

Preparation and Characterization of the First Binary Titanium Azides, $\text{Ti}(\text{N}_3)_4$, $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Ti}(\text{N}_3)_5]$ and $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Ti}(\text{N}_3)_6]$ and on Linear Ti-N-NN Coordination^{*,†}

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Whereas numerous partially azide-substituted titanium compounds had previously been reported,^[1-7] no binary titanium azides were known. In a recent theoretical study, the group 4 metal tetrazides $\text{M}(\text{N}_3)_4$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Th}$) were predicted^[8] to be vibrationally stable, exhibiting tetrahedral structures with unique linear M-N-NN bond angles (see Figure 1). All previously characterized covalent binary azide species possess bent M-N-NN angles.^[9] In this paper, we wish to report the synthesis, isolation and characterization of the first binary titanium azide species $\text{Ti}(\text{N}_3)_4$, $[\text{Ti}(\text{N}_3)_5]^-$ and $[\text{Ti}(\text{N}_3)_6]^{2-}$, and provide explanations for the observed and predicted Ti-N-NN bond angles.

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[**] This work was funded by the Defense Advanced Research Projects Agency, with additional support from the Air Force Office of Scientific Research and the National Science Foundation. We thank Prof. G. A. Olah, and Drs. A. Morrish, D. Woodbury, and M. Berman, for their steady support, and Prof. R. Bau and Dr. R. Wagner for their help and stimulating discussions.

[†] Dedicated to Dr. Robert Corley on the occasion of his 70th birthday.

Report Documentation Page

Form Approved
OMB No. 0704-0188

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1. REPORT DATE 12 MAR 2004	2. REPORT TYPE	3. DATES COVERED -		
4. TITLE AND SUBTITLE Preparation and Characterization of the First Binary Titanium Azides		5a. CONTRACT NUMBER F04611-99-C-0025		
		5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Ralf Haiges; Jerry Boatz; Stefan Schneider; Thorsten Schroer; Muhammed Yousufuddin		5d. PROJECT NUMBER DARP		
		5e. TASK NUMBER A205		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ERC Incorporated,555 Sparkman Drive,Huntsville,AL,35816-0000		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT Where as numerous partially azide-substituted titanium compounds had previously been reported,[1-7] no binary titanium azides were known. In a recent theoretical study, the group 4 metal tetrazides M(N3)4 (M = Ti, Zr, Hf, Th) were predicted[8] to be vibrationally stable, exhibiting tetrahedral structures with unique linear M-N-NN bond angles (see Figure 1). All previously characterized covalent binary azide species possess bent M-N-NN angles.[9] In this paper, we wish to report the synthesis, isolation and characterization of the first binary titanium azide species Ti(N3)4, [Ti(N3)5]- and [Ti(N3)6]2-, and provide explanations for the observed and predicted Ti-N-NN bond angles.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified		
			18. NUMBER OF PAGES 20	19a. NAME OF RESPONSIBLE PERSON

The reaction of TiF_4 with $(\text{CH}_3)_3\text{SiN}_3$ in acetonitrile solution at room temperature results within minutes in complete fluoride-azide exchange and yields a clear orange solution of $\text{Ti}(\text{N}_3)_4$ according to Equation (1).



Removal of the volatile products (CH_3CN , $(\text{CH}_3)_3\text{SiF}$ and excess $(\text{CH}_3)_3\text{SiN}_3$) at ambient temperature results in the isolation of $\text{Ti}(\text{N}_3)_4$ as an amorphous orange solid. All attempts to obtain single crystals by recrystallization or sublimation were unsuccessful.

As expected for a highly endothermic, covalent polyazide species, $\text{Ti}(\text{N}_3)_4$ is very shock sensitive and can explode violently when touched with a metal spatula or by rapid change in temperature (e.g. freezing with liquid nitrogen). Its identity was established by the observed material balance, and vibrational and NMR spectroscopy. The presence of covalent azido ligands^[10-15] is confirmed by the observed ^{14}N NMR shifts of $\mathbf{d} = -134$ ppm (N_β , $\Delta\nu_{1/2} = 26$ Hz), -195 ppm (N_γ , $\Delta\nu_{1/2} = 39$ Hz) and -255 ppm (N_α , extremely broad) in DMSO solution at 25°C .

The observed Raman and IR spectra of solid $\text{Ti}(\text{N}_3)_4$ are shown in Figure 2, and the observed frequencies and intensities are listed in the experimental section. The experimental vibrational spectra deviate significantly from those calculated for free $\text{Ti}(\text{N}_3)_4$ at the B3LYP level of theory,^[8, 16] and resemble those of higher-coordinated compounds with bent M-N-NN bonds. Therefore, the predicted^[8] tetrahedral structure with linear Ti-N-NN bonds could not be confirmed in this study. The discrepancy between the calculated and observed spectra arises from solid state effects. The Ti atoms in $\text{Ti}(\text{N}_3)_4$ are coordinatively unsaturated seeking higher coordination numbers by the formation of nitrogen bridges, and crystal-structure data will be

required for a reliable determination of the precise arrangement of the azido ligands in solid $\text{Ti}(\text{N}_3)_4$. The growing of single crystals for such a study will be difficult because the compound is hard to recrystallize and does not sublime without decomposition. The structure determination of free monomeric $\text{Ti}(\text{N}_3)_4$ and proof for its predicted tetrahedral structure with linear Ti-N-NN bonds will be even more difficult.

