Azide Complexes (2)

Polyazide Chemistry: Preparation and Characterization of $Te(N_3)_4$ and $[P(C_6H_5)_4]_2[Te(N_3)_6]$ and Evidence for $[N(CH_3)_4][Te(N_3)_5]$**

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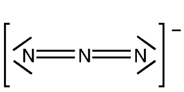
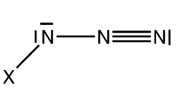
The azido group is highly energetic and adds about 70 kcal mol^{-1} to the energy content of a molecule. It is, therefore, not surprising that polyazides are highly endothermic compounds, and that their energy content increases with an increasing number of azido ligands. Compared to the relatively stable azide anion, which possesses two double bonds, the bonds in covalent azides are polarized towards a single and a triple bond, which greatly facilitates N_2 elimination and enhances their shock sensitivity.





Consequently, the synthesis and characterization of covalent binary azides containing multiple azido ligands can present great experimental challenges, and binary tellurium azides are no exception to this general rule.

Whereas numerous, partially azide-substituted tellurium compounds have been reported,[1–14] only one binary tellurium azide, the $[Te(N_3)_3]^+$ ion, has previously been reported.[5] In this paper, we wish to communicate the synthesis and characterization of three novel binary tellurium azides, $Te(N_3)_4$, $[Te(N_3)_5]^-$, and $[Te(N_3)_6]^{2-}$.

In the presence of catalytic amounts of CsF, the reaction of TeF_6 with excess $(CH_3)_3SiN_3$ in acetonitrile solution at room temperature results in the reduction of Te^{VI} to Te^{IV}, while the azide ion is oxidized to dinitrogen. Furthermore, complete fluoride–azide exchange takes place, to yield a clear yellow solution of $Te(N_3)_4$ according to Equation (1).

$$TeF_6 + 6\,(CH_3)_3SiN_3 \xrightarrow{CH_3CN} Te(N_3)_4 + 6\,(CH_3)_3SiF + 3\,N_2 \qquad (1)$$

Removal of the volatile products (CH_3CN, $(CH_3)_3SiF$, and excess $(CH_3)_3SiN_3$) in vacuo results in the isolation of $Te(N_3)_4$ as a bright-yellow solid. In the absence of CsF, no fluoride–azide exchange reaction was observed even after several days at room temperature. The catalytic function of the fluoride ion in these reactions probably involves the generation of intermediate free azide ions from the reaction of $(CH_3)_3SiN_3$ and F^- ions, and these free azide ions might be the actual reagent. The need for fluoride-ion catalysis, found in our study, is in contrast to the results from a previous ^{19}F NMR study[9] in which TeF_6 was reported to undergo facile fluoride–azide exchange with $(CH_3)_3SiN_3$ in CD_3CN solution to produce all the members of the $TeF_n(N_3)_{6-n}$ ($n = 1$–5) series. In their study, these authors also observed the azide-ion-mediated reduction of Te^{VI} to Te^{IV} as a side reaction.

As expected for a highly endothermic, binary covalent polyazide, $Te(N_3)_4$ is very sensitive and can explode violently. Its identity was established by the observed material balance, and through vibrational and NMR spectroscopy. The presence of single $\delta(^{125}Te)$ signals at $\delta = 1427$ ppm (CH_3CN solution) and $\delta = 1376$ ppm (DMSO solution), and the absence of any signals that would indicate Te–F spin–spin coupling in CH_3CN solution at 25 °C confirm complete fluoride–azide exchange and a pronounced solvent dependency of these shifts. The observed ^{125}Te shifts are in accord with our expectations for a multi-azido-substituted Te^{IV} compound; the shift reported for the closest known analogue, $CH_3Te(N_3)_3$, is $\delta = 1405$ ppm.[12] Furthermore, the presence of covalent azido ligands[11–16] is confirmed by the observed ^{14}N NMR shifts of $\delta = -139.8$ ppm (N_β, $\Delta\nu_{1/2} = 63$ Hz) and -238 ppm (N_γ, $\Delta\nu_{1/2} = 680$ Hz) in DMSO solution at 25 °C. In addition to quadrupolar broadening, rapid ligand exchange on the NMR timescale by the Berry pseudorotation mechanism[17] might contribute to the observation of only one set of azide signals and the relative broadness of the N_β resonance.

