respect to the nonbonding monomer orbitals and that the extant $d_{x^2-y^2}$ $\sigma$–$\sigma^*$ splitting is at least 21,000 cm$^{-1}$. The spectral results are consistent with the magnetic properties of the complex in that spin-pairing energies for most systems are on the order of 20,000 cm$^{-1}$.[31] This view of metal–metal bond formation is further supported by the short metal–metal distances found in these complexes.[13,32]

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(31) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 671.

(32) F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, **4**, 1377 (1965).

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# Low-Spin Binuclear Titanium Complexes. I. Preparation and Characterization of Bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$[1a]

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Treatment of titanium tetrachloride, $TiCl_4$, with tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, results in formation of bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$. This latter species exhibits spin equilibrium with the value for the exchange integral, $J$, $\geqslant 378$ cm$^{-1}$. Characterization was effected by analytical analyses, magnetic susceptibility, and reaction with $N(CH_3)_3$ affording $2TiCl_3[N(CH_3)_3]_2$ and $[(CH_3)_2N]_2BCl$.

## Introduction

We have previously reported the preparation of di[bis(dimethylamino)chloroborane]tris[tetrachlorotitanium(IV)], $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$, by treatment of $TiCl_4$ with either $[(CH_3)_2N]_2BCl$ or $B_2[N(CH_3)_2]_4$.[2] In the latter case oxidation of $B_2[N(CH_3)_2]_4$ takes place to afford the coordinated ligand, $[(CH_3)_2N]_2BCl$. We now report the isolation and characterization of the reduction product which contains titanium in the formal oxidation state (III).

## Results and Discussion

**Isolation and Purification of Bis(dimethylamino)chloroboranehexachlorodititanium(VI), $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$.**—Treatment of tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, with a sixfold molar excess of titanium tetrachloride, $TiCl_4$, affords $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$, small amounts of dimethylaminotrichlorotitanium(IV), $(CH_3)_2NTiCl_3$, and a brown solid hereafter referred to as I. I is a microcrystalline material which was purified by repeated washing with $o$-$C_6H_4Cl_2$ and $CH_2Cl_2$ and demonstrated by X-ray powder diffraction to be free from occluded $(CH_3)_2NTiCl_3$, $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$, and the four crystalline modifications of $TiCl_3$; see Table I. Furthermore, the infrared spectrum of I does not contain absorptions at 481 cm$^{-1}$ (vvs) ($\nu_3$(TiCl)) characteristic of $TiCl_4$(l), 579 cm$^{-1}$ (vvs) ($\nu$(TiN)) characteristic of $(CH_3)_2NTiCl_3$, or 1644 (s) and 829 cm$^{-1}$ (vvs) ($\nu_{as}(^{10}BN_2)$ and $\nu_s(NC_2)$), respectively, characteristic of $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$.[2]

**Analytical Characterization of I.**—Hydrolysis of I results in the formation of bluish black $Ti_2O_3$ which is slowly oxidized in basic water to white $TiO_2$ with the evolution of $H_2$. Analytical data for I are summarized in Table II. The analytical recovery of mass was 94.3%, based on the initial sample weight (384.6 mg) and the assumption that the $CH_3$:N mole ratio is 2, *i.e.*, for $N(CH_3)_2$ moieties. The empirical formula for I is $Ti_{2.07}B_{1.00}Cl_{6.94}[N(CH_3)_2]_{1.98}$. The oxidative hydrolysis of I in basic solution is represented by

$$[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6 + 8OH^- \longrightarrow H_2 + 2(CH_3)_2NH + 2TiO_2 + BO_2^- + 7Cl^- + 2H_2O \quad (1)$$

The experimentally determined stoichiometry for the reaction between $B_2[N(CH_3)_2]_4$ and $TiCl_4$, with the idealized reaction coefficients in parentheses, is represented by

$$7.6(7.0)TiCl_4 + 2.0(2.0)B_2[N(CH_3)_2]_4 \longrightarrow 1.9(2.0)[(CH_3)_2]_2BCl\cdot Ti_2Cl_6 + 1.2(1.0)\{[(CH_3)_2]_2BCl\}_2\{TiCl_4\}_3 + 0.2(0)(CH_3)_2NTiCl_3 + 0.1(0)(CH_3)_2NBCl_2 \quad (2)$$

Owing to difficulties incurred during the separation of products and to exchange of groups between boron and titanium, the idealized and experimental reaction coefficients are considered to be in good agreement. An over-all reaction sequence consistent with the stoichiometry is

$$2B_2[N(CH_3)_2]_4 + 4TiCl_4 \longrightarrow 4[(CH_3)_2N]_2BCl + 4TiCl_3 \quad (3)$$

$$2[(CH_3)_2N]_2BCl + 4TiCl_3 \longrightarrow 2[(CH_3)_2]_2BCl\cdot Ti_2Cl_6 \quad (4)$$

$$2[(CH_3)_2N]_2BCl + 3TiCl_4 \longrightarrow \{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3 \quad (5)$$

Equation 3 represents the reduction of $TiCl_4$ to generate $TiCl_3$ and the formation of the ligand which subsequently complexes with $TiCl_4$ (eq 5) and *in situ* $TiCl_3$ (eq 4). Reaction 4 is believed to take place faster

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(1) (a) G. S. Kyker and E. P. Schram, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. INOR 165. (b) Work completed in partial fulfillment of the Ph.D. degree, June 1969. (c) To whom correspondence should be addressed.

(2) G. S. Kyker and E. P. Schram, *J. Am. Chem. Soc.*, **90**, 3672 (1968).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR (1) $[(CH_3)_2N]_2BCl\cdot(TiCl_3)_2$,[a] (2) $(CH_3)_2NTiCl_3$,[a] (3) $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$,[a] (4) $\alpha$-$TiCl_3$,[b] (5) $\beta$-$TiCl_3$,[b] (6) $\gamma$-$TiCl_3$,[b] AND (7) $\delta$-$TiCl_3$,[c]

| d, Å |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| 9.41 vs[d] | 7.93 s | 8.59 s | 5.87 s | 5.43 s | 5.91 m | 5.13 |
| 7.40 vs | 6.76 vs | 7.69 w | 4.98 vw | 2.89 vw | 5.24 w | 2.72 |
| 6.00 vs | 5.77 w | 5.77 vs | 2.95 m | 2.76 m | 4.60 vvw | 2.65 |
| 5.54 s | 5.08 m | 5.32 m | 2.92 m | 2.57 vw | 3.00 vvw | . . . |
| 4.54 vvw | 4.80 m | 4.97 m | 2.72 vs | 2.14 m | 2.94 w | 2.52 |
| 4.27 vvw | 4.36 w | 4.67 s | 2.12 s | 1.97 vw | 2.73 mw | . . . |
| 3.60 w | 3.66 m | 4.15 w | 1.78 s | 1.81 w | 2.52 ms |  |
| 3.31 m | 3.50 vw | 3.95 w | 1.70 w | 1.67 vw | 2.44 vvw |  |
| 2.89 s | 3.17 m | 3.74 w | 1.65 m | 1.52 vw | 2.34 vvw |  |
| 2.73 w | 3.02 m | 3.33 w | 1.52 vw | 1.45 vvw | 2.13 w |  |
| 2.65 w | 2.91 s | 3.03 m | 1.49 m | 1.39 vvw | 1.97 vw |  |
| 2.51 w | 2.79 s | 2.87 m | 1.47 m | 1.16 vvw | 1.78 ms |  |
| 2.41 vvw | 2.72 vw | 2.69 w | 1.37 m | 1.14 vvw | 1.70 w |  |
| 2.29 vvw | 2.65 vw | 3.62 w | 1.21 w | 1.09 vvw | 1.66 vw |  |
| 2.24 w | 2.55 m | 2.56 w | 1.14 w |  | 1.52 vw |  |
| 2.17 vvw | 2.46 vw | 2.45 vvw | 1.13 w |  | 1.48 w |  |
| 2.06 vvw | 2.40 vw | 2.33 vw |  |  | 1.46 vw |  |
| 2.00 w | 2.34 m | 2.16 vw |  |  | 1.26 vw |  |
| 1.92 vvw | 2.29 m | 2.07 vvw |  |  | 1.13 w |  |
| 1.85 w | 2.22 w | 2.04 vvw |  |  |  |  |
| 1.73 vvw | 2.18 m | 2.00 w |  |  |  |  |
|  | 2.08 w | 1.96 w |  |  |  |  |
|  | 1.98 w | 1.88 m |  |  |  |  |
|  | 1.88 w | 1.83 w |  |  |  |  |
|  | 1.83 vvw | 1.79 vvw |  |  |  |  |
|  | 1.77 vvw | 1.73 vvw |  |  |  |  |
|  | 1.74 vw | 1.65 vvw |  |  |  |  |
|  | 1.71 vw | 1.61 w |  |  |  |  |
|  | 1.47 vw | 1.57 w |  |  |  |  |
|  | 1.45 vvw |  |  |  |  |  |