The reaction of $\text{Ti}(\text{N}_3)_4$ with one equivalent of ionic azides leads to the formation of the $[\text{Ti}(\text{N}_3)_5]^-$ anion according to Equation (2).



The $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Ti}(\text{N}_3)_5]$ salt was isolated as an orange solid. It is less sensitive than $\text{Ti}(\text{N}_3)_4$ and does not explode upon freezing with liquid nitrogen. It was characterized by its ^{14}N NMR spectrum, and by infrared and Raman spectroscopy. The observed Raman and IR spectra of $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Ti}(\text{N}_3)_5]$ are shown in Figure 3. The experimental infrared and Raman frequencies and intensities are listed in the experimental section. Three well-resolved ^{14}N NMR resonances were found in DMSO at 25°C. The spectrum shows a sharp signal at $\delta = -133$ ppm ($\Delta\nu_{1/2} = 28$ Hz) for the N_β atoms, a medium-sharp resonance at $\delta = -194$ ppm ($\Delta\nu_{1/2} = 40$ Hz) for the N_γ atoms, and a very broad signal at $\delta = -263$ ppm ($\Delta\nu_{1/2} = 160$ Hz) for the N_α atoms, in accord with our expectations for covalently bound azido groups. The calculated structure for the free gaseous anion is that of a trigonal bipyramid, and its calculated frequencies are listed in the Theoretical Methods section.

By reaction of $\text{Ti}(\text{N}_3)_4$ with two equivalents of ionic azide, the $[\text{Ti}(\text{N}_3)_6]^{2-}$ anion is formed according to Equation (3).



$[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Ti}(\text{N}_3)_6]$ was isolated as an orange solid and is stable at room temperature. Because of the presence of two large counter-ions, it is much less sensitive and explosive than $\text{Ti}(\text{N}_3)_4$. It can even be heated to its melting point at 191°C without any signs of decomposition. The compound was characterized by its crystal structure,^[17] and vibrational and ^{14}N NMR spectroscopy. Single crystals were obtained from a solution in CH_3CN .

$[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Ti}(\text{N}_3)_6]$ crystallizes in the triclinic space group $P\bar{1}$ and is the first structurally characterized binary titanium azide. Figure 4 depicts the structure of the $[\text{Ti}(\text{N}_3)_6]^{2-}$ anion that is only slightly distorted from perfect S_6 symmetry. The structure consists of an asymmetric TiN_9 unit with three azido groups covalently bonded in a trigonal pyramidal fashion to the titanium. The remaining three azide groups are generated by symmetry (symmetry operation $-x+2,-y+1,-z$). The average Ti-N distance of 2.02 \AA is in good agreement with the one reported for $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{N}_3)_2$ ($2.03(1) \text{ \AA}$).^[6] In the $[\text{P}(\text{C}_6\text{H}_5)_4]^+[\text{Ti}(\text{N}_3)_6]^{2-}$ salt, the anions are well separated by twice as many large counter-ions, and the closest $\text{Ti}\cdots\text{N}$ contacts between neighboring anions are 7.1 \AA .

Further support for the presence of the $[\text{Ti}(\text{N}_3)_6]^{2-}$ ion is provided by the NMR spectrum. In analogy with $\text{Te}(\text{N}_3)_4$ and $[\text{Ti}(\text{N}_3)_5]^-$, the ^{14}N NMR spectra in DMSO show at $\mathbf{d} = -134 \text{ ppm}$ (N_β , $\Delta\nu_{1/2} = 30 \text{ Hz}$), -199 ppm (N_γ , $\Delta\nu_{1/2} = 35 \text{ Hz}$) and -264 ppm (N_α , $\Delta\nu_{1/2} = 165 \text{ Hz}$) resonances characteristic for covalent azides.

The observed Raman and IR spectra of $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Ti}(\text{N}_3)_6]$ are shown in Figure 5, and the observed frequencies and intensities are listed in the experimental section. Assignments of the observed spectra were made by comparison with those calculated at the B3LYP/SBKJC+(d) level of theory^[16] and are given in the experimental section.

