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Whereas the existence of numerous binary transition metal azido-complexes has been reported,[1-3] no binary Group 5 azides are known. Only a limited number of partially azide-substituted compounds of vanadium, niobium and tantalum have previously been reported.[4-21]

In this paper, we wish to communicate the synthesis and characterization of $Nb(N_3)_5$, $Ta(N_3)_5$ and their 1:1 adducts with CH_3CN, and of the anions $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$. The crystal structures of $Nb(N_3)_5 \cdot CH_3CN$ and $[PPh_4][Nb(N_3)_6]$ and the first experimental evidence for the existence of azido compounds with linear metal-N-N bonds are also reported.

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Experimental Evidence for Linear Metal-Azide Bonds. The Binary Group 5 Azides $Nb(N_3)_5$, $Ta(N_3)_5$, $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$, and 1:1 Adducts of $Nb(N_3)_5$ and $Ta(N_3)_5$ with CH_3CN [**] (Preprint)

Ralf Haiges[*]*, Jerry A. Boatz, Thorsten Schroer, Muhammed Yousufuddin, and Karl O. Christe*[*]

Dedicated to Professor Reint Eujen on the occasion of his 60th birthday

Whereas the existence of numerous binary transition metal azido-complexes has been reported,[1-3] no binary Group 5 azides are known. Only a limited number of partially azide-substituted compounds of vanadium, niobium and tantalum have previously been reported.[4-21]

In this paper, we wish to communicate the synthesis and characterization of $Nb(N_3)_5$, $Ta(N_3)_5$ and their 1:1 adducts with CH_3CN, and of the anions $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$. The crystal structures of $Nb(N_3)_5{\cdot}CH_3CN$ and $[PPh_4][Nb(N_3)_6]$ and the first experimental evidence for the existence of azido compounds with linear metal-N-N bonds are also reported.

The reactions of NbF_5 or TaF_5 with excess $(CH_3)_3SiN_3$ in SO_2 solution at -20 °C result in

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[*] Dr. R. Haiges, Dr. T. Schroer, Dr. M. Yousufuddin, Prof. Dr. K. O. Christe
Loker Research Institute and Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661 (USA)
Fax: (+1) 213-740-6679
E-mail: haiges@usc.edu, kchriste@usc.edu
Dr. J. A. Boatz
Space and Missile Propulsion Division
Air Force Research Laboratory (AFRL/PRSP)
10 East Saturn Boulevard, Bldg 8451
Edwards Air Force Base, CA 93524 (USA)

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complete fluoride-azide exchange and yield clear solutions of $Nb(N_3)_5$ or $Ta(N_3)_5$, respectively, [Eq. (1) (M = Nb, Ta)].

$$MF_5 + 5\,(CH_3)_3SiN_3 \longrightarrow M(N_3)_5 + 5\,(CH_3)_3SiF \qquad (1)$$

When the volatile compounds, SO_2, $(CH_3)_3SiF$ and excess $(CH_3)_3SiN_3$), are pumped off at -20 °C, pure, yellow, solid, room-temperature stable pentaazides are produced in quantitative yield. As expected for covalently bonded polyazides,[22] they are shock sensitive and can explode violently when touched with a metal spatula or by heating in the flame of a Bunsen burner. Their identity was established by the observed mass-balances, vibrational spectroscopy and their conversions with N_3^- into hexaazido-metalates and with CH_3CN into 1:1 acetonitrile donor-acceptor adducts, as shown by the crystal structures of $[P(C_6H_5)_4]^+[Nb(N_3)_6]^-$ and $Nb(N_3)_5{\cdot}CH_3CN$.

The observed infrared and Raman spectra of $Nb(N_3)_5$ and $Ta(N_3)_5$ are shown in Figures S1 and S2, respectively, of the Supplementary Material, and the observed frequencies and intensities are listed in the Experimental Section. They were assigned (see Tables S1 and S2 of the Supplementary Material) by comparison with those calculated at the B3LYP[23] and MP2[24] levels of theory using SBKJ-(d) basis sets.[25] The agreement between observed and calculated spectra is satisfactory and supports trigonal-bipyramidal structures (Table 1) for $Nb(N_3)_5$ and $Ta(N_3)_5$. The internal modes of the azido ligands are split into clusters of five due to in-phase and out-of-phase coupling of the individual motions. There are always one in-phase and four out-of-phase vibrations, with the in-phase one readily identifiable from its higher Raman intensity. The MN_5 skeletal modes can be derived from D_{3h} symmetry in which the double degeneracy of the E modes is lifted due to the presence of the azido ligands which lowers the overall symmetry to C_s and is likely to produce some distortion from D_{3h}.

Whereas trigonal-bipyramidal arrangements of the azido ligands have previously also been found for $[Fe(N_3)_5]^{2-}$,[26] and theoretically predicted for $Sb(N_3)_5$ and $As(N_3)_5$,[27,28] the details of these structures are very different. In $[Fe(N_3)_5]^{2-}$, $As(N_3)_5$ and $Sb(N_3)_5$, all five M-N-N bonds are strongly bent, and the two axial M-N bonds are significantly longer than the equatorial ones, as expected from VSEPR arguments.[29] In contrast, the axial M-N-N bonds in $Nb(N_3)_5$ and $Ta(N_3)_5$ are calculated to be almost linear, while the equatorial ones have angles of about 137 °. Furthermore, all five M-N bonds and the internal N-N distances of the five azido ligands are essentially the same.

Linear M-N-N bonds had previously been predicted also for the tetraazides of d^0 Ti(+IV), Zr(+IV), and Hf(+IV)[30] and for d^6 Fe(+II),[31] but the hexazido dianion of d^0 Ti(+IV) was shown experimentally to possess strongly bent Ti-N-N bonds.[1] These findings show that the linearity of the M-N-N bonds cannot be caused by either a trigonal-bipyramidal structure, multiple M-N bonds, or a d^0 electronic configuration *per se*.

The occurrence of linear metal-N-N groups can be predicted by theoretical calculations.[30,31] A plausible explanation for the linearity of these M-N-N bonds has recently been given,[1] based on an analogy with the known crystal structure of $Zr(BH_4)_4$.[32] A model was proposed in which the N_α atom of the azides acts as a tridative ligand. A detailed analysis of the occurrence of linear M-N-N bonds in the periodic system and of the nature of these bonds is presently being carried out by us and will be the subject of a future publication.

By using CH_3CN instead of SO_2 as solvent for the reactions of NbF_5 and TaF_5 with excess $(CH_3)_3SiN_3$, yellow solutions of $CH_3CN\cdot Nb(N_3)_5$ and $CH_3CN\cdot Ta(N_3)_5$, respectively, were obtained [Eq. (2) (M = Nb, Ta)].

$$MF_5 + 5\,(CH_3)_3SiN_3 \longrightarrow CH_3CN\cdot M(N_3)_5 + 5\,(CH_3)_3SiF \qquad (2)$$

Removal of the volatile compounds (CH_3CN, $(CH_3)_3SiF$ and excess $(CH_3)_3SiN_3$) at -20 °C results in the isolation of the acetonitrile-adducts of the pentaazides. Although still dangerous and explosive, both acetonitrile-adducts are less shock-sensitive than the corresponding donor-free pentaazides.

Both acetonitrile-adducts were isolated as yellow solids and were characterized by vibrational spectroscopy, their conversion with N_3^- into the hexaazido-metalates and, in the case of $CH_3CN{\cdot}Nb(N_3)_5$, by its crystal structure.[33] The observed Raman spectra of $CH_3CN{\cdot}Nb(N_3)_5$ and $CH_3CN{\cdot}Ta(N_3)_5$ are shown in Figures 1 and S3, respectively, and their frequencies and intensities are given in the Experimental Section. A comparison with the calculated spectra is given in Tables S3 and S4 of the Supplementary Material, and the given assignments are in accord with those previously reported[34,35] for the related $CH_3CN{\cdot}SbF_5$ adduct.

$CH_3CN{\cdot}Nb(N_3)_5$ crystallizes in the monoclinic space group *P*2(1)/*c*. The X-ray structure analysis[33] (Figure 2) reveals the presence of isolated $CH_3CN{\cdot}Nb(N_3)_5$ units. The closest Nb···N and N···N contacts between neighboring molecules are 3.98 Å and 3.04 Å, respectively.

The molecule consists of a pseudo-octahedral NbN_6 skeleton with CH_3CN and one azido group in the axial positions. The equatorial positions are occupied by the remaining 4 azido groups which, interestingly, are all bent away from the axial azido ligand. The axial Nb-N_3 distance is about 0.09 Å shorter than the four equatorial ones. The most interesting feature, however, is the fact that the axial azido group exhibits a large Nb-N-NN bond angle of 168.8(3)°, compared to an average angle of 137.8° for the four equatorial ligands, and suggests the presence of a tridative azido ligand. The small deviation of the observed axial Nb-N-N angle from the ideal 180° is attributed to solid state effects, because our theoretical calculations for the free gaseous molecule at the B3LYP and MP2 levels of theory with an SBKJ+(d) basis set resulted in

Nb-N-N angles of 179.6° and 178.3°, respectively. For free $CH_3CN{\cdot}Ta(N_3)_5$, analogous calculations gave values of 179.6 and 180.0 °. The significant shortening of the axial $Nb\text{-}N_3$ distance might be attributed to a *trans*-effect caused by the opposite long $Nb\text{-}NCCH_3$ bond.

The average $Nb\text{-}N_{azide}$ distance of 1.997 Å in $CH_3CN{\cdot}Nb(N_3)_5$ is significantly shorter than those of 2.081 Å and 2.105 Å found for the terminal azides of two isomers of $[Cp^*NbCl(N_3)(\mu\text{-}N_3)]_2(\mu\text{-}O)$[16] and 2.27 Å found for the cluster $[Nb_6Br_{12}(N_3)_6]^{4-}$,[18] but slightly longer than that of 1.92 Å found in $[NbCl_5(N_3)]^-$ [19] and is attributed to varying degrees of ionicity of the azide ligands in these compounds.

The reactions of the pentaazides with ionic azides, such as $[P(C_6H_5)_4]^+N_3^-$, in CH_3CN solution produce the corresponding $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$ salts, respectively, [Eq. (3) (M = Nb, Ta].

$$M(N_3)_5 \ + \ [P(C_6H_5)_4]N_3 \longrightarrow [P(C_6H_5)_4][M(N_3)_6] \qquad (3)$$

The hexaazido niobates and tantalates were isolated as yellow-orange solids and are stable at room temperature. The compounds were characterized by the observed material balances, vibrational spectroscopy, and in the case of $[P(C_6H_5)_4][Nb(N_3)_6]$ by its crystal structure.[36] The observed vibrational spectra of $[P(C_6H_5)_4][Nb(N_3)_6]$ and $[P(C_6H_5)_4][Ta(N_3)_6]$ are shown in Figures S4 and S5, respectively, and their frequencies and intensities are given in Table 2 and the Experimental Section, respectively. The free gaseous $[Nb(N_3)_6]^-$ anion is predicted to have perfect S_6 ($\equiv C_{3i}$) symmetry, which is quite rare,[37] and, therefore, a complete vibrational analysis was carried out (Table 2). $[Ta(N_3)_6]^-$ is slightly distorted from S_6 to C_1 symmetry, but its structure is almost identical to that of $[Nb(N_3)_6]^-$, and the splittings of its degenerate modes are extremely small (Table S5 of the Supplementary Material).