[a] Data for samples prepared in this work. [b] G. Natta, *Atti Accad. Nazl. Lincei., Rend., Classe Sci. Fis. Mat. Nat.*, **24** (2), 1 (1958). [c] G. Natta, P. Corradini, and G. Allegra, *J. Polymer Sci.*, **51,** 399 (1961). [d] Visually estimated intensities: v, very; s, strong; m, medium; w, weak.

TABLE II

ANALYTICAL CHARACTERIZATION OF I, $[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6$

|  | % by wt |  |  |  | Mole ratio $H_2$:compd |
|---|---|---|---|---|---|
|  | Ti | Cl | B | N |  |
| Calcd | 21.60 | 56.00 | 2.44 | 6.32 | 1.00 |
| Found | 21.60 | 56.10 | 2.45 | 6.34 | 0.97 |

than crystallization of $TiCl_3$ because it has been demonstrated the $\alpha$-$TiCl_3$ does *not* react with $[(CH_3)_2N]_2BCl$ to afford I. Based on the method of preparation, it has been assumed that I contained coordinated bis(dimethylamino)chloroborane; however, formulations such as $Cl_3TiB[N(CH_3)_2]_3\cdot TiCl_4$ (involving a Ti–B bond) and $\{[(CH_3)_2N]_2B\}^+\{Ti_2Cl_7\}^-$ are equally consistent with the analytical data.

**Evidence for the Presence of Coordinated $[(CH_3)_2N]_2BCl$ in I. Displacement by $(CH_3)_3N$.**—Equations 6–8 represent the expected reactions for $(CH_3)_3N$ with three possible formulations for I.

$$\{[(CH_3)_2N]_2B\}^+\{Ti_2Cl_7\}^- + (1+n)(CH_3)_3N \longrightarrow \{[(CH_3)_2N]_2BN(CH_3)_3\}^+\{Ti_2Cl_7\cdot nN(CH_3)_3\}^- \quad (6)$$

$$Cl_3TiB[N(CH_3)_2]_2\cdot TiCl_4 + (1+n)(CH_3)_3N \longrightarrow TiCl_4\cdot N(CH_3)_3 + [(CH_3)_2N]_2BTiCl_3\cdot nN(CH_3)_3 \quad (7)$$

$$[(CH_3)_2N]_2BCl\cdot Ti_2Cl_6 + 4(CH_3)_3N \longrightarrow [(CH_3)_2N]_2BCl + 2TiCl_3\cdot[N(CH_3)_3]_2 \quad (8)$$

$$Cl^- + [(CH_3)_2N]_2BN(CH_3)_3^+ \longrightarrow (CH_3)_2BCl + (CH_3)_3N \quad (9)$$

For the reaction represented by eq 6, $(CH_3)_3N$ is expected to attack the electrophilic boronium ion; the possibility of a chloride shift from Ti to B, eq 9, is not considered likely in the presence of excess amine because the amine is a stronger nucleophile than $Cl^-$ toward boron. Equation 7 represents the nucleophilic displacement of $(CH_3)_2N$ moieties by $(CH_3)_3N$; the associated formulation for I should result in the formation of $TiCl_4\cdot N(CH_3)_3$. Finally, if the formulation represented for I in eq 8 is correct, then $[(CH_3)_2N]_2BCl$ and $Cl_3Ti[N(CH_3)_3]_2$ should be formed.

Trimethylamine reacts with I in the interval −15 to 0° to afford $[(CH_3)_2N]_2BCl$, $TiCl_3\cdot[N(CH_3)_3]_2$, and small amounts of unidentified species; data pertaining to this slow heterogeneous reaction are summarized in Table III. The quantity of $(CH_3)_3N$ combined with I varies from 82 to 92% of that calculated for the idealized reaction, eq 8. The amount of $[(CH_3)_2N]_2BCl$ liberated from I varies from 23 to 64%, while the quantity of $Cl_3Ti[N(CH_3)_3]_2$ isolated (reaction 3) is 86% of the calculated. No evidence was found for the presence of yellow $TiCl_4\cdot N(CH_3)_3$ in the nonvolatile reaction residue, green $TiCl_3\cdot[N(CH_3)_3]_2$; this conclusion is based on solid-state infrared and X-ray powder pattern data.

TABLE III

STOICHIOMETRY ASSOCIATED WITH THE REACTION BETWEEN $N(CH_3)_3$ AND I

| Reaction conditions | | | Amt of reactant, in mmol | | | Amt of $N(CH_3)_3$ lost,[b] mmol | Amt of product, mmol | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | Temp, °C | Time, hr | I | $N(CH_3)_3$[a] | $N(CH_3)_3$:Ti | | $[(CH_3)_2N]_2BCl$ | $TiCl_3 \cdot 2[N(CH_3)_3]_2$ | $N(CH_3)_3$:Ti[c] |
| 1 | 0–25 | 0.1 | 0.64 | 10.51 | 16.5 | 2.41 | 0.15 | ... | 1.87 |
| 2 | 0 | 11.0 | 0.73 | 32.50 | 44.6 | 2.40 | 0.47 | ... | 1.65 |
| 3 | 0 | 39.0 | 1.50 | 20.42 | 13.6 | 5.18 | 0.50 | 2.57 | 1.71 |
| 4 | 10 | 50.0 | 1.17 | 18.65 | 16.0 | 4.14 | 0.72 | ... | 1.77 |

[a] Purity 98%; see Experimental Section. [b] Determined from $PVT$ measurements. [c] In the green reaction residue.

Because $(CH_3)_3N$ will reduce $TiCl_4$ at 25° to afford $Cl_3Ti \cdot [N(CH_3)_2]_2$, it was necessary to demonstrate that a similar reduction did not take place with I. Treatment of $TiCl_4$ with excess $(CH_3)_3N$ at 0° for 144 hr and subsequent removal of the unreacted amine at −45°, *in vacuo*, affords yellow $TiCl_4 \cdot N(CH_3)_3$. Also, no green color was observed which is characteristic of $Cl_3Ti \cdot [N(CH_3)_3]_2$.