Although the occurrence of linear Ti-N-NN bond angles could not be confirmed experimentally, we have confirmed by independent computations the correctness of the previous predictions^[8] for free gaseous $\text{Ti}(\text{N}_3)_4$. Furthermore, it was shown, both computationally and experimentally by our crystal structure determination, that in higher coordinated binary titanium azide species, such as $[\text{Ti}(\text{N}_3)_6]^{2-}$, and in the main group tetra-azides $\text{M}(\text{N}_3)_4$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) the M-N-NN bond angles are normal and strongly bent. It was also shown that the occurrence of linear M-N-NN bond angles should not be limited to group 4 tetra-azides, but might also occur in compounds, such as $\text{Fe}(\text{N}_3)_2$.^[18] Normal coordinate analyses were carried out for the binary Ti-azides of this study and showed that the modes due to the azido ligands were highly characteristic, while those of the TiN_n skeletal modes were strongly mixed and, therefore, are not reported in this paper. However, the TiN_n stretching mode clusters clearly exhibit the frequency decreases expected for increasing polarities of the Ti-N bonds with increasing negative formal charges. Thus, the range of the TiN_n stretching modes decreases from 472 - 371 cm^{-1} in $\text{Ti}(\text{N}_3)_4$ to 448 - 355 cm^{-1} in $\text{Ti}(\text{N}_3)_5^-$ and 398 - 307 cm^{-1} in $[\text{Ti}(\text{N}_3)_6]^{2-}$.

In the previous theoretical paper on the linearity of the M-N-NN bond angles for $\text{M} = \text{Ti}, \text{Zr}$ and Hf , the linearities of the M-N-NN angles was explained by M-N-N-N conjugation.^[8] In our opinion, the linearity of the M-N-NN angles is due to a nearly ideal overlap between the three valence electron pairs on the *a*-nitrogen atoms of the azide ligands and the lobes of the *d*-orbitals on the central metal atom. Because the *d*-orbitals of the (+IV) central metal atoms are unoccupied, the three valence electron pairs of the *a*-nitrogens can donate electron density equally into three lobes of the empty *d*-orbitals resulting in the *a*-nitrogen acting as a tridentate donor ligand. The symmetry of the central axes of these *d*-orbitals is tetrahedral. Therefore, this tridentate type of overlap is possible only for the tetra-coordinated azides of group 4 transition

metals with d^0 configurations. For other coordination numbers or electron configurations, the α -nitrogens act usually as monodentate donors with only one pair donating and two sterically active free valence electron pairs, thus resulting in strongly bent M-N-NN bond angles. An excellent example for the validity of our explanation is the known crystal structure of $\text{Zr}(\text{BH}_4)_4$ (see Figure 6) involving a (+IV) group 4 d^0 transition metal central atom and 4 trihapto BH_4 ligands.^[19] Another example for a special geometry, dictated by the empty d^0 -orbitals of a (+IV) group 4 transition metal is $\text{Ti}(\text{O}_2\text{ClO}_2)_4$ in which the perchlorato groups act as bidentate ligands.^[20]

Experimental Section

Caution! *Covalent azides are potentially hazardous and can decompose explosively under various conditions! They should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs). Teflon containers should be used, whenever possible, to avoid hazardous fragmentation. Pure $\text{Ti}(\text{N}_3)_4$ has to be cooled or heated carefully and slowly. A sample at ambient temperature must not be cooled directly with liquid nitrogen. Doing so can result in violent explosions. Ignoring safety precautions can lead to serious injuries.*

Materials and Apparatus: All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass vacuum line. All Teflon reaction vessels were passivated with ClF_3 prior to use. Nonvolatile materials were handled in the dry argon atmosphere of a glove box.

Raman spectra were recorded at $-80\text{ }^{\circ}\text{C}$ in the range $4000\text{--}80\text{ cm}^{-1}$ on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd-YAG laser at 1064 nm with power levels of less than 200 mW . Pyrex melting point tubes that were baked out at $300\text{ }^{\circ}\text{C}$ for 48 h at 10 mTorr vacuum or Teflon-FEP tubes with stainless steel valves that were passivated with ClF_3 were used as sample containers. Infrared spectra were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ on a Midac, M Series, FT-IR spectrometer using KBr or AgCl pellets. The pellets were prepared inside the glove-box using an Econo press (Barnes Engineering Co.).

^{14}N NMR spectra were recorded unlocked at 36.13 MHz on a Bruker AMX 500 spectrometer using solutions of the compounds in DMSO in sealed standard glass tubes. Neat CH_3NO_2 (0.00 ppm) was used as the external reference.

The starting materials TiF_4 and $[\text{P}(\text{C}_6\text{H}_5)_4]\text{I}$ (both from Aldrich) were used without further purification. $(\text{CH}_3)_3\text{SiN}_3$ (Aldrich) was purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. $[\text{P}(\text{C}_6\text{H}_5)_4]\text{N}_3$ was prepared from $[\text{P}(\text{C}_6\text{H}_5)_4]\text{I}$ and AgN_3 .

