Torr, reservoir temperature slowly increased from 25 to 74°, and condensation tip at 13°. No green crystals, *i.e.*, $TiCl_3 \cdot [N(CH_3)_3]_2$, were produced even at 74°. A small amount of brown residue remained in the reservoir.

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Low-Spin Binuclear Titanium Complexes. II. An Infrared and an Electronic Spectrophotometric Study of Bis(dimethylamino)chloroboranehexachlorodititanium(VI)[1a]

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The infrared spectrum of bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$, is interpreted in terms of complexed dimethylamino moieties. Strong vibrational coupling in the complex results in increased ν(BN) and decreased ν(BCl) frequencies as compared to the free ligand. The ν(TiCl) vibrations as well as the charge-transfer spectrum indicate five-coordinate Ti in $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$.

Introduction

Bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ (hereafter referred to as I), has been prepared by reduction of titanium tetrachloride, $TiCl_4$, with tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$.[1a] I is of interest because it exhibits intramolecular antiferromagnetism and, as will be shown, is coordinately unsaturated; these properties in conjunction suggest the possibility of catalytic activity toward olefin polymerization. In order to elucidate the mode of bonding in I, an infrared and electronic absorption investigation was carried out.

Results and Discussion

Characterization of $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ (I) *via* Infrared Spectroscopy.—The infrared spectra of I (mull) and $[(CH_3)_2N]_2BCl(l)$ are shown in Figure 1a and b, respectively; the infrared data are summarized in Table I. Absorptions above *ca.* 500 cm^{-1} in the vibrational spectrum of I are easily assigned to ligand modes because TiCl vibrations are known to occur only below *ca.* 500 cm^{-1}; see Table II. Assignments of group frequencies to ligand vibrations were made by correlation of band frequencies, intensities, and shapes to those observed for $[(CH_3)_2N]_2BCl$. In these assignments due consideration was given to the presence of isotope bands, *i.e.*, ^{10}B and ^{11}B, as well as to frequency shifts and intensity changes expected for ligand modes upon complexation.[2] Also, it is assumed that the symmetry of the C_4N_2BCl skeleton of the ligand (C_{2v}) is not perturbed by complexation to such an extent that some vibrations become infrared active and some inactive. However, splitting of certain ligand modes might be expected as symmetry is lowered to C_s upon coordination.

TABLE I
INFRARED FREQUENCIES AND ASSIGNMENTS FOR (a) $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ (MULL) AND (b) $[(CH_3)_2N]_2BCl(l)$

	Freq, cm^{-1} (± 5 cm^{-1})	
Assignments	a	b
$\nu(CH_3)$	3483 w	3017 m
	3124 m	2933 s, sh
	3020 w, sh	2895 vs
	2940 vw, sh	2845 m, sh
$\nu_{as}(^{10}BN_2)$	1668 w, sh	1544 vs, sh
	1644 m, sh	
$\nu_{as}(^{11}BN_2)$	1612 vs	1530 vvs
?	1561 w	
$\delta_{as}(CH_3)$	1467 vvs	1482 w
		1452 s
$\delta_s(CH_3)$	1413 m	1408 vs, sh
		1400 vvs
$\nu_s(BN_2)$	1466 s, sh	1349 s
$\rho(CH_3)$	1278 vvw	1215 vvs
	1251 vs	1191 vs
	1181 vs	1152 vs
	1147 s	1143 vvs
	1131 m, sh	1107 vw
$\nu_{as}(NC_2)$	1054 vs	
	1021 vs	1074 vvs
	992 s	
?	971 w	
	944 vw	
$\nu(BCl)$	862 m	922 m
$\nu_s(NC_2)$	825 m	907 vs
	798 m	
$\delta(^{10}BN_2)$		600 w
$\delta(^{11}BN_2)$	654 s	579 vs
$\nu(TiCl)$	383 vvs	
	322 m	
	276 s	

CH_3 Modes.—The CH asymmetric and symmetric stretching vibrations, $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$, shift from the range 2805–2933 cm^{-1} in the spectrum of free

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(1) (a) Part I: G. S. Kyker and E. P. Schram, *Inorg. Chem.*, **8**, 2306 (1969). (b) Completed in partial fulfillment of the Ph.D. degree, 1969. (c) To whom correspondence should be addressed.

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

TABLE II

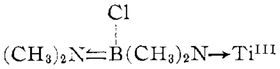
TITANIUM–CHLORINE VIBRATIONS FOR SOME SELECTED COMPOUNDS—A CRITERION FOR COORDINATION NUMBER

