

A Mixed-Valence Titanium(III)-Titanium(IV) Tetramer and Related Compounds<sup>†</sup>

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The mixed-valence compound  $[\text{NH}_4^+\cdot\text{NH}_3]_2[\text{Ti}_4\text{Br}_4(\text{NH}_2)_{12}^{2-}]$  was produced in the reaction of potassium borohydride and titanium(IV) bromide in liquid ammonia at room temperature. Similar ammonium salts of either Ti(III) or Ti(IV) were also prepared. The reactions of these compounds with sodium acetylide in liquid ammonia evolve acetylene equivalent to the ammonium ions present, thus providing the charge of the complex, and yield novel titanium acetylide derivatives. The acetylides convert into titanium carbonitride upon thermal treatment to 800 °C.

## Introduction

A series of novel compounds was isolated in the course of exploratory work on the chemistry of titanium halides in liquid ammonia. This work was undertaken to study synthetic approaches to titanium-containing precursors of ceramic materials. Current interest on advanced ceramic materials centers around materials such as carbides, nitrides, borides, and silicides which have properties unmatched by metallic alloys or other structural materials. The design and syntheses of appropriate precursors for conversion by thermal or photolytic means into advanced ceramics is a preparative approach that can particularly benefit from the contribution of chemists. Reference 1 gives a historical perspective of the use of precursors and the potential advantages of this approach. Alternative routes include high-temperature reactions, plasmas, chemical vapor deposition, etc.

Oxygen is an element that can be detrimental to the properties of some of the above-mentioned ceramic materials; thus, liquid ammonia is, among a number of solvents that are not oxygen compounds, a useful medium to conduct synthetic chemistry.

Titanium chemistry in liquid ammonia relevant to the preparation of precursors includes past efforts<sup>2,3</sup> to synthesize  $\text{Ti}(\text{NH}_2)_4$  and  $\text{Ti}(\text{NH}_2)_3$  via metathetical reactions between the corresponding thiocyanates and potassium amide. In addition to this, the chemistry of titanium halides<sup>4-7</sup> in liquid ammonia provides a fertile ground for intermediates. Titanium(IV) halides undergo ammonolysis to yield initially  $\text{TiX}(\text{NH}_2)_3\cdot 2\text{NH}_3$ ; however, the ammonia of solvation is lost upon continued pumping at room temperature. Evidence was obtained<sup>4</sup> in the case of the iodide derivative, which is soluble, showing the presence of anionic species of the type  $[\text{TiX}_n(\text{NH}_2)_{6-n}^{2-}]$ . The titanium(III) halides do not ammonolyze but form a number of solvates. The room-temperature stable phase is  $\text{TiX}_3\cdot 4\text{NH}_3$ . Spectroscopic evidence<sup>7</sup> points to the fact that the solvates are not molecular compounds but rather complex salts similar to the aquo complexes such as  $[\text{TiX}_2(\text{H}_2\text{O})_4]^+\text{X}^-$ . Most of the past efforts concerning the chemistry of titanium halides in liquid ammonia were aimed at establishing the stoichiometry of the ammonolysis and the composition of the solvates as a function of temperature. In the present study, the products isolated from reactions between the ammonolytic mixtures or solvates and alkali-metal borohydrides, amides, and acetylides are revealing of the structure of some of these compounds and also provide precursors for conversion into ceramic materials.

## Results and Discussion

**Mixed-Valence Compounds.** Titanium(IV) bromide was allowed to react with potassium borohydride in liquid ammonia at room temperature in a sealed ampule provided with a side arm. This treatment produced after a few days a forest green insoluble crystalline precipitate and an olive green supernatant. The supernatant was decanted into the side arm and ammonia distilled back to wash the precipitate. This procedure was repeated a few times. The supernatant became deep purple as it was being

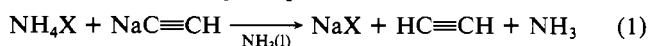
concentrated. Finally, the ampule was opened and the ammonia removed. The green precipitate, compound I, was found to contain Ti, Br, and  $\text{NH}_3$  in the ratios 1:1:4, respectively. The Ti(III) content of compound I was established by titration with Ce(IV) and found to correspond to 51.2%, 48.3%, and 53.4% of the total titanium for materials obtained in three independent preparations. These results indicate that I is at least a mixed-valence dimer but its tetrameric character is suggested by additional evidence described below.

Treatment of compound I with excess potassium amide at -50 °C in liquid ammonia, which was expected to substitute the bromide by amide, led instead to partial substitution producing a compound, Ia, containing K, Ti, Br, and  $\text{NH}_3$  in a 0.25:1:0.75:3 relation. Total substitution of bromide by amide did indeed take place as observed in a separate experiment but only at room temperature, leading in that case to a condensed material, Ib, containing K, Ti, and N in a 1:1:2 ratio. This compound is formulated as  $\text{K}_2\text{Ti}_2(\text{N})(\text{NH}_3)_3$  after consideration of the ionic balances although reduction could have taken place to produce  $\text{KTi}(\text{NH}_2)_2$ , which is a known compound.

Evidence suggesting the tetrameric character of I is also derived from the composition of purple solids, Ic, isolated from the initially soluble fraction of the  $\text{TiBr}_4\text{-KBH}_4$  reaction mixture. These solids were found to contain Ti, Br, B, and  $\text{NH}_3$  in the relation 1:0.75:0.25:2.5. In addition to this a compound, Id, was derived from the reaction of  $\text{KBH}_4$  and  $\text{TiBr}_4$  conducted at -50 °C, which showed Ti, Br, and  $\text{NH}_3$  in the ratios of 1:0.75:5.25. Compound Id contained Ti(III) corresponding to 28% of the total titanium or within experimental error one Ti(III) in every four titanium atoms.