Because of the presence of a large counter-ion which serves as an inert spacer and suppresses detonation propagation, these salts are much less shock sensitive than neat $Nb(N_3)_5$ and $Ta(N_3)_5$, and are thermally surprisingly stable. Single crystals of $[P(C_6H_5)_4][Nb(N_3)_6]$ were obtained by re-crystallization from CH_3CN. The salt crystallizes in the rare orthorhombic space group *P*2(1)2(1)2. The X-ray structure analysis[36] of $[P(C_6H_5)_4][Nb(N_3)_6]$ (Figure 3) reveals no significant cation-anion and anion-anion interactions. The closest Nb···N and N···N contacts between neighboring anions are 4.20 Å and 3.15 Å, respectively. The structure of the $[Nb(N_3)_6]^-$ anion in the solid is distorted from the perfect S_6 symmetry, predicted by our theoretical calculations for the free gaseous anion, and is similar to those of $[As(N_3)_6]^-$[28], $[Sb(N_3)_6]^-$,[27] $[Si(N_3)_6]^-$[38] $[Ge(N_3)_6]^-$[39] and $[Ti(N_3)_6]^{2-}$,[1] and contrary to that of $[Te(N_3)_6]^{2-}$[40] which contains a sterically active free valence electron pair on its central atom. The average Nb-N distance of 2.027 Å in $[Nb(N_3)_6]^-$ is larger than that of 1.997 Å found for $CH_3CN{\cdot}Nb(N_3)_5$, as expected from the formal negative charge in the former which increases the ionic character of the azide ligands. The relatively large variation in the Nb-N-N bond angles, which range from 131.7 to156.2 °, is attributed to intramolecular repulsion effects among the ligands.

In summary, this paper reports the synthesis and characterization of the first examples of binary Group 5 azides and provides the first experimental proof for the existence of linear metal-N-N bonds.

Experimental Section

Caution! *Covalent azides are potentially hazardous and can decompose explosively under various conditions! The polyazides of this work are extremely shock-sensitive and can explode violently upon the slightest provocation. They should be handled only on a scale of less* *than 1 mmol. Because of the high energy content and high detonation velocities of these azides, their explosions are particularly violent and can cause, even on a one mmol scale, significant damage. The use of appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs) is mandatory. Teflon containers should be used, whenever possible, to avoid hazardous shrapnel formation. The manipulation of these materials is facilitated by handling them, whenever possible, in solution to avoid detonation propagation, the use of large inert counter-ions as spacers, and anion formation which increases the partial negative charges on the terminal* N_γ *atoms and thereby reduces the* N_β-N_γ *triple bond character and strengthens the weak* N_α-N_β *single bond.* ***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 or stainless steel/Teflon-FEP vacuum line.[41] All 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 directly in the Teflon reactors in the range 3600–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer, using a Nd-YAG laser at 1064 nm with power levels less than 50 mW(!). Infrared spectra were recorded in the range 4000-400 cm^{-1} on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the glove box using an Econo mini-press (Barnes Engineering Co.) and transferred in a closed container to the spectrometer before placing them quickly into the sample compartment which was purged with dry nitrogen to minimize exposure to atmospheric moisture and potential hydrolysis of the sample.

The starting materials NbF_5, TaF_5 (both Ozark Mahoning) and $[P(C_6H_5)_4]I$ (Aldrich) were used without further purification. $(CH_3)_3SiN_3$ (Aldrich) was purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. $[P(C_6H_5)_4]N_3$ and $[P(C_6H_5)_4]F$ were prepared from $[P(C_6H_5)_4]I$ and stoichiometric amounts of AgN_3 and AgF, respectively, in aqueous solution, filtering off the precipitated AgI .

Preparation of $M(N_3)_5$ (M = Nb, Ta): A sample of NbF_5 (0.55 mmol) or TaF_5 (0.59 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of 1 g of SO_2 and $(CH_3)_3SiN_3$ (5.5 mmol) *in vacuo* at -196 °C. The mixture was warmed to -30 °C. After 2 hours, the temperature was raised to -20 °C and all volatile material was pumped off, leaving behind solid $M(N_3)_5$.

$Nb(N_3)_5$: 0.175 g, expected for 0.55 mmol: 0.166 g; Raman (-80 °C): $\tilde{\nu}$ =2155 [10.0], 2106 [5.5], (ν_{as} N_3), 1385 [1.6], (ν_s N_3), 628 [0.7], 590 sh, (δ N_3), 427 sh, (ν_{as} NbN_3 *eq*), 413 [3.2], (ν_s NbN_3 *eq*), 360 sh, (ν_s NbN_2 *ax*), 288 [0.7], (δ_{sciss} NbN_3 *eq*), 234 [0.7], (ρ NbN_2 *ax*); infrared (KBr): 2124 vs, 2088 vs, (ν_{as} N_3), 1374 m, 1347 s, (ν_s N_3), 591 mw, 569 w, (δ N_3), 450 sh, (ν_{as} NbN_3 *eq*), 440 mw, (ν_{as} NbN_2 *ax*), 422 w, (ν_s NbN_3 *eq*).

$Ta(N_3)_5$: 0.247 g, expected for 0.59 mmol = 0.231 g; Raman (-80 °C): $\tilde{\nu}$ =2182 [10.0], 2129 [3.3], (ν_{as} N_3), 623 [1.1], 590 sh, (δ N_3), 450 sh, (ν_{as} TaN_3 *eq*), 426 [2.5], (ν_s TaN_3 *eq*), 390 sh, (ν_s TaN_2 *ax*), 256 [1.7] (δ_{sciss} TaN_3 *eq*), 221 [2.0], (ρ TaN_2 *ax*); infrared (KBr): 2141 vs, 2103vs, (ν_{as} N_3), 1403 ms, 1364 m, (ν_s N_3), 613 mw, 578 w, (δ N_3), 410 mw, (ν_{as} TaN_2 *ax*).

In addition to these bands, the following weak infrared bands were observed which are attributed to overtones or combination bands: $Nb(N_3)_5$: 1667 w, 1263 w, 1195 sh, 1176 w, 1037 vvw, 696 w, 660 w; $Ta(N_3)_5$: 1669 w, 1508 vw, 1274 sh, 1252 w, 1203 w, 1180 sh, 1036 vw, 850 w, 712 w, 683 w.

Preparation of $CH_3CN·M(N_3)_5$ (M = Nb, Ta): A sample of NbF_5 (0.39 mmol) or TaF_5 (0.37 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of 2 mL CH_3CN and $(CH_3)_3SiN_3$ (3.7 mmol) *in vacuo* at -196 °C. The mixture was warmed to -20 °C. After 2 hours, all volatile material was pumped off at this temperature, leaving behind solid $CH_3CN·M(N_3)_5$.

$CH_3CN·Nb(N_3)_5$: 0.129 g, expected for 0.39 mmol: 0.136 g. Raman (-80 °C): $\tilde{\nu}$=2928 [1.8], (ν_s CH_3), 2315 [1.2], 2289 [1.1], (ν CN), 2140 [10.0], 2121 [1.5], 2097 [1.9], 2090 [1.6], 2074 [2.2], 2058 [1.4], (ν_{as} N_3), 1415 [1.3], 1363 [1.2], 1351 [1.1], 1331 [1.1], (δ CH_3) and (ν_s N_3), 947 [1.0], (ν CC), 620 [1.2], 610 [1.0], 599 [1.2], 580 [1.1], 566 [1.0], 557 [1.1], (δ N_3), 441 [3.1], 435 [2.8], 423 [1.7], 419 [1.7], 411 [2.0], (ν NbN_x), 281 [1.1], 266 [1.3], 256 [1.3], 248 [1.4], 226 [1.6], (δ NbN_x), 189 [1.3], 180 [1.3], 139 [1.6], 96 [2.9], (torsional modes).

$CH_3CN·Ta(N_3)_5$: 0.175 g, expected for 0.37 mmol: 0.161 g. Raman (-80 °C): $\tilde{\nu}$=2933 [1.7], (ν_s CH_3), 2319 [0.5], 2291 [0.5], (ν CN), 2172 [10.0], 2162 [1.2], 2123 [1.2], 2103 [1.1], (ν_{as} N_3), 1389 [0.4], 1361 [0.4], (δ CH_3) and (ν_s N_3), 948 [1.0], (ν CC), 592 [0.3], (δ N_3), 438 [2.1], 417 [0.6], (ν NbN_x), 250 [0.7], 266 [1.3], 226 [0.6], (δ NbN_x), 192 [0.9], (torsional mode).

Preparation of $[M(N_3)_6]^-$ salts (M = Nb, Ta): Neat PPh_4N_3 (0.25 mmol) was added to a frozen solution of $M(N_3)_5$ (0.25 mmol) in CH_3CN (15 mmol) at –78 °C. The reaction mixture was warmed to -25 °C and occasionally agitated. After 2 hours, all volatiles were removed at ambient temperature in a dynamic vacuum, leaving behind the solid $[M(N_3)_6]^-$ salts.

$[P(C_6H_5)_4][Nb(N_3)_6]$: orange solid, 0.160 g, expected for 0.25 mmol: 0.171 g. The IR and Raman spectra of $[Nb(N_3)_6]^-$ are given in Table1.

$[P(C_6H_5)_4][Ta(N_3)_6]$: pale yellow solid, 0.207 g, expected for 0.25 mmol: 0.193 g. Raman bands due to $[Ta(N_3)_6]^-$ (-80 °C): $\tilde{\nu}$=2159 [10.0], 2111 [1.0], 2103 [1.0], 2091 [0.8], 2081 [0.7],

(ν_{as} N_3), 1355 [0.8], (ν_s N_3), 609 [0.6], 582 [0.4], (δ N_3), 437 [2.8], 372 [0.7], 364 [0.8], 353 [0.8], (ν TaN_6), 225 [1.8], 215 [1.8], (δ TaN_6), 168 [2.6], 160 [2.6], (torsions); infrared bands due to $[Ta(N_3)_6]^-$ (KBr): 2124 vs, 2113 vs, 2096 vs, 2087 vs, (ν_{as} N_3), 1383 m, 1372 m, 1360 ms, 1348 s, (ν_s N_3), 648 vw, 615 m, 600 mw, 585 mw, 576 w, (δ N_3), 433 w, 418 mw, 414 mw, (ν TaN_6).

Theoretical Methods: The molecular structures, harmonic vibrational frequencies, and infrared and Raman vibrational intensities were calculated using second order perturbation theory (MP2, also known as MBPT(2)[24]) and also at the DFT level using the B3LYP hybrid functional,[23a] which included the VWN5 correlation functional.[23b] The Stevens, Basch, Krauss, and Jasien (SBKJ) effective core potentials and the corresponding valence-only basis sets were used.[25a] The SBKJ valence basis set for nitrogen was augmented with a d polarization function[25b] and a diffuse s+p shell,[25c] denoted as SBKJ+(d). Hessians (energy second derivatives) were calculated for the final equilibrium structures to verify them as local minima; i.e., having a positive definite Hessian. All calculations were performed using the electronic structure code GAMESS.[42]

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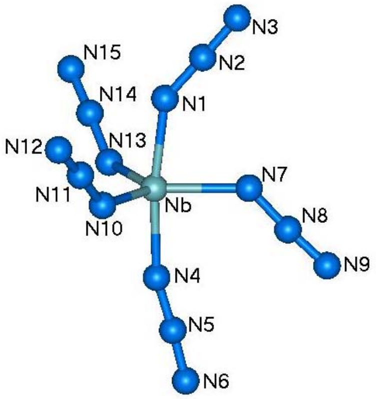
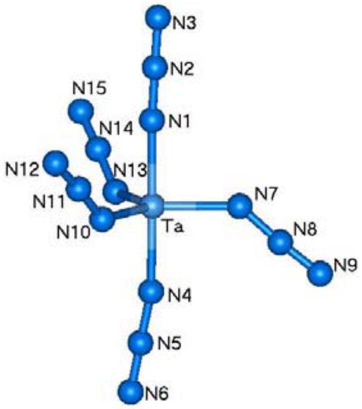
Table 1. Stuctures of $Nb(N_3)_5$ and $Ta(N_3)_5$ calculated at the B3LYP/SBKJ+(d) level of theory (MP2/SBKJ+(d) values in parentheses).