Compound	Phase	CN	r(MCl), Å	Ref	ν(MCl), cm^{-1}	Symmetry	Ref
$TiCl_4$	Gas	4	2.18	*a*	506 vs (t_2)	Td	*b*
$TiCl_4 \cdot N(CH_3)_3$	Solid	5	. . .	*c*	456 s (e), 376 s (e), 344 m (a_1)	C_3	*c*
$TiCl_3 \cdot 2N(CH_3)_3$	Solid	5	. . .	*d*	387 s, b, 330 m, 254 m	D_{3h}?	*e*
$TiBr_3 \cdot 2N(CH_3)_3$	Solid	5	. . .	*d*	323 s (a_2''), 238 ms (e)	D_{3h}	*e*
$TiCl_3 \cdot 2S(CH_3)_2$	Solid	5	. . .	*d, f*	390 s, b, 232 m, 280 b	C_{4v}	*d*
$TiCl_3 \cdot 2SC_4H_4$	Solid	5	. . .	*d, f*	390 s, 324 m, 290 m	C_{4v}	*d*
$[(H_5C_2)_2NH_2]TiCl_5$	Solid	5	. . .	*g*	385 vs, 346 vs, 212 m, 170 m (bending)	D_{3h}?	*g*
$[(H_5C_2)_2NH_2]_2TiCl_6$	Solid	6	*Ca.* 2.34	*i*	325 vs, b (t_{1u})	O_h	*h*
$(NH_4)_2TiCl_6$	Aq soln	6	*Ca.* 2.34	*i*	330 (ν_3), 193 (ν_4)	O_h	*j*
$[(CH_3)_4N]_2TiCl_6$	Solid	6	*Ca.* 2.34	*i*	324 vs (ν_3), 183 m (ν_4)	O_h	*g*
$[(H_5C_2)_4N]_2TiCl_6$	Solid	6	*Ca.* 2.34	*i*	321 vs (ν_3), 182 m (ν_4)	O_h	*g*
$TiCl_4 \cdot 2THF^m$	Solid	6	*Ca.* 2.34	*k*	371 s, 298 m	C_{2v}	*k*
$TiCl_4 \cdot 1,4\text{-}D^m$	Solid	6	*Ca.* 2.34	*k*	389 s, 340 w	C_{2v}	*k*
$TiCl_4 \cdot 2A^m$	Solid	6	*Ca.* 2.34	*k*	387 s, b, 318 w	C_{2v}	*k*
$TiCl_4 \cdot 2py^m$	Solid	6	*Ca.* 2.34	*k*	368, 280	C_{2v}	*k*
$TiCl_4 \cdot 2,2'bipy^m$	Solid	6	. . .	. . .	384 s, 366 sh, 307 w	C_{2v}	*k*
$TiCl_4 \cdot phen^m$	Solid	6	. . .	. . .	379 s, 356 sh, 303 w	C_{2v}	*k*
$TiCl_3 \cdot 3THF$	Solid	6	. . .	. . .	360 s, 331 s, 300 m	. . .	*k*
$TiCl_3 \cdot 3A$	Solid	6	. . .	. . .	365 s, *ca.* 334 m, b	. . .	*k*
α-$TiCl_3$	Solid	6	*Ca.* 3.6	*l*	289 (bridge)	. . .	*k*
$TiCl_4 \cdot 2B^m$	Solid	8	2.44	*k*	317 (b_2), 325 (sh) (e)	D_{2d}	*k*

[a] By electron diffraction: M. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37,** 393 (1941). [b] M. F. A. Dove, J. A. Creighton, and L. A. Woodward, *Spectrochim. Acta*, **18,** 267 (1962). [c] The infrared spectrum of the solid is identical with that in C_6H_6 solution: I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 6596 (1965). Complex is monomeric in C_6H_6: G. W. A. Fowles and R. A. Hoodless, *ibid.*, 33 (1963). [d] By X-ray diffraction; *i.e.*, $TlCl_3 \cdot 2N(CH_3)_3$ is isomorphous (powder pattern) to $TiBr_3 \cdot 2N(CH_3)_3$ for which a *trans*-trigonal-bipyramidal structure was found *via* a single crystal X-ray study: B. J. Russ and J. S. Wood, *Chem. Commun.*, 745 (1966). [e] G. W. A. Fowles, T. E. Lester, and R. A. Walton, *J. Chem. Soc., A*, 198 (1968). [f] Both complexes were considered to be five-coordinate because ν_{as}(MCl) shifts to lower energy when the complexes dissolve in excess base; the first charge-transfer band in the uv spectrum of both complexes shifts to lower energy upon dissolving in excess base. These shifts are consistent with the presence of five-coordinate monomers in the solid state which dissolve in excess base as six-coordinate complexes. [g] J. A. Creighton and J. H. S. Green, *J. Chem. Soc., A*, 808 (1968). [h] R. A. Walton and B. J. Brisdon, *Spectrochim. Acta*, **23A,** 2222 (1967). [i] By X-ray diffraction; *e.g.*, for Cs_2TiCl_6 (2.35 Å) and Rb_2TiCl_6 (2.33 Å): G. Engel, *Z. Krist.*, **90,** 341 (1935). [j] D. M. Adams and D. C. Newton, *J. Chem. Soc., A*, 2262 (1968). [k] R. J. H. Clark, *Spectrochim. Acta*, **21,** 955 (1965). [l] X-Ray diffraction: G. Natta, P. Corradini, and G. Allegra, *J. Polymer Sci.*, **51,** 399 (1961). [m] Abbreviations: THF, tetrahydrofuran; D, dioxane; A, acetonitrile; py, pyridine; 2,2′-bipy, 2,2′-bipyridyl; phen, *o*-phenanthroline; B, *o*-phenylenebis(dimethylarsine). For *cis* (C_{2v}) complexes four ν(MCl) are allowed in the infrared spectra ($2\,A_1 + B_1 + B_2$) whereas for a *trans* D_{4h} complex only one ν(MCl) mode is allowed (E_u)—these complexes are considered to have the *cis* (C_{2v}) structure.