The above evidence not only suggests that compound I is tetrameric but also that this structure already exists in a common Ti(IV) precursor of I, Ic, and Id, which might well be  $[\text{TiBr}(\text{NH}_2)_3\cdot 2\text{NH}_3]_4$ .

Compound I could be formulated as  $\text{Ti}_4\text{Br}_4(\text{NH}_2)_{10}\cdot 6\text{NH}_3$  in accordance with the ionic and mass balance dictated by the chemical and valence analyses. However, this is not the case since the IR spectrum of I shows among other N-H vibrations that of ammonium ions as a strong band centered at 1410  $\text{cm}^{-1}$ ; thus, compound I must be a salt. Reactions of compound I with monosodium acetylide in liquid ammonia provided a means to establish the charge of the tetramer since ammonium ions react with the acetylide to release acetylene in a direct stoichiometric 1:1 relation according to eq 1.



Therefore, measurement of the amount of acetylene released from the reaction gives a value of -2.34 for the charge of the

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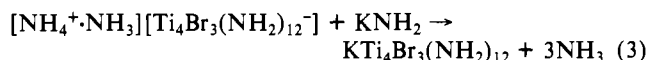
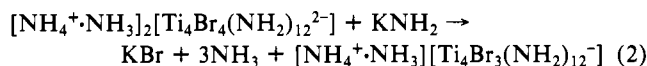
- (1) Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, *62*, 889.
- (2) Schmitz-DuMont, O.; Ross, B. Z. *Anorg. Allg. Chem.* **1966**, *342*, 82.
- (3) Schmitz-DuMont, O.; Simons, P.; Broja, G. Z. *Anorg. Allg. Chem.* **1949**, *258*, 307.
- (4) Fowles, G. W. A.; Nicholls, D. J. *Chem. Soc.* **1959**, 990.
- (5) Fowles, G. W. A.; Nicholls, D. J. *Chem. Soc.* **1961**, 95.
- (6) Kottarathil, T.; Lepoutre, G. J. *Chim. Phys. Phys.-Chim. Biol.* **1976**, *73*, 849.
- (7) Nicholls, D.; Ryan, T. A. *J. Inorg. Nucl. Chem.* **1977**, *39*, 961.

tetramer. Treatment of  $\text{NH}_4\text{Br}$  under similar conditions in a parallel experiment released acetylene in an amount that was 96.0% of that theoretically anticipated. The slight excess, about 17%, of acetylene evolved over the theoretical amount for a  $-2.0$  charge in the case of compound I is within the variance observed for similar determinations for this and other compounds, to be discussed later. These results then lead to the formulation of compound I as  $[\text{NH}_4^+]\text{[Ti}_4\text{Br}_4(\text{NH}_2)_{12}^{2-}]\cdot 2\text{NH}_3$ .

The product of the acetylide treatment was isolated after repeated washings with liquid ammonia. This material, compound Ie, required extensive digestion with acid for dissolution, suggesting its polymeric character. Compound Ie showed an idealized composition corresponding to  $\text{Ti}_4(\text{C}\equiv\text{C})(\text{NH})_6$ .

There are many examples of acetylide complexes of the transition-metal elements;<sup>8,9</sup> some are complex salts incorporating the alkali metal from the initial acetylide reagent while the neutral ones appear to be polymeric. Their mode of preparation is similar to that followed for compound Ie. Apparently no titanium acetylides have been reported to date; perhaps these are not formed because of competing polymerization reactions unless stabilized by certain ligands as in compound Ie.

The course of the reaction between compound I and potassium amide at  $-50^\circ\text{C}$  suggests that the 2 mol of ammonia of solvation is associated with the ammonium ion since the product of that reaction, compound Ia ( $\text{KTi}_4\text{Br}_3(\text{NH}_2)_{12}$ ), does not have any ammonia of solvation. That reaction can be visualized as proceeding by the steps



In eq 2 one bromide ion is abstracted as KBr and 1 equiv of ammonium with its associated ammonia is neutralized by the amide ion. In eq 3 the remaining ammonium ion is displaced by potassium and neutralized by amide. The order of these two steps can be reversed without affecting the final outcome.

When the charge and number of ligands for the tetrameric unit has been established, the question arises as to what would be a plausible structure for such a unit. A set of double amido bridges between each metal center is an attractive possibility by analogy with the zirconium and hafnium tetramers  $\text{M}_4(\text{OH})_8(\text{H}_2\text{O})_{16}^{8+}$ , which are joined by double hydroxo bridges.<sup>10</sup> However, such a structure demands eightfold coordination because the two sets of hydroxo bridges around each zirconium are orthogonal. This situation is not too plausible for titanium, which is most likely octahedral. An arrangement of two double bridges and two single bridges is feasible in joining octahedra; also feasible is a double bridge and three single bridges as found in the structure of  $\text{Cr}_2\text{F}_5$ , which is a mixed-valence Cr(II)–Cr(III) compound.<sup>11</sup> Either possibility is equally likely for compound I. The  $\text{Ti}_4(\text{NH}_2)_{12}\text{Br}_4^{2-}$  core of compound I also resembles the tetrameric  $\text{Ru}_4(\text{OH})_{12}^{4+}$  unit known<sup>12</sup> as a solution species, which shows interestingly enough, similar to Id and I, a redox chemistry whereby either one or two of the metal centers can be reduced to Ru(III) while the integrity of the tetrameric unit is still preserved.