The observed Raman spectrum of solid $Te(N_3)_4$ is shown in Figure 1, and the observed infrared and Raman frequencies and intensities are listed in the Experimental Section. Assignments of the observed spectra were made by comparison with those calculated at the B3LYPSBKJC + (d) level of theory.[18]

These calculations resulted in two minimum-energy structures of C_2 symmetry (Figure 2 a and b). Both structures are derived from pseudo trigonal bipyramids, in which one of the equatorial positions is occupied by the sterically active free valence-electron pair of the tellurium center. The two structures differ in energy by only 1.8 kcal mol^{-1}. Their main structural difference is the orientation of the axial azido ligands. In structure **2a**, the axial azido ligands point in the same direction and toward the free valence-electron pair of the Te center. This compresses the free pair in the axial direction and exerts additional pressure on the two equatorial

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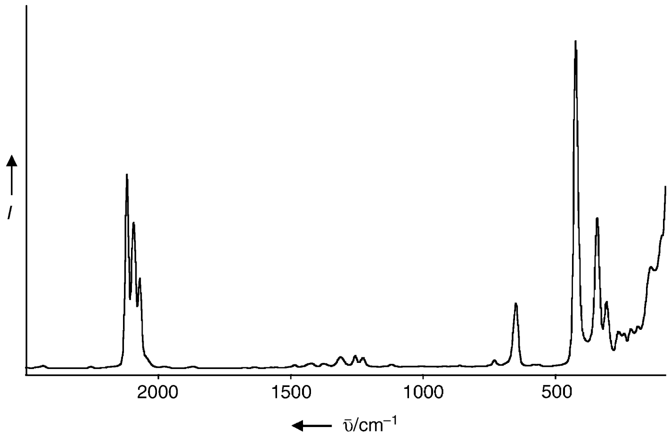

Figure 1. Raman spectrum of solid $Te(N_3)_4$.

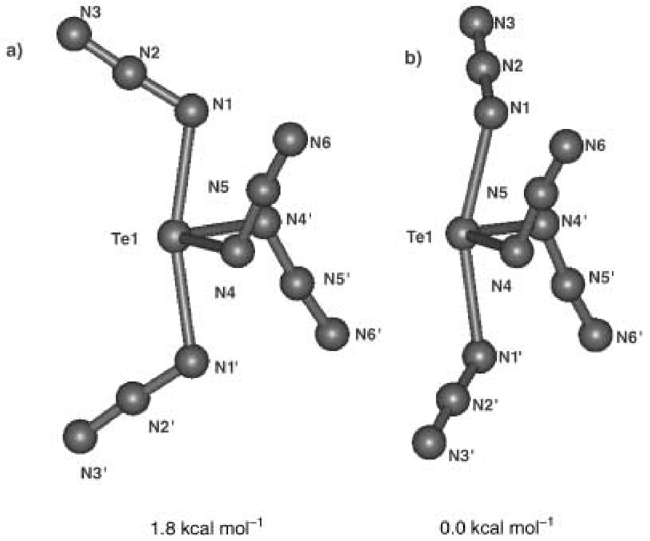

Figure 2. The two minimum energy structures calculated for $Te(N_3)_4$ at the B3LYPSBKJC+(d) level of theory.

ligands, compressing their bond angle by 11° compared to structure **2b**, in which the axial azido ligands point in different directions and away from the free pair.

The vibrational spectra, calculated for **2a** and **2b**,[18] are almost identical and do not permit a distinction between the two models. Nevertheless, they strongly support the presence of highly covalent azido ligands, the absence of Te–F bonds, and the identification of this compound as $Te(N_3)_4$. Because the two isomers have similar Te–N skeletal geometries and differ only in the orientation of the highly fluxional azido ligands, the vibrational spectra should deviate significantly only in the torsional modes. However, these modes are difficult to observe because of their low frequencies and intensities. A further complication might arise from the solid state, where coordinatively unsaturated polyazides might seek higher coordination numbers by the formation of nitrogen bridges. Consequently, crystal-structure data are required for a reliable determination of the precise arrangement of the azido ligands.

