0.98 vvw	
2.55 vw	2.97 m	0.97 vvw	
2.07 vvw			
1.81 vvw			

[a] M. J. Brock and M. J. Hannum, *Anal. Chem.*, **27**, 1374 (1955). [b] Visually estimated intensities.

$BCl_2{}^+Cl^-$ has a $Cl_2BN_2H_2C_4$ skeleton of essentially C_{2v} symmetry. Therefore, certain skeletal vibrations of this boronium salt can be assigned by reference to vibrational assignments for $[(CH_3)_2N]_2BCl$, also of C_{2v} symmetry.[3] In the process of assigning group frequencies in the spectrum of the boronium salts, consideration must also be given to (1) frequency shifts in ligand modes which result from the change in the coordination number of boron (3 to 4) and from protonation of the dimethylamino groups and (2) appearance of the new modes ν(NH), $\nu_{as}(BCl_2)$, $\nu_s(BCl_2)$, and $\delta(BCl_2)$ as the result of the formation of NH and an additional BCl bond. The infrared spectrum of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ is shown in Figure 1a and data are summarized in Table II. The spectrum of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ contains intense absorptions in the interval 2300–2777 cm^{-1} which are assigned to $\nu(NH\cdots Cl)$, where the dots represent a hydrogen bond. This assignment is based on the fact that the spectrum of $(CH_3)_2NH_2{}^+Cl^-$ contains intense absorptions in the 2400–2800-cm^{-1} interval which have been assigned to $\nu(NH\cdots C^{\cdot})$.[4] It is interesting to note that NH stretching frequencies have been calculated to occur between 3100 and 3300 cm^{-1} for compounds in which hydrogen bonding is absent.[5] These calculations are verified for salts in which hydrogen bonding is inherently unlikely; *e.g.*, ν(NH) is found in the interval 3214–3158 cm^{-1} for $[CH_3NH_3]^+[BCl_4]^-$ and $[C_5H_5NH]^+[BCl_4]^-$.[6] The charge density on the resulting anion is less than on Cl^-; thus, the decreased hydrogen bonding is understandable. Therefore, if II contains the $Ti_2Cl_7{}^-$ anion, a corresponding absence of hydrogen

---

(3) G. S. Kyker and E. P. Schram, *J. Am. Chem. Soc.*, **90**, 3678 (1968).

(4) J. Bellanato, *Spectrochim. Acta*, **16**, 1344 (1960).

(5) B. Chenon and C. Sandorfy, *Can. J. Chem.*, **36**, 1181 (1958).

(6) W. Kynaston, B. E. Larcombe, and H. S. Turner, *J. Chem. Soc.*, 1772 (1960).

TABLE II

INFRARED FREQUENCIES AND GROUP VIBRATIONAL ASSIGNMENTS FOR (a) $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ AND (b) $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$

	Freq, cm^{-1} (± 5 cm^{-1})	
Assignments	(a)	(b)
$\nu(NH)$		3189 s
$\nu(CH)$	3020 m	3061 m, sh
	2957 vs, sh	2979 vw
	2931 vs	2749 vvw
	2881 vs, sh	
$\nu(NH\cdots Cl)$	2777 vs	2682 vvw
	2666 vvs	2481 vvw
	2505 m	2421 vvw
	2486 m, sh	2287 vvw
	2468 m	2192 vvw
	2432 w, sh	
	2298 vw	
$\delta_{as}(CH_3)$	1652 vvw	1462 vvs
	1472 vs	1433 vs, sh
	1463 vs, sh	
	1444 m	
	1427 m	
$\delta_s(CH_3)$	1415 s	1402 s
	1376 s	1385 s, sh
		1366 s
$\delta(NH)$	1361 s	1265 m
$\rho(CH_3)$		1226 w
$\rho(CH_3)$	1168 vw	1199 w
	1145 s	1170 m
	1132 s	1147 m, sh
	1107 vw, sh	1130 s
$\rho(CH_3)$	1055 vvw	1046 w
$\nu_{as}(NC_2)$	1017 vs	1020 vs
	1007 vs	1008 vs
		991 vs
$\rho(CH_3)$	971 vvw	952 m
$\nu_{as}(^{10}BN_2)$	940 s	924 s
$\nu_{as}(^{11}BN_2)$	924 vvs	899 vs
	907 s	881 s
$\nu_s(NC_2)$	866 s	838 vs
	851 vvs	825 s, sh
	835 vvs	
$\nu_s(^{10}BN_2)$	812 m, sh	
$\nu_s(^{11}BN_2)$	802 s	804 s
$\nu_{as}(BCl_2)$	771 vvs	778 s
	754 m, sh	749 m
$\nu_s(BCl_2)$	727 m	732 s
$\delta(BN_2)$	539 s	579 vvw
		527 w
$\delta(BCl_2)$	508 vvs	496 m
	468 vvw?	
$\nu_{as}(TiCl)$		446 m, sh
		408 vvs, sh

