# Stereospecific Synthesis and Absolute Configuration of (−)-Dioxodi-μ-oxo-D(−)-1,2-propylenediaminetetraacetatodimolybdate(V)[1,2]

BY RICHARD M. WING AND KENNETH P. CALLAHAN[3]

The binuclear dioxo-bridged molybdenum(V) species prevalent in 3–6 $M$ hydrochloric acid has been placed in an optically dissymmetric environment through a stereospecific reaction with D(−)-1,2-propylenediaminetetraacetic acid. The absolute configuration of the binuclear molybdenum complex has been established. The ORD and CD spectra, richer in content than electronic spectral data previously available, are discussed.

## Introduction

Molybdenum has been demonstrated in several instances to be a necessary cofactor for a number of redox enzymes, in particular those involved in the fixation of molecular nitrogen.[4-6] Further, monomeric molybdenum(V) was identified from its electron spin resonance (esr) signal when xanthine oxidase was added to an oxidizable substrate.[7]

In spite of the interest thus generated in the chemistry of molybdenum(V) and, in particular, the relationship between the paramagnetic $MoO^{3+}$ monomer and the various, usually diamagnetic binuclear species formed by it at low acidity,[8-11] few experiments have been done which may aid in describing the electronic structures[12] of the various dimers.

After preliminary X-ray studies in this laboratory[13] established the ethylenediaminetetraacetic acid (EDTA) complex of molybdenum(V) to contain the dioxo-bridged $Mo_2O_4$ unit (Figure 1), a rapid intramolecular racemization process (Figure 2) was postulated[14,15] to explain the equivalence of the ethylenic protons in the nmr spectrum. Were a methyl group to be substituted onto the ethylenic backbone, the racemization process would be stopped because of steric repulsions between the methyl group and the metal–oxygen plane. The resultant structure would be a static, (±) racemic mixture with the methyl group in

an equatorial position (a 50:50 mixture of $H_B$ in Figure 2a and $H_A$ in Figure 2c).

We have carried out the synthesis of an optically active dioxo-bridged Mo(V) dimer using propylenediaminetetraacetic acid (PDTA) as the ligand, determined its absolute configuration, and reported its electronic, circular dichroism (CD), and optical rotatory dispersion (ORD) spectra. As is often the case, the latter two spectra allow a more detailed view of the electronic structure of the complex than does the electronic spectrum, thereby permitting a more complete discussion of the bonding.

## Experimental Section

(±)-1,2-Propylenediaminetetraacetic acid was prepared by the method of Dwyer and Garvan.[16]

D(−)-1,2-Propylenediaminetetraacetic Acid Monohydrate.—1,2-Propylenediamine was resolved by the method of Dwyer, *et al.*[17] The diastereoisomer was converted to the optically active hydrochloride, $[\alpha]D$ +3.90°, lit.[18] value 3.99–4.10°. This product was converted to D(−)-$H_4$PDTA by a modification of the method of Dwyer and Garvan.[16] The yield of pure product was not as good as that previously obtained, but the experimental convenience is greater.

Chloroacetic acid (71 g, 0.75 mol) in water (40 ml) was cooled to 10° and a solution of sodium hydroxide (70 g, 1.75 mol) in water (125 ml) was added slowly with a dropping funnel. The solution was magnetically stirred and surrounded by an ice bath to keep the temperature below 20°. D(+)-Propylenediamine dihydrochloride (18.25 g, 0.125 mol) in water (35 ml) was then added and the resulting solution was allowed to stand in a stoppered flask at room temperature for 7 days. The mixture was then acidified with concentrated hydrochloric acid (40 ml) and evaporated on a steam bath with a current of air to a volume of 150 ml; the resulting solids were filtered off. The filtrate was passed through a column of Dowex 50W-X4 cation-exchange resin (H+ form, Bio-Rad Laboratories, Richmond, Calif.) and eluted with 3 l. of boiling water. The column was heated with a heat gun during the elution. The levorotatory eluate was concentrated to a small volume on a rotary evaporator and treated with acetone, forming a gummy white solid which crystallized overnight at 4° to give D(−)-$H_4$PDTA·$H_2O$, mp 198°, $[\alpha]D$ −45°; lit.[16] mp 198°, lit.[16] $[\alpha]D$ −47°.