The reaction of $Te(N_3)_4$ with ionic azides leads to the formation of the $[Te(N_3)_6]^{2-}$ ion, according to Equation (2).

$$Te(N_3)_4 + 2\,[P(C_6H_5)_4]N_3 \xrightarrow{CH_3CN} [P(C_6H_5)_4]_2[Te(N_3)_6] \qquad (2)$$

The $[P(C_6H_5)_4]_2[Te(N_3)_6]$ salt is a yellow solid which is stable at room temperature and, because of the presence of two large counterions, is much less sensitive to shock than $Te(N_3)_4$. It was characterized from its crystal structure,[19] and by infrared, Raman, and ^{125}Te and ^{14}N NMR spectroscopy.

$[P(C_6H_5)_4]_2[Te(N_3)_6]$ crystallizes in the triclinic space group $P\bar{1}$ and is the first structurally characterized anionic tellurium(IV) azide.[20] The structure of the dianion shows roughly 50% positional disorder in two azide groups, i.e., N10-N11-N12 and N16-N17-N18. Figure 3 depicts the TeN_6 skeleton that is strongly distorted from octahedral symmetry by the sterically active free valence-electron pair of the Te center. If this electron pair were sterically inactive, one would expect perfect S_6 symmetry for a $Te(N_3)_6$ species, as predicted by our theoretical studies for $Te(N_3)_6$ and $[Te(N_3)_6]^{2-}$. The possibility of the distortion in $[Te(N_3)_6]^{2-}$ being caused by nitrogen bridging with other anions can be ruled out because, in its $P(C_6H_5)_4^+$ salt, the anions are well separated by twice as many large counterions, and the closest Te···N contacts between neighboring anions are 6.2 Å.

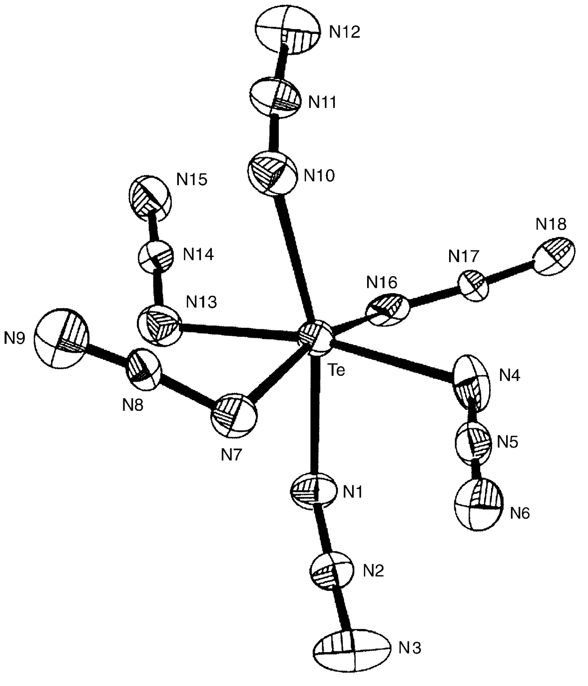

Figure 3. ORTEP drawing of the dianionic part of the crystal structure of $[P(C_6H_5)_4]_2[Te(N_3)_6]$. Thermal ellipsoids are shown at the 50% probability level without any disordered components. Selected bond lengths [Å] and angles [°]: Te-N1 2.136(2), Te-N4 2.240(2), Te-N7 2.094(2), Te-N10 2.416(2), Te-N13 2.197(2), Te-N16 2.542(2), N1-N2 1.228(2), N2-N3 1.115(3), N10-N11 1.223(3), N11-N12 1.143(10), N16-N17 1.206(10), N17-N18 1.159(10); N1-N2-N3 174.4(3), N13-N14-N15 177.6(3), Te-N10-N11 109.3(2), Te-N4-N5 121.2(2), N1-Te-N16 78.0(4), N7-Te-N10 80.63(8), N1-Te-N7 83.59(8), N4-Te-N7 83.79(9), N1-Te-N13 84.32(8), N7-Te-N13 85.33(8), N10-Te-N13 87.89(8), N1-Te-N4 88.87(9), N13-Te-N16 88.5(3), N4-Te-N10 95.87(8), N4-Te-N16 100.1(3), N10-Te-N16 117.1(4).