Preparation of $\text{Ti}(\text{N}_3)_4$: A sample of TiF_4 (0.96 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of $3\text{ mL CH}_3\text{CN}$ and $(\text{CH}_3)_3\text{SiN}_3$ (4.32 mmol) *in vacuo* at $-196\text{ }^{\circ}\text{C}$. The mixture was allowed to warm to room temperature. Within minutes, the mixture turned yellow, and the color intensified while the reaction proceeded. After 1 hour , all volatile material was pumped off, leaving behind an orange solid (0.20 g , weight calculated for $0.96\text{ mmol Ti}(\text{N}_3)_4 = 0.21\text{ g}$). The obtained orange solid was characterized by vibrational and NMR spectroscopy. IR (AgCl): $\tilde{\nu} = 2141(\text{vs})/2093(\text{vs})/2051(\text{vs})$ ($\nu_{\text{as}}\text{N}_3$), $1376(\text{s, br})/1253(\text{s})$ ($\nu_{\text{s}}\text{N}_3$), $684(\text{s})/668(\text{s})/665(\text{s})/575(\text{m})/561(\text{m})$ (δN_3), $458(\text{w})\text{ cm}^{-1}$ (νTiN_n). Raman (50mW , $-80\text{ }^{\circ}\text{C}$): $\tilde{\nu} = 2160(10.0)/2141(4.0)/2108(2.9)/2100(1.8)/2079(2.8)$ ($\nu_{\text{as}}\text{N}_3$), $1407(1.0)/1385(0.2)/1366(0.2)/$

1283(0.3)/1269(0.3) ($\nu_s\text{N}_3$), 671(0.3)/574(0.4) (δN_3), 472(9.6)/454(4.9)/391(2.2)/371(1.8) (νTiN_n), 310(1.7), 270 (1.7), 227 (0.8), 168 (2.1), 135(2.0) cm^{-1} .

Preparation of [PPh₄][Ti(N₃)₅]. A solution of Ti(N₃)₄ (0.5 mmol) in 3 mL CH₃CN was added to a mixture of PPh₄N₃ (0.5 ml) in 2 mL CH₃CN at -64 °C. The reaction mixture was warmed to ambient temperature where it formed a clear orange solution. After 2 hours, all volatiles were slowly removed in a dynamic vacuum at 20 °C, leaving behind an orange solid (0.450 g, weight calculated for 0.5 mmol [PPh₄][Ti(N₃)₅] = 0.443 g). IR of [Ti(N₃)₅]⁻ (KBr): $\tilde{\nu}$ =2100(vs)/2070(vs)/2058(vs) ($\nu_{\text{as}}\text{N}_3$), 1373(m)/1356(s)/1320(s) ($\nu_s\text{N}_3$), 621(m)/595(w)/591(w)/580(vw) (δN_3), 448(w)/440(vw) cm^{-1} (νTiN_n). Raman of [Ti(N₃)₅]⁻ (50 mW, -80 °C): $\tilde{\nu}$ =2133(10.0)/2110(4.4)/2083(2.9)/2070(2.2) ($\nu_{\text{as}}\text{N}_3$), 1367(0.3)/1342(0.3)/1325(0.2)/1314(0.1) ($\nu_s\text{N}_3$), 623(0.2)/608(0.1)/597(0.1) (δN_3), 445(3.4)/438(1.0)/412(0.6)/398(2.2)/363(0.9)/355(0.7) (νTiN_n), 306(0.9), 245(1.3), 210(0.9), 174(1.6) cm^{-1} .

Preparation of [PPh₄]₂[Ti(N₃)₆]. A solution of Ti(N₃)₄ (0.5 mmol) in 3 mL CH₃CN was added to a mixture of PPh₄N₃ (1.0 ml) in 2 mL CH₃CN at -64 °C. The reaction mixture was warmed to ambient temperature and an orange precipitate was formed. After 8 hours, all volatiles were removed in a dynamic vacuum at 20°C, leaving behind an orange solid (0.768 g, weight calculated for 0.5 mmol [PPh₄]₂[Ti(N₃)₆] = 0.778 g). Single crystals were grown from a solution in CH₃CN by slow evaporation in a dynamic vacuum. IR of [Ti(N₃)₆]²⁻ (KBr): $\tilde{\nu}$ =2109(m)/2061(vs)/2041(vs) ($\nu_{\text{as}}\text{N}_3$), 1356(s)/1322(s) ($\nu_s\text{N}_3$), 622(m)/615(m)/595(w) cm^{-1} (δN_3). Raman of [Ti(N₃)₆]²⁻ (50 mW, -90 °C) $\tilde{\nu}$ =2110(10.0)/2063(1.2)/2038(0.3) ($\nu_{\text{as}}\text{N}_3$), 1366(0.7)/1341(0.7)/1325(0.4) ($\nu_s\text{N}_3$), 631(0.2)/622(0.3)/608(0.3) (δN_3), 398(5.4)/316(1.1)/307(1.1) (νTiN_n), 246(1.3), 210 (1.8), 103(0.5), 95(0.5) cm^{-1} .