bonding is to be expected. The spectrum of II does indeed contain strong bands, in the interval 3100–3300 cm^{-1}, which is consistent with the absence of hydrogen bonding. The CH modes overlap, to some extent, with the NH stretching vibrations; however, the absorptions in the interval 2800–3020 cm^{-1} are assigned to $\nu(CH)$. For comparison, the CH stretching modes in the spectrum of $[(CH_3)_2N]_2BCl$ are found in the interval 2805–3017 cm^{-1}.[3] The infrared spectrum of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ contains absorptions in the interval 1427–1472 cm^{-1} which are assigned to $\delta_{as}(CH_3)$ and in the interval 1376–1415 cm^{-1} which are assigned to $\delta_s(CH_3)$. For comparison, the asymmetric and symmetric methyl deformations in the spectrum of $[(CH_3)_2N]_2BCl$ are found at 1452 and 1400 cm^{-1}, respectively.[3] The absorption at 1361 cm^{-1} in the spectrum of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ is assigned to $\delta(NH)$. This assignment is based on two facts. First, the infrared spectrum of $[CH_3(H)N]_3B$ contains an absorption at 1277 cm^{-1} which can be attributed to $\delta(NH)$.[7] Second, hydrogen bonding is known to result in a shift of $\delta(NH)$ to higher energy, relative to those observed for compounds in which hydrogen bonding is absent.[8] Thus, the 1361-cm^{-1} absorption is considered the correct choice for $\delta(NH)$. The absorptions in the interval 1107–1168 cm^{-1} in the spectrum of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ are assigned to $\rho(CH_3)$. In the spectrum of $[(CH_3)_2N]_2BCl$, $\rho(CH_3)$ occurs at 1143 cm^{-1} with a shoulder at 1152 cm^{-1}.[3] The splitting of these two absorptions to four bands in the spectrum of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$ may result from the lower "local symmetry" of the dimethylamino moieties, C_s, in the boronium salt with respect to that in the aminoborane, C_{2v}. Also, the absorptions at 1215 and 1191 cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCl$, assigned to $\rho(CH_3)$,[3] are absent in that of the boronium salt. These modes may be infrared inactive in C_s symmetry. Packing in the crystalline state may also decrease the amplitude of these out-of-plane vibrations so that the intensities would be extremely low. The $\nu(NC_2)$ asymmetric and symmetric modes are found at 1074 and 907 cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCl$. In proceeding to the infrared spectrum of $[(CH_3)_2NH]_2BCl_2{}^+Cl^-$, these modes are expected to shift to lower energy as a result of protonation of the dimethylamino moieties. For example, $\nu_{as}(NC_2)$ and $\nu_s(NC_2)$ modes shift from 1079 and 930 cm^{-1}, respectively, in the infrared spectrum of $(CH_3)_2NH$[9] to 1022 cm^{-1} ($\Delta = -57$ cm^{-1}) and 867 cm^{-1} ($\Delta = -61$ cm^{-1}), respectively,

---

[7] D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 5239 (1960).

[8] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

[9] J. E. Stewart, *J. Chem. Phys.*, **30**, 1259 (1959).

in the spectrum of $(CH_3)_2NH_2^+Cl^-$.[4] Indeed, similar shifts in these NC_2 modes are found in proceeding from the infrared spectrum of $[(CH_3)_2N]_2BCl$ to that of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$, *i.e.*, $\nu_{as}(NC_2)$ and $\nu_s(NC_2)$ shift -60 and -83 cm^{-1}, respectively, upon complexation.[3] Therefore, similar frequency shifts in the NC_2 modes are expected in proceeding from $[(CH_3)_2N]_2BCl$ to $[(CH_3)_2NH]_2BCl_2^+Cl^-$. In the spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ the $\nu_s(NC_2)$ is assigned to the bands at 851 and 835 cm^{-1}, $\Delta = -67$ cm^{-1}. The splitting of these bands apparently results from the lower local symmetry of the dimethylamino moieties in this salt, C_s, relative to that in $[(CH_3)_2N]_2BCl$, C_{2v}. In the spectrum of $[(CH_3)_2NH]_2BCl^+Cl^-$ the absorptions at 925 and 943 cm^{-1} have been assigned to $\nu_{as}(^{10}BN_2)$ and $\nu_{as}(^{11}BN_2)$, respectively.[10] These assignments appear reasonable because protonation of the dimethylamino moieties should decrease the BN bond order relative to that in the unprotonated aminoborane. Also, the transition from three- to four-coordinate boron is expected to result in a shift of ν(BN) to lower energy because of decreased s character in the BN bond. The absorptions at 812 (m, sh) and 802 (s) cm^{-1} in the spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ are assigned to $\nu_s(^{10}BN_2)$ and $\nu_s(^{11}BN_2)$, respectively. These assignments are based on the presence of the ^{10}B isotope bands, the lower intensity of ν_s relative to ν_{as}, and the fact that this band is generated by addition of HCl to $[(CH_3)_2N]_2BCl$. In the spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$, the absorptions in the interval 842–849 cm^{-1} have been assigned to $\nu(BCl_2)$.[10] The frequencies of these absorptions appear to be too high for ν(BCl) in a four-coordinate boron because these modes have generally been assigned to absorptions in the range 630–783 cm^{-1}, *i.e.*, 630–750 cm^{-1} for BCl_4^- [6] and 755–783 cm^{-1} for $(CH_3)_3N \cdot BCl_3$.[11] Therefore, the absorptions at 771 and 727 cm^{-1}, in the spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$, are assigned to $\nu_{as}(BCl_2)$ and $\nu_s(BCl_2)$, respectively. The absorption centered at 539 cm^{-1} in the infrared spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ is assigned to $\delta(BN_2)$, *i.e.*, a net shift of -42 cm^{-1} from the same mode in the spectrum of $[(CH_3)_2N]_2BCl$ (579 cm^{-1}). This shift of $\delta(BN_2)$ to lower energy apparently results from a weakening of the BN bond as a result of protonation of the dimethylamino moieties and the transition from three- to four-coordinate boron. The absorption centered at 539 cm^{-1} in the infrared spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ is assigned to $\delta(BCl_2)$. In support of this assignment, the spectrum of $(CH_3)_2NBCl_2(g)$ contains a band at 525 cm^{-1} which has been assigned to $\delta(BCl_2)$.[12]