$R(Nb-N_1) = 2.025(2.013)$
$R(Nb-N_4) = 2.001(2.002)$
$R(Nb-N_7) = 2.048(2.060)$
$R(Nb-N_{10}) = 2.008(2.014)$
$R(Nb-N_{13}) = 2.008(2.014)$
$R(N_1-N_2) = 1.234(1.241)$
$R(N_4-N_5) = 1.230(1.241)$
$R(N_7-N_8) = 1.243(1.249)$
$R(N_{10}-N_{11}) = 1.240(1.245)$
$R(N_{13}-N_{14}) = 1.240(1.245)$
$R(N_2-N_3) = 1.162(1.208)$
$R(N_5-N_6) = 1.163(1.210)$
$R(N_8-N_9) = 1.162(1.210)$
$R(N_{11}-N_{12}) = 1.160(1.208)$
$R(N_{14}-N_{15}) = 1.160(1.208)$
$\alpha(N_1-Nb-N_4) = 171.9(169.0)$
$\alpha(N_1-Nb-N_7) = 82.8(81.4)$
$\alpha(N_1-Nb-N_{10}) = 91.0(92.1)$
$\alpha(N_1-Nb-N_{13}) = 91.0(92.1)$
$\alpha(N_4-Nb-N_7) = 89.1(87.6)$
$\alpha(N_4-Nb-N_{10}) = 93.2(93.6)$
$\alpha(N_4-Nb-N_{13}) = 93.2(93.6)$
$\alpha(N_7-Nb-N_{10}) = 121.3(121.3)$
$\alpha(N_7-Nb-N_{13}) = 121.3(121.3)$
$\alpha(N_{10}-Nb-N_{13}) = 117.2(117.1)$
$\alpha(Nb-N_1-N_2) = 145.3(147.2)$
$\alpha(Nb-N_4-N_5) = 165.0(157.3)$
$\alpha(Nb-N_7-N_8) = 131.8(130.8)$
$\alpha(Nb-N_{10}-N_{11}) = 137.2(138.8)$
$\alpha(Nb-N_{13}-N_{14}) = 137.2(138.8)$

$R(Ta-N_1) = 1.997(1.996)$
$R(Ta-N_4) = 1.991(1.993)$
$R(Ta-N_7) = 2.003(1.997)$
$R(Ta-N_{10}) = 2.008(2.009)$
$R(Ta-N_{13}) = 2.008(2.009)$
$R(N_1-N_2) = 1.226(1.235)$
$R(N_4-N_5) = 1.225(1.234)$
$R(N_7-N_8) = 1.240(1.242)$
$R(N_{10}-N_{11}) = 1.240(1.244)$
$R(N_{13}-N_{14}) = 1.240(1.244)$
$R(N_2-N_3) = 1.163(1.209)$
$R(N_5-N_6) = 1.163(1.209)$
$R(N_8-N_9) = 1.160(1.206)$
$R(N_{11}-N_{12}) = 1.160(1.206)$
$R(N_{14}-N_{15}) = 1.160(1.206)$
$\alpha(N_1-Ta-N_4) = 179.2(177.9)$
$\alpha(N_1-Ta-N_7) = 89.4(90.2)$
$\alpha(N_1-Ta-N_{10}) = 90.2(89.8)$
$\alpha(N_1-Ta-N_{13}) = 90.2(89.8)$
$\alpha(N_4-Ta-N_7) = 91.4(91.8)$
$\alpha(N_4-Ta-N_{10}) = 89.4(89.2)$
$\alpha(N_4-Ta-N_{13}) = 89.4(89.2)$
$\alpha(N_7-Ta-N_{10}) = 119.6(119.1)$
$\alpha(N_7-Ta-N_{13}) = 119.6(119.1)$
$\alpha(N_{10}-Ta-N_{13}) = 120.9(121.7)$
$\alpha(Ta-N_1-N_2) = 176.9(178.5)$
$\alpha(Ta-N_4-N_5) = 169.3(173.8)$
$\alpha(Ta-N_7-N_8) = 137.7(143.0)$
$\alpha(Ta-N_{10}-N_{11}) = 137.1(138.9)$
$\alpha(Ta-N_{13}-N_{14}) = 137.1(138.9)$

Table 2. Comparison of observed and unscaled calculated vibrational frequencies [cm^{-1}] and intensities for $[Nb(N_3)_6]^{-}$[a] in point group S_6

			observed		Calculated (IR) [Raman]	
		description	IR	Ra	B3LYP/SBK+(d)	MP2/SBK+(d)
A_g	ν_1	$\nu_{as}N_3$		2131 (10.0) 2112 (5.6)	2218 (0) [1428]	2129 (0) [1388]
	ν_2	ν_sN_3		1342 (2.0)	1432 (0) [49]	1283 (0) [60]
	ν_3	δN_3		616 (2.8)	588 (0) [8.8]	565 (0) [39]
	ν_4	δN_3			580 (0) [2.2]	524 (0) [2.3]
	ν_5	ν_sNbN_6		433 (5.3) 414 (4.8)	401 (0) [147]	402 (0) [367]
	ν_6	δ_sNbN_6		225 (3.5)	249 (0) [13]	242 (0) [51]
	ν_7	τ			74 (0) [14]	72 (0) [31]
	ν_8	τ			34 (0) [37]	32 (0) [39]
E_g	ν_9	$\nu_{as}N_3$		2080 (2.1) 2060 (2.3)	2164 (0) [1063]	2146 (0) [110]
	ν_{10}	ν_sN_3			1413 (0) [50]	1279 (0) [154]
	ν_{11}	δN_3			582 (0) [8.4]	550 (0) [73]
	ν_{12}	δN_3			580 (0) [0.63]	521 (0) [4.2]
	ν_{13}	ν_sNbN_6		339 (2.7)	334 (0) [12]	350 (0) [38]
	ν_{14}	δ_sNbN_6		217 (3.5)	238 (0) [34]	234 (0) [31]
	ν_{15}	τ			87 (0) [36]	89 (0) [92]
	ν_{16}	τ			36 (0) [69]	38 (0) [80]
A_u	ν_{17}	$\nu_{as}N_3$	2121 s 2080 vs		2185 (4084) [0]	2152 (2577) [0]
	ν_{18}	ν_sN_3	1336 ms		1406 (677) [0]	1271 (338) [0]
	ν_{19}	δN_3	640 vw		580 (0.91) [0]	549 (100) [0]
	ν_{20}	δN_3	624 w		574 (49) [0]	505 (8.0) [0]
	ν_{21}	$\nu_{as}NbN_6$	409 mw		400 (536) [0]	418 (629) [0]
	ν_{22}	$\delta_{as}NbN_6$			276 (15) [0]	262 (31) [0]
	ν_{23}	τ NbN_6			140 (2.8) [0]	114(0.48) [0]
	ν_{24}	τ			27 (0.006) [0]	29 (0.022) [0]
	ν_{25}	τ			24 (1.6) [0]	14 (0.37) [0]
E_u	ν_{26}	$\nu_{as}N_3$	2069 vs 2060 vs		2170 (4366) [0]	2141 (2681) [0]
	ν_{27}	ν_sN_3	1361 m 1351 m		1409 (739) [0]	1278 (314) [0]
	ν_{28}	δN_3	600 w		577 (126) [0]	544 (94) [0]
	ν_{29}	δN_3	583 vw		570 (38) [0]	502 (8.2) [0]
	ν_{30}	$\nu_{as}NbN_6$	409 mw	382 (2.8)	391 (874) [0]	404 (1045) [0]
	ν_{31}	$\delta_{as}NbN_6$			233 (26) [0]	223 (30) [0]
	ν_{32}	$\delta_{wag/rock}NbN_6$		151 (4.3)	154 (13) [0]	128 (31) [0]
	ν_{33}	τ			36 (4.8) [0]	38 (3.1) [0]
	ν_{34}	τ			15 (1.6) [0]	6 (1.9) [0]

[a] Calculated IR and Raman intensities are given in km mol^{-1} and $Å^4$ amu^{-1}, respectively; observed spectra are for the solid $[P(C_6H_5)_4]^+$ salt.

Figure 1. Raman spectrum of solid $CH_3CN{\cdot}Nb(N_3)_5$. The band marked by an asterisk (*) is due to the Teflon-FEP sample tube.

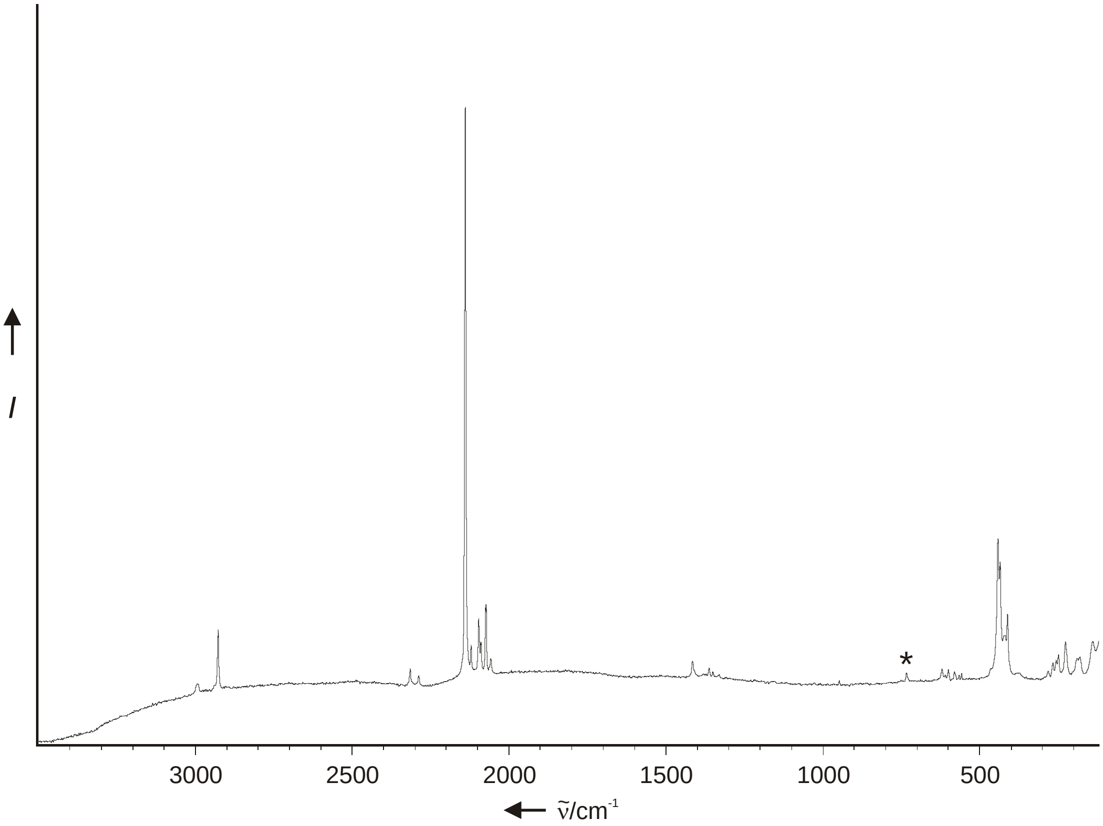


Figure 2. ORTEP drawing of $CH_3CN\cdot Nb(N_3)$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Nb-N1 2.031(3), Nb-N4 1.998(3), Nb-N7 2.004(3), Nb-N10 2.017(3), Nb-N13 1.935(3), Nb-N16 2.259(3), N1-N2 1.217(4), N2-N3 1.139(4), N4-N5 1.212(4), N5-N6 1.133(4), N7-N8 1.212(4), N8-N9 1.129(4), N10-N11 1.211(4), N11-N12 1.132(4), N13-N14 1.205(4), N14-N15 1.137(4), N16-C1 1.139(4), C1-C2 1.447(5), N1-Nb-N4 87.55(12), N1-Nb-N7 165.51(11), N1-Nb-N10 82.89(12), N1-Nb-N13 99.16(12), N1-Nb-N16 84.59(10), N4-Nb-N7 93.90(12), N4-Nb-N10 162.91(12), N4-Nb-N13 96.38(12), N4-Nb-N16 81.15(10), N7-Nb-N10 91.93(11), N7-Nb-N13 95.01(12), N7-Nb-N16 81.40(11), N10-Nb-N13 99.11(12), N10-Nb-N16 83.86(10), N13-Nb-N16 175.45(11), Nb-N1-N2 132.7(2), Nb-N4-N5 141.9(2), Nb-N7-N8 144.1(2), Nb-N10-N11 132.3(2), Nb-N13-N14 168.8(3), Nb-N16-C1 170.6(3).