From the bond angles observed for $[Te(N_3)_6]^{2-}$, it appears that the free pair is located primarily between the N10 and N16 atoms (widening of the N10-Te-N16 angle to 120.6(4)° (av)) and displaced somewhat toward N4. Therefore, the $[Te(N_3)_6]^{2-}$ structure is best described as a distorted pseudo pentagonal bipyramid, in which the free valence-electron pair of the Te center is sterically active and occupies one of the equatorial positions. Because of increased ligand crowding in the equatorial plane, the free pair is located somewhat above the N1-N7-N10-N16 plane. This interpretation of the structure is also supported by the observed Te–N bond lengths, which exhibit remarkable differences and can be separated into three sets of pairs: N1 (2.136(2)) and N7 (2.094(2)), N4 (2.240(2)) and N13 (2.197(2)), and N10 (2.416(2)) and N16 (2.535(9) Å (av)). The N1-N2-N3 and N7-N8-N9 ligands are highly covalent, as shown by their very short Te–N bond lengths of about 2.1 Å and the large differences between the N_α–N_β and N_β–N_γ bonds. In contrast, the N_3 ligand, composed of N16-N17-N18, is partially ionic with a Te–N bond length of 2.535(9) Å (av) and with similar N_α–N_β and N_β–N_γ bond lengths.

In contrast to the observed crystal structure, the global minimum energy structure, predicted for free gaseous $[Te(N_3)_6]^{2-}$ at the B3LYPSBKJC+(d) level of theory,[18] shows ideal S_6 symmetry. Local minima of C_1 symmetry with asymmetric arrangements of the azido groups were also found which are only slightly higher in energy. The distortions in these C_1 structures are relatively minor and are caused by mutual repulsion effects among the azido ligands. These findings indicate that in our calculations the free valence-electron pair of the Te center is sterically inactive. Similar problems with correctly predicting the steric activity of free valence-electron pairs by these methods have been encountered by us for related species, such as $[IF_6]^-$. This ion is known to have a sterically active free valence-electron pair and a strongly distorted octahedral structure,[21,22] but the theoretical studies predict an ideal octahedral structure with a sterically inactive free valence-electron pair.[23]

The NMR spectra provide further support for the presence of the $[Te(N_3)_6]^{2-}$ ion. The observed ^{125}Te shift of 1250 ppm (CH_3CN, 25 °C) is in the range expected for a covalent multi-azido-substituted Te^{IV} compound (see above) and, relative to $Te(N_3)_4$, its shielding is increased by 177 ppm due to the addition of two negatively charged azide ions. By analogy with $Te(N_3)_4$, the ^{14}N NMR spectra (CH_2Cl_2, 25 °C) show resonances characteristic for covalent azido groups at $\delta = -138.6$ (N_β, $\Delta\nu_{1/2} = 33$ Hz) and -239 ppm (N_γ, $\Delta\nu_{1/2} = 240$ Hz), while N_α is too broad for a reliable assignment. Again, the observation of a single set of signals implies rapid exchange of the different type of ligands on the NMR time scale.

The observed infrared and Raman spectra of $[P(C_6H_5)_4]_2[Te(N_3)_6]$ are shown in Figure 4, and the observed frequencies are listed in the Experimental Section. Again, the agreement between the observed and the calculated spectra is good for the azido vibrations, however, the agreement is poor for the skeletal TeN_6 modes because of the failure of the calculations to properly predict the distortion caused by the steric activity of the free valence-electron pair of the Te center.