Assignments for Group Frequencies in the Vibrational Spectrum of $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}$ (II).—The infrared spectrum of the cation in $[(CH_3)_2NH]_2BCl^+Cl^-$ is not expected to change drastically upon substitution of Cl^- by $Ti_2Cl_7^-$. However, ν(NH) is expected to shift to higher energy because of decreased hydrogen bonding in the $Ti_2Cl_7^-$ derivative. As previously discussed, this decrease in hydrogen bonding is a consequence of decreased charge density on chlorine in $Ti_2Cl_7^-$ relative to that on Cl^-. The infrared spectrum of II is shown in Figure 1b and data are summarized in Table II. As expected, the infrared spectrum of II is similar to that of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ in many respects; however, certain contrasts are immediately apparent. The infrared spectrum of II contains only weak absorptions in region 2200–2800 cm^{-1}, $\nu(NH \cdots Cl)$, but an absorption is found at 3189 cm^{-1}, *i.e.*, in the region expected for ν(NH) in a compound exhibiting no hydrogen bonding. It should be noted that similar shifts in ν(NH) occur when Cl^- is replaced by $FeCl_4^-$ in $[(CH_3)_2NH]_2BCl_2^+Cl^-$; ν(NH) shifts from 2800 to 3120 cm^{-1}.[10] Thus, the occurrence of ν(NH) at 3189 cm^{-1} in the spectrum of II is consistent with an ionic formulation similar to that of $[(CH_3)_2NH]_2BCl_2^+[FeCl_4]^-$, *i.e.*, $\{[(CH_3)_2NH]_2BCl_2\}^+$-$\{Ti_2Cl_7\}^-$. The envelope of bands centered at 899 cm^{-1} in the spectrum of II, assigned to $\nu_{as}(BN_2)$, has shifted -25 cm^{-1} from the envelope assigned to the same mode in the spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$. Although the definite cause of this shift is unknown, the decrease in hydrogen bonding in proceeding from the Cl^- to the $Ti_2Cl_7^-$ derivative would appear to be the most likely. The $\nu_{as}(NC_2)$ mode in the spectrum of II (1020, 1008, 991 cm^{-1}) is split into three bands while the same mode in $[(CH_3)_2NH]_2BCl_2^+Cl^-$ consists of only two bands (1017, 1007 cm^{-1}). Also, the $\nu_s(NC_2)$ mode, in the spectrum of II, consists of a single band with a shoulder on the low-energy side whereas the same mode is split into three well-defined bands in that of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ (866, 851, 835 cm^{-1}). These differences are apparently a consequence of the different "site symmetries" of the cation in the lattice of these two salts because in both cases complexation of the dimethylamino moieties to titanium(III) is improbable because protonation of the amino moieties has taken place. The intensities of the absorptions assigned to $\delta(BN_2)$ and $\delta(BCl_2)$ in the spectrum of II, relative to the other band intensities, are much lower than those in that of $[(CH_3)_2NH]_2BCl_2^+Cl^-$. It appears that the site symmetry of $[(CH_3)_2NH]_2BCl_2^+$, in II, is such that these deformations are less infrared active than in $[(CH_3)_2NH]_2BCl_2^+Cl$.

The absorption at 1265 cm^{-1} in the infrared spectrum of II is assigned to δ(NH). It should be noted that the infrared spectrum of $[(CH_3)_2NH]_3B$ contains an absorption at 1277 cm^{-1} which is also assignable to δ(NH).[7] The band assigned to δ(NH), in the spectrum of II, shifts to 1361 cm^{-1} in the spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$. This shift to higher energy most likely results from the increased hydrogen bonding in this latter boronium salt. Similar shifts of δ(NH) to higher energy have also been attributed to hydrogen bonding.[13] The very intense absorptions at 446 and 408 cm^{-1}, in the spectrum of II, are absent in that of $[(CH_3)_2NH]_2$-

---

(10) H. Noth and S. Lukas, *Ber.*, **95**, 1505 (1962).

(11) R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964).

(12) A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J. Chem. Soc.*, 995 (1964).

(13) H. J. Becker, *Spectrochim. Acta*, **19**, 575 (963).

$BCl_2^+Cl^-$. Therefore, these absorptions do not arise from vibrations of $[(CH_3)_2NH]_2BCl_2^+$ and are assigned to ν_{as}(TiCl) associated with $Ti_2Cl_7^-$, possibly indicative of five-coordinate titanium.[1a] In conclusion, the infrared spectrum of II is considered to be consistent with the ionic formulation $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$.

Electronic Absorption Spectrum of II.—The absorption spectrum of II, Figure 2, contains no d ← d transitions in the near-infrared and visible regions which are characteristic of five- or six-coordinate titanium(III) complexes, respectively. However, very broad, poorly defined charge-transfer bands are found at 27.39 and 35.69 kK. The frequency of the lowest energy charge-transfer band is close to that observed for I, 27.59 kK, and may be characteristic of five-coordinate titanium(III).[1a] Indeed, this conclusion would be consistent with the interpretations of the infrared spectrum of II in which ν_{as}(TiCl) is thought to be characteristic of five-coordinate titanium(III).

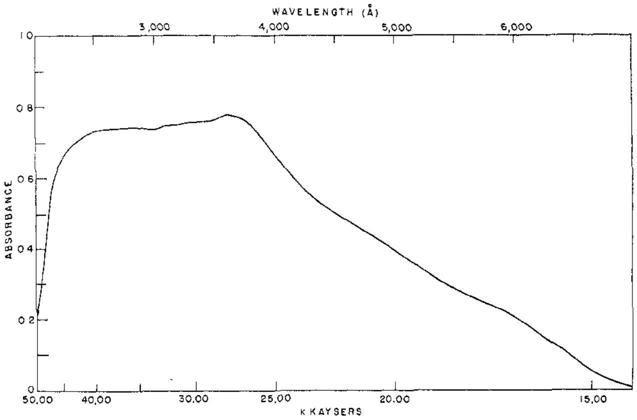

Figure 2.—Electronic absorption spectrum of $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$ (solid state).

Magnetochemistry of II.—The molar magnetic susceptibility of II is 535 × 10^{-6} cgsu (not corrected for TIP) at 297.5°K (μ_{eff}^{cor} = 0.80 BM per Ti(III)). The exchange of electron spin between the titanium(III) atoms is most likely of the intramolecular type because the susceptibility is independent of field strength. The magnetic moment of II at 297.5°K, 0.80 BM per titanium(III), is slightly lower than that observed for I at 297.2°K, 0.89 BM per titanium(III). In both cases these data are not corrected for TIP.