Theoretical Methods. The molecular structures and harmonic vibrational frequencies were calculated at the DFT level using the B3LYP hybrid functional,^[16a] which included the VWN5 correlation functional.^[16b] The SBKJC^[16c] effective core potential and the corresponding valence-only basis set was used for titanium. The all-electron 6-31G basis set,^[16d] augmented with a d polarization function^[16e] and a diffuse s+p shell^[16f] and denoted as 6-31+G(d), was used for nitrogen. All calculations were performed using the GAMESS^[16g] quantum chemistry program. Unscaled calculated frequencies (cm⁻¹) and (infrared, km/mol) and [Raman, Å⁴/amu] intensities for Ti(N₃)₄: 2293 (0.0) [794], 2251 (5737) [1022], 1497 (0.0) [4.5], 1475 (2005) [48], 573 (110) [0.3], 571 (0.0) [0.3], 569 (0.0) [0.0], 516 (933) [67], 373 (0.0) [103], 192 (17) [7.3], 167 (0.0) [14.0], 14.8 (0.0) [50], 14.0 (0.0) [71]. [Ti(N₃)₅]⁻ (pseudo-trigonal bipyramid of C_i symmetry): 2248 (72) [751], 2212 (3406) [42], 2206 (1441) [160], 2202 (1836) [77], 2200 (142) [278], 1445 (48) [28], 1433 (390) [4.3], 1415 (180) [16], 1404 (174) [17], 1402 (384) [6.9], 620 (50) [0.3], 618 (18) [0.8], 615 (57) [0.7], 602 (13) [1.2], 601 (12) [0.1], 599 (10) [0.7], 595 (12) [0.8], 594 (1.0) [0.4], 584 (19) [0.9], 577 (43) [0.4], 487 (325) [1.2], 475 (347) [0.7], 456 (534) [1.8], 401 (1.2) [77], 322 (0.3) [4.2], 263 (2.6) [8.6], 252 (5.3) [7.3], 231 (3.9) [7.2], 228 (0.8) [19], 200 (0.7) [8.1], 131 (2.8) [4.8], 103 (1.1) [11], 94 (0.2) [12], 91 (0.5) [7.1], 66 (0.1) [1.9], 54 (1.1) [4.6], 40 (0.1) [18], 36 (0.1) [22], 33 (0.6) [18], 30 (0.2) [19], 24 (1.1) [2.4], 19 (0.7) [8.1]. [Ti(N₃)₆]²⁻: 2234 (1.4) [798], 2186 (3723) [9.5], 2185 (2778) [90], 2180 (2776) [74], 2168 (25) [180], 2167 (468) [134], 1438 (3.6) [70], 1429 (161) [18], 1428 (19) [46], 1425 (182) [23], 1424 (186) [24], 1424 (165) [17], 626 (4.1) [5.9], 622 (34) [1.2], 621 (39) [2.8], 620 (59) [3.9], 620 (0.0) [2.9], 616 (3.1) [3.9], 608 (5.2) [0.2], 605 (8.8) [0.0], 604 (3.9) [0.1], 599 (9.4) [0.1], 599 (9.9) [0.0], 598 (0.6) [0.4], 409 (675) [0.4], 404 (540) [0.9], 404 (601) [1.2], 364 (1.2) [78], 284 (0.2) [11], 280 (0.1) [8.4], 264 (3.0) [7.0], 261 (5.4) [0.2], 250 (3.5) [6.1], 235 (3.6) [8.7],

209 (0.1) [19], 205 (0.2) [7.4], 151 (1.2) [25], 150 (0.2) [15], 142 (0.4) [25], 78 (1.9) [2.2], 63 (0.1) [11], 62 (2.7) [0.4], 44 (2.2) [20], 40 (0.5) [28], 39 (0.0) [14], 33 (1.0) [28], 28 (2.0) [2.7], 23 (0.1) [13], 21 (1.2) [4.1], 16 (0.1) [4.5], 15 (1.2) [6.8].

Received: , 2004

Keywords: Crystal structure, Titanium azides, Vibrational spectra, NMR spectra, Theoretical calculations

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Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 232521.

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Figure 1. Predicted tetrahedral structure of free gaseous $\text{Ti}(\text{N}_3)_4$ with linear Ti-N-NN bonds.

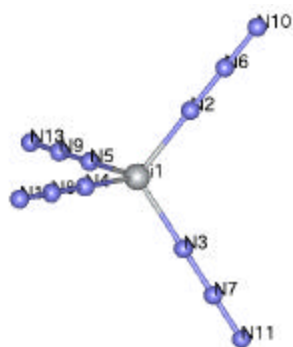


Figure 2. IR and Raman spectra of solid $\text{Ti}(\text{N}_3)_4$.