In summary, the displacement of $[(CH_3)_2N]_2BCl$ and formation of $Cl_3Ti \cdot [N(CH_3)_3]_2$ by treatment of I with $N(CH_3)_3$ provides strong evidence for the covalent formulation $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$. This formulation suggests I is paramagnetic; therefore the magnetic susceptibility of I was investigated.

**Magnetochemistry of I.**—The magnetic susceptibility of I as a function of temperature and field strength is summarized in Table IV and graphically represented as a function of temperature in Figure 1. The magnetic moment, $\mu_{eff}$, for I as a function of temperature is shown in Figure 2. The reported values for $\mu_{eff}$ are per two Ti and are not corrected for TIP. For example, at 133°K, if one assumes a TIP of $100 \times 10^{-6}$ cgsu per Ti, the moment per Ti is 0.40 BM.

TABLE IV

THE DEPENDENCE OF THE MAGNETIC SUSCEPTIBILITY AND MOMENT OF I ON TEMPERATURE AND FIELD STRENGTH

| Temp, °K | 3.6[b] | 5.4 | 7.1 | 8.4 | 9.0 | $10^6\chi_M$(av), cgsu | $10^6\chi_M^{cor}$(av),[c] cgsu | $\mu_{eff}$,[d] BM (per 2 Ti(III)) |
|---|---|---|---|---|---|---|---|---|
| | $10^6\chi_M$,[a] cgsu | | | | | | | |
| 96.8 | 364 | 310 | 410[e] | 345 | 340 | 340 | 543 | 0.65 |
| 97.2 | ... | ... | 419[e] | 343 | 331 | 337 | 540 | 0.65 |
| 108.7 | ... | ... | 348 | 296 | 310 | 318 | 521 | 0.68 |
| 111.0 | ... | ... | 322 | 302 | 312 | 312 | 515 | 0.68 |
| 112.2 | ... | ... | 318 | 296 | 319 | 311 | 514 | 0.70 |
| 114.9 | ... | ... | 327 | 334 | 300 | 320 | 523 | 0.70 |
| 116.0 | ... | ... | 314 | 331 | 310 | 318 | 521 | 0.69 |
| 118.7 | ... | ... | 280 | 302 | 305 | 296 | 499 | 0.71 |
| 121.7 | ... | ... | 293 | 348 | 298 | 313 | 516 | 0.73 |
| 131.7 | ... | ... | 300 | 305 | 304 | 303 | 506 | 0.75 |
| 133.0 | 318 | 316 | 313 | 307 | 296 | 310 | 513 | 0.74 |
| 135.4 | ... | ... | 305 | 302 | 293 | 300 | 503 | 0.81 |
| 153.7 | 283 | 378 | 321 | 336 | 315 | 324 | 527 | 0.83 |
| 163.7 | ... | ... | 304 | 339 | 325 | 323 | 526 | 0.92 |
| 190.2 | ... | ... | 345 | 377 | 332 | 351 | 554 | 0.96 |
| 209.5 | ... | ... | 348 | 341 | 347 | 345 | 548 | 1.01 |
| 231.2 | ... | ... | 319 | 362 | 347 | 343 | 546 | 1.08 |
| 255.2 | ... | 349 | 350 | 373 | 373 | 361 | 564 | 1.14 |
| 278.2 | ... | ... | 387 | 379 | 375 | 380 | 583 | 1.20 |
| 294.7 | ... | ... | 396 | 408 | 390 | 398 | 601 | 1.20 |
| 295.2 | ... | ... | 404 | 403 | 386 | 398 | 601 | 1.21 |
| 297.2 | 437 | 416 | 390 | 411 | 384 | 408 | 611 | 1.25 |
| 309.2 | ... | ... | 423 | 437 | 411 | 425 | 627 | 1.31 |
| 331.7 | ... | ... | 444 | 450 | 421 | 438 | 641 | 1.33 |
| 341.7 | ... | ... | 451 | 444 | 420 | 438 | 641 | 1.33 |

[a] Standard deviations, $\sigma$ (95% confidence level), for $\chi_M$ at 97.2, 121.7, and 294.7°K are ±15, ±12, and ±10 cgsu, respectively. [b] Field strength $\times 10^3$ (oersteds). [c] $\chi_M^{ligand} = 203 \times 10^{-6}$ cgsu (obtained by summing Pascals constants). [d] Not corrected for TIP. [e] Value rejected.

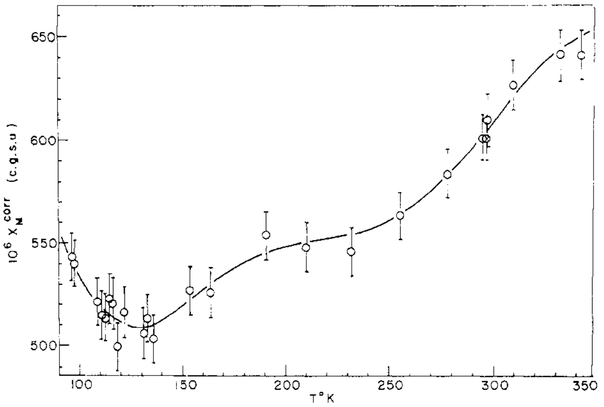

Figure 1.—Molar magnetic susceptibility of $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ as a function of temperature.

The magnetic susceptibility of I is independent of field strength (within experimental error) in the temperature interval 97–342°K and is non-Curie–Weiss in behavior. These data are interpreted in terms of a localized intramolecular exchange interaction between Ti(III) moieties associated with $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$. This antiferromagnetic behavior results in formation of singlet and triplet spin states in thermal equilibrium. For such a system the exchange integral $J$ can be calculated from the equation derived for $^1L \rightleftharpoons {}^3L$ models, *e.g.*, $Cu_2(CH_3CO_2)_2 \cdot 2H_2O$[3] and $[(\pi\text{-}C_5H_5)_2TiCl]_2$:[4] $\chi_M = (0.5/T)[1 + {}^1/_3 \exp(J/kT)]^{-1}$, where $T$ is the temperature in degrees Kelvin, $k$ is the Boltzmann constant, and $J$ is the exchange integral (cm$^{-1}$). The temperature of maximum susceptibility, $T$, is replaced by $T_c$ (Néel temperature) and $d\chi_M/dt = 0$. Solving the resulting equation for $T_c$ affords $J = -1.6kT_c$; thus, the exchange integral $J$ may be evaluated providing $T_c$ is known. Unfortunately the decomposition of I at $T > 350$°K precludes susceptibility measurements which would define the Néel temperature. However, if one assumes that the Néel temperature for I is $\gtrsim 350$°, then $J \gtrsim 378$ cm$^{-1}$ which indicates relatively strong metal–metal interaction. For comparison, the exchange integrals and magnetic moments of several low-spin Ti and Cu species are summarized in Table V. The magnitude of the exchange integral can, to a limited extent, be correlated with the mechanism by which exchange occurs. Molecular orbital calculations on $[(\pi\text{-}C_5H_5)_2TiCl]_2$, assuming metal–metal bond-

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(3) B. C. Guha, *Proc. Roy. Soc.* (London), **A206**, 353 (1951).
(4) R. L. Martin and G. Winter, *J. Chem. Soc.*, 4709 (1965).