In summary, the infrared spectrum of II confirms the presence of $[(CH_3)_2NH]_2BCl_2^+$ and is indicative of five-coordinate titanium(III). The lowest energy charge-transfer band in the electronic absorption spectrum of II occurs in the same frequency interval as those observed for other five-coordinate titanium(III) complexes and the magnetic moment of II is consistent with the presence of a binuclear titanium(III) cluster, $Ti_2Cl_7^-$, in which considerable exchange occurs between adjacent metal atoms.

Preparation and Characterization of Dimethylammonium Heptachlorodititanate(VI), $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$.—The boronium salt $[(CH_3)_2NH]_2BCl_2^+Cl^-$ decomposes in the interval 180–200°, *in vacuo*, to afford $(CH_3)_2NH_2^+Cl^-$ and $(CH_3)_2NBCl_2$;[10] therefore the thermal degradation of $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$ (II) was investigated to determine if a similar mode of decomposition would take place. Indeed, II decomposes in the interval 98–180°, *in vacuo*, to afford $(CH_3)_2NBCl_2$ and a nonvolatile brown solid; no $(CH_3)_2NH_2^+Cl^-$ sublimed from the hot zone. The yield of $(CH_3)_2NBCl_2$ is 94% of that calculated for the degradation equation

$$\underset{\text{II}}{\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-} \xrightarrow[98\text{–}180°]{in\ vacuo} (CH_3)_2NBCl_2 + \underset{\text{III}}{[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-}$$

The quantitative recovery of $(CH_3)_2NBCl_2$ was not achieved because the monomer partially converted to the nonvolatile dimer during transport. Thus, the yield of $(CH_3)_2NBCl_2$ is considered to be essentially quantitative for the degradation.

The nonvolatile brown solid produced in the pyrolysis of II is formulated as $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ (III) on the basis of the stoichiometry of the decomposition of II and the interpretation of infrared data. Furthermore, X-ray powder pattern data for this brown solid, Table III, contain no lines characteristic of $(CH_3)_2NH_2^+Cl^-$ or II (see Table I) and the various crystalline modifications of $TiCl_3$.[2] Also, the infrared spectrum of III (Figure 3b; data in Table IV), contains no absorptions at 1030 and 890 cm^{-1} characteristic of $(CH_3)_2NH_2^+Cl^-$ or at 1130 and 991 cm^{-1} characteristic of II (see Figure 1 and Table II). On the bases of the combined infrared and X-ray data, III does not contain $(CH_3)_2NH_2^+Cl^-$, undecomposed II, or $TiCl_3$. The solid-state infrared spectrum of III was compared to that of $(CH_3)_2NH_2^+Cl^-$, in order to prove the presence of the dimethylammonium cation in the salt.

Table III

X-Ray Powder Diffraction Data for $[(CH_3)_2NH_3]^+[Ti_2Cl_7]^-$ (*d*, Å)

8.80 vs[a]	3.18 vvw	1.94 m
7.73 m	3.07 vw	1.86 vvw
6.94 s	2.93 vs	1.80 m
6.37 vs	2.78 w	1.72 vw
5.45 w	2.54 s	1.67 vw
5.15 m	2.44 vvw	1.60 vw
4.77 m	2.36 w	1.56 vw
4.06 w	2.14 m	1.52 vw
3.85 vs	2.06 m	1.47 vvw
3.44 vvw	1.99 w	1.42 vvw

[a] Visually estimated intensities.

Solid-State Infrared Spectrum of III. Dimethylammonium Ion Vibrations.—The infrared spectra of $(CH_3)_2NH_2^+Cl$ and $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ (III) are shown in Figure 3a and b, respectively, and data are summarized in Table IV, columns a and b, respectively. The vibrational spectrum of $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ (III) is similar to that of $(CH_3)_2NH_2^+Cl^-$; however,