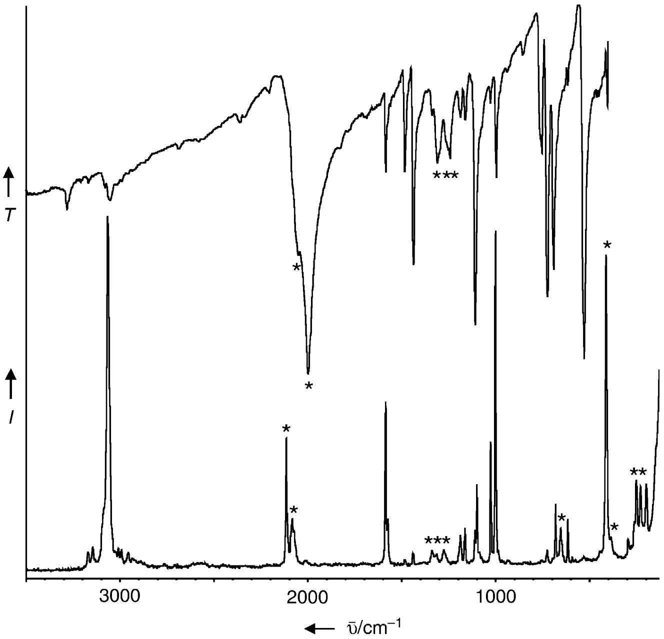

Figure 4. IR and Raman spectra of $[P(C_6H_5)_4]_2[Te(N_3)_6]$. The bands belonging to the $[Te(N_3)_6]^{2-}$ ion are marked with asterisks.

During an attempted synthesis of the $[Te(N_3)_7]^-$ ion from $[TeF_7]^-$ and trimethylsilylazide (either neat or in CH_3CN solution at room temperature), single crystals of $[N(CH_3)_4]^+[Te(N_3)_5]^-$ were obtained and identified by their crystal structure. Again the reduction of Te^{VI} to Te^{IV} by N_3^- ions had occurred [Eq. (3)]:

$$[TeF_7]^- + 7\,(CH_3)_3SiN_3 \rightarrow [Te(N_3)_5]^- + 7\,(CH_3)_3SiF + 3\,N_2 \qquad (3)$$

The structure had a low *R* factor of 0.016 and clearly showed the expected pseudooctahedral geometry with the free valence-electron pair of the Te center occupying one of the axial positions. However, this structure suffers from a partial occupancy of one equatorial azide position by a chloride ion (which is introduced during recrystallization from a CH_2Cl_2 solution), a positional disorder of a second equatorial azide ligand, and a twofold disorder of the $[N(CH_3)_4]^+$ ion along a C_3 axis. Consequently, this structure is not discussed in further detail because an ordered structure for this anion has already been obtained by Klapötke and coworkers.[20]

Tellurium azides are remarkable in that the nature of their Te–N bonds can vary in closely related compounds, or even within the same compound, from highly ionic to highly covalent with correspondingly large changes in bond lengths. For example, in R_3TeN_3 (R = CH_3 or C_6H_5),[14] the Te–N bond lengths have average values of about 3.0 Å and the two N–N bonds in the azido groups are almost identical in length, which indicates the presence of highly ionic azides. The other extreme, that is the presence of highly covalent azido ligands, is found in the $[Te(N_3)_3]^+$ ion[5] and $RTe(N_3)_3$ (R = Et, *n*Pr, *i*Pr, or 2,4,6-$Me_3C_6H_2$).[12] In these compounds, the Te–N bond lengths range from 1.99 to 2.25 Å, and the N_α–N_β and N_β–N_γ lengths differ by about 0.1 Å. As might be expected, compounds with bond lengths that fall between these extremes are also known. For example, the Te–N bond in $[(C_6H_5)_2TeN_3]_2O$ is 2.397(8) Å in length.[10]

Although the bond lengths for $Te(N_3)_4$ could not be measured experimentally, the values of 2.071 and 2.185 Å, predicted for the free gaseous molecule at the B3LYPSBKJC + (d) level of theory,[18] and the observed vibrational and NMR spectra suggest the presence of highly covalent Te–N bonds, similar to those predicted for free $Te(N_3)_6$. In contrast, the Te–N bond lengths observed for $[Te(N_3)_6]^{2-}$ cover a wide range from 2.094(2) to 2.542(9) Å, which indicates the simultaneous presence of highly covalent and partially ionic Te–N bonds within the same ion. The increase of 0.20 Å in the predicted average Te–N bond length on going from $Te(N_3)_6$ to $[Te(N_3)_6]^{2-}$ can be explained by a higher ionicity of the Te–N bonds in $[Te(N_3)_6]^{2-}$, caused by the two formal negative charges.

Experimental Section

Caution! Covalent azides are potentially hazardous and can decompose explosively under various conditions. They should be handled only on a small scale with appropriate safety precautions (face shields, leather gloves, and protective clothing).