The course of the borohydride reduction that produced compound I is interesting. Apparently it involved, at one stage, borohydride incorporation into the titanium coordination sphere to produce a soluble purple intermediate from which small amounts of an insoluble purple solid (Ic) containing boron was derived. On the other hand, when the reaction was conducted at  $-50^\circ\text{C}$ , larger amounts of a purple solid were obtained that on washing with ammonia released boron and produced the boron-free green product Id,  $\text{Ti}_4\text{Br}_3(\text{NH}_2)_{12}\cdot 9\text{NH}_3$ . It is evident that borohydride

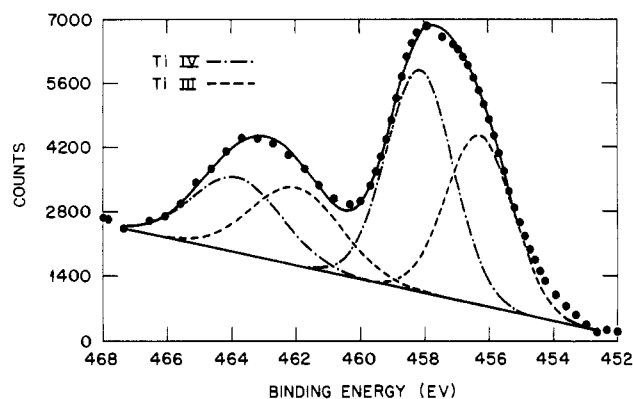


Figure 1. Deconvoluted ESCA spectra of compound I showing the Ti 2p binding energy range. Dots show the calculated fit.

is readily displaced in these intermediates by the much more nucleophilic amide ligand provided by the reaction medium.

The role of the solvent in the borohydride reaction is illustrated by the products obtained under different conditions. Total incorporation of borohydride was obtained, to produce  $\text{Ti}(\text{BH}_4)_3$  in the neat reaction system of  $\text{TiCl}_4$  vapor and  $\text{LiBH}_4$ ,<sup>13</sup> while  $\text{TiCl}(\text{BH}_4)_2$  was obtained<sup>14</sup> in pentane and  $\text{Ti}(\text{BH}_4)_3\cdot\text{Et}_2\text{O}$  in ether.<sup>15</sup>

Compound I was further characterized by physical techniques. The IR spectrum showed broad bands centered at 3200 and 640  $\text{cm}^{-1}$ , bands at 1590, 1410, and 1230  $\text{cm}^{-1}$ , and a shoulder at 860  $\text{cm}^{-1}$ . The electronic spectrum was obtained in a reflectance cell sealed under argon. This spectrum showed a gradual rise into the UV region with weak peaks at 260, 360, 490, and 640 nm. The X-ray diffraction pattern is rather weak, showing the following "d" values in order of decreasing intensity: 8.0 m, 3.33 w, 4.05 w, and 2.36 w. X-ray photoelectron spectroscopy (XPS or ESCA) showed an area relation of the  $2p_{1/2}$  peak of 0.49:0.51 for the Ti(IV) and Ti(III) resolved components while the  $2p_{3/2}$  peak was resolved into a 0.57:0.43 relation for the Ti(IV) and Ti(III) components. The deconvoluted spectrum is shown in Figure 1. These results are in agreement with those derived by chemical analysis for the oxidation state of compound I. The binding energies for the  $2p_{3/2}$  peaks of Ti(IV) and Ti(III) were 458.2 and 456.3 eV, respectively. These compare with 458.7 eV for Ti(IV) in  $\text{TiO}_2$  and 454.8 eV for Ti(II) in TiO reported by Ranqvist et al.<sup>16</sup> It is seen that the Ti(III) value is intermediate between those of TiO and  $\text{TiO}_2$  but somewhat higher than the 455.3 eV reported<sup>16</sup> for TiN, which could formally be considered as a Ti(III) compound. However, it seems that in the nitride, as well as in the boride and carbide, the electron transfer from titanium to the other element is less than that predicted by the stoichiometry of these compounds.

The photoelectron spectra of compound I were rerun after exposing the sample to air. In this case the Ti(III) component disappears altogether and the Ti(IV) signal decreases in strength relative to the N (1s) and Br (3d) signals. Apparently oxidation and hydrolysis produce  $\text{NH}_4\text{Br}$  as a coating on the compound in the same way that rust coats exposed iron although on a slower scale.

**Titanium(III) Compounds.** Titanium(III) chloride was loaded together with an excess of  $\text{NaBH}_4$  into an ampule provided with a side arm. Ammonia was distilled in, and the ampule was sealed. The reaction mixture was allowed to stand for 10 days at  $35^\circ\text{C}$ . This produced a purple supernatant, which was decanted, and ammonia was distilled back to wash the precipitate. This operation was repeated a few times before opening the ampule and removing the ammonia. The analysis of the insoluble product, compound

(8) Nast, R. *Spec. Publ.—Chem. Soc.* **1959**, No. 13, 103.

(9) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1960**, 1718.

(10) Muha, G. M.; Vaughan, P. A. *J. Chem. Phys.* **1960**, *33*, 194.

(11) Steinfink, H.; Burns, J. H. *Acta Crystallogr.* **1964**, *17*, 823.

(12) Maya, L. *J. Inorg. Nucl. Chem.* **1979**, *41*, 67.

(13) Hoekstra, H. R.; Katz, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 2488.

(14) Franz, K.; Noth, H. Z. *Anorg. Allg. Chem.* **1973**, *397*, 247.

(15) Noth, H. *Angew. Chem.* **1961**, *73*, 380.

(16) Ramqvist, L.; Hamrin, K.; Johanson, G.; Fahlman, A.; Nordling, C. J. *Phys. Chem. Solids* **1969**, *30*, 1835.