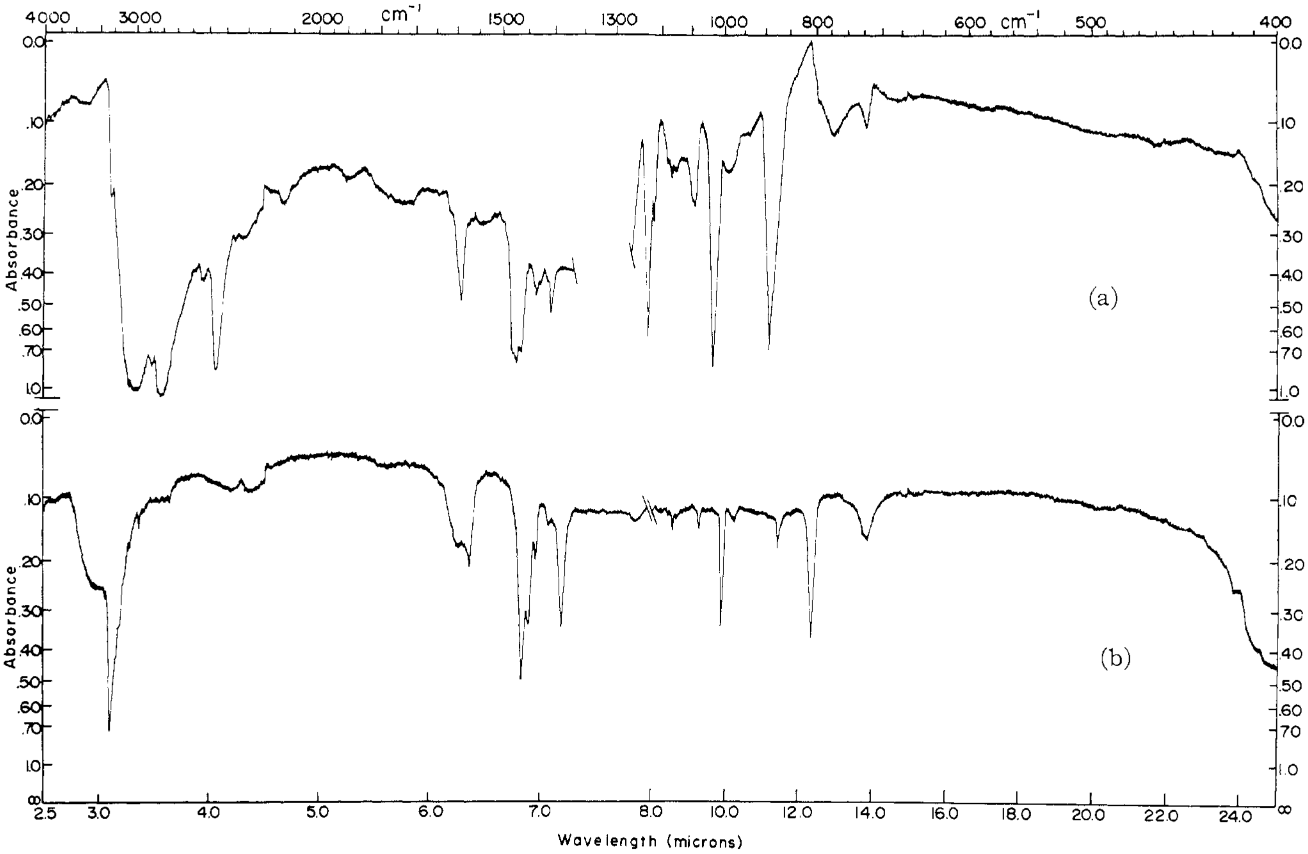

Figure 3.—Infrared spectra of (a) $[(CH_3)_2NH_2]^+Cl^-$ (mull) and (b) $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ (mull).

differences are apparent which may be understood when one considers the different magnitudes of hydrogen bonding in these two salts. The intense absorptions in the interval 2300–2900 cm^{-1}, $\nu(NH\cdots Cl)$,[4] in the spectrum of $(CH_3)_2NH_2{}^+Cl^-$ are absent in that of $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$. Instead the latter compound exhibits absorptions in the 3131–3300-cm^{-1} region which are assigned to overlapping NH and CH stretching modes. Similar shifts have been observed for $\nu(NH)$ in proceeding from $(CH_3)_2NH_2{}^+Cl^-$ to $[(CH_3)_2NH_2]^+[FeCl_4]^-$ and have already been attributed to decreased hydrogen bonding in the latter salt. The occurrence of $\nu(NH)$ in the interval 3131–3300 cm^{-1} in the spectrum of III is consistent with the presence of the $Ti_2Cl_7{}^-$ moiety which exhibits small $H\cdots Cl$ bonding interactions. The spectrum of III contains bands at 1599 and 1573 cm^{-1} which are assigned to $\delta(NH_2)$. For comparison, these modes occur at 1612 and 1586 cm^{-1} in the spectrum of $(CH_3)_2NH_2{}^+Cl^-$.[4] The $\nu_{as}(NC_2)$ and $\nu_s(NC_2)$ modes shift from 1030 and 880 cm^{-1}, respectively, in the spectrum of $(CH_3)_2NH_2{}^+Cl^-$ to 1009 ($\Delta = -21$ cm^{-1}) and 806 cm^{-1} ($\Delta = -74$ cm^{-1}), respectively, in the spectrum of III. The exact causes of these shifts are unknown; however, the decrease in hydrogen bonding in proceedfrom $(CH_3)_2NH_2{}^+Cl^-$ to III appears important. Similar shifts (-25 and -80 cm^{-1}) in these NC_2 modes have been observed in proceeding from $(CH_3)_2NH_2Cl$ (1030 and 880 cm^{-1}) [4] to $[(CH_3)_2NH_2]^+[BCl_4]^-$

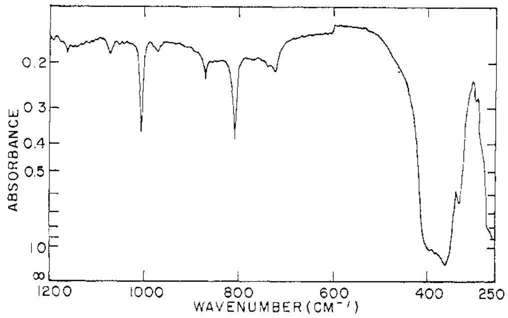

Figure 4.—Far-infrared spectrum of $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ (mull).

(1005 and 800 cm^{-1}),[6] *i.e.*, in proceeding from a salt in which hydrogen bonding is present to one in which there are only weak $H\cdots Cl$ interactions as evidenced by a normal frequency for $\nu(NH)$. The far-infrared spectrum of III, Figure 4, contains bands at 392 (vs, b), 361 (vs, b), 350 (vs, sh), 332 (s), 297 (w), 283 (m, sh), 270 (vs, sh), and 255 (vs) cm^{-1}. The absorptions at 392 and 361 cm^{-1} are assigned to $\nu_{as}(TiCl)$. The 392-cm^{-1} band is characteristic of five-coordinate titanium(III) while the 361-cm^{-1} band is characteristic of six-coordinate titanium(III).[1a] Therefore, it appears possible that the structure of III is comprised of two titanium(III) moieties of different coordination number, *i.e.*, 5 and 6. This spectrum is in contrast to that of I which contained a single band at 383 cm^{-1}, assigned to

TABLE IV
INFRARED FREQUENCIES AND GROUP VIBRATION ASSIGNMENTS FOR (a) $(CH_3)_2NH_2{}^+Cl^-$ AND (b) $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$