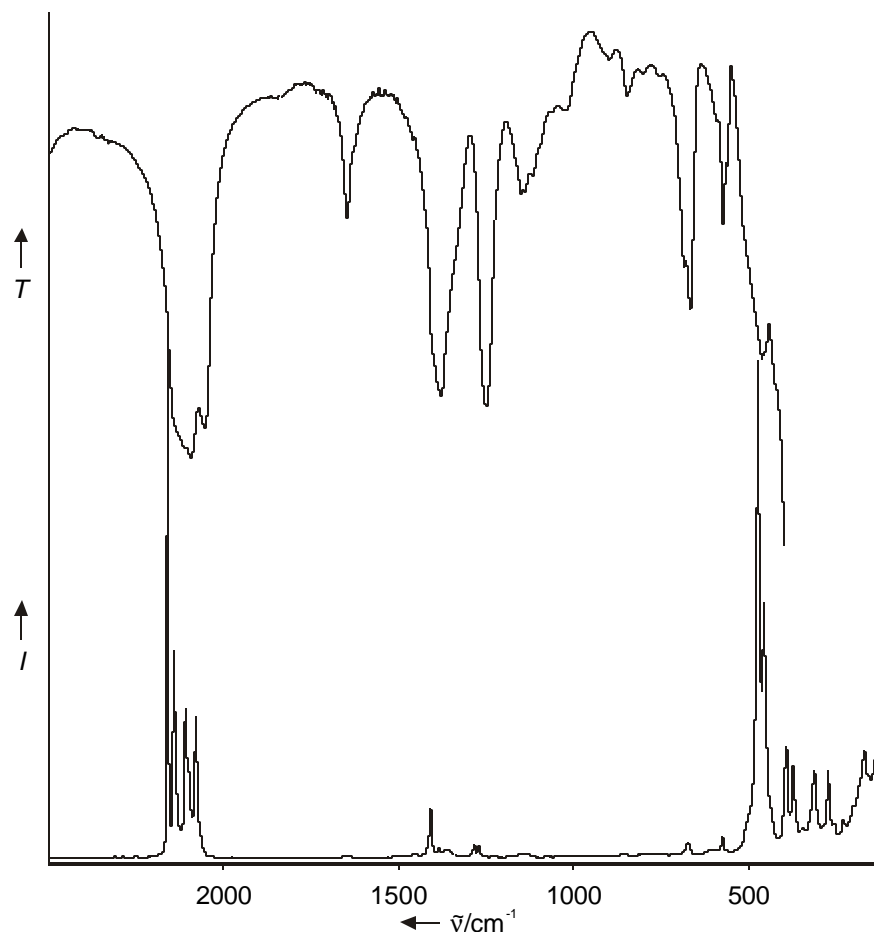


Figure 3. IR and Raman spectra of $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Ti}(\text{N}_3)_5]$. The bands belonging to the $[\text{Ti}(\text{N}_3)_5]^-$ anion are marked with asterisks.