(−)-Disodium Dioxodi-μ-oxo-D(−)-1,2-propylenediaminetetraacetatodimolybdate(V).—D(−)-$H_4$PDTA (1.26 g, 4 mmol) was dissolved in water (5 ml) and the solution was made basic with sodium hydroxide (0.28 g, 7 mmol). To this solution was added with stirring 16.5 ml of 0.5 $F$ Mo(V) solution (prepared by reduc-

(1) Supported in part by the National Science Foundation under Grant GP-8055.

(2) The symbols D and L are used to denote the absolute configurations of optically active organic molecules. The symbols (+) and (−) denote the sign of rotation of the optically active substance at the Na D line. Racemates are denoted as (±).

(3) Lockheed Propulsion Co. Summer Fellow, 1967.

(4) D. I. Arnon in "Trace Elements in Plant Physiology," IUBS Colloquia Series No. 1, Chronica Botanica Co., Waltham, Mass., 1950, p 31.

(5) R. H. Burris in "Annual Reports on Plant Physiology," Vol. 17, L. Machlis, Ed., Annual Reviews, Inc., Palo Alto, Calif., 1966, p 155.

(6) R. W. F. Hardy and E. Knight, Jr., in "Progress in Phytochemistry," L. Reinhold, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, p 387.

(7) G. Palmer, R. C. Bray, and H. Beinert, *J. Biol. Chem.*, **239**, 2657 (1964).

(8) L. Sacconi and R. Cini, *J. Am. Chem. Soc.*, **76**, 4239 (1954).

(9) G. P. Haight, Jr., *J. Inorg. Nucl. Chem.*, **24**, 663 (1962).

(10) C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, **1**, 831 (1962).

(11) J. T. Spence and M. Haydanek, *ibid.*, **6**, 1489 (1967).

(12) P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **26**, 1967 (1964).

(13) R. M. Wing and K. P. Callahan, unpublished results.

(14) L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, **6**, 2146 (1967).

(15) R. M. Wing, K. P. Callahan, L. V. Haynes, and D. T. Sawyer, Abstracts, 3rd Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 1967, No. 198.

(16) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).

(17) F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959).

(18) J. C. Bailar, H. B. Jonassen, and A. D. Gott, *ibid.*, **74**, 3131 (1952).
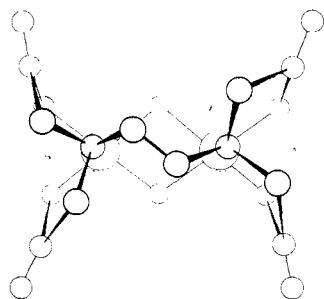
Figure 1.—Structure of the $Mo_2O_4EDTA^{2-}$ ion looking down the molecular twofold axis.



a       b       c
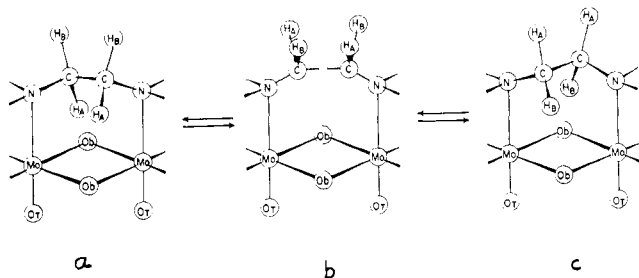
Figure 2.—Description of the intramolecular racemization process of $Mo^V$EDTA. The center figure is a hypothetical transition state for the equilibration of the enantiomers depicted at the right and left.

tion of a Mo(VI) solution in 3 $M$ hydrochloric acid with mercury).[19] Ethanol (95%) was added to this solution until a persistent cloudiness was obtained. Cooling at 4° for 1 hr yielded a flocculent tan solid. This solid, dried *in vacuo* over $Mg(ClO_4)_2$ overnight, showed extensive surface decomposition after 10 hr. The solid was dissolved in water, the insoluble decomposition products were removed by filtration, and the filtrate was again treated with ethanol to yield a light tan solid. Two more recrystallizations from water–ethanol afforded red-brown crystals which showed a much slower rate of decomposition. *Anal.* Calcd for $C_{11}H_{14}N_2O_{12}Mo_2Na_2$: C, 21.87; H, 2.34; N, 4.64. Found: C, 21.88; H, 2.56; N, 4.73; $[\alpha]D$ −252°.