II, showed Ti, Cl, and ammonia in a relation of 1:2:4. The oxidation-state analysis showed all the titanium being present as Ti(III). As in the case of compound I this material showed also the presence of ammonium ions in the IR spectrum, which was remarkably similar in every respect to that of compound I other than the intensity of the  $\text{NH}_4^+$  band. The reaction with sodium acetylide, performed in order to establish the charge of compound II, produced acetylene corresponding to a charge of  $-0.97$  per titanium. There is no direct evidence for a tetrameric character of compound II; however, the similarity in the IR spectra and the formation of a similar intermediate, the purple supernatant, as well as the stoichiometry of the acetylide product, suggests that compound II might also be a tetramer. Attempts to isolate a partially substituted product by treatment with sodium amide at  $-50^\circ\text{C}$ , which could have clarified whether compound II was tetrameric, led instead to total substitution, producing  $\text{NaTi}(\text{NH})_2$ . Compound II is formulated as  $[\text{NH}_4^+\cdot\text{NH}_3]_4[\text{Ti}_4\text{Cl}_8(\text{NH}_2)_8^{4-}]$  by similarity to compound I.

Titanium trichloride does not ammonolyze.<sup>7</sup> It seems therefore that displacement of one chloride per titanium, as observed in the formation of compound II, was promoted by the presence of borohydride. Apparently an intermediate containing borohydride as a ligand is formed, which finally yields compound II.

The acetylide derivative, compound IIa, showed an idealized composition corresponding to  $\text{Ti}_4(\text{C}\equiv\text{C})_2(\text{NH})_4$ . This material is similar to Ie derived from compound I, but in this case the C:Ti ratio is doubled. It is seen that the amount of acetylene incorporation is proportional to the excess halide over the ammonium ion present; thus, in compound I there are 2 equiv of bromide in excess of the ammonium ion present while in compound II there are 4 equiv of chloride in excess of the ammonium ion present.

Additional acetylide reactions were conducted with use of in one case  $\text{TiCl}_3$  and in another the preformed ammine  $\text{TiCl}_3\cdot 4\text{NH}_3$ . The products of these reactions showed the same C:Ti ratio as IIa but incorporated sodium. The product derived from  $\text{TiCl}_3$ , IIb, showed an idealized composition corresponding to  $\text{NaTi}_4(\text{C}\equiv\text{C})_2(\text{NH})_4\text{NH}_2$ , resembling the saltlike acetylides prepared by Nast et al.<sup>8</sup> On the other hand, the product from the ammine, IIc, seemed unusual in that the ionic balance requires the presence of nitride ligands or a partial conversion of the acetylide to carbide. The two alternatives are  $\text{Na}_4\text{Ti}_4(\text{C}\equiv\text{C})_2(\text{NH})_4$  or  $\text{Na}_4\text{Ti}_4(\text{C}\equiv\text{C})_2\text{N}_4$ . Compound IIc appears to be a precursor related to a series of complex carbides and nitrides having empirical formulas corresponding to  $\text{Ti}_4\text{M}^{\text{II}}_2[\text{C}_2\text{N}]$ , where  $\text{M}^{\text{II}} = \text{Zn}, \text{Cd}, \text{Sn}$ .<sup>17-19</sup>

**Titanium(IV) Compounds.** In the sequence given by the Ti(III) compound  $\text{Ti}_4\text{X}_8(\text{NH}_2)_8^{4-}$  and the mixed-valence compound  $\text{Ti}_4\text{X}_4(\text{NH}_2)_{12}^{2-}$  it would be expected that the Ti(IV) compound  $\text{Ti}_4\text{X}_4(\text{NH}_2)_{12}$  would be a neutral moiety; however, this was not the case. The Ti(IV) compound with the nominal formula of  $\text{TiBr}(\text{NH}_2)_3$ , compound III, turned out to also contain ammonium ions as found by IR and the production of acetylene in the reaction with sodium acetylide. This reaction evolved acetylene corresponding to a charge of  $-2.02$  for the titanium tetramer, thus leading to a formulation of  $[\text{NH}_4^+]_2[\text{Ti}_4\text{Br}_4(\text{NH})_4(\text{NH}_2)_6^{2-}]$  for compound III after consideration of the charge balance.

Compound III is the ammonolysis product of  $\text{TiBr}_4$  obtained after removal of ammonium bromide and continued pumping at room temperature. It derives from the solvate having the nominal composition  $\text{TiBr}(\text{NH}_2)_3\cdot 2\text{NH}_3$ . A plausible formulation of the solvate is  $[\text{NH}_4^+]_2[\text{Ti}_4\text{Br}_4(\text{NH}_2)_{14}^{2-}]\cdot 4\text{NH}_3$ , which structurally could be visualized as a tetrahedron of titanium atoms with amido bridges running through the six edges and eight terminal amido ligands, two on each vertex in addition to one terminal halide ligand per titanium atom.

Compound III failed to yield compound I upon treatment with potassium borohydride; it produced instead a gummy green ma-

terial that stuck to the walls of the ampule. Apparently compound III is condensed to such an extent, involving imido bridges, that it fails to form the amido- and/or bromo-bridged tetramer. On the other hand, compound I is formed as a crystalline precipitate when the borohydride reaction is simultaneously conducted with the ammonolysis.

The product of the acetylide reaction with III, compound IIIa, showed an idealized composition corresponding to  $\text{Ti}_4(\text{C}\equiv\text{C})(\text{N}-\text{H})_7$ . In a parallel acetylide reaction, started with a different batch of compound III, which was slightly contaminated with residual ammonium bromide ( $\sim 10\%$  by weight), the product IIIb had a composition corresponding to  $\text{NaTi}_4(\text{C}\equiv\text{C})(\text{NH})_7\text{NH}_2$ . In the latter case the acetylene evolved corresponded to a charge of  $-2.5$  for the tetramer, although this number is somewhat uncertain because of the correction applied to account for the presence of ammonium bromide.