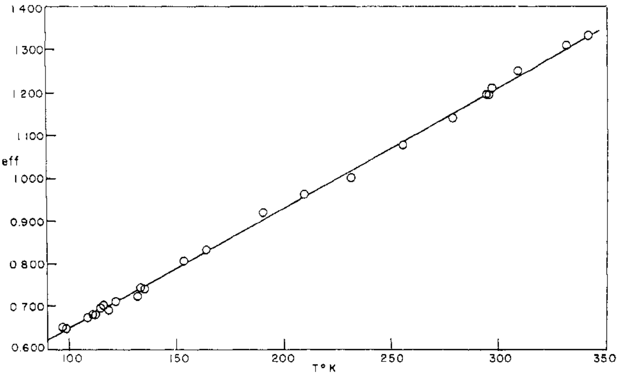

Figure 2.—Magnetic moment of $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ as a function of temperature.

TABLE V
VALUES FOR THE EXCHANGE INTEGRAL $J$ FOR COMPOUNDS OF TITANIUM(III) AND COPPER(II)

| Compound | $T_c$, °K | $J$, cm$^{-1}$ | $\mu_{eff}$,[a] BM | $T$, °K | Ref |
|---|---|---|---|---|---|
| $Cu_2(C_3H_7CO_2)_4(C_6H_5NH_2)_2$ | 107 | 119 | 1.73 | 305.5 | *b* |
| $[(\pi\text{-}C_5H_5)_2TiCl]_2$ | 170 | 192 | 1.32 | 296 | *c, d* |
| $Cu_2(CH_3CO_2)_4(H_2O)_2$ | 255 | 284 | 1.42 | 300.3 | *e* |
| $\alpha$-$TiCl_3$ | 265 | 294 | 1.31 | 308.6 | *f* |
| $Cu_2(C_3H_7CO_2)_4(C_5H_5N)_2$ | 295 | 325 | 1.37 | 300.6 | *b* |
| $TiCl_3 \cdot 2THT$[k] | *Ca.* 320 | 355 | 1.12 | 293.2 | *g* |
| $TiCl_3 \cdot 2S(CH_3)_2$ | *Ca.* 320 | 355 | 1.05 | 293.1 | *g* |
| $Cu_2(HCO_2)_4(C_5H_5N)_2$ | 495 | 550 | 0.63 | 314 | *h* |
| $Cu_2(dpt)_4$[l] | ... | >1000 | ... | ... | *i* |
| $[(CH_2)_2N]_2BCl \cdot Ti_2Cl_6$ (I) | 340 | 378 | 1.25 | 297 | *j* |

[a] Magnetic moment per formula weight. [b] E. Kokot and R. L. Martin, *Inorg. Chem.*, **3,** 1306 (1964). [c] R. L. Martin and G. Winter, *J. Chem. Soc.*, 4709 (1965). [d] D. F. Evans, *ibid.*, 2003 (1959). [e] B. N. Figgis, and R. L. Martin, *ibid.*, 3838 (1956). [f] J. Lewis, D. J. Machin, I. E. Newman, and R. S. Nyholm, *ibid.*, 2036 (1962). [g] W. A. Fowles, T. E. Lester, and R. A. Walton, *ibid.*, *A*, 198 (1968). [h] R. L. Martin and H. Waterman, *ibid.*, 2960 (1959). [i] C. M. Harris, B. F. Hoskins, and R. L. Martin, *ibid.*, 3728 (1959). [j] This work. [k] THT = tetrahydrothiophene. [l] dpt = 1,3-diphenyltriazene.

ing, indicate $J$ should be several thousand reciprocal centimeters.[4] This high value for $J$ requires $[(\pi\text{-}C_5H_5)_2TiCl]_2$ to be diamagnetic which is in disagreement with experimental fact. However, inclusion of multicentered orbitals, constructed from Cl and Ti orbitals, results in lowering $J$ to a few hundred reciprocal centimeters. The exchange is thought to occur through multicentered bonding, localized superexchange, or a mixture of the two.[4] In Cu(II) complexes such as $Cu_2(CH_3CO_2)_4 \cdot 2H_2O$, the relatively high value of $J$ (284 cm$^{-1}$) is thought to result from significant metal–metal bonding.[5]

The exchange integral for $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$ is greater than 378 cm$^{-1}$; this relatively high value for $J$ is consistent with direct Ti–Ti interactions. The antiferromagnetic properties of I as well as the lack of d–d transitions in the electronic absorption spectrum are both consistent with a high population of the singlet state.[6] The apparent minimum in the magnetic susceptibility curve of I may be associated with: (1) the presence of a small amount of a paramagnetic impurity; (2) a phase change at *ca.* 130°K; or (3) the presence of ferromagnetic coupling in the lattice. The most likely paramagnetic impurities in I are $\alpha$-, $\beta$-, $\gamma$-, and $\delta$-$TiCl_3$. None of these species was present as determined by X-ray studies. However, the 97–130°K temperature interval of the $\chi_M^{cor}$ *vs.* $T$°K plot exhibits normal Curie behavior; *i.e.*, $\chi_M^{cor}$ decreases with increasing temperature in a hyperbolical manner. The presence of a small amount of an unidentified paramagnetic material in I would account for this section of the curve. Ferromagnetic coupling in the lattice of I most likely is not the cause of the minimum because the susceptibility exhibited no field dependence at temperatures below or above this minimum. A transformation from a paramagnetic to an antiferromagnetic phase at *ca.* 130° could account for this minimum; *i.e.*, the overlap of the curve of the paramagnetic phase ($\chi_M$ decreases with $T$°K) with that of the antiferromagnetic phase ($\chi_M$ increases with $T$°K) would result in a minimum. The susceptibility measurements above and below the minimum, at *ca.* 130°K, were reproducible on raising and lowering the temperature of the samples; therefore, if a phase change takes place, it must be reversible. Indeed, phase transformations appear to be quite common for Ti(III) compounds; *e.g.*, $TiCl_3$ exists in four crystalline modifications,[7,8] and $Ti_2O_5$ is dimorphic with a rapid reversible phase transformation occurring at *ca.* 390°K.[9] Also, the susceptibility of $[(\pi\text{-}C_5H_5)_2TiCl]_2$ exhibits undue scattering in the vicinity of the maximum centered at 170°K; this scattering is thought to reflect a minor phase change.[4]

## Experimental Section

**Apparatus and Procedures.**—Many of the reagents used in this investigation react with water and/or oxygen; therefore all manipulations were carried out in a dry inert atmosphere inside a glove box or in a vacuum line. A glove box, obtained from Kewaunee Scientific Equipment, Adrian, Mich., was used for most routine manipulations where exposure times of the sample to the atmosphere were short, *i.e.*, in transferring nonvolatile samples from storage containers into reaction vessels. This glove box was continually purged with nitrogen (minimum purity 99.996+% by volume), obtained from Liquid Carbonic. This gas was dried by passage through two drying tubes containing Linde Molecular Sieve (5A) and phosphorus pentoxide. A Dri-Lab glove box, obtained from Vacuum-Atmosphere Corp., Los Angeles, Calif. (Model No. HE-43-2), and equipped with a Dri-Train (Model No. HE-373BIN), was used when prolonged exposure of extremely moisture- and/or oxygen-sensitive samples was necessary, *i.e.*, in grinding samples for bulk magnetic susceptibility measurements and in mounting of single crystals for X-ray diffraction studies.

Volatile reagents which did not react with mercury or stopcock lubricant were manipulated in a standard vacuum line. All ground-glass surfaces, unless stated therwise, were lubricated with Apiezon N grease; spherical joints were sealed with Kel-F-200 wax. Because titanium tetrachloride vigorously attacks mercury and Apiezon N lubricant, this reagent was handled in a mercury-free vacuum system. The components of this system were connected by 18/9 spherical joints and "quick-opening threaded glass valves" (4.0-mm bore with Teflon stems) here-

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(5) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(6) G. S. Kyker and E. P. Schram, *Inorg. Chem.*, **8,** 2313 (1969).

