Experimental and Theoretical Studies of Homoleptic Tellurium Cyanides $Te(CN)_x$: Crystal Structure of $Te(CN)_2$

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Dedicated to Professor H. Schmidbaur on the occasion of his 70th birthday

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The labile tellurium cyanide species $Te(CN)_2$ and $Te(CN)_4$ have been prepared by treatment of tellurium(IV) tetrahalides with cyanide. Both are thermosensitive solids and, in addition, the tetracyanide was found to be pyrophoric. The crystal structure of $Te(CN)_2$ has been determined. The structures of $Te(CN)_2$, $Te(CN)_4$, and $Te(CN)_6$ have been calculated at various levels of theory.

Introduction

A search for low-valent tellurium pseudohalides leads to few reports on the existence of dicyanotellane, $Te(CN)_2$ (**1**). This almost "forgotten" molecule was first prepared in 1908 by the reaction of $TeBr_4$ with excess AgCN,[1] and since then it has had a scanty publication history.[2−4] Somewhat surprising is the fact that **1** had been investigated by IR spectroscopy,[3] and used for an attempted synthesis only once, respectively.[4] The stable dicyanides of the lighter homologues of **1**, $S(CN)_2$ and $Se(CN)_2$, have been characterized in more detail,[5,6] while the $O(CN)_2$ molecule probably only exists as an intermediate and has been studied by theoretical methods.[7] The Te^{II} dihalides $TeHal_2$ (Hal = Cl, Br, I) are not stable towards disproportionation in the condensed phase,[8] but have been investigated in the gas phase;[9,10] the difluoride TeF_2 does not seem to exist at all. To the best of our knowledge, structurally characterized binary covalent main-group cyanides—apart from HCN, $(CN)_2$, and the halogen derivatives HalCN—are limited to $P(CN)_3$, $As(CN)_3$, $S(CN)_2$, and $Se(CN)_2$, whose reports date back to the 1960s.[11,12] This let us believe that the elucidation of the structural and spectroscopic properties of $Te(CN)_2$ (**1**) might be worthwhile.

Results and Discussion

Similar to the original procedure, $Te(CN)_2$ (**1**) can be obtained in analytically pure form from the reaction of $TeBr_4$ or TeI_4 with excess AgCN by separation of its colorless solutions in Et_2O under meticulously anhydrous conditions [Equation (1)].

$$\mathrm{TeHal_4 + 3\,AgCN \xrightarrow[-\,3\,AgHal]{60\,^\circ C\,/\,C_6H_6} Te(CN)_2\ (\mathbf{1}) + HalCN} \qquad (1)$$

$$\mathrm{Hal = Br,\ I}$$

After evaporation of the solvents, careful sublimation of the faintly brownish residue in vacuo ($<10^{-4}$ mbar/<80 °C) yielded an almost colorless solid, which is very sensitive towards hydrolysis; above 100 °C slow decomposition to elemental tellurium and cyanogen occurs.

The vibrational spectra (IR/Raman) of solid **1** exhibit the symmetric and antisymmetric C≡N stretching vibrations at 2176/2177 (A_1) and 2168/2170 (B_1), and bands at 410/409 (A_1 Te−C stretch), 398/395 (B_2 Te−C stretch), 296/− (B_1 TeCN deformation), 277/279 (A_2 TeCN deformation), and 147/136 cm^{-1} (A_1 CTeC deformation). The significant differences in frequencies and intensities (see Figure 1) obtained from the calculated values for the gas phase may result from intermolecular interactions in solid **1** (vide infra). Even if appropriate scaling factors for the calculated vibrational frequencies of **1** were available for all methods, this would give only partial improvement of the computed spectra because of a non-linear systematic difference in the Te−C and C≡N stretching vibrations. In the mass spec-