**Infrared Spectra of the Acetylide Derivatives.** The spectra of the acetylides showed weak bands at  $2030$  and  $2180\text{ cm}^{-1}$ , with the exception of compound IIa, which showed a single band at  $2080\text{ cm}^{-1}$ . These values are in agreement with observations of similar acetylide derivatives of other transition elements.<sup>20</sup> The relatively weak intensity of the bands suggests that the acetylide ligands are bridging.<sup>21</sup> The spectra also showed weak N-H stretching vibrations around  $3200\text{ cm}^{-1}$  and N-H deformation vibrations in the  $1600$ – $1200\text{ cm}^{-1}$  region. The most salient feature in all the spectra was a very strong and broad band centered at  $600\text{ cm}^{-1}$ , which is assigned to M-C and M-N stretching in accordance with reported values for these vibrations.<sup>20,22</sup>

**Pyrolysis of Titanium Acetylide Derivatives.** A few of the acetylide derivatives were pyrolyzed under dynamic vacuum up to  $800^\circ\text{C}$  while the condensable volatiles were trapped at  $-196^\circ\text{C}$ . In all cases decomposition started at about  $100^\circ\text{C}$ . Condensable volatiles collected up to about  $300^\circ\text{C}$  while additional noncondensable gases were produced up to the final temperature. The condensable volatiles were identified by their IR spectra as  $\text{NH}_3$  and  $\text{HC}\equiv\text{CH}$ . In addition to these, a small amount, about  $10\%$  of the total, of what appeared to be  $\text{HCN}$  was also produced. The presence of  $\text{HCN}$  was suggested by a sharp band at  $712.9\text{ cm}^{-1}$ , the only strong IR band for this compound, and the fact that this component was partially removed by fractionation through a  $-95^\circ\text{C}$  trap.

The Raman spectrum of the pyrolysis residue, derived from compound IIIa, showed bands at  $194$ ,  $270$ ,  $418$ , and  $610\text{ cm}^{-1}$ . These frequencies fall within the variance of  $\pm 8\text{ cm}^{-1}$  observed for each band in the spectra of either TiN or TiC.

The solid residues of the pyrolysis were titanium carbonitrides with the exception of that derived from compound IIc, which retained sodium to yield a complex carbide similar to the complex  $\text{Ti}_4\text{M}^{\text{II}}_2\text{C}_2$  compounds prepared by Jeitschko et al.<sup>17-19</sup> but differing in that the  $\text{M}^{\text{II}}_2$  component is replaced by  $\text{M}^{\text{I}}_4$ .

No features were present in the infrared spectra of the pyrolysis products, thus confirming the conversion of the acetylide-imide derivatives into an ionic carbonitride lattice.

The results of the pyrolysis experiments are summarized in Table I.

## Conclusions

Titanium(IV) halides yield in liquid ammonia a tetrameric unit showing an interesting substitutional and redox chemistry while titanium(III) halides undergo a partial substitution of halide by amide that is promoted by the presence of borohydride.

Titanium acetylide complexes can be prepared in liquid ammonia by the reaction of sodium acetylide and titanium halides or their ammonolytic products. Separation of the alkali-metal byproduct is readily accomplished in this reaction medium. These complexes, having a relatively high titanium content, provide

(17) Jeitschko, W.; Holleck, H.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* **1964**, *95*, 1004.

(18) Jeitschko, W.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* **1964**, *95*, 178.

(19) Jeitschko, W.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* **1963**, *94*, 672.

(20) Hagihara, N. *Mem. Inst. Sci. Ind. Res., Osaka, Univ.* **1978**, *35*, 61.

(21) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1960.

(22) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1970.

**Table I.** Pyrolysis of Acetylides

compd	idealized formula	wt loss to 800 °C, %	formula of residue	C content, %		calcd wt loss, %	remarks
				calcd	found		
Iib	NaTi <sub>4</sub> (C≡C) <sub>2</sub> (NH) <sub>4</sub> NH <sub>2</sub>	23.9	Ti <sub>4</sub> N <sub>2</sub> C <sub>2</sub>	9.85	9.16	28.1	(a) sodium mirror analyzed, accounts for 65% of init Na (b) X-ray shows Ti(N,C)
Iic	Na <sub>4</sub> Ti <sub>4</sub> (C≡C) <sub>2</sub> (NH) <sub>2</sub>	21.3	Na <sub>4</sub> Ti <sub>4</sub> C <sub>2</sub>	7.8	8.54	21.5	mostly amorphous, shows weak lines of Ti(N,C)
IIIa	Ti <sub>4</sub> (C≡C)(NH) <sub>7</sub>	24.6	Ti <sub>4</sub> N <sub>3</sub> C	4.88	3.1	23.4	X-ray shows Ti(N,C), Raman shows Ti(N,C)
IIIb	NaTi <sub>4</sub> (C≡C)(NH) <sub>7</sub> NH <sub>2</sub>	32.0	Ti <sub>4</sub> N <sub>3</sub> C	4.88	4.66	31.7	X-ray shows Ti(N,C), sodium mirror produced