$[(CH_3)_2N]_2BCl$ to the interval 2940–3124 cm^{-1} in that of the complexed ligand, *i.e.*, I. This shift to higher energy has also been observed in the spectrum of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$.[2] The asymmetric methyl deformation $\delta_{as}(CH_3)$, shifts from 1452 to 1467 cm^{-1} ($\Delta = +15$ cm^{-1}) upon complexation; the symmetric deformation, $\delta_s(CH_3)$, shifts from 1400 to 1413 cm^{-1} ($\Delta = +13$ cm^{-1}). The other $\rho(CH_3)$ absorptions undergo similar shifts; however, the changes in frequency and intensity of these modes are not considered definitive as to the mode of bonding exhibited by $[(CH_3)_2N]_2BCl$ in I.

BN_2 Modes.—The asymmetric $^{10}BN_2$ and $^{11}BN_2$ stretching modes, $\nu_{as}(^{10}BN_2)$ and $\nu_{as}(^{11}BN_2)$, shift from 1544 and 1530 to 1644 and 1612 cm^{-1}, respectively ($\Delta = +100$ and $+82$ cm^{-1}), upon complexation. A shift of similar magnitude is exhibited by the symmetric BN_2 stretching mode, $\nu_s(BN_2)$, *i.e.*, from 1349 (free ligand) to 1466 cm^{-1} (complexed ligand), $\Delta = +117$ cm^{-1}. Similarly, the $^{10}BN_2$ and $^{11}BN_2$ deformations shift from 600 and 579 to 654 cm^{-1} (unresolved), $\Delta = +75$ cm^{-1}. The occurrence of the BN_2 modes at unusually high energy (*e.g.*, $\nu_{as}(^{11}BN_2)$ is generally found in the interval 1499–1530 cm^{-1} for aminoboranes) is a most striking aspect of the infrared spectrum of I. It is interesting to note that relatively high-energy BN_2 modes have also been observed in the solid-state infrared spectrum of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$.[2] These high-energy BN_2 modes were attributed to coupling of these vibrations with other ligand modes as a result of complexation of $N(CH_3)_2$ moieties to titanium(IV). An alternate explanation for the high-energy BN_2 bands in the spectrum of I is the occurrence of considerable BN double-bond character which results from a noncomplexed dimethylamino group, *i.e.*



$$(CH_3)_2N \overset{\leftarrow}{=} \overset{\displaystyle Cl}{\overset{\vdots}{B}}(CH_3)_2N \rightarrow Ti^{III}$$

High-Energy BN_2 Modes Arising from Considerable BN Double-Bond Character as a Result of Noncomplexed Dimethylamino Moieties.—The infrared spectrum of $H[(CH_3)_2N]_2BCH_3{}^+I^-$ contains a band at 1576 cm^{-1} which is assigned to $\nu_{as}(^{11}BN_2)$.[3] The same mode is found at 1502 cm^{-1} in the spectrum of $[(CH_3)_2N]_2BCH_3(g)$; therefore, a shift of $+74$ cm^{-1} occurs upon addition of 1 mol of HI. This high-energy BN_2 mode was

(3) H. Noth and P. Fritz, *Z. Anorg. Allgem. Chem.*, **322,** 297 (1963).

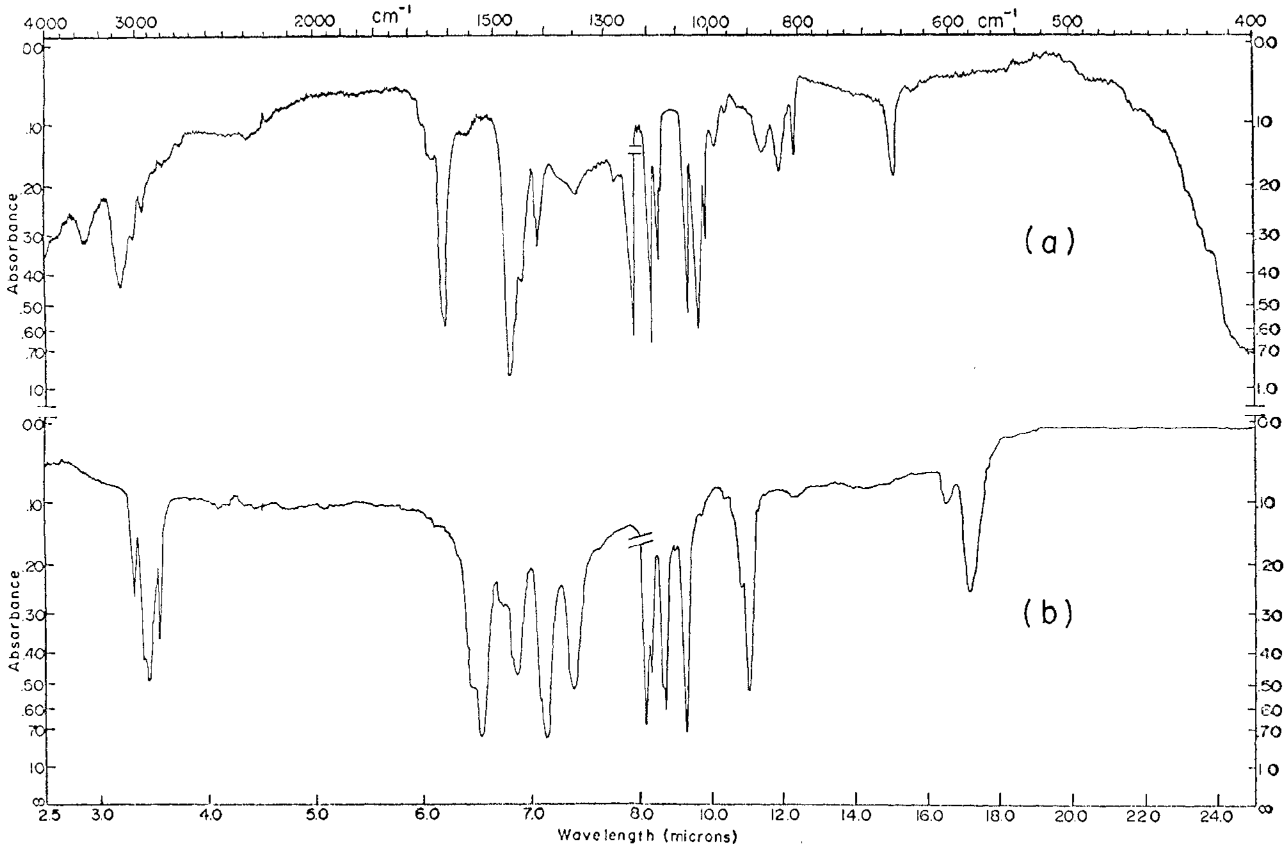
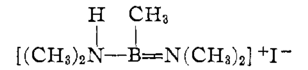