Assignments[a]	Freq, cm^{-1} ($\pm$5 cm^{-1}) (a)	(b)
ν(NH) + ν(CH)	3468 vvs	3327 m, b
ν(CH)	3211 m, sh	3222 vvs
ν(CH) + ν(NH)	2999 vvs	3181 s, sh
ν(CH)	2853 vs	3131 m, sh
	2781 vs	
ν(NH)	2521 s	2378 vw
	2453 vs	2284 vw
	2311 m, sh	
Combination	2128 w	1782 vvw
$\nu_7 + \nu_{27}$	1893 vw	
	1726 w, b	
	1612 w, sh	1599 m
$\delta(NH_2)$	1586 m	1573 m
	1534 vw	
	1475 s, sh	1464 vs
$\delta_{as}(CH_3)$	1469 vs	1449 s
	1452 s, sh	1437 m
	1433 m	1412 w
$\omega(NH_2)$	1425 m, sh	
	1412 m, sh	
$\delta_s(CH_3)$	1404 m	1389 s
$\rho(CH_3)$	1236 s	1270 vvw
	1186 m	
$\rho(CH_3)$	1169 m	1166 w
	1149 m	
$\rho(CH_3)$	1096 s, sh	1078 w
	1087 s	
$\nu_{as}(NC_2)$	1030 vvs	1009 s
	987 m	976 vw
$\rho(NH_2)$	890 vvs	873 w
$\nu_s(NC_2)$	880 vs, sh	806 vs
?	766 w	722 w
?	716 w	
$\delta(N(CH_3)_2)$	>400 w	416 m, sh

[a] Assignments for $(CH_3)_2NH_2{}^+Cl^-$ from J. Bellanato, *Spectrochim. Acta*, **16**, 1334 (1960).

ν_{as}(TiCl). The band at 332 cm^{-1} in III is assigned to CNC bending and the envelope of bands at 283, 270, and 255 cm^{-1} is assigned to ν_s(TiCl).

In summary, the interpretation of the vibrational spectrum of III is consistent with the formulation $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$. The differences between the vibrational spectra of the dimethylammonium ion in III and $(CH_3)_2NH_2{}^+Cl^-$ can be explained by consideration of the relative amounts of hydrogen bonding in the two salts.

Electronic Absorption Spectrum of III.—The electronic transitions associated with III (Figure 5) consist of two well-defined charge-transfer bands centered at 37.02 and 27.02 kK. In addition, a broad low-intensity band is found at *ca.* 21.74 kK which is most likely a weak d–d transition. The charge-transfer spectra of six-coordinate Ti(III) complexes contain bands in the region of 21 kK, while those of five-coordinate Ti(III) complexes are in the vicinity of 27 kK.[1a] Therefore, the charge-transfer spectrum of III is considered to be consistent with the presence of both five- and six-coordinate titanium(III) and is in accord with the interpretation of the far-infrared spectrum.

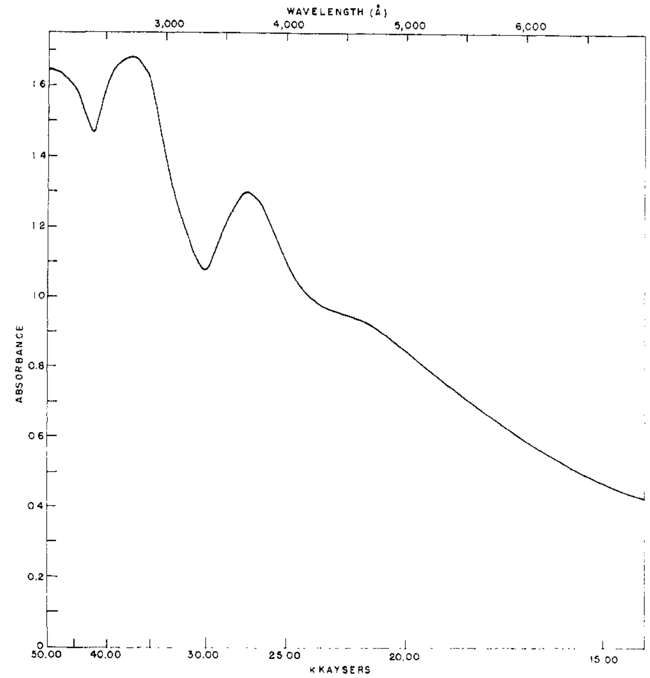

Figure 5.—Electronic absorption spectrum of $[(CH_3)_2NH_2]^+$-$[Ti_2Cl_7]^-$ (solid state).

Magnetochemistry of III.—The molar magnetic susceptibility of $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ is 791 × 10^{-6} cgsu (not corrected for TIP) at 294.2°K ($\mu_{eff}{}^{cor}$ = 0.96 BM per titanium(III)). The susceptibility is field independent and is therefore indicative of intramolecular exchange between adjacent titanium(III) moieties. The structural aspects associated with III and II, which result in their strong antiferromagnetic properties, apparently do not require complexation of $[(CH_3)_2N]_2BCl$ to titanium(III) moieties, *i.e.*, a bridging aminoborane between two metal atoms. Thus, it appears that the exchange in III, as well as in II, results from direct metal–metal interactions, a superexchange through bridging chlorine atoms, or perhaps a combination of both.

Thermal Degradation of III.—Decomposition of III begins at 220°, *in vacuo*, as evidenced by a change from brown to dark brown. After 2 hr at 263° the salt decomposes to a nonvolatile violet solid and a yellow solid (*ca.* 30% of the total mass) which sublimes from the hot zone. X-Ray powder data for this violet solid are summarized in Table V. Although the X-ray data for this material are similar to those for α-, β-, γ-, and δ-$TiCl_3$,[2] some lines exhibit marked differences in wavelength and intensity. It appears likely that this violet solid may be a new crystalline modification of $TiCl_3$. Furthermore, the solid-state infrared spectrum of this violet solid contained no absorptions above 400 cm^{-1}; therefore $(CH_3)_2NH_2{}^+$ has been removed, possibly in the yellow solid.