(7) W. Klemm, E. Holze, and W. Basuldo, General Papers, 16th International Congress on Pure and Applied Chemistry, Paris, 1957, p 43.

(8) G. Natta, P. Corradini, and G. Allegra, *J. Polymer Sci.*, **51,** 399 (1961).

(9) S. C. Abrahams, *Phys. Rev.*, **130,** 2230 (1963).

after referred to as Teflon stopcocks, which were obtained from the Fisher and Porter Co., Warminster, Pa. This greaseless mercury-free vacuum system was sealed to the standard line and both vacuum systems operated at a low pressure of $10^{-7}$ Torr as determined periodically by use of a McLeod gauge.

Nonvolatile samples were weighed in sealed vials under a dry nitrogen atmosphere. Volatile samples were distilled into a weighing vial which had been previously evacuated and weighed. This vial was comprised of a sample reservoir, a Teflon stopcock, and an O-ring joint for connection to the inlets of the lower manifold. Volatile materials were expanded in calibrated sections of the vacuum line; the moles of volatile compounds were then calculated from $PVT$ measurements, assuming ideal gas behavior. Solid samples were recrystallized and filtered in a vacuum filtration apparatus. **X-Ray powder diffraction patterns** were obtained by irradiating samples hermetically sealed in 0.5-mm Lindemann glass capillaries with nickel-filtered copper K$\alpha$ radiation. **Infrared** solid samples were ground with Fluorolube (previously dried over Molecular Sieve Type 4A) for studies in the region 4000–1350 cm$^{-1}$ and with Nujol (previously dried over sodium) for studies in the region 1350–400 cm$^{-1}$ and were subsequently contained between potassium bromide disks. These mulls were then enclosed in a holder which was fitted with Teflon gaskets to provide a dry inert atmosphere around the edges of the mull and to prevent reaction with the atmosphere during special measurements. Infrared spectra of neat liquids were obtained in a similar manner. Spectra of volatile compounds in the region 4000–400 cm$^{-1}$ were obtained on samples contained in a gas cell of 10-cm path length. This cell was equipped with potassium bromide optics, a Teflon stopcock (4.0-mm bore) and an O-ring joint for attachment to the vacuum line. A Perkin-Elmer Model 337 grating infrared spectrophotometer was used for all measurements. Infrared spectra were calibrated by reference to the 1601.4- and 906.7-cm$^{-1}$ absorptions of a polystyrene film (0.05-mm thickness). **Magnetic susceptibility measurements** were made by the Gouy method. Pyrex Gouy tubes (5.0 cm × 0.5-cm o.d.) were fitted with 10/30 ground-glass joints. These tubes were calibrated with $Hg[Co(NCS)_4]$ according to the method of Figgis and Nyholm.[10] The tube constants $\beta$ were calculated from

$$\beta = [4981 \times 10^{-6}/(T + 10)^\circ\mathrm{K}][w/F']$$

where $w$ is the specimen weight in grams and $F'$ is the force (corrected for diamagnetism of the tube) exerted on the specimen. The magnetic susceptibility per gram of compound, $\chi_g$, was calculated from

$$10^6\chi_g = \frac{\alpha + \beta F'}{w}$$

where $\alpha$ is a constant allowing for displacement of air and is equal to 0.029 times the specimen volume. This constant could be omitted in these calculations since the Gouy tubes were filled with dry nitrogen during calibration. The tube constant $\beta$ was determined at each temperature and field strength, in the manner previously described using the standard $Hg[Co(NCS)_4]$. The force exerted on the specimen $F'$ is equal to $(F - \delta)$ where $F$ is the observed force and $\delta$ is the diamagnetic correction of the tube. The term $w$ is the weight of the specimen in grams. The molar magnetic susceptibility, $\chi_M$, was calculated from the equation $\chi_M = \chi_g(\text{mol wt})$. The corrected molar magnetic susceptibility, $\chi_M{}^{cor}$, is obtained by adding the Pascal's constants of the ligands to $\chi_M$. Magnetic moments (units of Bohr magnetons) of I per Ti were calculated from the equation which is derived as follows

$$\chi_M{}^{cor} = \chi_M{}^{cor}{}_{Ti(1)} + \chi_M{}^{cor}{}_{Ti(2)}$$

$$\chi_M{}^{cor} = N\mu_{eff}{}^2/3kT$$

$$\chi_{M_{Ti(1)}} = \chi_{M_{Ti(2)}}$$

$$\chi_M{}^{cor} = (N/3kT)(2\mu_{eff})^2$$

$$\mu_{eff/Ti} = (3k/N)^{1/2}(2^{-1/2})(\chi_M{}^{cor}T)^{1/2}$$

$$\mu_{eff/Ti} = 2.84(2^{-1/2})(\chi_M{}^{cor}T)^{1/2}$$

The variable-temperature Gouy balance consisted of a Varian magnet, Model 4004, equipped with a power supply (V-2300-A) and a current regulator (V-2301-A). The 4-in. magnet pole pieces were tapered to 2-in. pole faces. Magnet currents of 1.5, 2.0, 3.1, and 3.6 A were reported to produce fields of 3.5, 5.4, 7.1, 8.4, and 9.0 kG, respectively. The samples were suspended within a cryostat which could be centered between the pole faces of the magnet. The top of the cryostat was attached *via* an O-ring joint to the glove box which encloses the balance. The entire system was flushed with dry nitrogen during measurements. Force measurements were made with a Sartorius Standard Selecta Model Automatic balance equipped with below-the-pan suspension and recorder attachment. The projection scale can be read to *ca.* 0.02 mg. The precision for this balance is ±0.062 mg in the mass range 1–30 g. The accuracy claimed for this balance is ±0.05 mg. Temperatures in the intervals 90–220, 220–290, and 290–340°K were maintained by use of liquid nitrogen, a Dry Ice–2-propanol slush bath, and water, respectively, in connection with an electric heating element contained in the cryostat. Temperature measurements were made with a platinum resistance thermometer.

**Reagents.**—Unless otherwise stated cylinder gases were obtained from the Matheson Co., Inc., Joliet, Ill. All solvents were rigorously dried over calcium hydride unless specified otherwise. All reagents were manipulated by standard procedures inside a drybox or vacuum line. ***o*-Dichlorobenzene** (Analyzed Reagent, bp 179.2–180.2°) was obtained from J. T. Baker Chemical Co., Phillipsburg, N. J., and used without further purification. The 20° vapor tension of the dry solvent was 1.0 Torr. **Dichloromethane**, obtained from Matheson Coleman and Bell, was distilled through a trap maintained at −63° into one at −126°. The 0° vapor tension of the −126° condensate was 137.0 Torr at 0°. **Tetrakis(dimethylamino)diborane(4)**, obtained from the U. S. Borax Research Corp., Anaheim, Calif., was distilled utilizing a Nester–Faust spinning-band column. The colorless distillate had a constant boiling point of 69° at 3.5 Torr. **Titanium tetrachloride** (purity of 99.9+% by weight), obtained from Dr. G. Macwood, The Ohio State University, was used without further purification. **Titanium trichloride** (H-127-351, $\alpha$ modification), obtained from Stauffer Chemical Co., Weston, Mich., was freed of small amounts of titanium tetrachloride by heating *in vacuo*. A sample of this solid was analyzed. *Anal.* Calcd for $TiCl_3$: Cl, 74.0; $H_2$ evolution in basic solution, 0.50 mmol/mol of $TiCl_3$. Found: Cl, 74.8; $H_2$ evolution in basic solution, 0.48 mmol/mol of $TiCl_3$. An X-ray powder pattern of a sample of this solid was identical with that reported for $\alpha$-$TiCl_3$. **Trimethylamine** was stirred with excess phosphorus pentoxide for 7 days at 25° to remove water and species containing labile hydrogen. The volatile liquid was fractionated through traps maintained at −78, −126, and −196°. The −126° condensate was identified as $(CH_3)_3N$ by its −78 and 0° vapor tensions of 7.0 and 683.0 Torr. This sample of trimethylamine was shown to contain *ca.* 2% dimethylamine by gas–liquid partition chromatography.