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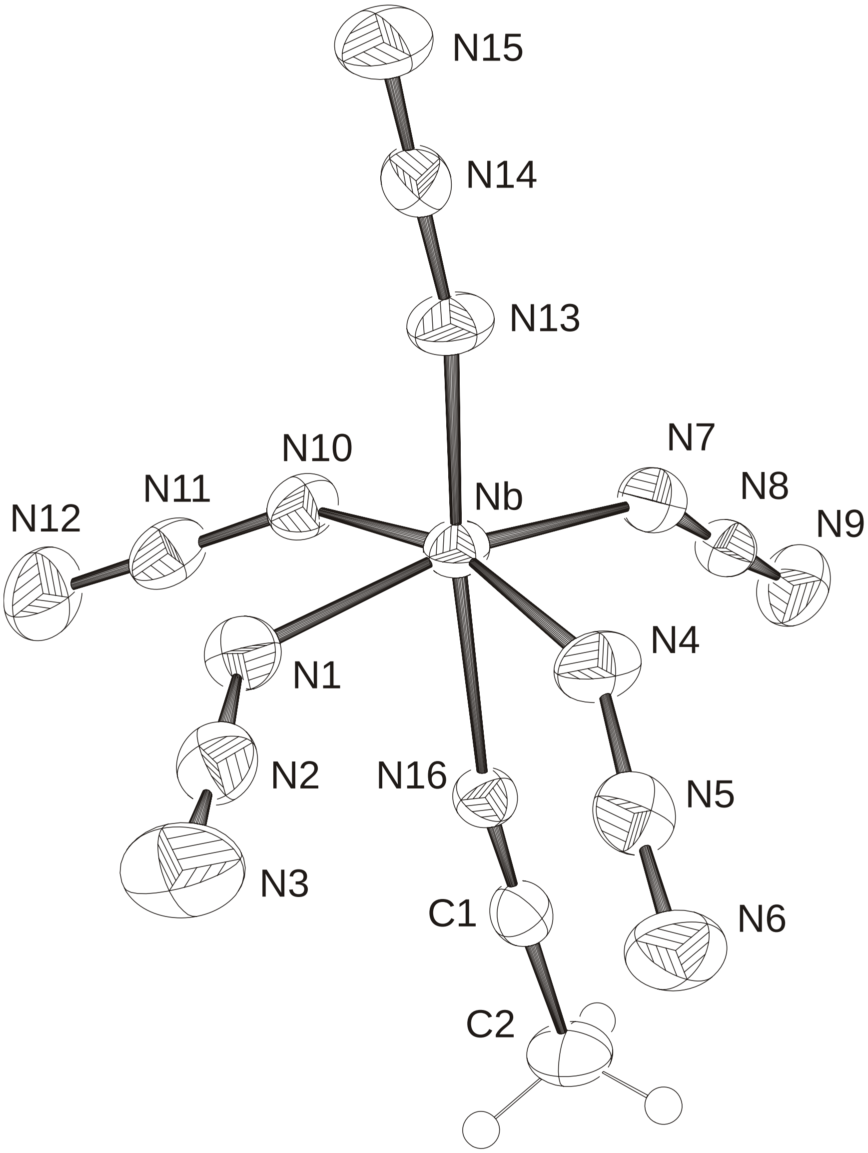
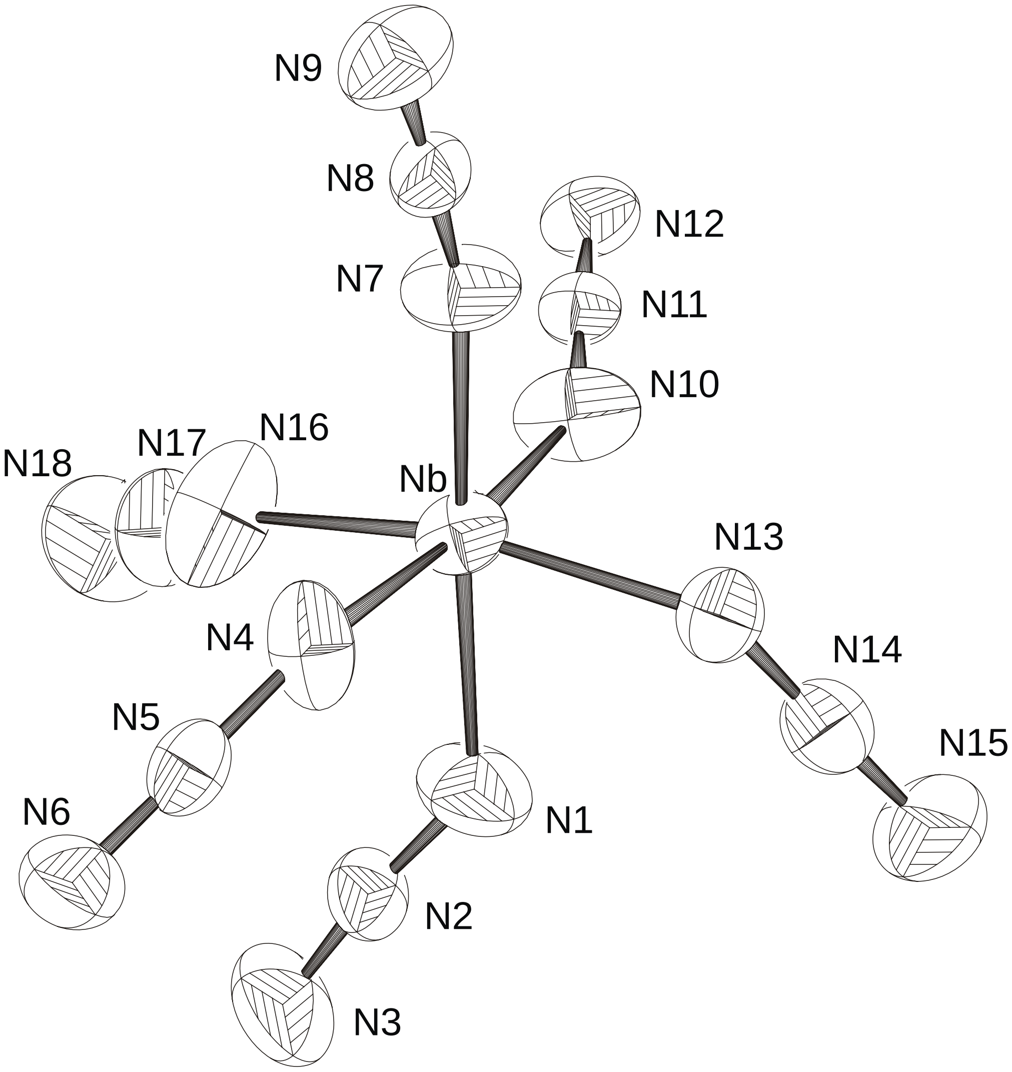


Figure 3. ORTEP drawing of the anionic part of the crystal structure of $[P(C_6H_5)_4][Nb(N_3)_6]$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Nb-N1 2.078(5), Nb-N4 2.035(4), Nb-N7 1.989(4), Nb-N10 2.008(4), Nb-N13 2.032(4), Nb-N16 2.026(5), N1-N2 1.164(5), N2-N3 1.126(6), N4-N5 1.198(5), N5-N6 1.128(5), N7-N8 1.192(5), N8-N9 1.133(5), N10-N11 1.196(5), N11-N12 1.118(5), N13-N14 1.203(6), N14-N15 1.137(6), N16-N17 1.173(6), N17-N18 1.137(6), N1-Nb-N4 89.54(19), N1-Nb-N7 173.25(18), N1-Nb-N10 94.23(18), N1-Nb-N13 80.45(18), N1-Nb-N16 85.2(2), N4-Nb-N7 86.30(18), N4-Nb-N10 174.15(18), N4-Nb-N13 95.40(15), N4-Nb-N16 86.78(17), N7-Nb-N10 90.34(17), N7-Nb-N13 94.63(17), N7-Nb-N16 99.86(19), N10-Nb-N13 89.63(18), N10-Nb-N16 89.1(2), N13-Nb-N16 165.46(18), Nb-N1-N2 134.4(4), Nb-N4-N5 141.2(4), Nb-N7-N8 156.2(4), Nb-N10-N11 152.3(4), Nb-N13-N14 131.7(4), Nb-N16-N17 142.3(4).

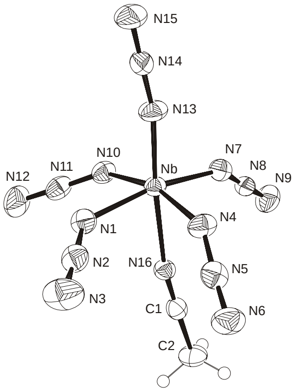


Synopsis

R. Haiges*, J. A. Boatz, T. Schroer, M. Yousufuddin, K. O. Christe*

Experimental Evidence for Linear Metal-Azide Bonds. The Binary Group 5 Azides $Nb(N_3)_5$, $Ta(N_3)_5$, $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$, and 1:1 Adducts of $Nb(N_3)_5$ and $Ta(N_3)_5$ with CH_3CN

Linear M-N-N bonds: The first binary group 5 azides, $Nb(N_3)_5$, $Ta(N_3)_5$, $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$, and 1:1 adducts of $Nb(N_3)_5$ and $Ta(N_3)_5$ with CH_3CN, have been prepared and characterized. The crystal structures of the $M(N_3)_5\cdot CH_3CN$ adducts provide the first experimental evidence for the existence of linear metal-N-N bonds.



$CH_3CN\cdot Nb(N_3)_5$

Re-revised anie.200501372

Supplementary Material

Experimental Evidence for Linear Metal-Azide Bonds. The Binary Group 5 Azides $Nb(N_3)_5$, $Ta(N_3)_5$, $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$, and 1:1 Adducts of $Nb(N_3)_5$ and $Ta(N_3)_5$ with CH_3CN [**]

Ralf Haiges[*], Jerry A. Boatz, Thorsten Schroer, Muhammed Yousufuddin, and Karl O. Christe[*]

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[*] Dr. R. Haiges, Dr. T. Schroer, Dr. M. Yousufuddin, Prof. Dr. K. O. Christe
Loker Research Institute and Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661 (USA)
Fax: (+1) 213-740-6679
E-mail: haiges@usc.edu, kchriste@usc.edu
Dr. J. A. Boatz
Space and Missile Propulsion Division
Air Force Research Laboratory (AFRL/PRSP)

10 East Saturn Boulevard, Bldg 8451
Edwards Air Force Base, CA 93524 (USA)

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Figure S1. IR and Raman spectrum of solid $Nb(N_3)_5$. The band marked by an asterisk (*) is due to the Teflon-FEP sample tube.