In summary the synthesis of $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ (III) is accomplished through the series of reactions

TABLE V
X-RAY POWDER DIFFRACTION DATA FOR THE VIOLET SOLID OBTAINED FROM THERMAL DEGRADATION OF $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ (d, Å)

5.89 vs[a]	2.13 m	1.49 vw
5.45 m	2.03 vvw	1.48 vw
3.05 vvw	1.79 s	1.46 vvw
2.94 vvw	1.69 w	1.22 vvw
2.74 vs	1.66 w	1.14 w
2.55 vvw	1.53 vw	

[a] Visually estimated intensities.

represented by eq 1 and 2. The solid-state infrared

$$\underset{\text{I}}{[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6} + 2HCl \longrightarrow \underset{\text{II}}{\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-} \quad (1)$$

$$\underset{\text{II}}{\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-} \xrightarrow[\textit{in vacuo}]{\Delta} (CH_3)_2NBCl_2 + \underset{\text{III}}{[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-} \quad (2)$$

spectrum of $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ is consistent with the presence of the cation $(CH_3)_2NH_2^+$ and the anion $Ti_2Cl_7^-$. The presence of both five- and six-coordinate titanium(III) moieties in $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$ is inferred from the far-infrared and charge-transfer spectra. The magnetic properties of $[(CH_3)_2NH_2]^+$-$[Ti_2Cl_7]^-$ are consistent with a $Ti_2Cl_7^-$ moiety in which appreciable exchange occurs between adjacent titanium(III) atoms.

Proposed Structure for Bis(dimethylamino)dichloroboronium Heptachlorodititanate(VI), $\{[(CH_3)_2N]_2BCl_2\}^+\{Ti_2Cl_7\}^-$ (II).—The structure of the anionic portion of II, $Ti_2Cl_7^-$, is considered to involve a triple chlorine bridge with two trigonal-bipyramidal Ti atoms sharing a common face. The bases for this geometry are: (1) the cation has been identified as $[(CH_3)_2NH]_2BCl_2^+$ by infrared spectroscopy and its mode of decomposition; therefore, the anion stoichiometry involves $Ti_2Cl_7^-$; (2) the far-infrared and electronic absorption spectra have been interpreted in terms of five-coordinate Ti; (3) the magnetic susceptibility of II indicates a binuclear species; and (4) the proposed structure is more symmetrical than the possible alternate proposals with the pseudo-precedent being the geometry of $Ti_2Cl_9^{3-}$ ion which involves a triple chlorine bridge.[14]

We are investigating the reactions of I with Lewis bases as well as those of oxidative addition and will report these results shortly.

Experimental Section

Procedures.—All reactions were carried out in the vacuum system previously described; similarly, the infrared and electronic spectral techniques as well as magnetic measurement procedures have been described.[1a,2]

Reactions of I with HCl. Synthesis and Characterization of $\{[(CH_3)_2NH]_2BCl_2\}^+\{Ti_2Cl_7\}^-$ and $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$.—I (538.6 mg, 1.21 mmol) was treated with HCl (9.85 mmol) at *ca.* 3 atm and 50° for 237 hr. The color of the residue was brown; all materials volatile at 25° were distilled from the reaction vessel and through a −78° trap into one maintained at −196°. A small amount of light yellow liquid, which collected in the −78° trap, was not investigated further. The volatile material distilling through the −78° trap was identified as pure HCl (8.82 mmol) by its −126° vapor tension of 30.0 Torr and its vapor-phase infrared spectrum. Hydrogen chloride (1.03 mmol) reacted with I (1.21 mmol); thus, the composition of the brown residue is I·0.85HCl. This reaction was continued under the conditions described. Volatiles were intermittently distilled from the reaction vessel, and the purity of the HCl, passing through −78° trap, was verified by its vapor tension. The progress of this heterogeneous gas–solid reaction is summarized in Table VI. The product of the reaction of HCl with I is a brown solid having the composition I·2.03HCl.

TABLE VI
COMPOSITION OF BROWN RESIDUE, I·xHCl, AS A FUNCTION OF REACTION TIME AND TEMPERATURE

Reaction		Amt of HCl recovered, mmol	Amt of HCl lost, mmol	HCl:I mole ratio in brown residue
Time, hr	Temp, °C			
237	50	8.82	1.03	0.85
551	55	8.54	1.32	1.09
647	55	8.30	1.55	1.28
Additional HCl (2.62 mmol) Was Added to the Reaction Mixture				
719	61	10.77	1.70	1.41
863	60	10.67	1.80	1.49
959	71	10.37	2.10	1.74
1007	80	10.12	2.35	1.94
1028	88	10.01	2.46	2.03

Thermal Degradation of I·2.03HCl.—This brown solid (612.6 mg, 1.21 mmol) was contained in a reaction vessel and slowly heated, *in vacuo*, in the interval 98–115° for 65 hr. The colorless liquid, which slowly evolved, was condensed into an adjacent trap maintained at −196° and subsequently identified as monomeric $(CH_3)_2NBCl_2$ by its vapor-phase infrared spectrum and its vapor tension. The quantity of $(CH_3)_2NBCl_2$ evolved, during thermal degradation, was 0.79 mmol. The brown residue was heated in the interval 150–160° for 23 hr. A small amount of yellow solid sublimed above the hot zone, and a colorless liquid slowly collected in a −196° trap. This liquid was identified as pure $(CH_3)_2NBCl_2$. The brown residue was maintained in the interval 160–180° for 6 hr. A colorless liquid, identified as $(CH_3)_2NBCl_2$, collected in a −196° trap; a small quantity of yellow solid sublimed above the hot zone. The total quantity of $(CH_3)_2NBCl_2$ evolved was 1.14 mmol. Thus, *ca.* 94% of the boron in I·2.03HCl has been converted to $(CH_3)_2NBCl_2$. Quantitative recovery of $(CH_3)_2NBCl_2$ was not possible because some of the monomer converted to the nonvolatile dimer during collection and *PVT* measurements. The brown residue was maintained in the interval 180–188° for 24 hr; no volatiles were evolved and the residue was still brown. Qualitative tests on the brown residue confirmed the absence of boron. The solid-state infrared spectrum of the brown residue is shown in Figure 3, infrared data are summarized in Table IV, and X-ray data are summarized in Table III.