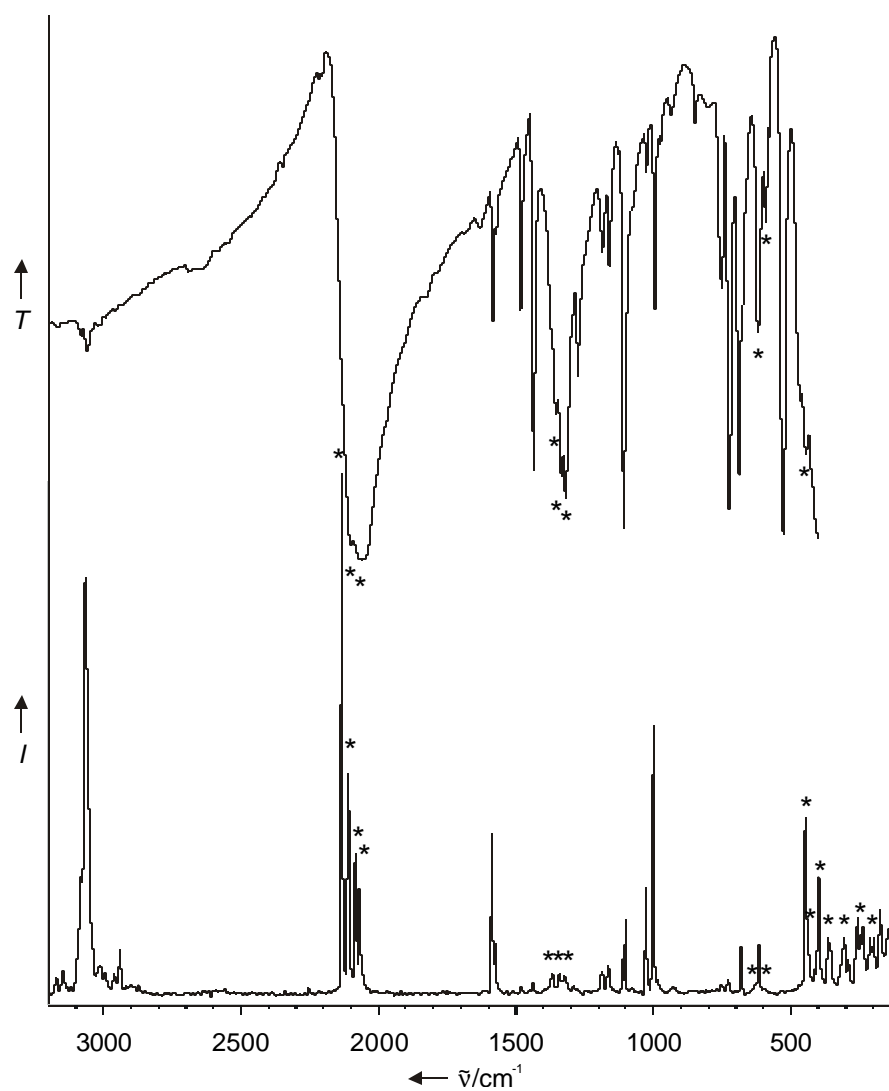


Figure 4. ORTEP drawing of the dianionic part of the crystal structure of $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Ti}(\text{N}_3)_6]$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [\AA] and angles [$^\circ$]: Ti-N1 2.002(2), Ti-N4 2.019(2), Ti-N7 2.048(2), N1-N2 1.173(2), N2-N3 1.138(2), N4-N5 1.200(2), N5-N6 1.146(3), N7-N8 1.197(2), N8-N9 1.140(3), N1-N2-N3 177.5(2), N4-N5-N6 177.6(2), N(7)-N(8)-N(9) 176.9(2), N1-Ti-N4 91.68(9), N1-Ti-N7 90.18(7), N4-Ti-N7 89.73(9), Ti-N1-N2 140.64(14), Ti-N4-N5 126.01(13), Ti-N7-N8 129.67(14)

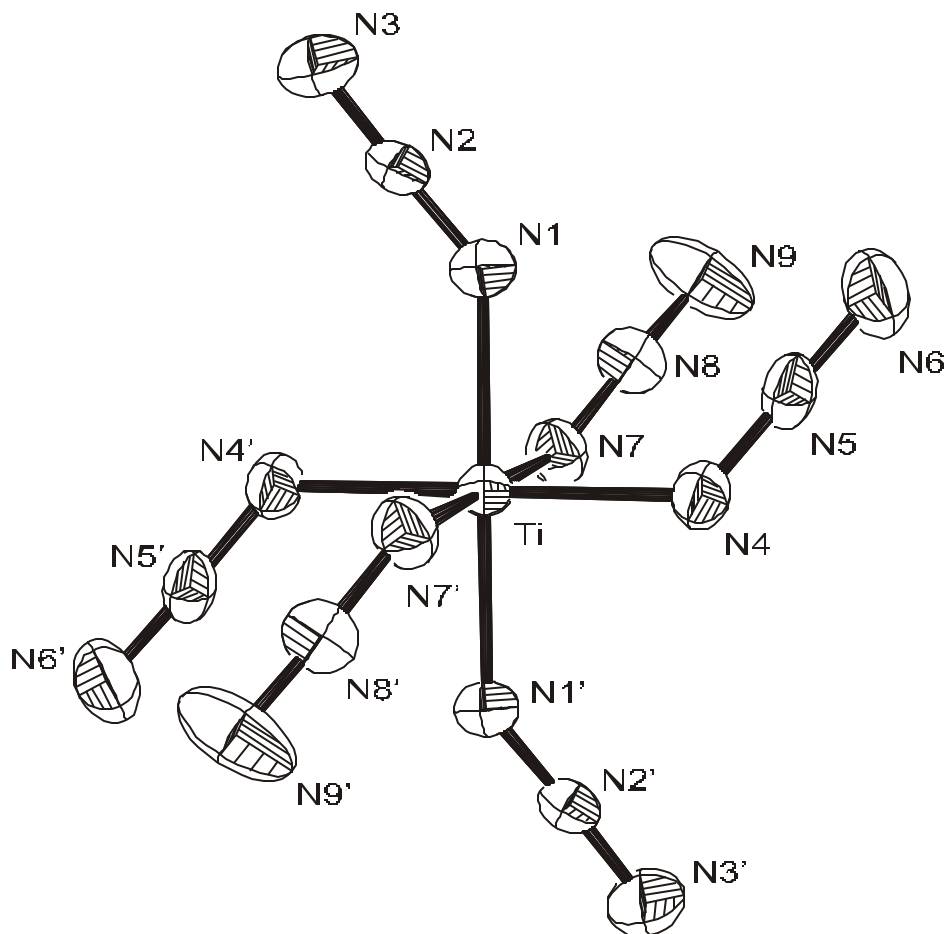


Figure 5. IR and Raman spectra of $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Ti}(\text{N}_3)_6]$. The bands belonging to the $[\text{Ti}(\text{N}_3)_6]^{2-}$ anion are marked with asterisks.