**Analytical Methods.**—Samples were sealed in precalibrated hydrolysis flasks equipped with break-seals. Sulfuric acid (25% aqueous solution) was contained above the break-seal and degassed *in vacuo*. The sample was then maintained at −196° and the Pyrex break-seal was shattered by lowering a magnet hermetically sealed inside 4-mm o.d. Pyrex tubing. Noncondensable gas, if evolved, was pumped into a calibrated Toepler system and the amount of gas was determined by $PVT$ measurements. Hydrogen was identified by combustion to water over copper oxide at 300°. The hydrolysis solution was then washed into a volumetric flask; aliquots of this solution were subse-

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(10) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

quently removed and analyzed for boron, nitrogen, chloride ion, and titanium content as previously described.[2]

**Syntheses and Characterizations of Bis(dimethylamino)-chloroboranehexachlorodititanium(VI).**—(1) Tetrakis(dimethylamino)diborane(4) (4.0 ml, 17.22 mmol) and *o*-dichlorobenzene (30 ml) were syringed into a 100-ml flask which was subsequently attached to the lower manifold of a mercury-free vacuum system. The reagents were maintained at 0° while all noncondensable gas, $N_2$, was pumped from the apparatus. Titanium tetrachloride (11.25 ml, 102.3 mmol) was distilled into the flask as well as dichloromethane (20 ml). Addition of the $CH_2Cl_2$–$TiCl_4$ solution to the *o*-$C_6H_4Cl_2$–$B_2[N(CH_3)_2]_4$ solution was accomplished by maintaining the flask at −95°. Vigorous stirring was effected by means of a Teflon-coated magnet which was driven by a magnetic field maintained outside the reaction vessel. A green coloration formed as the reagents were mixed at −95°. The reaction mixture was maintained at 0° and vigorously stirred for 12 hr during which time a tan solid precipitated from a dark red solution. Filtration of this solution, *in vacuo*, resulted in separation of a light brown solid from the dark red solution. This brown solid was transferred to another filtration apparatus and washed with a 50:50 solution by volume of $CH_2Cl_2$ and *o*-$C_6H_4Cl_2$ until the filtrate was colorless and then ground into a fine powder and alternately washed with *o*-$C_6H_5Cl_2$ and $CH_2Cl_2$ in a vacuum extraction apparatus until the washings were colorless. Finally the brown solid was dried for 24 hr at 25° *in vacuo*. Concerning the dark red filtrate, yellow needlelike crystals slowly formed over a span of 7 days at 25°. Filtration of this solution resulted in the retention of a yellow solid on a frit and the passage of a reddish brown filtrate into the adjacent flask. This yellow solid was dried *in vacuo* for 1 day at 20° and subsequently identified as $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ by its solid-state infrared spectrum.[11]

Distillation of all materials volatile at 25° from the filtrate afforded a nonvolatile greenish brown solid. An investigation of this residue by solid-state infrared spectroscopy revealed the presence of $(CH_3)_2NTiCl_3$ (*ca.* 90% by mass), $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ (*ca.* 3%), and $[(CH_3)_2NBCl_2]_2$ (*ca.* 7%). The volatile mixture was distilled through a series of traps maintained at −23° (*o*-$C_6H_4Cl_2$ condensed and subsequently identified by its 20° vapor tension of 1.0 Torr), −63° (unreacted $TiCl_4$ collected and later identified by vapor-phase infrared spectroscopy), and −196° ($CH_2Cl_2$ condensed and subsequently identified by its 0° vapor tension of 145.0 Torr and vapor-phase infrared spectroscopy).

**Analytical Characterization of Brown $Ti_2BCl_7[N(CH_3)_2]_2$.**—A sample of this material (988.7 mg) was treated with 25% aqueous sulfuric acid. A violet solution immediately developed; no noncondensable gas was evolved while the solution was stirred at 25° for 24 hr. Treatment of this acid hydrolysis solution with 25% aqueous NaOH (previously degassed) resulted in the formation of a blue-black precipitate and evolution of $H_2$. The blue-black solid slowly converted to a white solid over a span of 7 days; $H_2$ slowly evolved. Concentrated sulfuric acid was cautiously added to the basic solution until all hydrous titanium(IV) oxide went into solution. Aliquots of this hydrolysis solution were subsequently analyzed. *Anal.* Calcd for $Ti_2BCl_7[N(CH_3)_2]_2$: Ti, 21.60; Cl, 56.00; B, 2.44; N, 6.32; mol of $H_2$/mol of compound, 1.00. Found: Ti, 21.00; Cl, 56.90; B, 2.40; N, 6.05; mol of $H_2$/mol of compound, 0.98. The analytical recovery of mass was 96.2% for the 988.7-mg sample, assuming that the $(CH_3)$:N ratio is 2:1, *i.e.*, $-N(CH_3)_2$ groups.

**Magnetic Susceptibility Measurements on $Ti_2BCl_7[N(CH_3)_2]_2$.**—Magnetic susceptibility data for a sample of this material (0.6620 g), obtained at 296.0°K and a field strength of 8 kG, are summarized as follows: $\delta = -0.0021$ g; $F = -0.00009$ g; $\beta = 456.5$; $\chi_M^{cor} = 571.2 \times 10^{-6}$ cgsu.

(2) Titanium tetrachloride (8.5 ml, 77.6 mmol), dissolved in $CH_2Cl_2$ (35 ml), was contained in a 100-ml reaction vessel fitted to a 50-ml tip flask *via* 19/38 ground glass joints. Tetrakis(dimethylamino)diborane(4) (3.0 ml, 12.9 mmol), dissolved in $CH_2Cl_2$ (25 ml) and contained in the tip flask, was slowly added with vigorous stirring to the $TiCl_4$–$CH_2Cl_2$ solution maintained at −78°. The resultant solution underwent the following color changes: black (−78 to −30°) green (−30 to 0°), and brown (after 2 hr at 0°). All materials volatile at 25° were distilled from the reaction vessel; a brown nonvolatile residue remained in the vessel and a red liquid collected in a −196° trap. When the brown solid was maintained at 60° *in vacuo*, a volatile red liquid slowly evolved and was condensed into a trap maintained at −196°. After a period of 48 hr the evolution of volatiles ceased and a brown residue remained in the reaction vessel. This material was washed three times with benzene in a filtration apparatus and subsequently dried *in vacuo* at 25° for 12 hr.

**Analytical Characterization of $Ti_2BCl_7[N(CH_3)_2]_2$.**—Data for a 192.1-mg sample of this solid were collected. *Anal.* Calcd for $Ti_2BCl_7[N(CH_3)_2]_2$: Ti, 21.60; Cl, 56.00; B, 2.44; N, 6.32. Found: Ti, 19.85; Cl, 56.90; B, · · ·; N, 6.02.