All reactions were carried out in teflon-FEP ampules closed by stainless steel valves. Volatile materials were handled in a stainless steel–teflon-FEP or pyrex glass vacuum line. Nonvolatile materials were handled in the dry argon atmosphere of a glove-box. All reaction vessels and the stainless steel line were passivated with ClF_3 prior to use.

Raman spectra were recorded in the range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd-YAG laser at 1064 nm. Pyrex melting point tubes were baked out at 300 °C for 48 h at 10^{-2} Torr and teflon-FEP tubes with stainless steel valves, passivated with ClF_3, were used as sample containers. Infrared spectra were recorded 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.). NMR spectra were recorded unlocked at 500.13 MHz (^1H), 125.76 MHz (^{13}C), 202.46 MHz (^{31}P), 158.03 MHz (^{125}Te) and 36.13 MHz (^{14}N) on a Bruker AMX 500 spectrometer using solutions of the compounds in acetonitrile or dichloromethane in sealed standard glass tubes. Neat TMS ($\delta = 0.00$ ppm) was used as external reference for ^1H and ^{13}C, 85% aqueous H_3PO_4 ($\delta = 0.00$ ppm) as external reference for ^{31}P, saturated aqueous $Te(OH)_6$ ($\delta = 710.9$ ppm)[24] as external reference for ^{125}Te and neat CH_3NO_2 ($\delta = 0.00$ ppm) was the external reference for ^{14}N.

The starting materials TeF_6 (Ozark Mahoning) and $[(C_6H_5)_4P]I$ (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. $[(C_6H_5)_4P]N_3$ was prepared from $[(C_6H_5)_4P]I$ and AgN_3.

Preparation of $Te(N_3)_4$: On the stainless steel vacuum line, TeF_6 (0.438 mmol) was condensed at −196 °C into a teflon-FEP ampoule containing CsF (0.05 mmol). The ampoule was then attached to a glass vacuum line and after evacuation, CH_3CN (50 mmol) and $(CH_3)_3SiN_3$ (3.21 mmol) was condensed into the ampoule at −196 °C. The mixture was allowed to warm to ambient temperature, resulting in weak gas-evolution and a yellow-colored solution. After 8 h, the temperature was lowered to −20 °C, and all volatile compounds were pumped off over a period of 8 h, leaving behind a yellow liquid. Additional pumping at ambient temperature for 2 h resulted in a bright yellow solid (0.130 g, weight calculated for 0.438 mmol $Te(N_3)_4 = 0.129$ g). Inspection of the volatile material trapped at −196 °C by gas-FTIR spectroscopy showed CH_3CN and $(CH_3)_3SiF$[25,26] as the sole reaction by-product. IR: $\tilde{\nu} = 2111(w)/2082(m)/2063(m)/2048(s)/1998\ (vs)\ (\nu_{as}N_3)$, $1294(mw)/1251(m)/1241\ cm^{-1}\ (mw)\ (\nu_sN_3)$. Raman: $\tilde{\nu} = 2116(4.2)/2085(1.7)/2075\ (1.3)/2065(0.7)/2057(0.4)\ (\nu_{as}N_3)$, $1334(0.6)/1313(0.6)/1277(0.7)/1260(0.4)\ (\nu_sN_3)$, $654(1.4)/647(0.9)/639(0.5)\ (\delta N_3)$, $412(10.0)/385(1.1)\ cm^{-1}\ (\nu TeN)$.

Preparation of $[(C_6H_5)_4P]_2[Te(N_3)_6]$: $[(C_6H_5)_4P]N_3$ (0.6 mmol) was loaded into a teflon-FEP ampoule containing $Te(N_3)_4$ (0.3 mmol), followed by the addition of CH_3CN (30 mmol) in vacuo at −196 °C. The mixture was warmed to room temperature, which resulted in the formation of an orange solution. After 3 h, all volatile material was pumped off, leaving behind an orange solid (0.310 g, weight calculated for 0.3 mmol $[(C_6H_5)_4P]_2[Te(N_3)_6] = 0.317$ g). Single crystals were grown from a solution in CH_3CN. IR: $\tilde{\nu} = 2110(vs)/2060(vs)\ (\nu_{as}N_3)$, $1317(m)/1236\ cm^{-1}\ (m)\ (\nu_sN_3)$. Raman: $\tilde{\nu} = 2119(4.3)/2094(3.3)/2070(2.1)\ (\nu_{as}N_3)$, $1312(0.3)/1257(0.4)/1227(0.3)\ (\nu_sN_3)$, $649(1.9)\ (\delta N_3)$, $424(10.0)\ (\nu_{sym}TeN_{2eq})$, $343(4.6)\ (\nu_{sym}TeN_{2ax})$ and $(\nu_{as}TeN_{2eq})$, $307(2.1)\ (\nu_{as}TeN_{2ax})$, 262(1.2), 241(1.1), 216(1.3), 183(1.4), 138(3.4) cm^{-1}.