Figure 1.—Infrared spectra of (a) $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ (mull) and (b) $[(CH_3)_2N]_2BCl(l)$.

attributed to extensive BN double-bond character which is consistent with the valence bond formulation



$$[(CH_3)_2\overset{\overset{H}{|}}{N}-\overset{\overset{CH_3}{|}}{B}=N(CH_3)_2]^+I^-$$

It is interesting to note that this salt reacts with HCl to afford the boronium salt $[(CH_3)_2NH]_2B(Cl)(CH_3)^+Cl^-$; this addition of HCl is accompanied by a disappearance of the 1576-cm^{-1} absorption. The infrared spectrum of $H_2[(CH_3)_2N]_3B^{2+}I^-{}_2$ also contains an absorption assigned to a BN stretching mode at 1558 cm^{-1}.[3] The $\nu_{as}(BN_2)$ mode is found at 1507 cm^{-1} in $[(CH_3)_2N]_3B(g)$;[1] therefore, addition of 2 mol of HI results in a shift of of the BN mode to higher energy ($\Delta = +51$ cm^{-1}). This high-energy BN vibration was again attributed to a structure involving considerable BN double-bond character, *i.e.*, $[(CH_3)_2NH]_2B\overset{+}{=}N(CH_3)_2{}^+I^-{}_2$.[3]

High-Energy BN_2 Modes Arising from Coupling of These Vibrations with Other Vibrations of the Same Symmetry as a Result of Complexation of $-N(CH_3)_2$ Moieties to Ti(III).—Goubeau has reported that the infrared spectrum of $(CH_2NH)_2B(CH_3)$ contains absorptions at 1583 and 1534 cm^{-1} which are assigned to $\nu_{as}(^{11}BN_2)$ and $\nu_s(^{11}BN_2)$, respectively.[4] These high-energy BN_2 modes were attributed to coupling of these vibrations with $\nu(BC)$ as a result of the relatively strained five-membered ring. These BN_2 stretching frequencies should be compared to the analogous noncyclic compound $[(CH_3)_2N]_2BCH_3$ in which $\nu_{as}(BN_2)$ and $\nu_s(BN_2)$ are found at 1502 and 1364 cm^{-1}, respectively.[2] Because a B=N moiety is isoelectronic with C=C, a comparison was made to coupled vibrations in methylcycloalkene derivatives. In such derivatives coupling between $\nu(C{=}C)$ and $\nu(C{-}CH_3)$ is reported to result in a shift of $\nu(C{=}C)$ to higher energy; see Table III.[4]

TABLE III

EXAMPLES OF COUPLED INFRARED VIBRATIONS

	$\nu(C{=}C)$, cm^{-1}				
	Unsubstituted	Monomethyl deriv	$\Delta\nu$	Dimethyl deriv	$\Delta\nu$
cis-2-Hexene	1658	1669	+11	...	...
Cyclohexene	1652	1674	+22	...	...
Cyclopentene	1611	1658	+47	...	...
Maleic anhydride	1587	1646	+59	1679	+92

If noncomplexed dimethylamino moieties are present in I, the BN_2 and NC_2 modes of the free group would be expected to occur at frequencies close to those observed for the free ligand; see Table I. Indeed, treatment of I with excess $[(CH_3)_2N]_2BCl$ results in the formation of $\{[(CH_3)_2N]_2BCl\}_2 \cdot \{Ti_2Cl_6\}$. The infrared spectrum of this complex is shown in Figure 2 and summarized in Table IV. Absorptions characteristic of noncomplexed $N[(CH_3)_2]_2$ moieties are: 2803–3018 cm^{-1}

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(4) J. Goubeau and A. Z. Appel, *Z. Anorg. Allgem. Chem.*, **279**, 83 (1955).