(3) The synthesis of the brown solid was accomplished in a manner identical with that described in method 2. All materials volatile in the interval 50–70° were distilled from the brown residue over a span of 3 days. The brown residue was washed with hot *o*-dichlorobenzene (55°) and dried at 25° *in vacuo* for 48 hr.

**Analytical Characterization of $Ti_2BCl_7[N(CH_3)_2]_2$.**—Data for a 405.3-mg sample of this material were collected. *Anal.* Calcd for $Ti_2BCl_7[N(CH_3)_2]_2$: Ti, 21.60; Cl, 56.00; B, 2.44; N, 6.32; mmol of $H_2$/mmol of compound, 1.00. Found: Ti, 23.30; Cl, 55.60; B, 2.16; N, 6.08; mmol of $H_2$/mmol of compound, 1.04. The analytical recovery of mass was 95.2% based on the sample weight of 405.3 mg, assuming the $(CH_3)$:N mole ratio is 2:1. Carbon, hydrogen, and nitrogen analyses were performed by a microcombustion method; samples were briefly exposed to the atmosphere during weighing. *Anal.* Calcd for $Ti_2BCl_7[N(CH_3)_2]_2$: C, 10.81; N, 6.32; H, 2.71. Found: C, 11.60; N, 5.61; H, 2.71.

(4) $Ti_2BCl_7[N(CH_3)_2]_2$ was prepared and purified in a manner identical with that described in method 2; however, the brown residue was maintained at 50° *in vacuo* for 54 hr to remove excess solvent and other volatile contaminants.

**Analytical Characterization of $Ti_2BCl_7[N(CH_3)_2]_2$.**—Data for a 384.6-mg sample were collected. *Anal.* Calcd for $Ti_2BCl_7[N(CH_3)_2]_2$: Ti, 21.60; Cl, 56.00; B, 2.44; N, 6.32; mmol of $H_2$/mmol of compound, 1.00. Found: Ti, 21.60; Cl, 56.10; B, 2.45; N, 6.34; mmol of $H_2$/mmol of compound 0.97. The analytical recovery of mass was 94.3% based on an initial sample weight of 384.6 mg, assuming the $(CH_3)$:N mole ratio is 2.0:1.0. Carbon, hydrogen, and nitrogen analytical data were obtained by a microcombustion technique in which samples were exposed briefly to the atmosphere. *Anal.* Calcd for $Ti_2BCl_7[N(CH_3)_2]_2$: C, 10.81; N, 6.32; H, 2.71. Found: C, 12.00; N, 6.18; H, 5.50. The empirical formula of the brown solid is $Ti_{2.07}B_{1.00}Cl_{6.94}[N(CH_3)_2]_{1.98}$. This compound is hereafter referred to as I.

Magnetic susceptibility data for I are summarized in Table IV.

**Experimentally Determined Stoichiometry for the Reaction between $B_2[N(CH_3)_2]_4$ and $TiCl_4$.**—Titanium tetrachloride (8.6731 g, 45.85 mmol) was added to $B_2[N(CH_3)_2]_4$ (0.8680 g, 4.38 mmol). The reaction conditions were identical with those in (1) above. Titanium tetrachloride and $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ were separated from the reaction mixture as previously described. The $TiCl_4$ contained monomeric $(CH_3)_2NBCl_2$ which slowly precipitated from solution as the nonvolatile dimer. The masses of the dimer and $TiCl_4$ were determined and $TiCl_4$ was distilled from the weighing flask. The remaining mass was dimeric $(CH_3)_2NBCl_2$. Dimethylaminotrichlorotitanium(IV), $(CH_3)_2NTiCl_3$, a green solid, was sublimed from the brown solid at 70°. Also, some of this green solid was extracted from $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ with $CH_2Cl_2$. The masses of unreacted materials and products are summarized: $TiCl_4$, 5.5140 g, 29.10 mmol; $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$, 1.8200 g, 4.10 mmol; $\{[(CH_3)_2N]_2$-

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

$\mathrm{BCl\}_2\{TiCl_4\}_3}$, 2.0670 g, 2.47 mmol; $[(CH_3)_2NBCl_2]_2$, 25.0 mg, 0.10 mmol; $(CH_3)_2NTiCl_3$, 100 mg, 0.50 mmol. The mass of unreacted $TiCl_4$ and products recovered was 99.9% of that of the starting materials.

**Physical Properties of $[(CH_3)_2N]_2BCl\cdot(TiCl_3)_2$ (I).**—I is insoluble at 25° in $n$-$C_5H_{12}$, $CH_2Cl_2$, $[(CH_3)_2N]_2BCl$, $TiCl_4$, and $C_6H_6$ but slightly soluble in $o$-$C_6H_4Cl_2$. I, sealed in a capillary tube under 1 atm of dry nitrogen, decomposes in the interval 150–235° to afford a mixture of brown, black, and purple solids.

**Reaction of I with Trimethylamine, $N(CH_3)_3$.**—The $N(CH_3)_3$ used in the following reactions contained *ca.* 2% $HN(CH_3)_2$ as estimated from gas chromatographic analyses. Because $HN(CH_3)_2$ reacts with B–Cl and Ti–Cl moieties to afford $B-N(CH_3)_2$ and $Ti-N(CH_3)_2$ groups with liberation of HCl, small quantities of $[(CH_3)_2N]_3B$, $(CH_3)_2NH^+Cl^-$, and other unidentified products were formed by this side reaction.

(1) Treatment of I (285.0 mg, 0.64 mmol) with 252 Torr of gaseous $N(CH_3)_3$ (10.51 mmol) at 26° resulted in the formation of a yellow-green solid. This residue was treated with liquid amine until no further loss of reagent took place as confirmed by *PVT* measurements on the unreacted base. All materials volatile at 25° were distilled from the reaction vessel and through a series of traps maintained at −16, −78, and −196°. A white crystalline solid (*ca.* 10 mg) was recovered from the −16° trap. A colorless liquid (0.15 mmol), recovered from the −78° trap, was examined *via* vapor-phase infrared spectroscopy and found to consist of *ca.* 60% $[(CH_3)_2N]_2BCl$ and *ca.* 40% $[(CH_3)_2N]_3B$. A gas chromatogram of the volatile mixture contained two unresolved signals of *ca.* equal area at 5.42 and 5.62 min. Trimethylamine, collected from the −196° trap, was identified by −78 and 0° vapor tensions of 6.8 and 682.0 Torr, respectively, a vapor-phase infrared spectrum, and a gas chromatographic retention time of 3.80 min. The quantity of boron recovered as volatile aminoboranes was 22.8% of the total boron in I. The amount of $N(CH_3)_3$ which reacted with I was 2.41 mmol; the amine:titanium mole ratio in the yellow-green residue was 1.87.