Preparation of $[N(CH_3)_4][Te(N_3)_5]$: A sample of $[N(CH_3)_4][TeF_7]$ (0.5 mmol) was loaded into a Teflon-FEP ampoule in a glove-box, followed by the addition of CH_3CN (50 mmol) in vacuo at −196 °C. The mixture was warmed to room temperature to form a solution, cooled again to −196 °C, and $(CH_3)_3SiN_3$ (4.0 mmol) was condensed into the mixture. The ampoule was allowed to warm to ambient temperature resulting in a yellow solution. All volatile components were pumped off to leave a yellow solid residue (0.199 g, weight calculated for 0.5 mmol of $[N(CH_3)_4]\ [Te(N_3)_5 = 0.206$ g). Recrystallization of the crude product from CH_2Cl_2 solution by cooling to −30 °C resulted in yellow crystals. Raman (selected values): $\tilde{\nu} = 2109(8.4)/2094(1.9)/2074(1.9)/2057(2.6)/2047(2.7)/2036(2.0)\ (\nu_{as}N_3)$, $1311(1.7)/1266(1.2)\ (\nu_sN_3)$, $679(0.9)/664(0.8)/656(0.7)\ (\delta N_3)$, $400(10.0)/337(6.7)\ cm^{-1}\ (\nu TeN)$. IR (selected values): $\tilde{\nu} = 2086(vs)/2057(vs)/2022(vs)\ (\nu_{as}N_3)$, $1306(s)\ (\nu_sN_3)$, $645(w)\ cm^{-1}\ (\delta N_3)$. ^{14}N NMR (CH_3CN, 25 °C): $\delta = -138$ (N_β, $\Delta\nu_{1/2} = 40$ Hz), −233 (N_γ, $\Delta\nu_{1/2} = 210$ Hz), −337.8 ppm ($(CH_3)_4N$, $\Delta\nu_{1/2} = 6$ Hz); ^{125}Te NMR (CH_3CN, 25 °C) $\delta = 1256$ ppm.

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[19] Crystal data for $C_{48}H_{40}N_{18}P_2Te$: $M_r = 1058.52$, triclinic, space group $P\bar{1}$, $a = 10.198(1)$, $b = 15.170(1)$, $c = 15.927(2)$ Å, $\alpha = 78.781(2)$, $\beta = 88.424(2)$, $\gamma = 78.315(2)°$, $V = 2366.6(4)$ Å^3, $Z = 2$, $F(000) = 1072$, $\rho_{calcd} = 1.485\ \mathrm{g\,cm^{-3}}$, $\mu = 0.753\ \mathrm{mm^{-1}}$, approximate crystal dimensions $0.19 \times 0.14 \times 0.04\ \mathrm{mm^3}$, θ range = 1.30 to 25.33°, $\mathrm{Mo_{K\alpha}}$ ($\lambda = 0.71073$ Å), $T = 85$ K, 12464 measured data (Bruker 3-circle, SMART APEX CCD with χ axis fixed at 54.74°, using the SMART V 5.625 program, Bruker AXS: Madison, WI, 2001), of which 8426 ($R_{int} = 0.0141$) unique. Lorentz and polarization correction (SAINT V 6.45 program, Bruker AXS), absorption correction (SADABS program, Bruker AXS). Structure solution by Patterson methods (SHELXTL 6.14, Bruker AXS), full-matrix least-squares refinement on F^2, data-to-parameters ratio: 13.20:1, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0305$, $wR2 = 0.0772$, $R1 = 0.0348$, $wR2 = 0.0796$ (all data), GOF on $F^2 = 1.054$. CCDC-217066 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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