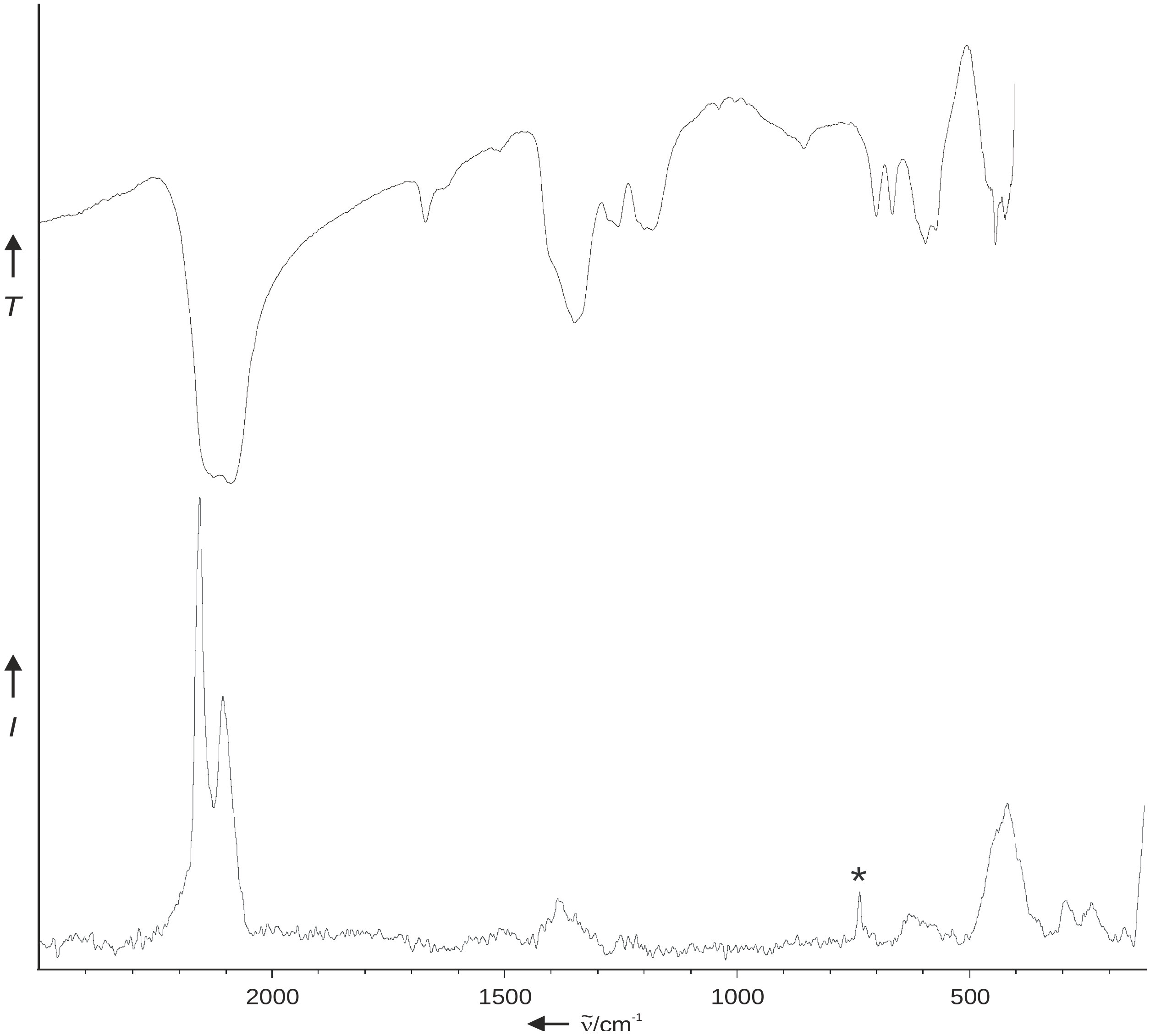

Figure S2. IR and Raman spectra of $Ta(N_3)_5$. The band marked by an asterisk (*) is due to the Teflon-FEP sample tube.

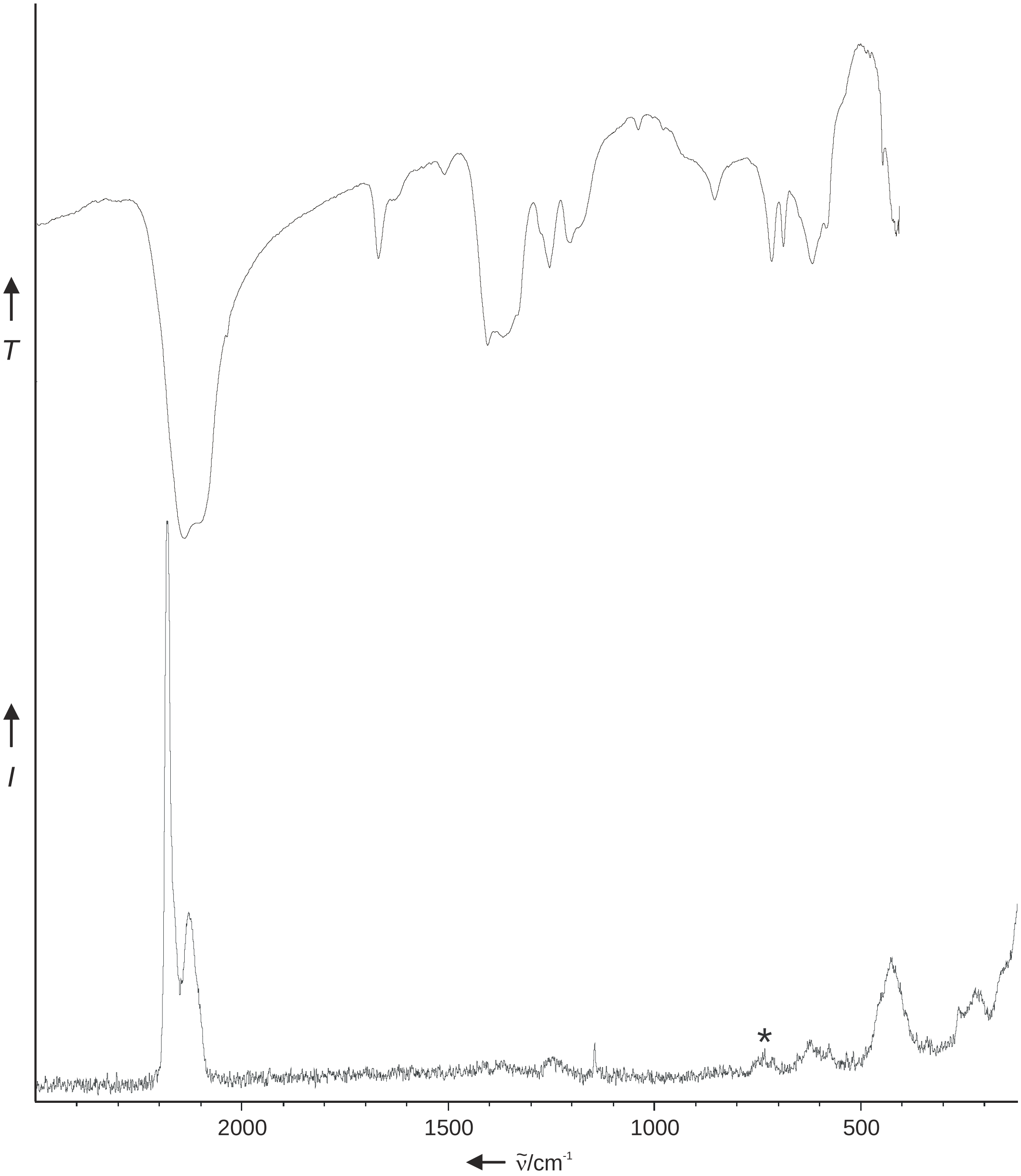

Figure S3. Raman spectrum of solid $CH_3CN \cdot Ta(N_3)_5$. The band marked by an asterisk (*) is due to the Teflon-FEP sample tube.

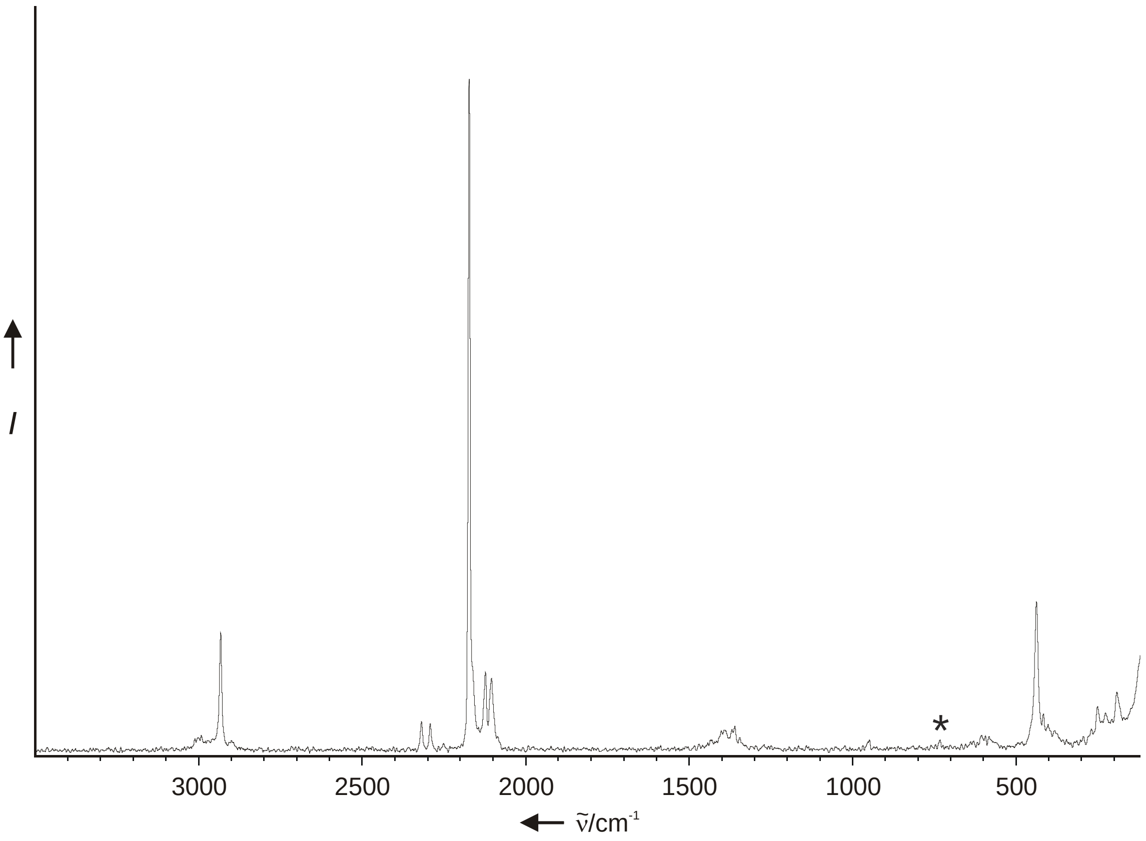

Figure S4. IR and Raman spectra of $[PPh_4][Nb(N_3)_6]$. The bands belonging to the $[Nb(N_3)_6]^-$ ion are marked with a diamond (♦).