(2) I (665.0 mg, 1.50 mmol), maintained at −196°, was treated with liquid $N(CH_3)_3$ (20.42 mmol). The reactants were slowly warmed; no reaction took place until *ca.* −15° where a yellow-green solid formed. This mixture was maintained at 0° for 39 hr. All materials volatile at 26° were distilled from the reaction vessel to afford a nonvolatile yellow-green residue. The volatile mixture was separated and identified by the methods described in the preceding reaction. The following quantities of components were separated from the volatile mixture: *ca.* 8 mg of white solid; 0.50 mmol of a mixture of *ca.* 70% $[(CH_3)_2N]_2BCl$ and 30% $[(CH_3)_2N]_3B$; 15.24 mmol of $N(CH_3)_3$. The amount of volatile boron-containing species recovered from the reaction mixture represents 30% of the boron contained in I. Trimethylamine (5.18 mmol) reacted with 1.50 mol of I; the amine:titanium mole ratio in the nonvolatile residue was 1.71. Attempts to separate the components of the yellow-green nonvolatile residue by fractional crystallization from $N(CH_3)_3$ were unsuccessful. The solids dissolved to afford a brownish green solution; concentration of this solution resulted in precipitation of a mixture consisting of green, yellow, and brown solids. Treatment of the residue with $C_6H_6$ resulted in the solution of a green solid; a yellow solid precipitated from the solution. Filtration afforded a yellow solid (*ca.* 10 mg) and a brownish green filtrate. This yellow solid was not investigated further. Solvent was distilled from the filtrate to afford a blue-green solid mixed with a small amount of brown solid. Heating this mixture at 35° *in vacuo* for 5 days afforded a blue-green sublimate. This sublimate was identified as $TiCl_3\cdot[N(CH_3)_3]_2$ by infrared spectroscopy [3098 (s), 3006 (vvs), 2990 (vvs), 2960 (m, sh), 2936 (vvs), 2911 (vvs), 2887 (vs, sh), 2855 (vs), 2916 (s), 2794 (s), 2697 (m, sh), 2456 (w), 2217 (vvw), 2044 (vvw), 1967 (vvw), 1517 (w), 1474 (vvs), 1460 (vvs), 1442 (vvs, sh), 1402 (vvs), 1246 (vvs), 1106 (vs), 1038 (w), 990 (vvs), 890 (w), 852 (m, sh), 810 (vvs), 500 (vvs, b), 438 (vvs), 400 (vvs)] and X-ray powder diffraction measurements.[12] The mass of $TiCl_3\cdot[N(CH_3)_3]_2$ recovered from the sublimator was 699.0 mg (2.57 mmol). A brown residue which remained in the reservoir of the sublimator contained B, Ti(III), $Cl^-$, and aminoboranes; $\nu(BN_2)$ was centered at 1528 $cm^{-1}$.

(3) I (516.0 mg, 1.17 mmol), maintained at −196°, was treated with liquid $N(CH_3)_3$ (18.65 mmol). Reaction took place at *ca.* −10° to afford a green solid. The mixture was maintained at −10° for 50 hr; a green solid precipitated from a light green amine solution. All materials volatile at 15° were distilled from the reaction vessel over a span of 24 hr. The components of the volatile mixture were separated and identified in the manner previously described. The following quantities of pure components were obtained: *ca.* 12 mg of white solid, 0.72 mmol of a mixture of *ca.* 90% $[(CH_3)_2N]_2BCl$ and 10% $[(CH_3)_2N]_3B$, and 14.51 mmol of unreacted $N(CH_3)_3$. The composition of the aminoborane mixture was estimated by vapor-phase infrared spectroscopy. A $^1H$ nmr spectrum of the mixture, dissolved in $CH_2Cl_2$, consisted of two signals centered at $\tau$ 7.27 ($\tau$ 7.27 observed for $[(CH_3)_2N]_2BCl$ in $CH_2Cl_2$) and $\tau$ 7.39 ($\tau$ 7.47 observed for $[(CH_3)_2N]_3B$ in $CH_2Cl_2$). The relative intensity of the $\tau$ 7.27 to the $\tau$ 7.39 absorptions was *ca.* 2.0:1.0. The amount of aminoboranes, displaced by $N(CH_3)_3$, represents 61% of the boron content of I. Trimethylamine (4.14 mmol) reacted with 1.17 mmol of I; the amine:titanium mole ratio is 1.77:1.00. Concerning the nonvolatile yellow-green residue, this material consisted mainly of $TiCl_3\cdot[N(CH_3)_3]_2$ as deduced from solid-state infrared spectroscopy and an X-ray diffraction powder pattern.

(4) I (323 mg, 0.73 mmol), maintained at −196°, was treated with $N(CH_3)_3$ (32.5 mmol). The reaction mixture was slowly warmed to *ca.* 0° at which temperature reaction occurred to afford a yellow-green solid. The mixture was maintained at 0° for 11 hr, and all materials volatile at 26° were distilled from the reaction mixture over a span of 9 hr and separated as previously described. The following amounts of materials were obtained: *ca.* 8 mg of white solid, 0.47 mmol of a mixture consisting of *ca.* 70% $[(CH_3)_2N]_2BCl$ and 30% $[(CH_3)_2N]_3B$, and 30.1 mmol of $N(CH_3)_3$. The quantity of aminoboranes recovered from the reaction mixture represents 65% of the boron content of I. Trimethylamine (2.40 mmol) reacted with 0.73 mmol of I; the amine:titanium mole ratio in the nonvolatile product is 1.65. A study of the infrared data combined with X-ray diffraction powder data indicates that this residue consists mainly of $TiCl_3\cdot[N(CH_3)_3]_2$.

**Reaction of Titanium Tetrachloride with Trimethylamine.**—Titanium tetrachloride (7.3915 g, 38.95 mmol), maintained at −196°, was treated with liquid $N(CH_3)_3$ (40.7 mmol). The solution was red in the interval −100 to *ca.* −10°; a homogeneous-appearing yellow solid formed at *ca.* −5°. No green color characteristic of $TiCl_3\cdot[N(CH_3)_3]_2$ was present. All materials volatile at −45° were distilled from the reaction vessel and condensed in a trap maintained at −196°. After 2 hr the evolution of volatile materials ceased. Trimethylamine (1.86 mmol), recovered from the −196° trap, was identified by its −78° vapor tension of 6.8 Torr and vapor-phase infrared spectrum which contained no absorptions at 492 $cm^{-1}$ (the $\nu_3$ fundamental of gaseous $TiCl_4$). The analytical composition of the yellow solid is $[TiCl_4]_{38\cdot95}[N(CH_3)_3]_{38\cdot84}$, or a 1:1 adduct. The solid-state infrared spectrum contains absorptions at 3103 (s), 3010 (m), 2978 (m), 2931 (m, sh), 2890 (s), 2851 (m, sh), 1460 (vvs), 1401 (vs), 1370 (m, b), 1243 (vvs), 1224 (w, sh), 1165 (w), 1105 (vvs), 979 (vvs), 861 (vs), 808 (vvs), 537 (vvs), and 490–400 (vvs, b) $cm^{-1}$. The *d* spacings, obtained from an X-ray powder diffraction study on this 1:1 adduct, compare favorably with those appearing in the literature.[12]

**Thermal Stability of $TiCl_4\cdot N(CH_3)_3$.**—A sample of $TiCl_4\cdot N(CH_3)_3$ was contained in a vacuum sublimator and the yellow crystalline solid sublimed under the following conditions: $10^{-6}$

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(12) M. Antler and A. W. Laubengayer, *J. Am. Chem. Soc.*, **77**, 5250 (1955).

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)chloroboranehexachloroditititanium(VI)[1a]

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The infrared spectrum of bis(dimethylamino)chloroboranehexachloroditititanium(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 $\nu(BN)$ and decreased $\nu(BCl)$ frequencies as compared to the free ligand. The $\nu(TiCl)$ vibrations as well as the charge-transfer spectrum indicate five-coordinate Ti in $[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6$.

## Introduction

Bis(dimethylamino)chloroboranehexachloroditititanium(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, $cm^{-1}$ ($\pm 5$ $cm^{-1}$) | |
|---|---|---|
| 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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(2) G. S. Kyker and E. P. Schram, *J. Am. Chem. Soc.*, **90**, 3678 (1968).