# Donor-Acceptor Complexes of Tellurium Polycationic Clusters with Cyanogen

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Dedicated to Professor Reinhard Nesper on the Occasion of His 60th Birthday

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Abstract. The reactions of cyanogen with  $Te_6[AsF_6]_4$  and  $Te_4[AsF_6]_2$  in SO<sub>2</sub> solutions yield  $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$  (1) and  $Te_4[AsF_6]_2 \cdot C_2N_2$  (2) as red crystals in quantitative yield. The complexes 1 and 2 are also generated in moderate yield by the reaction of Te,  $AsF_5$  and  $C_2N_2$  in liquid SO<sub>2</sub>, but by-products are formed. These reactions show the ability of cyanogen to act as a donor towards tellurium polycations. In the crystal structures, discrete octahedral  $[AsF_6]^-$  ions are present and linear cyanogen molecules, which coordinate the tellurium atoms of the polycations  $\eta^2$  by both nitrogen atoms. In the crystal structure of 1, the trigonal-prismatic

### Introduction

The formation of polycationic clusters of various size, shape, and charge is a well-known feature of the elements of the chalcogen series, of which tellurium has the richest structural chemistry [1]. The highly electrophilic chalcogen polycations are prepared by three main synthetic routes: in acidic melts [2], in solution, e.g. liquid SO<sub>2</sub>, AsF<sub>3</sub>, benzene [3] or super acidic solutions e.g. HF/AsF<sub>5</sub> [4], and in chemical vapor transport reactions using volatile metal halides as oxidants towards elemental chalcogens [5]. By all three routes ionic compounds are obtained, whose anions, as weak conjugate bases of strong Lewis acids, stabilize the "naked" polycationic clusters. The most common and straight forward possibility to transform elemental tellurium to cationic clusters is the use of  $MF_5$  (M = As, Sb) as two electron oxidizing agents. The reduction to MF<sub>3</sub> liberates  $F^-$  ions, which generate with MF<sub>5</sub> the weakly coordinating [MF<sub>6</sub>]<sup>-</sup> ions, representing suitable, weakly basic counterions. Liquid SO<sub>2</sub> is a convenient solvent for reactions of this kind. It is inert against AsF<sub>5</sub> und dissolves tellurium polycations without decomposition. It has weakly basic properties, since generally SO<sub>2</sub> containing crystals are isolated from its solutions with SO<sub>2</sub> coordinating the cationic clusters. Examples are the structures of

Gerhard-Domagk-Str. 1 53121 Bonn, Germany  ${\rm Te_6}^{4+}$  clusters are bridged by cyanogen molecules to one-dimensional zig-zag chains. The crystal structure of **2** contains squareplanar  ${\rm Te_4}^{2+}$  clusters, which are bridged by cyanogen molecules to two-dimensional sheets. The complexes **1** and **2** represent the first chalcogen polycationic cluster compounds containing a nitrogen ligation. The new compounds are unstable with respect to loss of cyanogen but stable under an atmosphere of C<sub>2</sub>N<sub>2</sub>. The Raman spectra of **1** and **2** were investigated and assigned. A serviceable and convenient way to handle air-sensitive and cold liquids by a transfer needle technique is described.

Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub>·SO<sub>2</sub> [6] and Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·2SO<sub>2</sub> [7]. Here, the SO<sub>2</sub> molecules are coordinated with their oxygen atoms to the cationic clusters and act either as terminal  $\mu_1$ -ligands or bridge the edges as  $\mu_2$ -ligands.

To the best of our knowledge, no polycationic cluster compounds containing a ligation by a nitrogen donor are known. Cyanogen, NC-CN, has some properties, which make it a solvent similar to SO<sub>2</sub>. It has a boiling point of -21 °C (SO<sub>2</sub> -10 °C) and can thus be handled at ambient temperature with a vapor pressure of about 3 bar. It has two weak nucleophilic centers at the terminal nitrogen atoms and is able to act as a  $\sigma$ -donor ligand. Only six structurally characterized coordination compounds of cyanogen are presented in the literature. Two of them are based on antimony pentahalides, SbCl<sub>5</sub>·NCCN·SbCl<sub>5</sub> and  $SbF_5 \cdot NCCN$  [8], the others on transition metals,  $\{[Ag(NCCN)_2][AsF_6]\}_n$  [9],  $[Cd[AsF_6]_2(NCCN)_2(SO_2)]_n$ [10], trans-[Ni(CN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]  $\cdot$  (C<sub>2</sub>N<sub>2</sub>)<sub>2</sub> [11] and [Zn(NCCN)<sub>6</sub>][AsF<sub>6</sub>]<sub>2</sub> [12].