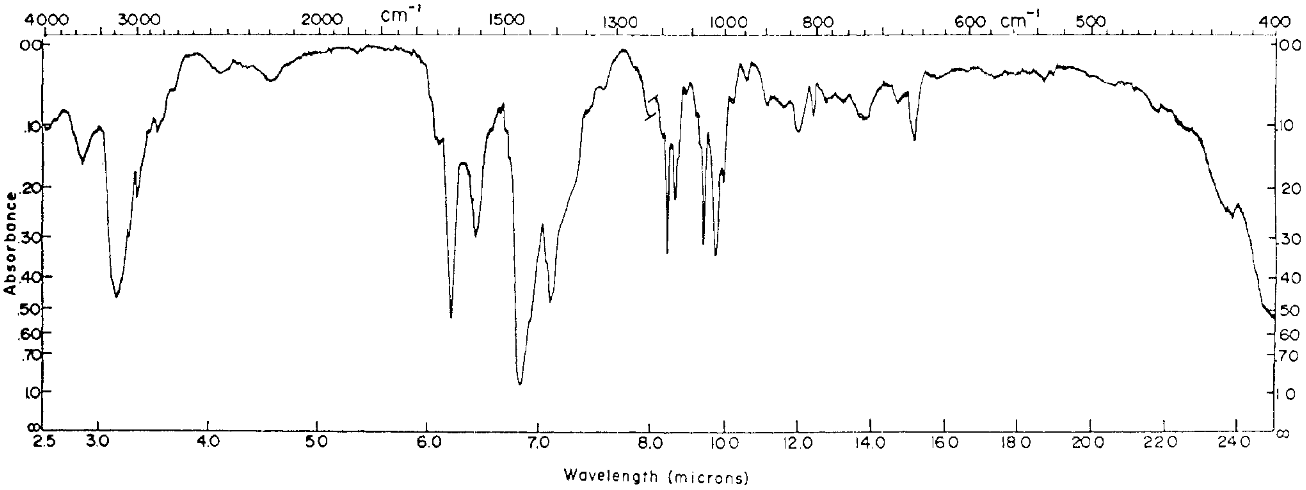

Figure 2.—Infrared spectrum of $\{[(CH_3)_2N]_2BCl\}_2\{Ti_2Cl_6\}$ (mull).

(ν(CH)); 1528–1559 cm^{-1} ($\nu_{as}(BN_2)$); 1304 and 1365 cm^{-1} ($\nu_s(BN_2)$); 1206 and 1137 cm^{-1} ($\rho(CH_3)$); 1083, 1071, and 1056 cm^{-1} ($\nu_{as}(NC_2)$); 887 cm^{-1} (ν(BCl) + $\nu_s(NC_2)$); and 585 s cm^{-1} ($\nu(BN_2)$). The infrared spectrum of I does not contain the absorptions which are characteristic of noncomplexed dimethylamino groups; therefore, the high-energy BN$_2$ modes most likely result from coupling of these modes with other ligand vibrations of the same symmetry as a result of the complexation of $N(CH_3)_2$ moieties to titanium(III).

TABLE IV
INFRARED FREQUENCIES AND GROUP VIBRATIONAL ASSIGNMENTS FOR $\{[(CH_3)_2N]_2BCl\}_2\{Ti_2Cl_6\}$

Assignments	Freq, cm^{-1} ($\pm$5 cm^{-1})	Assignments	Freq, cm^{-1} ($\pm$5 cm^{-1})
ν(C–H)^a	3236 m, sh	$\rho(CH_3)^a$	1246 m
	3184 s		
	3102 m, sh	$\rho(CH_3)^b$	1206 s
ν(C–H)^b	3018 m	$\rho(CH_3)^a$	1185 s
	2928 s		1104 m
	2900 s, sh		
	2855 m, sh	$\rho(CH_3)^b$	1137 m
	2803 w		
		$\nu_{as}(NC_2)^b$	1083 m
?	1692 vvw		1071 m
?	1666 vw		1056 m
$\nu_{as}(BN_2)^a$	1640 m, sh	$\nu_{as}(NC_2)^a$	1039 w, sh
	1617 s, sh		1025 m
	1609 s		1000 m
$\nu_{as}(BN)_2{}^b$	1584 m	ν(BCl)?	984 w
	1559 vvs		940 w
	1556 vvs, sh	ν(BCl) + $\nu_s(NC_2)^b$	887 w
	1528 m, sh	$\nu_s(NC_2)^a$	869 w
$\delta_{as}(CH_3)^{a,b}$	1487 m, sh		829 w
	1465 vvs		802 w
$\nu_s(BN_2)^a$	1446 s, sh	$\delta(^{10}BN_2)^a$	675 w
	1421 m, sh	$\delta(^{11}BN_2)^a$	657 w
$\delta_s(CH_3)^{a,b}$	1413 s	$\delta(BN_2)^b$	585 w
	1386 s	?	496 vw
$\nu_s(BN_2)^b$	1365 s	CNC bend	417 s, sh
	1304 m	ν_{as}(TiCl) ?	*Ca.* 400 vvs

^{a} Complexed. ^{b} Noncomplexed.