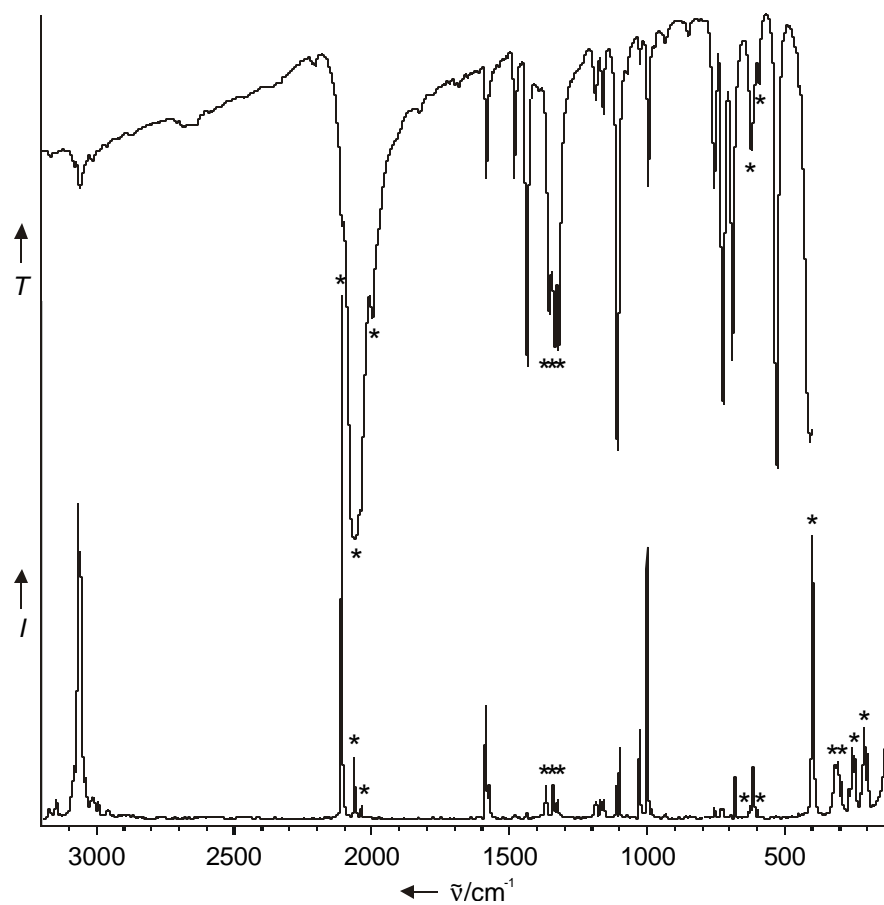
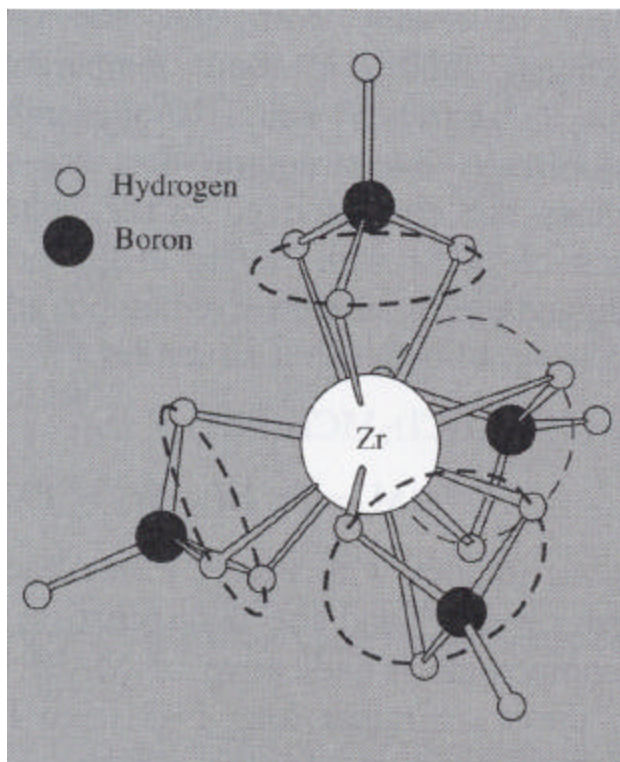


Figure 6. Crystal structure of $\text{Zr}(\text{BH}_4)_4$ demonstrating the perfect geometrical overlap of a tridentate donor into the empty d^0 orbitals of a (+IV) group 4 transition metal atom.



Synopsis

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Binary Titanium Azides.
Preparation and Characterization
of $\text{Ti}(\text{N}_3)_4$, $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Ti}(\text{N}_3)_5]$
and $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Ti}(\text{N}_3)_6]$

Theory predicts that $\text{Ti}(\text{N}_3)_4$ should exhibit unprecedented linear Ti-N-NN bond angles. $\text{Ti}(\text{N}_3)_4$ and its mono- and di-anions, the first examples of binary titanium azides, were prepared and characterized. They do not possess linear Ti-N-NN angles because their coordination numbers exceed 4. The predicted linearity of the Ti-N-N bonds is explained by the α -N atoms of the azide groups acting as tridentate donors into the empty tetrahedral d^0 -orbitals of a (+IV) group 4 metal atom.