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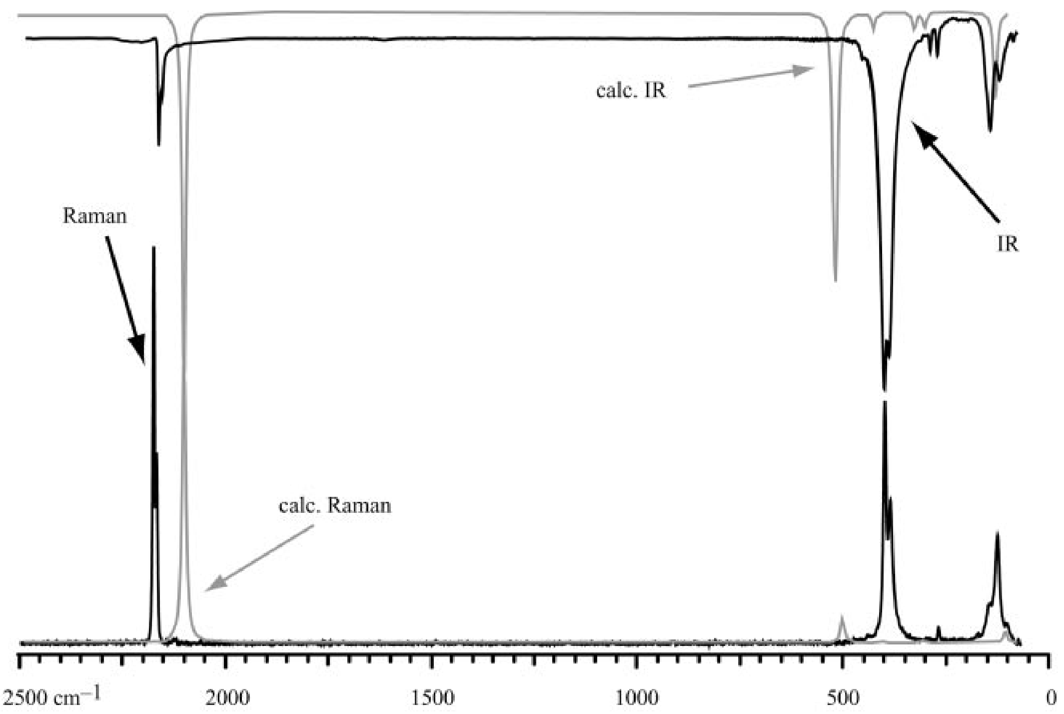

Figure 1. Experimental and calculated vibrational spectra of **1**, unscaled frequencies obtained at the MP2(FC)/MDF28-cc-pVQZ level

trum (EI), the parent ion is detected at $m/z = 182$, along with the fragments $[TeCN]^+$ at $m/z = 156$ and Te_2^+ at $m/z = 256$. The ^{125}Te NMR spectrum shows a single resonance at $\delta = 567$ ppm in [D$_8$]THF ($\delta = 585$ ppm in Et_2O). In the ^{13}C NMR spectrum in [D$_8$]THF, a resonance at $\delta = 86.2$ ppm with a coupling $^1J_{C-Te}$ of 330.2 Hz is found. The broad ^{14}N NMR resonance at $\delta = -70$ ppm ($\Delta\nu_{1/2} = 1300$ Hz) is overlapped by the sharp resonance for dinitrogen at $\delta = -71.5$ ppm. A minor second resonance at $\delta = -123$ ppm ($\Delta\nu_{1/2} = 170$ Hz) is assigned to cyanogen.

From saturated solutions of **1** in diethyl ether to which small amounts of *n*-heptane were added, off-white needles were formed under strictly anhydrous conditions at −25 °C after an extended period (18 months). In contrast, slow sublimation produced only amorphous solids. A single crystal suitable for X-ray diffraction was obtained only after several attempts because **1** in solution mostly decomposed faster than it crystallized. X-ray diffraction revealed a molecular structure with space group $R\bar{3}c$. Whereas the calculated gas phase structures of **1** at all theoretical levels applied

Table 1. Experimental parameters from X-ray diffraction and calculated parameters of $Te(CN)_2$ (**1**), $Te(CN)_4$ (**2**), and $Te(CN)_6$ in the gas phase at different levels of theory