NC$_2$ Modes.—The asymmetric and symmetric NC$_2$ stretching modes of the ligand $[(CH_3)_2N]_2BCl$ are expected to shift to lower energy upon complexation.[2] In the spectrum of I, $\nu_{as}(NC_2)$ shifts from 1074 (free ligand) to 1021 cm^{-1} (complexed ligand), $\Delta = -53$ cm^{-1}, and $\nu_s(NC_2)$ shifts from 907 to 825 cm^{-1}, $\Delta = -82$ cm^{-1}. The asymmetric mode is split into three bands as a result of complexation; similar splitting is observed in the symmetric NC$_2$ stretching modes.

BCl Modes.—The absorption assigned to ν(BCl), *i.e.*, 922 cm^{-1}, in the spectrum of free $[(CH_3)_2N]_2BCl$ is not present in the frequency range expected for this mode in that of I, *i.e.*, 900–940 cm^{-1}. This vibration must exist because the presence of $[(CH_3)_2N]_2BCl$ in I has been demonstrated by displacement with $(CH_3)_3N$.[1a] However, coupling of ν(BCl) with ν(BN) could result in a lowering of this frequency; therefore it is assigned to the band of medium intensity at 862 cm^{-1}, $\Delta = -60$ cm^{-1}. Indeed, a strong coupling between $\nu(BN_2)$ and ν(BC) in diazoborocyclopentane, $(CH_2NH)_2BCH_3$, has been reported to result in a relatively high BN$_2$ stretching frequency and a relatively low BC stretching frequency.[4] This BC stretching mode is found at 858 cm^{-1}, *i.e.*, much below the frequency range characteristic of ν(BC), *i.e.*, 1100–1200 cm^{-1}.[5]

In summary, the ligand vibrational spectrum of I is consistent with a covalent formulation involving both dimethylamino moieties of $[(CH_3)_2N]_2BCl$ complexed to titanium.

TiCl Modes.—The far-infrared spectrum of I, Figure 3, contains bands at 383 (vvs), 322 (s), 276 (vs), and 260 (m, sh) cm^{-1}. These absorptions occur in the region in which TiCl stretching modes are generally observed.[6] Metal–chlorine bending modes are generally found below 200 cm^{-1} (see ref *k*, Table II) and thus occur below the energy range of the instrument, 250 cm^{-1}. Assignment of bands in this low-energy

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(5) J. W. Dawson, P. Fritz, and K. Niedenzu, *J. Organometal. Chem.*, **5**, 13 (1966).

(6) R. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

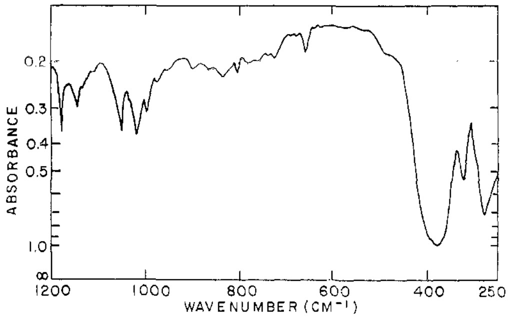

Figure 3.—Far-infrared spectrum of $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ (mull).

region is a formidable task because absorptions due to ligand modes (CNC bending), *e.g.*, 385 (wm) and 363 cm^{-1} (wm) for $B_2[N(CH_3)_2]_4$[7] and $B[N(CH_3)_2]_3$,[8] respectively, and to ν(Ti–N) (240–250 cm^{-1})[9] modes which are also present in addition to TiCl modes. However, the high frequency and intensity of the 383-cm^{-1} band in the spectrum of I preclude its assignment to CNC bending and it is assigned to ν_{as}(TiCl). The less intense absorptions at lower energy may result from CNC bending and Ti–N modes.

In order to provide a basis for further discussion of the low-energy absorptions in the spectrum of I, a brief survey of the far-infrared spectra of titanium trichloride complexes, including their interpretation and significance, is appropriate. Clark has studied the far-infrared spectra of several titanium trichloride complexes and the dependence of the TiCl stretching frequency on coordination number and oxidation state (see ref *k*, Table II). In general ν_{as}(TiCl) decreases with increasing coordination number and decreasing oxidation state of the metal. The lowering of ν_{as}(MCl) with increasing coordination number for Ti(IV) complexes is easily seen from inspection of the data contained in Table II, *e.g.*, $TiCl_4$ (506 cm^{-1}), $TiCl_4 \cdot N(CH_3)_3$ (456 cm^{-1}), $[(CH_3)_4N]_2TiCl_6$ (324 cm^{-1}), and $TiCl_4 \cdot 2B$ [B = *o*-phenylenebis(dimethylarsine)] (317 cm^{-1}). The increase in coordination number of the metal results in an increase in the TiCl bond length, *e.g.*, 2.18 Å in $TiCl_4$ (four-coordinate), 2.34 Å in $TiCl_4 \cdot 2$(ligand) (six-coordinate), and 2.44 Å in $TiCl_4 \cdot 2B$ (eight-coordinate); therefore, the lowering of ν_{as}(TiCl) results from a decrease in TiCl bond order with increasing coordination lumber.