**Table II.** Analytical Results

compd	idealized formula	calcd wt, %					found wt, %					remarks	
		Ti	NH <sub>3</sub>	Br or Cl	K or Na	C	Ti	NH <sub>3</sub>	Br or Cl	K or Na	B		C
I	[NH <sub>4</sub> <sup>+</sup> ·NH <sub>3</sub> ] <sub>2</sub> Ti <sub>4</sub> Br <sub>4</sub> (NH <sub>2</sub> ) <sub>12</sub>	24.78	35.17	41.34			26.1	33.9	40.6	0.2	0.4		from TiBr <sub>4</sub> and KBH <sub>4</sub> at room temp; 13.37% Ti(III) or 51.2% of ΣTi
I'	[NH <sub>4</sub> <sup>+</sup> ·NH <sub>3</sub> ] <sub>2</sub> Ti <sub>4</sub> Br <sub>4</sub> (NH <sub>2</sub> ) <sub>12</sub>	24.78	35.17	41.34			24.3	34.4	39.3	1.4	0.7		same as above; 11.73% Ti(III) or 48.3% of ΣTi
I''	[NH <sub>4</sub> <sup>+</sup> ·NH <sub>3</sub> ] <sub>2</sub> Ti <sub>4</sub> Br <sub>4</sub> (NH <sub>2</sub> ) <sub>12</sub>	24.78	35.17	41.34			24.7	34.8	40.6	0.2	0.5		same as above; 13.15% Ti(III) or 53.4% of ΣTi
Ia	KTi <sub>4</sub> (NH <sub>2</sub> ) <sub>12</sub> Br <sub>3</sub>	28.92	30.79	36.19	5.90		29.1	31.0	36.4	7.1			from I and KNH <sub>2</sub> at -50 °C
Ib	K <sub>2</sub> Ti <sub>2</sub> (N)(NH) <sub>3</sub>	41.12	29.18		33.56		40.2	27.2	1.1	31.7			from Ia and KNH <sub>2</sub> at room temp
Ic													isolated in small amounts from initially soluble fraction of I; Ti:Br:N:B = 1:0.75:2.5:0.25; purple solids
Id	Ti <sub>4</sub> Br <sub>3</sub> (NH <sub>2</sub> ) <sub>12</sub> ·9NH <sub>3</sub>	24.68	45.99	30.87			23.9	44.1	30.0	1.3	0.73		prepn described in text; 6.88% Ti(III) or 28% of ΣTi
Ie	Ti <sub>4</sub> (C≡CH)(NH) <sub>6</sub> NH <sub>2</sub>	59.39	36.88			7.44	58.5	35.0	0.1	2.6		7.6	from I and NaC≡CH
II	[NH <sub>4</sub> <sup>+</sup> ] <sub>4</sub> Ti <sub>4</sub> Cl <sub>8</sub> (NH <sub>2</sub> ) <sub>8</sub> ·4NH <sub>3</sub>	25.78	36.60	38.16			25.6	36.9	36.9	0.5	0.7		from TiCl <sub>3</sub> + NaBH <sub>4</sub> at 35 °C; 25.81% Ti(III) or 100% of ΣTi
IIa	Ti <sub>4</sub> (C≡C) <sub>2</sub> (NH) <sub>4</sub>	63.95	22.70			16.02	59.4	20.6	2.8	5.0		12.7	from II and NaC≡CH at room temp
IIb	NaTi <sub>4</sub> (C≡C) <sub>2</sub> (NH) <sub>4</sub> NH <sub>2</sub>	56.6	25.13		6.8	14.2	53.1	25.9	0.8	5.3		16.0	from TiCl <sub>3</sub> and NaC≡CH at room temp
IIc	Na <sub>4</sub> Ti <sub>4</sub> (C≡C) <sub>2</sub> (NH) <sub>4</sub>	48.9	17.36		23.5	12.3	47.6	17.4		23.0		11.8	from TiCl <sub>3</sub> ·4NH <sub>3</sub> and NaC≡CH at room temp
III	[NH <sub>4</sub> <sup>+</sup> ] <sub>2</sub> Ti <sub>4</sub> Br <sub>4</sub> (NH) <sub>4</sub> (NH <sub>2</sub> ) <sub>6</sub>	27.47	29.25	45.84			27.5	30.9	41.6				ammonolysis of TiBr <sub>4</sub> after removal of NH <sub>4</sub> Br
III'	[NH <sub>4</sub> <sup>+</sup> ] <sub>2</sub> Ti <sub>4</sub> Br <sub>4</sub> (NH) <sub>4</sub> (NH <sub>2</sub> ) <sub>6</sub>	27.47	29.25	45.84			24.1	28.0	47.9				ammonolysis of TiBr <sub>4</sub> after partial removal of NH <sub>4</sub> Br
IIIa	Ti <sub>4</sub> (C≡C)(NH) <sub>7</sub>	59.76	37.11			7.49	58.7	32.8		5.3		6.9	from III and NaC≡CH
IIIb	NaTi <sub>4</sub> (C≡C)(NH) <sub>7</sub> NH <sub>2</sub>	53.28	37.83		6.38	6.67	50.9	36.0		6.5		7.1	from III' and NaC≡CH

useful precursors for titanium carbonitride. The proportions of carbon and nitrogen in these materials are determined by the compositions of the precursors.

### Experimental Section

Electronic grade ammonia was further purified by contact with sodium metal. Titanium(IV) bromide (Alfa Inorganics) was sublimed prior to use. Sodium acetylide was prepared according to the procedure given in ref 23. All other reagents were of AR quality and were used without any additional purification.

Titanium, boron, and alkali-metal analyses were done by ICP. Nitrogen was determined as ammonium ion with an ion-selective electrode. Halides were also determined with ion-selective electrodes. Carbon was determined with a carbon analyzer by combustion as CO<sub>2</sub>. Infrared spectra were obtained with a Model 60 Digilab FTIR spectrophotometer. ESCA was done with use of Al K $\alpha$  radiation at 250 W.