Molecule	Method	Pseudo-potential	*E* [a.u.]	zpe [kJ mol^{-1}]	*d*(Te−C) [Å]	*d*(C−N) [Å]	<(C−Te−C) [°]	νCN [cm^{-1}][a]
$Te(CN)_2$ (**1**, C_{2v})	exp.	–	–	–	2.090(5)/ 2.091(6)[b]	1.131(7)/ 1.149(7) [b]	85.4(4)	2170/2177[c]
	B3LYP/cc-pVQZ	MDF28	−453.8442	40.57	2.054	1.153	94.46	2266/2274
	MP2(FC)/cc-pVQZ	MDF28	−452.6322	39.05	2.021	1.177	93.19	2100/2101
	CCD/cc-pVQZ	MDF28	−452.6691	–[d]	2.023	1.152	93.57	–[d]
	DHF/(20s18p11d+1s1p1d), cc-pVDZ	all-electron	−6978.4023	–	2.059	1.138	93.75	–
	LL-MP2/(20s18p11d+1s1p1d), cc-pVDZ	all-electron	−6796.9235	–	2.046	1.191	93.60	–
$Te(CN)_4$ (**2**, C_{2v})	B3LYP/cc-pVTZ	MDF28	−639.4585	88.91	2.074/2.227	1.152/1.155	84.35/104.06	2263/2265/ 2295/2300
	MP2(FC)/cc-pVTZ	MDF28	−637.7936	77.00	2.042/2.180	1.176/1.180	83.53/105.60	2053/2057/ 2086/2089
$Te(CN)_6$ (O_h)	B3LYP/cc-pVTZ	MDF28	−825.0674	125.49	2.118	1.153	90	2292−2297
	MP2(FC)/cc-pVTZ	MDF28	−823.0421	118.69	2.078	1.179	90	2062−2070

[a] Vibrational frequencies are unscaled. [b] Two different bond lengths due to lower symmetry of **1** in the crystal. [c] Raman frequencies. [d] Frequency analysis impossible due to exceedingly high memory requirements.

have the expected C_{2v} symmetry with a C−Te−C angle of about 95° (see Table 1), comparable to $TeCl_2$ in the gas phase with 97.0(6)°,[10] the crystal structure of **1** reveals two almost identical Te−C bond lengths [2.090(5) and 2.091(6) Å], but two slightly different C−N bond lengths [1.131(7) and 1.149(7) Å], with a C−Te−C angle of 85.4(2)° (see Figure 2). The Te−C distance in **1** is in the same range as found for diaryl-substituted tellanes Ar_2Te,[13] but with a more acute C−Te−C angle than the latter. Available structural data for $S(CN)_2$ and $Se(CN)_2$, as far as their poor quality allows conclusions, suggest a different structure in the solid state with C−S and Se−C angles of 96 and 99°, respectively.[5,12] This unusual small angle in **1** is most likely caused by the near square-planar coordination around Te^{II} created by the two covalent cyano groups attached to tellurium and two additional strong Te···N secondary interactions [2.745(5) and 2.758(5) Å] with two cyano-N atoms of two neighboring $Te(CN)_2$ molecules (see Figure 2), which are "pushed away" by the two lone pairs of Te^{II}. This can be conveniently visualized by the use of ELF analysis,[14] by using the experimental geometry of a part of the unit cell (see Figure 3). This coordination to adjacent molecules builds up a three-dimensional network, which connects all molecules of **1** contained in the unit cell. Furthermore, this network, when looked upon along the *c* axis, features small tubes of about 8 Å in diameter containing small residual electron densities, which have been assigned to disordered carbon atoms of a solvate, diethyl ether or *n*-heptane that was used during the crystallization process (see Figure 4).