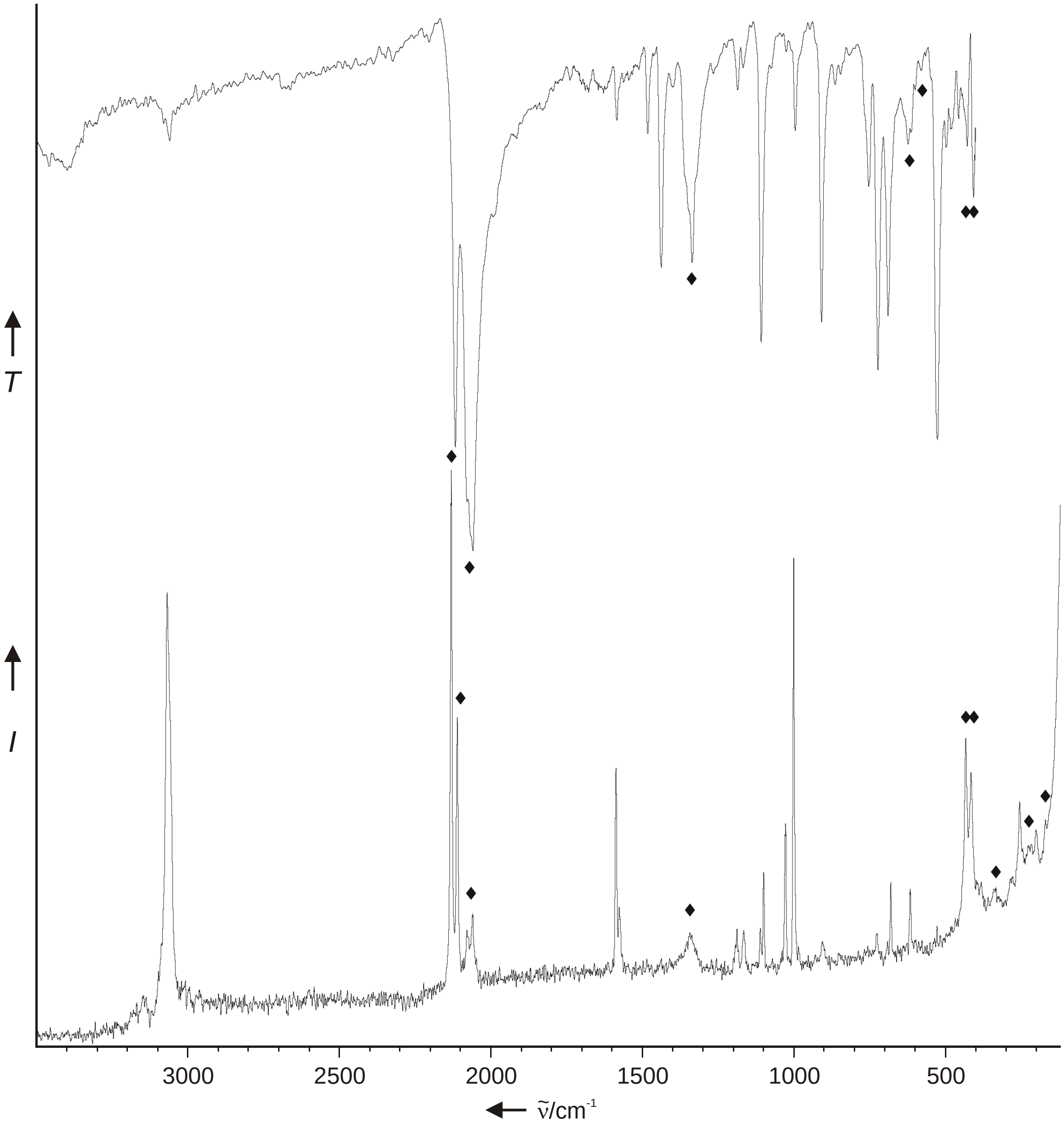

Figure S5. IR and Raman spectra of $[PPh_4][Ta(N_3)_6]$. The bands belonging to the $[Ta(N_3)_6]^-$ ion are marked with a diamond (♦). The band marked by an asterisk (*) is due to the Teflon-FEP sample tube.

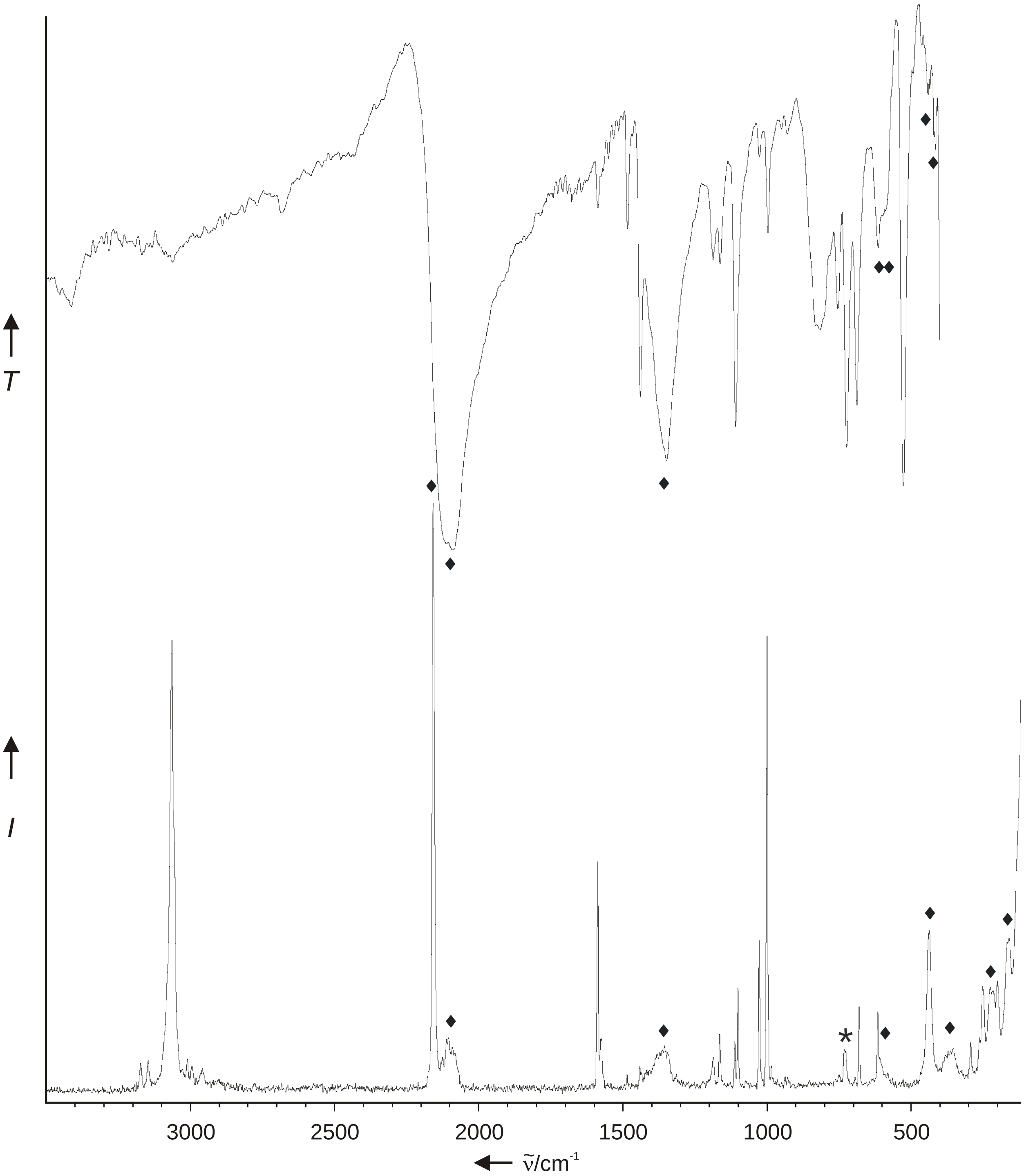

Table S1. Comparison of observed[a] and unscaled calculated vibrational frequencies [cm^{-1}] and intensities[b] for $Nb(N_3)_5$

		observed		calculated (IR)[Raman]	
	description	IR	Ra	B3LYP/SBK+(d)	MP2/SBK+(d)
ν_1	$\nu_{as}N_3$		2155 [10.0]	2235 (62) [1340]	2063 (806) [590]
ν_2	$\nu_{as}N_3$	2124 vs		2209 (2722) [241]	2074 (1918) [141]
ν_3	$\nu_{as}N_3$	2088 vs		2204 (1124) [250]	2061 (1261) [34]
ν_4	$\nu_{as}N_3$		2106 [5.5]	2200 (816) [306]	2059 (391) [246]
ν_5	$\nu_{as}N_3$			2179 (343) [210]	2044 (415) [28]
ν_6	$\nu_{s}N_3$		1385 [1.6]	1435 (172) [117]	1319 (36) [17]
ν_7	$\nu_{s}N_3$	1374 m		1403 (611) [31]	1312 (319) [16]
ν_8	$\nu_{s}N_3$			1375 (252) [8.4]	1294 (122) [20]
ν_9	$\nu_{s}N_3$	1347 s		1364 (453) [3.9]	1292 (206) [46]
ν_{10}	$\nu_{s}N_3$			1337 (350) [4.4]	1263 (111) [21]
ν_{11}	δN_3			598 (5.6) [2.8]	596 (5.8) [10]
ν_{12}	δN_3			587 (0.75) [5.8]	575 (83) [2.6]
ν_{13}	δN_3		628 [0.7]	583 (57) [90]	567 (79) [3.4]
ν_{14}	δN_3			580 (48) [2.5]	558 (115) [0.5]
ν_{15}	δN_3		590 sh	580 (51) [0.22]	533 (3.6) [0.39]
ν_{16}	δN_3	591 mw		579 (84) [6.6]	552 (39) [23]
ν_{17}	δN_3			571 (9.7) [77]	521 (4.8) [1.6]
ν_{18}	δN_3	569 w		567 (1.3) [2.1]	519 (6.5) [1.3]
ν_{19}	δN_3			559 (4.2) [0.63]	506 (0.25) [2.3]
ν_{20}	δN_3			552 (2.8) [1.2]	499 (6.4) [3.1]
ν_{21}	$\nu_{as}MN_3$ *eq*	450 sh		472 (164) [5.0]	468 (159) [7.8]
ν_{22}	$\nu_{as}MN_2$ *ax*	440 mw		463 (228) [2.9]	466 (247) [9.6]
ν_{23}	$\nu_{as}MN_3$ *eq*	422 w	427 sh	444 (202) [14]	455 (301) [14]
ν_{24}	$\nu_{s}MN_3$ *eq*		413 [3.2]	424 (100) [39]	416 (18) [238]
ν_{25}	$\nu_{s}MN_2$ *ax*		360 sh	363 (0.63) [15]	372 (0.07) [42]
ν_{26}	$\delta_{umbrella}MN_3$		288 [0.7]	285 (9.4) [29]	281 (8.8) [25]
ν_{27}	$\delta_{sciss}MN_3$			266 (1.4) [6.3]	253 (0.37) [11]
ν_{28}	$\delta_{sciss}MN_3$			243 (2.1) [16]	252 (1.2) [31]
ν_{29}	ρMN_2			227 (0.21) [1.2]	212 (0.003) [5.6]
ν_{30}	ρMN_2		234 [0.7]	208 (10) [36]	192 (8.6) [35]
ν_{31}	$\delta_{sciss}MN_2$			143 (0.48) [13]	153 (0.36) [13]
ν_{32}	$\delta_{sciss}MN_2$			134 (0.06) [1.9]	146 (0.11) [4.4]
ν_{33}	τ			103 (0.03) [6.5]	101 (0.11) [4.4]
ν_{34}	τ			100 (0.56) [7.2]	101 (1.9) [19]
ν_{35}	τ			90 (0.13) [0.99]	89 (0.13) [3.7]
ν_{36}	τ			57 (0.34) [15]	68 (0.33) [7.2]
ν_{37}	τ			53 (1.1) [6.3]	48 (1.1) [10]
ν_{38}	τ			45 (0.008) [13]	40 (0.05) [16]
ν_{39}	τ			43 (0.44) [23]	39 (0.17) [29]
ν_{40}	τ			41 (0.25) [20]	32 (0.012) [20]
ν_{41}	τ			29 (0.67) [16]	27 (0.44) [26]
ν_{42}	τ			18 (0.45) [1.7]	6 (0.61) [8.3]

[a] In addition to the bands listed in this table, the following weak infrared bands were observed which are attributed to overtones or combination bands: 1667 w, 1263 w, 1195 sh, 1176 w, 1037 vvw, 696 w, 660 w. [b] Calculated IR and Raman intensities are given in km mol^{-1} and Å^4 amu^{-1}.