All manipulations were done in an inert-gas glovebox and in a vacuum line. Reactions were done, unless otherwise stated, at room temperature in sealed heavy-walled ampules provided with side arms, which were used to decant the supernatant from the solid products. The products were washed with ammonia distilled from the side arm. This procedure was repeated many times.

Acetylene evolved in the sodium acetylide reactions was volumetrically measured after fractionation through a -130 °C (*n*-pentane) trap. This trap retained most of the NH<sub>3</sub> and allowed passage of all the HC≡CH produced and a small amount of ammonia. The residual ammonia in the acetylene fraction was determined after collecting the mixture into an aqueous solution containing excess standard acid. The amount of NH<sub>3</sub>

was subtracted from the volume of the HC≡CH-NH<sub>3</sub> mixture in order to arrive at the amount of acetylene produced. The titanium(III) content of the products was determined by dissolution into excess standard Ce(IV) solution and back-titrated with Fe(II) with use of ferroin as indicator.

All reactions, with the exception of that leading to compound Id, were conducted by loading a few millimoles of the reactants into heavy-walled ampules provided with a side arm. The ampules were sealed after introducing about 10–15 mL of liquid ammonia. The reaction mixtures were allowed to stand at room temperature for a few days and then fractionated by transfer of the supernatant into the side arm. Ammonia was distilled back to the straight portion of the ampule by insertion into an ice bath. The solids were resuspended and vigorously stirred. The resulting supernatant was transferred into the side arm, and the whole operation was repeated a few times. The products were recovered in the glovebox after removal of the ammonia.

The analytical results are summarized in Table II. The idealized formulas given are the closest compositions consistent with the analyses and an ionic balance.

Compound Id was isolated after a number of steps. Potassium borohydride and titanium(IV) bromide were made to react at -50 °C. This produced a small amount of a pale green insoluble residue showing an empirical formula corresponding to K<sub>8</sub>Ti<sub>4</sub>(NH<sub>2</sub>)<sub>19</sub>Br<sub>5</sub>. (Anal. Calcd: Ti, 15.87; NH<sub>2</sub>, 25.16; Br, 33.1; K, 25.88. Found: Ti, 15.9; NH<sub>2</sub>, 23.2; Br, 33.1; K, 25.5; B, 0.4.) The soluble portion was isolated after evaporation of NH<sub>3</sub> and resuspended in ammonia in a sealed ampule, and the suspension was maintained at room temperature for a few days. This produced a purple precipitate. The ampule was cooled to -63 °C and emptied through a frit. The purple solid on the frit was isolated and resuspended once more in liquid ammonia, and the suspension was stirred

at  $-60\text{ }^{\circ}\text{C}$  and filtered. The solid product remaining on the frit, compound Id, turned green, and the soluble fraction was proven to contain  $\text{KBH}_4$  upon analysis.

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**Registry No.**  $\text{TiBr}_4$ , 7789-68-6;  $\text{KBH}_4$ , 13762-51-1;  $\text{NH}_3$ , 7664-41-7;  $\text{TiCl}_3$ , 7705-07-9;  $\text{NaBH}_4$ , 16940-66-2.

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## Chromium(III)-Doped Pillared Clays (PILC's)

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Spectroscopic and catalytic properties of a low-iron-content bentonite clay were found to be sensitive to pillaring and to exchange with Cr(III) ions. These ions were introduced into the clay in both pillared and unpillared forms by the use of different synthetic conditions. Diffuse reflectance spectroscopy (DRS) and electron paramagnetic resonance (EPR) were used to monitor the environment of Cr(III) to determine whether it was in the interlamellar space of the clay or associated with an aluminum-hydroxy pillar. Catalytic behavior responded differently to Cr(III) in the different environments. Incorporating Cr(III) into an alumina pillar increased the kinetic stability and activity of the catalyst in decane cracking compared to a PILC catalyst containing no chromium.

### I. Introduction

It is known that smectite clays can be pillared with oligomeric metal hydroxide ions<sup>1-3</sup> to yield thermally stable materials with some properties similar to those of zeolites. Moreover, these materials have pores of a larger size range that allows catalytic conversion of high molecular weight hydrocarbons.<sup>2</sup>

Pillared montmorillonites have been prepared by ion exchanging the clay with several different agents, some of which are hydroxy-aluminum<sup>4</sup> cations  $\{[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}\}$ , zirconyl-aluminum-halo-hydroxy complexes<sup>4</sup>  $\{[\text{ZrOCl}_2\cdot\text{Al}_8(\text{OH})_{20}]^{4+}\}$ , colloidal silica,<sup>4</sup> polyoxy-chromium oligomers,<sup>5</sup> and zirconyl chloride<sup>6</sup>  $\{[\text{Zr}_4(\text{OH})_{16-n}(\text{H}_2\text{O})_{n+8}]^{n+}\}$  and fluoro-hydroxy-aluminum cations<sup>7</sup>  $\{[\text{Al}_{13}\text{O}_4\text{F}_x(\text{OH})_{24-x}]^{7+}\}$ .

These materials display different catalytic activities depending upon the type of pillar and upon the presence of other metallic ions or complexes. Propylene oligomerization has been examined with alumina-pillared clays (APC) and (Zr,Al)PC.<sup>8</sup> The catalytic cracking activity of APC has been extensively studied.<sup>2,9,10</sup> Increased acidity and related catalytic activity have been examined by pillaring preexchanged Ce- and La-clays.<sup>11,12</sup> By also adding other metal or metal complex ions to a pillared clay, other catalytic mechanisms have been induced; APC (Zr,Al)PC, and clays pillared with silica have been evaluated for use as the cracking component for hydrocracking vacuum gas oil.<sup>4</sup> Fischer-Tropsch (F-T) catalytic properties of metal cluster carbonyl complexes on APC<sup>13</sup> and the re-forming activity of Pt-Re on APC<sup>14</sup> have also been reported. Pillaring of a nickel-substituted montmorillonite produces hydroisomerization catalysts.<sup>15</sup> Also, Ru- $(\text{NH}_3)_6^{3+}$ -exchanged APC has been observed<sup>16</sup> to have activity for the reduction of  $\text{CO}_2$  by  $\text{H}_2$ .