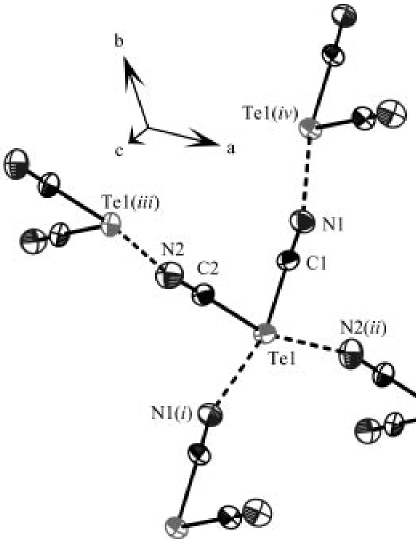

Figure 2. ORTEP plot of the molecular structure of **1** with thermal ellipsoids drawn at 50% probability; selected bond lengths [Å], distances [Å] and angles [°]: Te1−C1 2.090(5), Te1−C2 2.091(6), N1−C1 1.131(7), N2−C2 1.149(7); C1−Te1−C2 85.4(2), N1−C1−Te1 178.3(5), N2−C2−Te1 179.2(5); Te1···N1(*i*) 2.758(5), Te1···N2(*ii*) 2.745(5); C1−Te1···N1(*i*) 163.3(5), C1−Te1···N2(*ii*) 77.8(5), C2−Te1···N1(*i*) 78.0(5), C2−Te1···N2(*ii*) 163.2(5), N1(*i*)···Te1···N2(*ii*) 118.8(1); *i* = −1/3 + *x*, −1/6 + *x* − *y*, −1/6 + *z*; *ii* = 4/3 − *x* + *y*, −1/3 + *y*, −1/6 + *z*; *iii* = 1/3 + *x*, −1/3 + *x* − *y*, 1/6 + *z*; *iv* = 2/3 − *x* + *y*, 1/3 + *y*, −1/6 + *z*

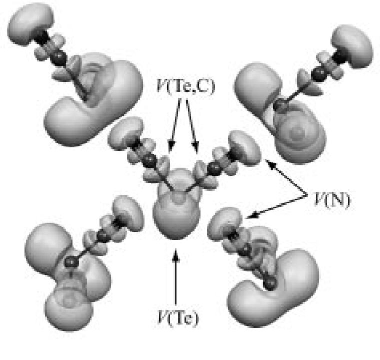

Figure 3. Ball-and-stick model with superimposed ELF isosurface of five $Te(CN)_2$ (**1**) molecules in the arrangement found by X-ray structure analysis (representing the full first coordination sphere for the central molecule, equivalent to Figure 2), single point calculation at the B3LYP/MWB46-VDZ level of theory; η = 0.78, grid increment 0.2 Å

The only report of a reaction of **1** is the attempted reaction with cyanide in MeCN solution, which did not furnish the tricyanotellurate(II) anion, $[Te(CN)_3]^-$.[4] Our experiments to halogenate **1** gave no clear results; reaction with XeF_2 in MeCN or EtCN led to colorless solutions, which were stable at −20°C for several hours. However, at higher temperatures, decomposition/dismutation reactions occurred, and sublimation of the dark residues thereof resulted in the isolation of starting material **1**.

The reaction of TeF_4 with Me_3SiCN, in a manner similar to the synthesis of $Te(N_3)_4$,[15] yields tellurium(IV) cyanide, $Te(CN)_4$ (**2**), one of the elusive neutral main-group tetracyanide species; a highly pyrophoric and thermally unstable solid. Compound **2** is obtained in CH_2Cl_2 or THF suspension at −20 °C [Equation (2)].

$$TeF_4 + 4\,Me_3SiCN \xrightarrow[-\,4\,Me_3SiF]{-20\,^{\circ}C\,/\,CH_2Cl_2} Te(CN)_4\ (\mathbf{2}) \qquad (2)$$

Above this temperature, rapid decomposition was observed that yielded a brownish oil, which was shown to contain **1** by ^{125}Te NMR spectroscopy. Reductive decomposition with extrusion of R−R species is also reported for some other R_4Te compounds.[16] After removal of all volatile materials from a suspension of **2** in CH_2Cl_2 at −20 °C, the remaining colorless powder was filled into a small Schlenk tube under argon for further investigations, upon which in two separate attempts a severe explosion destroyed parts of the glassware, presumably owing to thermal decomposition. The characterization of **2** is limited to Raman spectroscopy, since all other methods failed due to the enormous pyrophoric character, thermal sensitivity and insolubility. The fact that four equivalents of Me_3SiCN were consumed strongly suggests full substitution of all four fluorine atoms of TeF_4 to give the tetracyanide **2**. In the experimental Raman spectrum, four different C≡N stretching vibrations were detected, which complies with the basic considerations for two different cyano groups, axial and equatorial. The insolubility in all common solvents prevented crystallization and characterization by NMR spectroscopy.