Because $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ contains Ti(III), the frequency of the TiCl modes must be compared to those for other titanium trichloride complexes, *i.e.*, at lower energy than analogous Ti(IV) derivatives. The infrared spectrum of the five-coordinate complex $TiCl_3 \cdot [N(CH_3)_3]_2$ contains a band at 387 cm^{-1} assigned to ν_{as}(TiCl), while the same modes for six-coordinate complexes are generally found *ca.* 22 cm^{-1} to lower energy, *i.e.*, 360 and 365 cm^{-1} in the spectrum of $TiCl_3 \cdot 3THF$ and $TiCl_3 \cdot 3CH_3CN$, respectively; see Table II. The band at 383 cm^{-1}, assigned to ν_{as}(TiCl), in the spectrum of I is indicative of five-coordinate Ti(III) moieties in I.

It is most difficult to assign the remaining absorptions in the 250–350 cm^{-1} interval in an unambiguous manner because ligand CNC bending and Ti–Ti stretching modes may occur in this interval. However, the band at 322 (s) cm^{-1} in the spectrum of I is similar to the bands observed in the interval 323–346 cm^{-1} for other five-coordinate complexes; see Table II. This band most likely results from ν_s(TiCl) stretching; however, assignment of this absorption to CNC bending is also consistent with its observed intensity and frequency. The absorption at 276 cm^{-1} in the spectrum of I is close to the frequency expected for ν(Ti–Cl–Ti); *i.e.*, bridge frequency is found at 289 cm^{-1} in α-$TiCl_3$ (ref *k*, Table II). However, the infrared spectra of other five-coordinate titanium trichloride complexes also contain bands of medium intensity in the interval 254–290 cm^{-1}. This band in the spectrum of I is tentatively assigned to ν_s(TiCl); this assignment is based mainly on its relatively low frequency and intensity with respect to that of the 383-cm^{-1} bands, assigned to ν_{as} (TiCl), while the shoulder of medium intensity at 260 cm^{-1} is tentatively assigned to ν(Ti–N).

In conclusion, the far-infrared spectrum of I is interpreted to indicate a structure which contains five-coordinate Ti(III) moieties. This conclusion is based on the occurrence of ν_{as}(TiCl) in the region expected for five-coordinate titanium trichloride complexes, *i.e.*, close to 490 cm^{-1}, and on the similarity of its spectrum to those of other five-coordinate Ti(III) complexes.

Electronic Absorption Spectrum of $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$.—The electronic absorption spectrum of I, Figure 4, contains well-defined bands at 27.59, 37.65, and 44.45 kK. In order to ascertain if the frequency and intensity of these transitions could be related to structural aspects of the complexes, a survey of the charge-transfer spectra of titanium(III) and -(IV) complexes was made; see Table V. The intensities of these absorptions do not appear to be informative as to structure; however, an empirical correlation appears to exist between the frequency of the lowest energy charge-transfer band and the coordination number of the metal; *i.e.*, the frequency of the charge-transfer band shifts progressively to lower energy as the coordination number of the metal is increased. The following empirical facts summarize the relationship between the energy of the first charge-transfer bond and coordination number for titanium compounds containing Cl and N ligands: coordination number 4, $>\sim 35$ kK; coordination number 5, ~ 25–34 kK; coordination number 6, ~ 19–24 kK. Based on the relationship between coordination number and the energy of the first charge-transfer band, the electronic absorption spectrum of $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ (first band at 27.59 kK) is considered to suggest five-coordinate Ti. Recall that a similar conclusion was reached based on correlations of ν(TiCl) infrared frequencies with

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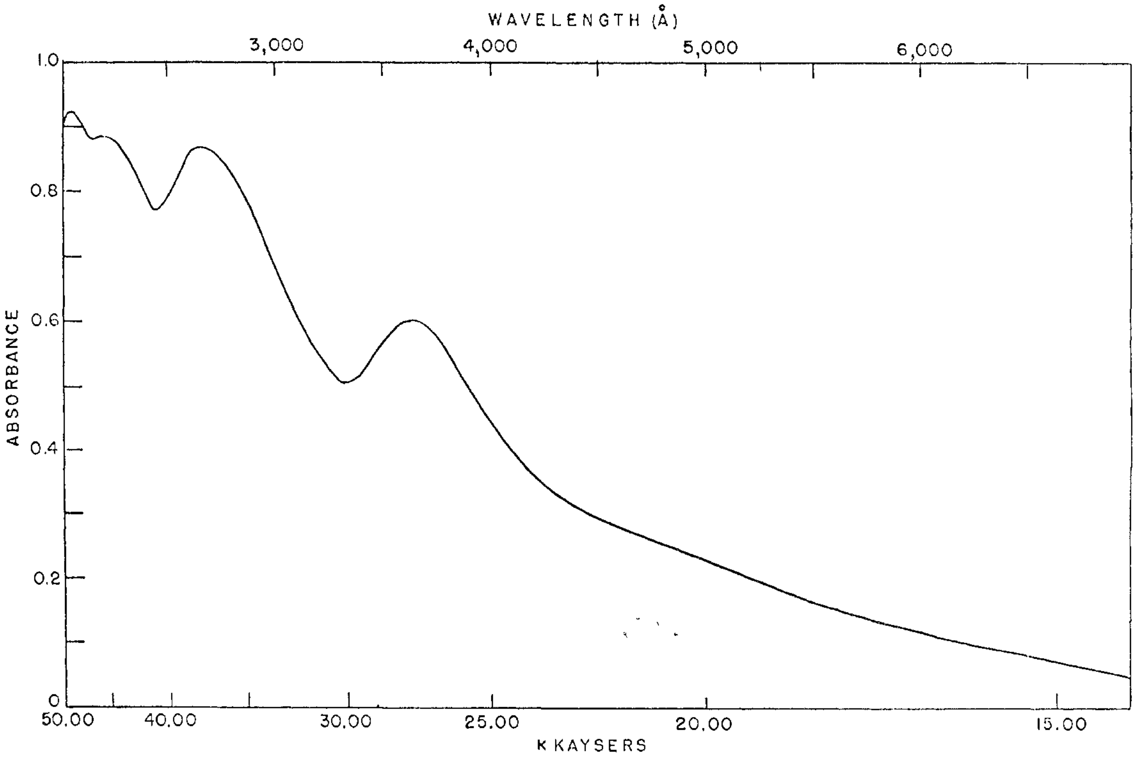