Here we report observed differences in the catalytic role played by a supported metal ion depending upon its apparent position in a pillared clay, i.e. in the micropore structure vs. in the pillars. Related work has attempted to substitute uranyl<sup>17</sup> and iron<sup>18</sup> ions directly into an alumina or zirconia pillar. Chromium ions were chosen because they can be tracked spectroscopically, as has been reported for Cr<sup>3+</sup>-exchanged zeolites by using infrared spectroscopy, electron paramagnetic resonance (EPR), and diffuse reflectance spectroscopy (DRS).<sup>19</sup> The photochemical and photocatalytic properties of tris(2,2'-bipyridine)chromium(III) in clays<sup>20</sup> have also been studied. Hydroxy-chromium cations in clays have been examined.<sup>21,22</sup> The catalytic activity of

chromium as chromia,  $\text{Cr}_2\text{O}_3$ , has been reported in reactions<sup>23</sup> involving alkylation, aromatization, cracking, cyclization, dehydrogenation, F-T, hydrodealkylation, hydrogenation, oxidation, re-forming, and the water gas shift reaction. Chromia-pillared clay catalysts have recently been studied for the dehydrogenation of cyclohexane to benzene.<sup>5</sup>

A relevant study has recently disclosed a class of hydroprocessing catalysts reported<sup>24</sup> to be comprised of, for example, a  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$  ion-exchanged smectite that is then cross-linked with hydroxy-Al oligomers. This material is calcined at 400-500  $^{\circ}\text{C}$  and treated with, for example, an ammonium molybdate solution to yield the hydroprocessing catalyst.

- (1) Vaughan, D. E. W.; Lussier, R. J. *Proc. Int. Conf. Zeol.*, 5th 1980, 94.
- (2) Vaughan, D. E. W.; Lussier, R. J.; Magee, J. S. U.S. Patent 4176090, 1979.
- (3) Lahav, N.; Shani, U.; Shabtai, J. *Clays Clay Miner.* 1978, 26, 107.
- (4) Ocelli, M. L.; Rennard, R. J., submitted for publication.
- (5) Pinnavaia, T. J.; Tzou, M. S.; Landau, S. D. *J. Am. Chem. Soc.* 1985, 107, 4783.
- (6) Yamanaka, S.; Brindley, G. W. *Clays Clay Miner.* 1979, 27, 119.
- (7) Fijal, J.; Shabtai, J. *Abstracts of Papers*, International Clay Conference, Denver, CO, 1985; No. 67.
- (8) Ocelli, M. L.; Hsu, J. T.; Galya, L. G. *J. Mol. Catal.* 1985, 33, 371.
- (9) Ocelli, M. L.; Innes, R. A.; Hwu, F. S. S.; Hightower, J. W. *Appl. Catal.* 1985, 14, 69.
- (10) Ocelli, M. L. *Ind. Eng. Chem. Prod. Res. Dev.* 1983, 22, 553.
- (11) Tokarz, M.; Shabtai, J. *Clays Clay Miner.* 1985, 33, 89.
- (12) Shabtai, J.; Lazar, R.; Oblad, A. G. *Proceeding of the 7th Inter. Congress on Catalysis*; Seiyama, T., Tanabe, K., Eds.; Kodansha-Elsevier: Tokyo, 1980; p 828.
- (13) Giannelis, E. P.; Rightor, E. G.; Pinnavaia, T. J. *Abstracts of Papers*, International Clay Conference, Denver, CO, 1985; No. 81.
- (14) Parulekar, V. N.; Hightower, J. W. *Abstracts of Papers*, 9th Meeting of the Catalysis Society, Houston, TX, 1985.
- (15) Gaaf, J.; van Santen, R.; Knoester, A.; van Wingerden, B. *J. Chem. Soc., Chem. Commun.* 1983, 655.
- (16) Challal, D.; Bergaya, F.; van Damme, H. *Bull. Soc. Chim. Fr.* 1985, 3, 393.
- (17) Ocelli, M. L.; Tanguay, J. F.; Suib, S. L. *J. Am. Chem. Soc.*, in press.
- (18) Kostapapas, A.; Suib, S. L.; Skoularikis, N. D.; Coughlin, R. W., submitted for publication.
- (19) Pearce, J. R.; Sherwood, D. E.; Hall, M. B.; Lunsford, J. H. *J. Phys. Chem.* 1980, 84, 3215.
- (20) Krenske, D.; Abdo, S.; van Damme, H.; Cruz, M.; Fripiat, J. J. *J. Phys. Chem.* 1980, 84, 2447. Abdo, S.; Canesson, P.; Cruz, M.; Fripiat, J. J.; van Damme, H., *J. Phys. Chem.* 1981, 85, 797.
- (21) Brindley, G. W.; Yamanaka, S. *Am. Mineral.* 1979, 64, 830.
- (22) Carr, M. *Clays Clay Miner.* 1985, 33, 357.
- (23) Wagner, F. S. In *Applied Industrial Catalysis*; Leach, B. E., Ed.; Academic: New York, 1983, Vol. 2, p 39.
- (24) Shabtai, J.; Fijal, J. U.S. Patent 4579832, 1986.

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