The complex with (±)-$H_4$PDTA was prepared in the same way and showed no evidence of decomposition. The nmr and ir spectra of the (±) and optically active compounds were identical, with the ir spectrum clearly indicating the presence of the dioxobridged $Mo_2O_4$ unit.[20]

**Partial Resolution of** (±)-$Na_2Mo_2O_4$**PDTA**.—(±)-*cis*-Dinitrobis(ethylenediamine)cobalt(III) nitrite was prepared and purified by the published procedure[21] and was resolved by the method of Dwyer and Garvan.[22]

**Levorotatory Isomer.**—(±)-$Na_2Mo_2O_4$PDTA (1.0 g, 1.66 mmol) was dissolved in water (5 ml) and added to a warm solution of (−)-*cis*-$[Co(en)_2(NO_2)_2]$Br (0.58 g, 1.66 mmol) in water (50 ml) and stirred until the solution became cloudy. Only a small amount of diastereoisomer could be obtained by scratching and cooling this solution; however, the addition of ethanol (95%), with stirring and cooling, produced the yellow diastereoisomer (−)-[(−)-*cis*-Co(en)_2(NO_2)_2]_2Mo_2O_4PDTA. The solid was filtered, washed with ethanol, dried in air, and then recrystallized from water–ethanol and dried over $P_2O_5$. The

aqueous filtrate was saved for the recovery of the dextrorotatory isomer. *Anal.* Calcd for $C_{19}H_{48}N_{14}O_{20}Co_2Mo_2$: C, 20.72; H, 4.18; N, 17.81; for monohydrate: C, 20.39; H, 4.32; N, 17.60. Found: C, 19.93; H, 4.33; N, 17.60; $[\alpha]D$ −10.45°.

The diastereoisomer so obtained may be converted into optically active $Na_2Mo_2O_4$PDTA. Diastereoisomer (0.50 g, 4.54 mmol) was triturated with excess sodium iodide in about 3 ml of water for 2 min and resolving agent filtered off as the insoluble iodide. The sodium salt of the optically active complex was obtained if the filtrate was heated with stirring and ethanol was added until cloudiness persisted. Heating was stopped at this point but stirring continued until solid particles were visible in the solution. The heating–stirring cycle was found necessary to prevent precipitation of the complex as an intractable oil. Cooling for several hours gave a solid compound. Rotations observed were variable; a typical sample gave $[\alpha]D$ −18.3°.

**Dextrorotatory Isomer.**—The filtrate from the resolution above was concentrated to a volume of 5–10 ml on a rotary evaporator and insoluble material was filtered off. Ethanol (95%) was added until cloudiness persisted, and then the solution was heated and stirred as described above. Cooling to 4° for several hours afforded a solid which was filtered, washed with ethanol, and dried in air. Recrystallization from water–ethanol and drying *in vacuo* over $P_2O_5$ yielded pure complex. *Anal.* Calcd for $C_{11}H_{14}N_2O_{12}Mo_2Na_2$: C, 21.87; H, 2.34; N, 4.64; for monohydrate: C, 21.24; H, 2.59; N, 4.50. Found: C, 21.62; H, 2.72; N, 4.55. Observed rotations were variable; a typical sample gave $[\alpha]D$ +20°.

Comparable results were obtained when (+)-*cis*-$[Co(en)_2(NO_2)_2]$Br was used as the resolving agent.