In order to obtain a derivative of **2**, we probed the possible existence of pentacyanotellurate(IV) $[Te(CN)_5]^-$; re-

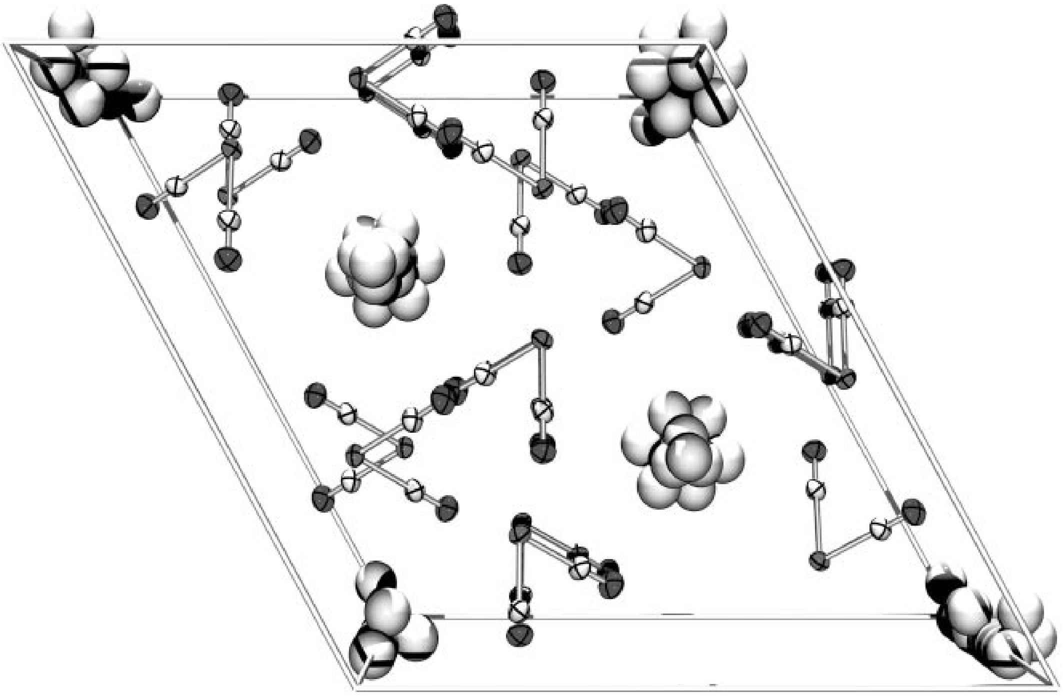

Figure 4. Unit cell of crystalline **1**, atoms within $0.5 \leq z \leq -1$ omitted, view along the *c*-axis (001), the residual electron densities assigned to carbon atoms [C11−C15, site occupation factor (SOF) = 0.207] of disordered solvate molecules are depicted as gray spheres within the free tubular spaces, thereof C11, C12, and C13 on a threefold axis

cently, we were able to characterize the stable azido analogue $[Te(N_3)_5]^-$.[15] Similar anions of the type $[aryl_5Te]^-$ can be trapped and have been proven to exist at low temperatures by ^{125}Te NMR spectroscopy.[17] Unfortunately, the reaction of $[Me_4N][TeF_5]$ with Me_3SiCN causes instantaneous decomposition to elemental tellurium, cyanide ion and cyanogen.

Since $Te(CN)_4$ (**2**) and $Te(N_3)_4$ [15,18] both seem to be highly sensitive compounds, and as examined for the hypothetical hexaazide,[18,19] we also investigated the possible existence of $Te(CN)_6$ with theoretical methods. The electronic structures of the $Te(CN)_2$ (**1**, C_{2v}), $Te(CN)_4$ (**2**, C_{2v}, see Figure 5), and $Te(CN)_6$ (O_h) molecules were calculated by using different ab initio and density functional methods (Table 1). All geometries have been fully optimized within C_1-symmetry and then recalculated in the obtained higher symmetry [**1** and **2**: C_{2v}; $Te(CN)_6$: O_h] at the level chosen, which led to minimum structures without imaginary frequencies. In addition, geometry optimization at the relativistic Dirac−Hartree−Fock level was performed for **1**, by using an energy-minimized relativistic Gaussian basis set for tellurium with either 4-component Dirac−Coulomb or Levy−Leblond Hamiltonians. The reductive decomposition of the $Te(CN)_x$ molecules yields energetic differences for the products $Te(CN)_{x-2}$ and one molecule of cyanogen of $75.78\ kJ\ mol^{-1}$ ($x = 2$), $-357.81\ kJ\ mol^{-1}$ ($x = 4$), and $-343.32\ kJ\ mol^{-1}$ ($x = 6$) at the MP2(FC)/MDF28-cc-pVDZ level, respectively (corrected for the atomization energy of tellurium: $196.7\ kJ\ mol^{-1}$), thereby adding strong evidence for the instability of **2** and, even more for the hypothetical $Te(CN)_6$, relative to **1**.