Table S2. Comparison of observed[a] and unscaled calculated vibrational frequencies [cm^{-1}] and intensities[b] for $Ta(N_3)_5$.

		observed		calculated (infrared) [Raman]	
	description	IR	Ra	B3LYP/SBK+(d)	MP2/SBK+(d)
ν_1	$\nu_{as}N_3$		2182 [10.0]	2260 (43) [1109]	2134 (696) [316]
ν_2	$\nu_{as}N_3$	2141 vs		2233 (3271) [125]	2132 (2089) [139]
ν_3	$\nu_{as}N_3$		2129 [3.3]	2217 (895) [259]	2097 (823) [53]
ν_4	$\nu_{as}N_3$	2103 vs		2214 (1202) [170]	2086 (1230) [10]
ν_5	$\nu_{as}N_3$			2210 (319) [246]	2085 (673) [48]
ν_6	ν_sN_3			1473 (7.2) [21]	1348 (29) [88]
ν_7	ν_sN_3	1403 ms		1451 (857) [19]	1334 (368) [6.5]
ν_8	ν_sN_3			1389 (15) [7.9]	1314 (124) [60]
ν_9	ν_sN_3	1364 m		1375 (615) [5.7]	1303 (149) [34]
ν_{10}	ν_sN_3			1370 (450) [10]	1299 (198) [51]
ν_{11}	δN_3			600(2.0) [1.5]	566 (1.6) [0.61]
ν_{12}	δN_3		623 [1.1]	599 (1.2) [15]	562 (0.98) [1.7]
ν_{13}	δN_3	613 mw		586 (13) [0.34]	547 (54) [0.10]
ν_{14}	δN_3			583 (19) [13]	545 (21) [10]
ν_{15}	δN_3		590 sh	576 (2.7) [66]	550 (1.2) [24]
ν_{16}	δN_3			572 (18) [0.59]	543 (0.59) [1.4]
ν_{17}	δN_3			565 (37) [1.7]	538 (1.1) [0.12]
ν_{18}	δN_3	578 w		563 (62) [9.8]	539 (18) [8.2]
ν_{19}	δN_3			560 (9.9) [1.7]	530 (16) [0.08]
ν_{20}	δN_3			552 (4.7) [311]	532 (27) [0.42]
ν_{21}	$\nu_{as}MN_3$ *eq*		450 sh	444 (137) [6.5]	443 (188) [4.0]
ν_{22}	$\nu_{as}MN_2$ *ax*			442 (149) [1.4]	445 (167) [1.7]
ν_{23}	$\nu_{as}MN_3$ *eq*		426 [2.5]	439 (29) [38]	431 (4.3) [172]
ν_{24}	ν_sMN_3 *eq*	410 mw		388 (265) [9.1]	391 (349) [7.1]
ν_{25}	ν_sMN_2 *ax*		390 sh	360 (12) [47]	359 (2.9) [53]
ν_{26}	$\delta_{umbrella}MN_3$			288 (10) [3.2]	282 (11) [4.1]
ν_{27}	$\delta_{sciss}MN_3$			268 (9.8) [10]	255 (20) [5.9]
ν_{28}	$\delta_{sciss}MN_3$		256 [1.7]	258 (5.5) [63]	259 (1.6) [16]
ν_{29}	ρMN_2			253 (3.7) [0.23]	238 (7.5) [0.08]
ν_{30}	ρMN_2		221 [2.0]	207 (22) [21]	189 (22) [4.6]
ν_{31}	$\delta_{sciss}MN_2$			150 (0.18) [5.0]	149 (0.85) [8.9]
ν_{32}	$\delta_{sciss}MN_2$			123 (1.5) [160]	141 (1.5) [11]
ν_{33}	τ			109 (0) [3.6]	115 (0.006) [2.4]
ν_{34}	τ			101 (0.10) [8.4]	94 (0.11) [13]
ν_{35}	τ			100 (0.11) [11]	93 (0.07) [23]
ν_{36}	τ			48 (1.0) [2.6]	42 (0.62) [6.7]
ν_{37}	τ			47 (0.002) [13]	44 (0.07) [11]
ν_{38}	τ			40 (0.36) [47]	35 (0.29) [28]
ν_{39}	τ			40 (0.11) [21]	33 (0.19) [15]
ν_{40}	τ			39 (0.13) [17]	35 (0.005) [24]
ν_{41}	τ			21 (0.65) [0.65]	12 (0.80) [0.73]
ν_{42}	τ			17 (0.70) [3.4]	9 (0.91) [2.2]

[a] In addition to the bands listed in this table, the following weak infrared bands were observed which are attributed to overtones or combination bands: 1669 w, 1508 vw, 1274 sh, 1252 w, 1203 w, 1180 sh, 1036 vw, 850 w, 712 w, 683 w. [b] Calculated IR and Raman intensities are given in km mol^{-1} and Å^4 amu^{-1}.

Table S3. Comparison of observed and unscaled calculated[a] vibrational frequencies [cm^{-1}] and intensities for $CH_3CN{\cdot}Nb(N_3)_5$.

		observed	calculated (infrared) [Raman]	
	description	Ra	B3LYP/SBK+(d)	MP2/SBK+(d)
ν_1	$\nu_s CH_3$	2928 (1.8)	3111 (1.1) [54]	3180 (1.8) [32]
ν_2	$\nu_{as} CH_3$		3110 (1.2) [52]	3179 (1.7) [56]
ν_3	$\nu_{as} CH_3$		3005 (0.82) [192]	3051 (0.83) [173]
ν_4	νCN	2315 (1.2) 2289 (1.1)	2378 (75) [138]	2218 (22) [62]
ν_5	$\nu_{as} N_3$	2140 (10.0)	2238 (751) [1019]	2168 (624) [67]
ν_6	$\nu_{as} N_3$	2121 (1.5)	2202 (1935) [364]	2131 (770) [16]
ν_7	$\nu_{as} N_3$	2097 (1.9)	2176 (1528) [163]	2129 (514) [45]
ν_8	$\nu_{as} N_3$	2090 (1.6)	2176 (1527) [163]	2102 (732) [609]
ν_9	$\nu_{as} N_3$	2074 (2.2) 2058 (1.4)	2153 (0.11) [205]	2100 (1690) [88]
ν_{10}	$\nu_s N_3$		1473 (470) [12]	1460 (17) [8.7]
ν_{11}	$\delta_{sciss} CH_3$	1415 (1.3)	1434 (14) [7.7]	1460 (11) [4.7]
ν_{12}	$\delta_{sciss} CH_3$		1434 (14) [7.6]	1404 (6.6) [8.7]
ν_{13}	$\nu_s N_3$	1351 (1.1)	1413 (246) [4.3]	1345 (252) [35]
ν_{14}	$\nu_s N_3$	1331 (1.1)	1394 (374) [2.2]	1294 (29) [22]
ν_{15}	$\nu_s N_3$		1394 (379) [2.3]	1288 (160) [11]
ν_{16}	$\nu_s N_3$		1391 (6.5) [4.0]	1276 (35) [22]
ν_{17}	$\delta_s CH_3$	1363 (1.2)	1375 (4.9) [16]	1274 (130) [16]
ν_{18}	$\delta_{rock} CH_3$		1046 (0.78)[0.10]	1068 (0.42) [0.67]
ν_{19}	$\delta_{wag} CH_3$		1046 (0.82) [0.10]	1066 (1.4) [0.69]
ν_{20}	νCC	947 (1.0)	934 (8.0) [5.6]	954 (12) [2.7]
ν_{21}	δN_3	620 (1.2)	609 (5.4) [1.7]	612 (14) [15]
ν_{22}	δN_3	610 (1.0)	598 (63) [2.9]	595 (22) [11]
ν_{23}	δN_3		598 (63) [2.9]	594 (111) [8.5]
ν_{24}	δN_3	599 (1.2)	594 (0.61) [0.12]	583 (92) [12]
ν_{25}	δN_3	580 (1.1)	573 (0.006) [0.05]	519 (3.1) [0.31]
ν_{26}	δN_3	566 (1.0)	565 (19) [0.50]	516 (0.46) [0.69]
ν_{27}	δN_3		565 (20) [0.53]	511 (1.5) [4.9]
ν_{28}	δN_3		564 (1.1) [0.03]	509 (6.2) [2.5]
ν_{29}	δN_3	557 (1.1)	557 (12) [1.0]	495 (3.2) [0.88]
ν_{30}	δN_3		557 (12) [1.0]	487 (15) [0.44]
ν_{31}	$\delta N\text{-}C\text{-}C$		456 (21) [0.12]	461 (233) [27]
ν_{32}	$\delta N\text{-}C\text{-}C$		456 (22) [0.12]	454 (261) [1.1]
ν_{33}	νNbN_{ax}	441 (3.1)	444 (224) [31]	451 (272) [17]
ν_{34}	$\nu_{as} NbN_4$	435 (2.8)	427 (278) [1.5]	429 (14) [4.0]
ν_{35}	$\nu_{as} NbN_4$	423 (1.7)	427 (277) [1.5]	428 (20) [81]
ν_{36}	$\nu_{sym} NbN_{4\ i\ p}$	419 (1.7)	411 (0.025) [87]	418 (20) [174]
ν_{37}	$\nu_{sym} NbN_{4\ oo\ p}$	411 (2.0)	352 (0) [3.6]	372 (6.1) [2.9]
ν_{38}	νNbN_{CH3CN}	281 (1.1)	296 (.006) [1.4]	294 (14) [1.5]
ν_{39}	$\delta_{as} NbN_4$	266 (1.3)	278 (17) [0.63]	265 (8.8) [1.2]
ν_{40}	$\delta_{as} NbN_4$	256 (1.3)	278 (17) [0.63]	262 (15) [15]
ν_{41}	δNbN_5	248 (1.4)	255 (0.02) [23]	247 (0.50) [15]
ν_{42}	δNbN_5	226 (1.6)	221 (0.64) [2.1]	232 (1.2) [19]
ν_{43}	δNbN_5		221 (0.66) [2.1]	224 (2.2) [1.7]
ν_{44}	$\delta_{CH3CN\text{-}NbN5}$		203 (0.10) [0.34]	202 (4.8) [6.5]
ν_{45}	$\delta_{CH3CN\text{-}NbN5}$		203 (0.09) [0.36]	190 (0.01) [2.7]
ν_{46}	δNbN_5	189 (1.3)	200 (0.09) [2.7]	182).96) [12]
ν_{47}	δNbN_5	180 (1.3)	183 (0) [16]	164 (0.01) [4.3]
ν_{48}	τ	139 (1.6)	119 (0.70) [6.6]	117 (0.28) [14]
ν_{49}	τ	96 (2.9)	118 (0.68) [6.6]	115 (1.1)[13]
ν_{50}	τ		83 (0) [0]	64 (2.7) [16]
ν_{51}	τ		52 (3.3) [31]	62 (0.05) [0.81]
ν_{52}	τ		48 (0.004) [24]	59 (0.11) [9.1]
ν_{53}	τ		38 (0.009) [16]	55 (1.7) [31]
ν_{54}	τ		34 (2.1) [1.7]	48 (0.48) [1.9]
ν_{55}	τ		34 (2.0) [1.9]	39 (1.5) [7.3]
ν_{56}	τ		29 (1.6) [3.4]	31 (1.9) [3.7]
ν_{57}	τ		28 (1.7) [3.3]	26 (0.49) [16]

ν_{58}	τ	12 (0.11) [145]	25 (0.89) [16]
ν_{59}	τ	9 (0.11) [15]	20 (0.55) [13]
ν_{60}	unhindered CH$_3$ τ	13i (0.04) [0.01]	16 (0.008) [19]

[a] Calculated IR and Raman intensities are given in km mol^{-1} and Å^4 amu^{-1}, respectively. The given assignments of the observed frequencies are for the calculated B3LYP frequencies. The MP2 values have not been matched with either the B3LYP values or the observed spectrum.