Figure 4.—Electronic absorption spectrum of $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$.

Table V

Charge-Transfer Spectral Data for Some Selected Titanium(III) and -(IV) Complexes—A Possible Criterion for Coordination Numbers

Complex	Phase	CN	Ref	Freq, kK[a]	Ref
$TiCl_4$	Gas	4	*b, c*	35.65, 43.15	*b*
$TiCl_4 \cdot N(CH_3)_3$	Solid	5	*d*	30.22, 46.05	*e*
$TiCl_3 \cdot 2N(CH_3)_3$	Solid	5	*f*	30.0, 37.0, 44.9	*g*
K_3TiCl_6	Solid	6	*h*	23.4, 30.0, 34.5, 37.8 sh, *ca.* 43 sh, 48.1	*h*
α-$TiCl_3$	Solid	6	*i*	18.9, 27.5	*j*
β-$TiCl_3$	Solid	6	*i*	24.12, 29.20, 38.20	*k*
γ-$TiCl_3$	Solid	6	*i*	19.00, 27.50	*l*
$TiCl_4 \cdot 2B$[m]	Solid	8	*n*	19.6	*o*

[a] 1 kK = 1000 cm^{-1}. [b] D. S. Alderice, *J. Mol. Spectry.*, **15,** 509 (1965). [c] By electron diffraction: M. Lister and L. E. Sutton, *Trans. Faraday Soc.*, 393 (1965). [d] Vibrational spectroscopy: I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 6559 (1965). [e] Data obtained in this work. [f] By X-ray diffraction—isomorphous to $TiBr_3 \cdot 2N(CN_3)_3$ which has been shown to have a *trans*-trigonal-bipyramidal structure *via* a single-crystal X-ray study: B. J. Russ and J. S. Wood, *Chem. Commun.*, 745 (1966). [g] M. W. Duckworth, G. W. A. Fowles, and P. T. Green, *J. Chem. Soc., A*, 1592 (1967). [h] *Via* infrared spectroscopy: B. J. Brisdon, *Spectrochim. Acta*, **23A,** 1969 (1967). [i] *Via* X-ray diffraction: G. Natta, P. Corradini, and G. Allegra, *J. Polymer Sci.*, **51,** 399 (1961). [j] C. Dijkgraaf and J. P. G. Rousseau, *Spectrochim. Acta*, **23A,** 1267 (1967). [k] R. J. H. Clark, *J. Chem. Soc.*, 417 (1964). [l] C. Dijkgraaf, *Nature*, **201,** 1121 (1964). [m] B = *o*-phenylenebis(dimethylarsine). [n] R. J. H. Clark, *Spectrochim. Acta*, **21,** 955 (1964). [o] R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2460 (1962).

coordination number. Additional data supporting a nonsaturated coordination sphere for Ti have been obtained. $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ reacts rapidly with both CH_3CN and pyridine without displacement of free

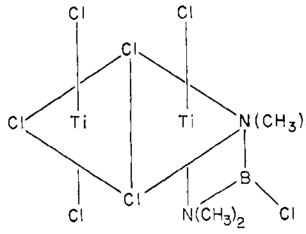

Figure 5.—Proposed structure for $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$.

$[(CH_3)_2N]_2BCl$; furthermore, CH_3CN reacts only very slowly with α-$TiCl_3$ (six-coordinate) to afford $TiCl_3 \cdot 3CH_3CN$; these data are interpreted in terms of I acting as a strong Lewis acid, *i.e.*, coordination number <6.[10]

Proposed Structure for Bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ (I).—The interpretation of the infrared and electronic spectra of I as well as the rapid reactions of I with Lewis bases is suggestive of a coordination number for Ti in I of 5. The proposed structure for I, depicted in Figure 5, consists of two trigonal-bipyramidal Ti atoms sharing a common edge with bridging Cl atoms. The low magnetic moment of I, *ca.* 0.4 BM per Ti (corrected for TIP) is considered a consequence of a metal–metal bond or superexchange, and the presence of coordinated $[(CH_3)_2N]_2BCl$ has been firmly established. Two other structures have been considered but subsequently discarded: (1) intramolecular bridging of the bis(amino)borane moiety between two Ti centers and (2) intermolecular bridging between two binuclear titanium

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[10] Unpublished work.

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 $\nu(BCl)$ 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.* $I \cdot 0.8[(CH_3)_2N]_2BCl$.

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

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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 $I \cdot 2HCl$, 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 $[(CH_3)_2NH]_2$-

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