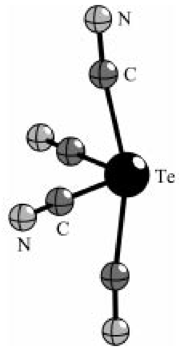

Figure 5. Calculated molecular structure of **2** (C_{2v}) at the MP2(FC)/MDF28-cc-pVTZ level of theory; selected bond lengths [Å] and angles [°]: $Te-C_{eq}$ 2.042, $C_{eq}-N_{eq}$ 1.177, $Te-C_{ax}$ 2.180, $C_{ax}-N_{ax}$ 1.179; $C_{eq}-Te-C_{eq}$ 105.60, $C_{ax}-Te-C_{ax}$ 158.50, $Te-C_{eq}-N_{eq}$ 177.73, $Te-C_{ax}-N_{ax}$ 172.21

Our present study involved the preparation and characterization of homoleptic tellurium cyanide species $Te(CN)_2$ (**1**) and $Te(CN)_4$ (**2**), as well as the calculation of their structures and that of hypothetical $Te(CN)_6$. A first comprehensive investigation of a chalcogen cyanide $Te(CN)_2$ (**1**), including an exact determination of its crystal structure is now at hand.

Experimental Section

General: All manipulations of air- and moisture-sensitive materials were performed under purified argon using flame-dried glass vessels and Schlenk techniques. Tellurium dioxide, silver cyanide and trimethylsilyl cyanide (Aldrich) were dried or distilled prior to use. Tellurium(IV) tetrahalides were prepared according to the literature.[8c,15] Ethers and hydrocarbons were dried with sodium/benzophenone and freshly distilled, CH_2Cl_2 was dried with CaH_2 and stored over molecular sieves (4 Å). Infrared spectra were recorded with a Bruker IFS 66/vS (as KBr and PE pellets), Raman spectra with a Perkin−Elmer 2000 NIR FT spectrometer fitted with an Nd-YAG laser (1064 nm). NMR spectra were recorded with a JEOL Eclipse 400 instrument, and chemical shifts are reported with respect to Me_4Si (^{13}C), $MeNO_2$ (^{14}N) and Me_2Te (^{125}Te). Mass spectra were recorded with a JEOL MStation JMS 700 spectrometer, tellurium-containing fragments refer to ^{130}Te. Elemental analysis: Analytical service (LMU).

$Te(CN)_2$ (1): In a flame-dried Schlenk tube connected with a D3 glass frit, $TeBr_4$ (3.5 mmol, 1.5 g), AgCN (37.3 mmol, 5.0 g) and benzene (10 mL) were stirred at 60 °C for 3 d. After the supernatant solution was decanted, the remaining residue was extracted with boiling diethyl ether (3 × 15 mL), and the ethereal extracts were filtered through the glass frit. Evaporation of all volatile material at 10^{-3} mbar and ambient temperature left a colorless solid, which was carefully sublimed at $<10^{-4}$ mbar and <80 °C; **1** has an off-white color (yield 68 %). M.p. 80−82 °C. IR: ν = 2176 (vs, νCN), 2168 (s, νCN), 462 (sh), 410 (vs, νTeC), 398 (vs, νTeC), 296 (w, δTeCN), 277 (w, δTeCN), 147 (m, δCTeC) cm^{-1}. Raman (200 mW, 25 °C): ν = 2177 (100, νCN), 2170 (50, νCN), 409 (69, νTeC), 395 (40, νTeC), 279 (5, δTeCN), 136 (30, δCTeC) cm^{-1}. ^{13}C NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 86.2 ($^1J_{C-Te}$ = 330.2 Hz) ppm. ^{14}N NMR (28.9 MHz, [D$_8$]THF, 25 °C): δ ($\Delta\nu_{1/2}$) = −70 (1300 Hz) ppm. ^{125}Te NMR (126.1 MHz, [D$_8$]THF, 25 °C): δ = 567 ppm. EI MS m/z (%) = 256 (20) [Te_2^+], 182 (90) [M^+], 156 (68) [$TeCN^+$], 130 (100) [Te^+]. C_2N_2Te (179.63): C 13.4, N 15.6; found C 13.6, N 15.4.