Table S4. Comparison of observed and unscaled calculated[a] vibrational frequencies [cm^{-1}] and intensities for $CH_3CN{\cdot}Ta(N_3)_5$.

	description	observed Ra	calculated (infrared) [Raman] B3LYP/SBK+(d)	MP2/SBK+(d)
ν_1	$\nu_s CH_3$		3109 (1.3) [56]	3181 (1.6) [46]
ν_2	$\nu_{as} CH_3$		3109 (1.3) [55]	3179 (2.0) [40]
ν_3	$\nu_{as} CH_3$	2933 [1.7]	3004 (0.96) [202]	3051 (0.71) [166]
ν_4	νCN	2319 [0.5]	2383 (74) [166]	2235 (23) [79]
ν_5	νCN	2291 [0.5]	2222(2045) [360]	2168 (1157) [5.2]
ν_6	$\nu_{as} N_3$	2172 [10.0]	2260 (655) [1025]	2154 (128) [363]
ν_7	$\nu_{as} N_3$	2162 [1.2]	2195 (1739) [125]	2167 (1155) [4.6]
ν_8	$\nu_{as} N_3$	2123 [1.2]	2195 (1735) [125]	2168 (1157) [5.2]
ν_9	$\nu_{as} N_3$	2103 [1.1]	2173 (0.007) [181]	2137 (2378) [92]
ν_{10}	$\nu_s N_3$		1487 (428) [28]	1462 (13) [7.1]
ν_{11}	$\delta_{sciss} CH_3$	1389 [0.4]	1434 (15) [8.2]	1460 (15) [7.1]
ν_{12}	$\delta_{sciss} CH_3$		1433 (15) [8.4]	1404 (4.1) [9.2]
ν_{13}	$\nu_s N_3$		1432 (264) [29]	1364 (260) [69]
ν_{14}	$\nu_s N_3$		1410 (417) [6.8]	1318 (59) [42]
ν_{15}	$\nu_s N_3$		1410 (418) [6.9]	1307 (110) [48]
ν_{16}	$\nu_s N_3$		1409 (0.08)[12]	1301 (181) [27]
ν_{17}	$\delta_s CH_3$	1361 [0.4]	1374 (3.7) [16]	1298 (89) [44]
ν_{18}	$\delta_{rock} CH_3$		1046 (0.91) [0.055]	1067 (0.41) [0.33]
ν_{19}	$\delta_{wag} CH_3$		1046 (0.93) [0.082]	1067 (0.4) [0.33]
ν_{20}	νCC	948 [0.3]	935 (7.5) [15]	958 (12) [3.5]
ν_{21}	δN_3		608 (5.7) [1.2]	592 (2.1) [11]
ν_{22}	δN_3		596 (29) [1.7]	572 (50) [7.1]
ν_{23}	δN_3		596 (28) [1.7]	576 (4.0) [7.3]
ν_{24}	δN_3	592 [0.3]	593 (0.09)) [28]	572 (46)) [6.6]
ν_{25}	δN_3		585 (0.03) [0]	535 (12) [0.37]
ν_{26}	δN_3		584 (1.5) [0.06]	529 (0.10) [0.35]
ν_{27}	δN_3		584 (41) [0.28]	534 (12) [0.30]
ν_{28}	δN_3		584 (43) [0.26]	529 (1.6) [0.06]
ν_{29}	δN_3		578 (0.11) [1.6]	523 (3.8) [0.28]
ν_{30}	δN_3		578 (0.19) [1.6]	523 (2.8) [0.32]
ν_{31}	δN-C-C		471 (1.8) [0.82]	439 (7.1) [0.05]
ν_{32}	δN-C-C		471 (1.9) [0.82]	440 (16) [23]
ν_{33}	νNbN_{ax}	438 [2.1]	424 (0.53) [83]	433 (21) [69]
ν_{34}	$\nu_{as} NbN_4$	417 [0.6]	410 (170) [20]	413 (188) [100]
ν_{35}	$\nu_{as} NbN_4$		398 (242) [0.27]	411 (268) [3.0]
ν_{36}	$\nu_{sym} NbN_{4\ i\ p}$		398 (242) [0.26]	412 (272) [0.67]
ν_{37}	$\nu_{sym} NbN_{4\ oo\ p}$		366 (0) [1.3]	382 (0.32) [3.1]
ν_{38}	νNbN_{CH3CN}		303 (0) [2.1]	297 (0.06) [0.37]
ν_{39}	$\delta_{as} NbN_4$		274 (33) [0.32]	253 (38) [2.0]
ν_{40}	$\delta_{as} NbN_4$		273 (32) [0.31]	253 (40) [1.9]
ν_{41}	δNbN_5	250 [0.7]	246 (3.5) [24]	236 (0.87) [0.83]
ν_{42}	δNbN_5	226 [0.6]	226 (0.43) [0.98]	228 (1.8) [30]
ν_{43}	δNbN_5		226 (0.43) [0.98]	215 (11) [1.2]
ν_{44}	$\delta_{CH3CN-NbN5}$		210 (0.32) [0.12]	215 (10) [1.4]
ν_{45}	$\delta_{CH3CN-NbN5}$		210 (0.32) [0.11]	183 (0.96) [0.79]
ν_{46}	δNbN_5		203 (1.2) [0.27]	182 (0.97) [0.83]
ν_{47}	δNbN_5	192 [0.9]	182 (0.0004) [15]	169 (0) [14]
ν_{48}	τ		126 (0) [0]	107 (2.6) [11]
ν_{49}	τ		115 (0.95) [6.0]	107 (2.4) [11]
ν_{50}	τ		115 (0.96) [6.0]	86 (0.005) [0.006]
ν_{51}	τ		57 (0.0004) [24]	45 (0.027) [24]
ν_{52}	τ		48 (3.7) [28]	42 (4.1) [33]
ν_{53}	τ		40 (2.0) [0.12]	34 (1.1) [2.2]
ν_{54}	τ		40 (2.1) [0.13]	37 (1.2) [2.6]
ν_{55}	τ		33 (1.0) [6.7]	30 (0.0025) [11]
ν_{56}	τ		33 (0.99) [6.7]	17 (0.78) [17]
ν_{57}	τ		30 (0.003) [15]	27 (0.019) [12]
ν_{58}	τ		26 (0.82) [11]	17 (0.34) [16]

ν_{59}	τ	26 (0.77) [11]	15 (0.40) [0.72]
ν_{60}	τ	10 (0.0004) [0.019]	7 (0.66) [0.44]

[a] Calculated IR and Raman intensities are given in km mol^{-1} and Å^{4} amu^{-1}, respectively. The given assignments of the observed frequencies are for the calculated B3LYP frequencies. The MP2 values have not been matched with either the B3LYP values or the observed spectrum.

Table S5. Comparison of observed and unscaled calculated vibrational frequencies [cm^{-1}] and intensities for $[Ta(N_3)_6]^{-[a]}$ in point group C_1

		observed		Calculated (IR) [Raman]	
	description	IR	Ra	B3LYP/SBK+(d)	MP2/SBK+(d)
ν_{1}	$\nu_{as}N_3$		2159 [10.0]	2238 (100) [940]	2281 (1924) [5.1]
ν_{2}	$\nu_{as}N_3$	2124 vs	2111 [1.0]	2199 (2670) [120]	2181 (1926) [5.1]
ν_{3}	$\nu_{as}N_3$	2113 vs	2103 [1.0]	2193 (2307) [130]	2168 (534) [0.86]
ν_{4}	$\nu_{as}N_3$	2096 vs	2091 [0.8]	2189 (3036) [38]	2169 (771) [0.59]
ν_{5}	$\nu_{as}N_3$	2087 vs	2081 [0.7]	2178 (8.1) [221]	2169 (59) [1.5]
ν_{6}	$\nu_{as}N_3$			2172 (176) [193]	2167 (0.021) [444]
ν_{7}	$\nu_{s}N_3$			1441 (14) [55]	1304 (0.0004) [123]
ν_{8}	$\nu_{s}N_3$	1383 m		1421 (197) [25]	1297 (7.1) [103]
ν_{9}	$\nu_{s}N_3$	1372 m		1417 (118) [28]	1298 (6.9) [103]
ν_{10}	$\nu_{s}N_3$	1360 ms	1355 [0.8]	1414 (336) [18]	1293 (157) [0.003]
ν_{11}	$\nu_{s}N_3$	1348 s		1412 (420) [7.7]	1292 (232) [67]
ν_{12}	$\nu_{s}N_3$			1409 (338) [13]	1292 (232) [67]
ν_{13}	δN_3	648 vw		605 (7.4) [0.49]	581 (0.0004) [8.6]
ν_{14}	δN_3	615 m	609 [0.6]	599 (30) [1.2]	563 (13) [4.7]
ν_{15}	δN_3	600 mw		597 (25) [1.6]	563 (12) [4.7]
ν_{16}	δN_3			595 (15) [1.9]	553 (23) [8.0]
ν_{17}	δN_3			594 (0.45) [0.60]	553 (23) [8.0]
ν_{18}	δN_3			592 (10) [0.54]	551 (20) [0.014]
ν_{19}	δN_3			590 (12) [1.4]	534 (0.04) [0.027]
ν_{20}	δN_3			586 (3.4) [0.35]	535 (0) [2.6]
ν_{21}	δN_3	585 mw		585 (16) [0.39]	534 (0.04) [0.029]
ν_{22}	δN_3			584 (20) [0.44]	530 (0.060) [1.1]
ν_{23}	δN_3		582 [0.4]	583 (16) [1.9]	530 (0.063) [1.1]
ν_{24}	δN_3	576 w		578 (17) [0.24]	521 (23) [0]
ν_{25}	νMN	433 w	437 [2.8]	418 (1.9) [73]	414 (0.0009) [155]
ν_{26}	νMN	418 mw		377 (281) [1.3]	389 (294) [0.10]
ν_{27}	νMN	414 mw	372 [0.7]	375 (288) [1.3]	389 (294) [0.10]
ν_{28}	νMN		364 [0.8]	369 (306) [0.63]	369 (357) [0]
ν_{29}	νMN		353 [0.8]	344 (7.4) [1.5]	341 (40) [5.2]
ν_{30}	νMN			337 (41) [2.1]	341 (40) [5.1]
ν_{31}	δMN			271 (31) [3.2]	266 (57) [4.8]
ν_{32}	δMN			261 (31) [2.7]	266 (57) [4.8]
ν_{33}	δMN			254 (9.6) [6.3]	256 (0) [27]
ν_{34}	δMN		225 [1.8]	233 (24) [13]	215 (4.5) [4.7]
ν_{35}	δMN			228 (17) [11]	215 (4.5) [4.7]
ν_{36}	δMN		215 [1.8]	221 (9.6) [7.4]	209 (40) [0]
ν_{37}	δMN		168 [2.6]	181 (0.76) [18]	167 (0) [19]
ν_{38}	δMN			176 (0.06) [7.5]	161 (0.28) [19]
ν_{39}	δMN		160 [2.6]	172 (0.34) [14]	161 (0.28) [19]
ν_{40}	τ			91 (0.55) [7.3]	79 (3.6) [0]
ν_{41}	τ			83 (0.13) [10]	44 (0.006) [19]
ν_{42}	τ			79 (0.48) [0.69]	44 (0.004) [19]
ν_{43}	τ			44 (2.4) [19]	43 (0) [28]
ν_{44}	τ			41 (0.81) [18]	37 (1.7) [16]
ν_{45}	τ			39 (1.2) [18]	37 (1.8) [16]
ν_{46}	τ			38 (0.47) [17]	28 (0.73) [28]
ν_{47}	τ			36 (2.8) [11]	28 (0.75) [28]
ν_{48}	τ			35 (1.4) [7.3]	27 (0.0004) [3.6]
ν_{49}	τ			30 (0.44) [3.9]	14 (0.60) [6.5]
ν_{50}	τ			27 (0.22) [10]	14 (0.58) [6.3]
ν_{51}	τ			22 (0.81) [6.5]	9 (2.8) [0.002]

[a] Calculated IR and Raman intensities are given in km mol^{-1} and $Å^4$ amu^{-1}, respectively; observed spectra are for the solid $[P(C_6H_5)_4]^+$ salt. The MP2 values have not been matched with either the B3LYP values or the observed spectrum.