**Physical Measurements.**—The ORD and CD spectra were taken in aqueous solutions in a 1-cm quartz cell using a Jasco Model ORD/UV/CD-5 spectrophotometer. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 621 spectrophotometer. Proton magnetic resonance spectra were measured on a Varian A-60 spectrometer.

**Analyses.**—The elemental analyses reported were performed by C. F. Geiger, Ontario, Calif.

## Results and Discussion

**Structure.**—From the known absolute configuration[23] of D(−)-propylenediamine and the steric requirement that the methyl group take an equatorial position, the absolute configuration of the complex formed between Mo(V) and D(−)-PDTA may be deduced and is shown in Figure 3. The visible-uv, ORD, and CD spectra of this compound, denoted (−)-$Mo^V$-D(−)-PDTA, are shown in Figure 4.

Despite the fact that no attempt was made to synthesize the corresponding complex with L(+)-PDTA we are confident of almost complete stereospecificity because of the isolation of compounds from the chemical resolution which show strong evidence for being optical isomers. Although the classical resolution procedure gave neither good nor reproducible optical purity thereby ruling out quantitative proof of the isolation of true optical isomers, the qualitative evidence obtainable from the ORD spectra (positions of maxima and minima, signs of rotation) of $Mo^V$PDTA formed by resolution with (+) and (−) resolving agent is in total agreement with the formulation of optical isomerism.

Although the absolute configuration of the complex is certain, the assignment of a term to designate the
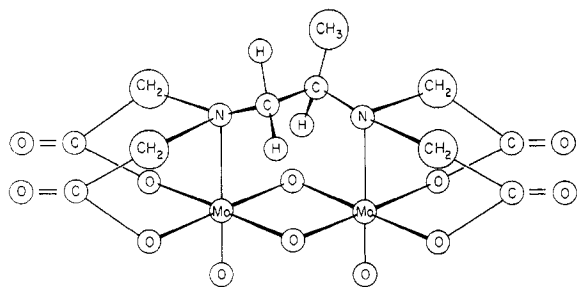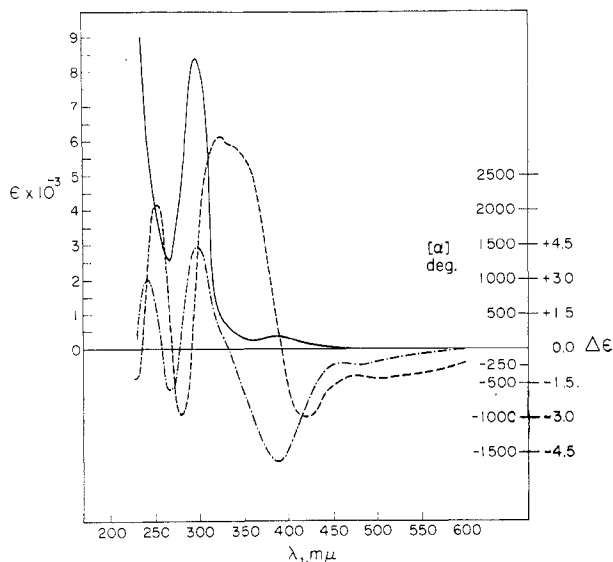
(19) D. E. Carrit, Ph.D. Thesis, Harvard University, 1947.

(20) R. M. Wing and K. P. Callahan, *Inorg. Chem.*, **8**, 871 (1969).

(21) H. F. Holtzclaw, Jr., D. P. Sheetz, and B. D. McCarty, *Inorg. Syn.*, **4**, 176 (1953).

(22) F. P. Dwyer and F. L. Garvan, *ibid.*, **6**, 195 (1960).

(23) (a) H. Reihlen, E. Weinbrenner, and G. V. Hessling, *Ann.*, **494**, 143 (1932); (b) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

Figure 3.—Absolute configuration of $(-)-Mo_2O_4$-D$(-)$-PDTA$^{2-}$.