$Te(CN)_4$ (2): In a flame-dried Schlenk tube, TeF_4 (1.0 mmol, 0.20 g) was suspended in dry CH_2Cl_2 (5 mL) at −20 °C. After addition of Me_3SiCN (4.4 mmol, 0.44 g) in one portion, the mixture was stirred at −20 °C for 7 h, then all volatile materials were evaporated in vacuo at this temperature. ***CAUTION:*** The remaining colorless powder tends to suddenly decompose when either exposed to temperatures above −20 °C or upon contact with air. Raman (200 mW, −20 °C): ν = 2204 (25, νCN), 2191 (45, νCN), 2149 (40, νCN), 2129 (15, νCN), 640 (65), 474 (35), 426 (br, 55), 381 (br, 55), 220 (75), 155 (50) cm^{-1}.

Crystal Data for 1: C_2N_2Te (179.63), colorless needle, 0.08 × 0.1 × 0.6 mm, hexagonal, space group $R\bar{3}c$, a = 16.288(1), b = 16.288(1), c = 21.267(1) Å, α = 90°, β = 90°, γ = 120°, V = 4886.3(4) Å^3, Z = 36, $\rho_{calcd.}$ = 2.198 g cm^{-3}, μ = 5.321 mm^{-1}, $F(000)$ = 2808, Siemens P4 diffractometer with CCD Area Detector, Mo-K_α, λ = 0.71073 Å, T = 193 K, 2θ range = 4.80−58.32°, $-10 \le h \le 19$, $-21 \le k \le 13$, $-28 \le l \le 28$, reflections collected: 7815, independent reflections: 1478 (R_{int} = 0.0414), observed reflections: 943 [$I > 4\sigma(I)$], SADABS absorption correction, structure solution: SHELXS-97, heavy-atom method, data/parameters ratio: 24.6:1 [16.8:1 for $I > 4\sigma(I)$], final R indices [$I > 4\sigma(I)$]: $R1$ = 0.0370, $wR2$ = 0.1079, $R1$ = 0.0511, $wR2$ = 0.1159 (all data), GOF on F^2 = 1.084, largest difference peak/hole: 1.319/−1.841 e Å^{-3}. Residual peaks (five with 1.15−2.4 e Å^{-3}) were considered to be carbon atoms (disordered diethyl ether or n-heptane) and refined isotropically (U_{eq} = 0.15) with the same SOF (0.207) for all atoms. CCDC-244701 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: Gaussian03 program package on Itanium2 (64 bit),[20] DFT and MP2(FC) methods, employing the MWB46 large-core and the MDF28 small-core pseudopotentials with the corresponding cc-pVnZ-PP basis sets for tellurium,[21] and the cc-pVnZ basis sets for carbon and nitrogen atoms;[22] (very) tight geometry optimizations for **1** and **2**, and $Te(CN)_6$ until max. force = 2/15 × 10^{-6} a.u., root-mean-square force = 1/10 × 10^{-6} a.u., max. displacement = 6/60 × 10^{-6} a.u., root-mean-square displacement = 4/40 × 10^{-6} a.u. Fully relativistic direct 4-component Dirac−Hartree−Fock and MP2 calculations have been performed with the DIRAC program package[23] on Pentium4 by using the Dirac−Coulomb-Hamiltonian, a relativistic dual family basis set for tellurium (20s18p11d+1s1p1d) applying strict kinetic balance,[24] and cc-pVDZ basis sets for carbon and nitrogen atoms. ELF values have been calculated with the ToPMoD package and visualized with Molekel 4.2.[25]

Acknowledgments

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