Magnetic Susceptibility of $[(CH_3)_2NH_2]^+[Ti_2Cl_7]^-$.—Data obtained for a 311.9-mg sample of the brown solid at 21° by use of a Gouy balance are given in Table VII. The force measurements summarized in this table are the average of four sets of data; the χ_M data are not corrected for TIP.

Reaction of I with HCl.—I (976.2, 2.21 mmol) was treated with gaseous HCl (2.48 mmol) at 25.5° and 172.0 Torr. A set of P_{HCl} data, obtained at 25.5° and constant volume (*ca.* 200 ml), as a function of reaction time is summarized in Table VIII. Hydrogen chloride (0.67 mmol) was recovered from the reaction mixture. The composition of the brown solid was I·0.82HCl. Additional HCl (6.27 mmol) was added to the reaction mixture. consisting of unreacted HCl (0.67 mmol) and a brown solid,

---

(14) R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1606 (1968).

TABLE VII

Magnet current, A	δ, g	F, g	F', g	$10^6\chi_M^{cor}$, cgsu	μ_{eff}/Ti, BM
6	−0.0013	−0.0002	+0.0011	808	0.98
8	−0.0021	−0.0007	+0.0014	796	0.97
10	−0.0027	−0.0011	+0.0016	769	0.96

TABLE VIII

Reaction time, min	p_{HCl}, Torr	Reaction time, min	p_{HCl}, Torr
0.0	172.0	7.0	46.8
1.0	134.0	8.0	46.0
2.0	105.0	9.0	45.0
3.0	80.0	10.0	44.9
4.0	70.0	11.0	44.9
5.0	58.0	25.0	42.2
6.0	51.0		

After 30 min the pressure had dropped from 450.0 to 437.7 Torr. Hydrogen chloride (2.25 mmol) reacted with I; the composition of the brown residue was I·1.02HCl. Unreacted HCl was condensed onto the brown solid; the reaction vessel was isolated from the adjoining U trap and the manometer by closing a Teflon stopcock. The pressure in this system at 26° was *ca.* 6 atm. After 24 hr HCl (2.44 mmol) had reacted with I; the composition of the brown solid was I·1.10HCl. Additional HCl (12.69 mmol) was added to the reaction mixture. After 72 hr at 20° HCl (3.49 mmol) had reacted with I; the composition of the brown solid was I·1.58HCl. The unreacted HCl was again added to the brown residue and the mixture was maintained at 60°. After 70 hr HCl (4.12 mmol) had reacted with I; the composition of the brown residue was I·1.87HCl. After an additional 24 hr the amount of HCl lost was 4.33 mmol; the composition of the brown residue was I·1.96HCl.

Magnetic Susceptibility Data for I·1.96HCl.—Five sets of weight deflection data were obtained at each field strength. Susceptibility data (not corrected for TIP) obtained for a 813.3-mg sample at 24.3° are summarized in Table IX. The solid-state infrared spectrum of I·1.96HCl is shown in Figure 1, infrared data are summarized in Table II, and X-ray powder diffraction data are summarized in Table I.

TABLE IX

Magnet current, A	β	δ, g	F', g	$10^6\chi_M^{cor}$, cgsu	μ_{eff}/Ti (av), BM
6	608.0	−0.0013	−0.0007	488	
8	473.0	−0.0021	−0.0010	587	0.80
10	391.0	−0.0027	−0.0016	530	

Thermal Degradation of I·1.96HCl.—A sample of I·1.96HCl (846.0 mg, 1.64 mmol), contained in a vacuum sublimator, was maintained in the interval 200–206°, *in vacuo*, for 72 hr. All volatile materials evolved during pyrolysis were condensed at −196°. The sublimate, collected on the condensation tip at 4.0°, consisted mainly of a brown solid contaminated with a small amount of purple solid. A brownish white material remained in the bottom of the sublimator. The volatile materials condensed in the −196° trap consisted of small amounts of yellow and green solids, a viscous red oil (*ca.* 10 mg), and a red liquid. These materials were distilled through a trap maintained at 10° into an adjacent trap maintained at −196°. The materials nonvolatile at 10° consisted of a yellow solid (*ca.* 20 mg), a viscous red oil (*ca.* 10 mg), and a green solid (*ca.* 2 mg). The volatile liquid collected in the −196° trap was identified as $(CH_3)_2NBCl_2$ (175.6 mg, 1.40 mmol) by a vapor-phase infrared spectrum.

Reaction of $[(CH_3)_2N]_2BCl$ with HCl.—Bis(dimethylamino)chloroborane (1.5425 g, 11.48 mmol) was treated with gaseous HCl (3.86 mmol) at −10°. A white solid immediately formed; the reaction mixture was stirred for 1 hr at 27°. All materials volatile at 27° were distilled from the reaction vessel and collected in a −196° trap. This colorless condensate was identified as unreacted $[(CH_3)_2N]_2BCl$ (1.2923 g, 9.63 mmol) by its 25° vapor tension of 5.5 Torr and its vapor-phase infrared spectrum. The composition of the white solid was $\{[(CH_3)_2N]_2BCl\}_{1.00}\{HCl\}_{2.09}$. This solid melts in the interval 145–158°. The solid-state infrared spectrum is shown in Figure 1; infrared data and assignments are summarized in Table II. The properties of this compound agreed well with those reported for $[(CH_3)_2NH]_2BCl_2^+Cl^-$ which has been prepared by treating $[(CH_3)_2N]_2BCl$ with excess HCl in ether.[10]

Acknowledgment.—We are pleased to acknowledge support of this work by the National Science Foundation under Grant GP-9308.