Figure 4.—Spectra of $(-)-Mo_2O_4$-D$(-)$-PDTA$^{2-}$: ———, electronic; – – – –, ORD; –·–·–·, CD.

configuration is made difficult by the lack of suitable model compounds and the lack of applicability of the commonly employed methods. The optically active compounds most closely related structurally to Mo$^V$-PDTA appear to be the binuclear cobalt complexes first prepared by Werner[24] and the similar complex containing D$(-)$-propylenediamine.[25] All these complexes, however, have two complete five-atom chelate rings with no shared coordinated atoms, enabling comparisons to be made with the complex Co(en)$_3$$^{3+}$, the absolute configuration of which has been determined by X-ray methods.[26] The fact that the two acetate rings on each molybdenum are bonded to the same nitrogen make this approach impossible and is also responsible in part for the lack of success in our attempt to apply the ring-pairing method of Legg and Douglas.[27] Correlations of absolute configurations have also been made

on the basis of the signs of CD transitions[28] but as yet have only been applied to d$^3$ and d$^6$ complexes. We have thus decided to defer assignment of a new symbol until further examples of compounds of this type have been studied.

**Bonding and Spectra.**—Gray and Hare[29] have given a molecular orbital treatment of the MoOCl$_5$$^{2-}$ ion and we will adopt their description except for a 45° rotation of the coordinate system about the $z$ (Mo–O) axis. This allows correlation of the monomer orbitals with those of the dimer, *vide infra*, and the only change is that the half-filled nonbonding b$_2$ orbital is now d$_{x^2-y^2}$ and the $\sigma^*$ (b$_1$) orbital is primarily d$_{xy}$.

Two monomer units are now brought together so as to share a common edge (the metal–metal direction being defined as the $y$ axis) and the dimer molecular orbitals are considered to be symmetric and antisymmetric combinations of the monomer orbitals.

Of the combinations that can be constructed, only those between the d$_{x^2-y^2}$ pair and the d$_{yz}$ pair will give rise to a serious perturbation from the monomer orbital energies. Since the d$_{yz}$ orbitals are already involved in $\pi$ bonding to the terminal oxygens, further interaction to form $\pi$ bonds with the bridge oxygens, while important, is not expected to give rise to any major spectral changes.

The effect of dimer formation on the d$_{x^2-y^2}$ orbital pair is, on the other hand, expected to be quite dramatic. Several important cross-dimer interactions involving these orbitals are possible, but the easiest to visualize and probably the most significant is described as a $\sigma$ bond between the two metals. A large splitting thereby arises between the $(+,+)$ bonding and $(+,-)$ antibonding combinations with the result that the dioxo-bridged dimer is almost completely spin-paired ($\mu_{eff}$ = 0.3 BM).[30]

There is little question that the lowest energy transition for the monomer (13,800 cm$^{-1}$) can be assigned to the $^2E(I) \leftarrow {}^2B_2$ transition.[29] Although the first band seen in the electronic spectrum of Mo$^V$PDTA is at 26,600 cm$^{-1}$, the ORD and CD clearly indicate another electronic transition at lower energy, centered at *ca.* 21,000 cm$^{-1}$. This is in agreement with Mitchell's observations[12] on the Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$$^{2-}$ ion.

There are two reasonable assignments for this low-energy transition. In one case the metal–metal $\sigma^*$ orbital is higher in energy than the metal–oxygen $\pi^*$ orbital (*i.e.*, E(I) for the monomer) and the first dimer transition is $^1\pi^*_{metal-oxygen} \leftarrow {}^1\sigma_{metal}$. Alternatively, the crossover has not occurred, and the transition is $^1\sigma^* \leftarrow {}^1\sigma$ ($^1B_2 \leftarrow {}^1A_1$, assuming local C$_{2v}$ symmetry for the dimer). On the basis that this 21,000-cm$^{-1}$ transition is so weak (presumably dipole forbidden), we feel that the first assignment is probably correct.

In spite of this ambiguity, it is clear that $\sigma_{d_{x^2-y^2},d_{x^2-y^2}}$ has been stabilized by a minimum of 7200 cm$^{-1}$ with

(24) See F. Basolo, *Chem. Rev.*, **52**, 459 (1953), for a listing.

(25) Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, **40**, 2206 (1967).

(26) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *ibid.*, **30**, 795 (1957).

(27) J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966). All of the chelate rings in Mo$^V$PDTA are either "adjacent" or "*trans*" rings which are excluded from consideration in the ring-pairing method. Furthermore, if a pseudoring is constructed across the bridging oxygens, application of this method indicates that the compound is optically inactive.

(28) See, for example, R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 331 (1962).

(29) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).

(30) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4570 (1962).

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]

(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).

# Low-Spin Binuclear Titanium Complexes.  I.  Preparation and Characterization of Bis(dimethylamino)chloroboranehexachlorodititanium(VI), [(CH$_3$)$_2$N]$_2$BCl·Ti$_2$Cl$_6$[1a]

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

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$_3$)$_2$N]$_2$BCl·Ti$_2$Cl$_6$. 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$_3$)$_2$N]$_2$BCl.

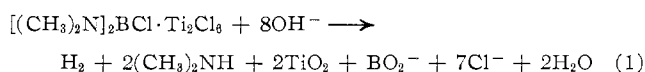## Introduction

We have previously reported the preparation of di[bis(dimethylamino)chloroborane]tris[tetrachlorotitanium(IV)], {[(CH$_3$)$_2$N]$_2$BCl}$_2${TiCl$_4$}$_3$, by treatment of TiCl$_4$ with either [(CH$_3$)$_2$N]$_2$BCl 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$_3$)$_2$-N]$_2$BCl. We now report the isolation and characterization of the reduction product which contains titanium in the formal oxidation state (III).
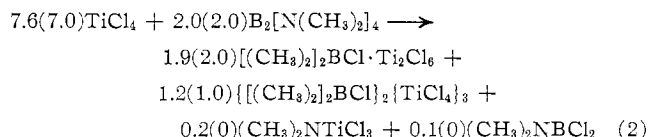
## Results and Discussion

**Isolation and Purification of Bis(dimethylamino)-chloroboranehexachlorodititanium(VI), [(CH$_3$)$_2$N]$_2$BCl·Ti$_2$Cl$_6$.**—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$_3$)$_2$N]$_2$-BCl}$_2${TiCl$_4$}$_3$, small amounts of dimethylaminotrichlorotitanium(IV), (CH$_3$)$_2$NTiCl$_3$, and a brown solid hereafter referred to as I. I is a microcrystalline material which was purified by repeated washing with $o$-C$_6$H$_4$Cl$_2$ and CH$_2$Cl$_2$ and demonstrated by X-ray powder diffraction to be free from occluded (CH$_3$)$_2$N-TiCl$_3$, {[(CH$_3$)$_2$N]$_2$BCl}$_2${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$_3$)$_2$-NTiCl$_3$, or 1644 (s) and 829 cm$^{-1}$ (vvs) ($\nu_{as}$($^{10}$BN$_2$) and $\nu_s$(NC$_2$)), respectively, characteristic of {[(CH$_3$)$_2$-N]$_2$BCl}$_2${TiCl$_4$}$_3$.[2]

(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).
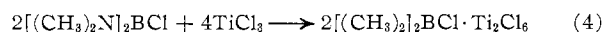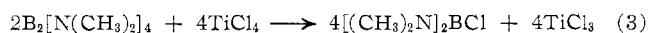
**Analytical Characterization of I.**—Hydrolysis of 1 results in the formation of bluish black Ti$_2$O$_3$ which is slowly oxidized in basic water to white TiO$_2$ with the evolution of H$_2$. Analytical data for I are summarized in Table II. The analytical recovery of mass was 94.3%, based on the initial 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

$$2B_2[N(CH_3)_2]_4 + 4TiCl_4 \longrightarrow 4[(CH_3)_2N]_2BCl + 4TiCl_3 \quad (3)$$
$$2[(CH_3)_2N]_2BCl + 4TiCl_3 \longrightarrow 2[(CH_3)_2N]_2BCl \cdot Ti_2Cl_6 \quad (4)$$
$$2[(CH_3)_2N]_2BCl + 3TiCl_4 \longrightarrow \{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3 \quad (5)$$

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