We conducted experiments for the oxidation of elemental tellurium by  $AsF_5$  in liquid  $C_2N_2$  and in  $C_2N_2/SO_2$  mixtures to explore the usability of cyanogen as a solvent for such reactions and to probe for its coordination abilities towards the polycationic clusters. We found that  $C_2N_2$  is suitable as a new solvent and acts as a new coordinating ligand towards the tellurium clusters  $Te_6^{4+}$  and  $Te_4^{2+}$ , what about we report in the following.

## **Experimental Section**

*Caution:* Cyanogen is severely poisonous, having a toxicity comparable to that of hydrogen cyanide. The maximum tolerable vapor

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concentration is 10 parts per million [13]. Cyanogen is highly inflammable and burns in air generating temperatures up to 5000 °C. AsF<sub>5</sub> is also highly toxic, liberating HF and As<sub>2</sub>O<sub>5</sub> on contact with humid air. All experiments have to be carried out in a well ventilated hood.

For all reactions, pressure stable "H-shaped" thick walled glass Schlenk tubes (diameter 2 cm, volume  $2 \times 40$  mL) equipped with two screw plug valves made of PTFE [14] and a medium porosity glass frit between the two compartments were used. All glass equipment (Simax<sup>®</sup> glass) was preheated two times under vacuum to remove adsorbed moisture (approx.  $350 \text{ °C} / 3 \times 10^{-3} \text{ mbar}$ ).

Tellurium was purified by sublimation at 350 °C under vacuum to remove TeO<sub>2</sub> and traces of TeO<sub>3</sub>, which are not volatile under these conditions. Cyanogen was prepared in an all-glass vacuum line by pyrolysis of silver evanide, which had itself been prepared from potassium cyanide and silver nitrate [15]. It was stored over  $P_4O_{10}$ and freshly distilled before use. The melting and boiling points of cyanogen are -28 °C and -21 °C, respectively [16]. The desired amount of C<sub>2</sub>N<sub>2</sub> was added into the reaction vessels using a vacuum line of calibrated volume or from a calibrated vessel using a stainless steel cannula. Liquid  $SO_2$  was dried by storing over  $P_4O_{10}$ and was freshly distilled into the reaction vessel for each experiment. Solutions of Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub> and Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub> are stable in liquid SO<sub>2</sub> and can be stored in glass vessels over years. For all reactions a cannula transfer technique was used to transfer the liquid SO<sub>2</sub> solutions of Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub> and Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub> at approximate -70 °C from a calibrated H-tube vessel to the reaction vessel kept at -140 °C. The technical layout of the apparatus is described in Figure 1. Since all investigated compounds are very sensitive towards loss of the volatile C<sub>2</sub>N<sub>2</sub>, samples were left inside the reaction vessel covered with some liquid SO2 or liquid cyanogen or were kept under a  $SO_2/C_2N_2$  gas atmosphere.



Figure 1. Technical layout of the apparatus to transfer the cold liquid SO<sub>2</sub>, liquid cyanogen, or solutions of  $Te_4[AsF_6]_2$  or  $Te_6[AsF_6]_4$  into SO<sub>2</sub>/C<sub>2</sub>N<sub>2</sub> mixtures under anhydrous conditions between "H-shaped" glass vessels. Explanation: 1) Stainless steel cannula. The ends of the stainless steel cannula are pointed, so they can be inserted through the septa. 2) PTFE high vacuum screw plug valve [14] 3) H-shaped thick-walled glass flask with two valves and a medium porosity glass frit between the two compartments 4) Teflon valve substituted by a septum 5) Penetrated septum by a stainless steel needle for argon pressure compensation 6) Cooling bath 7) Solution of  $Te_4[AsF_6]_2$  or  $Te_6[AsF_6]_4$  in liquid SO<sub>2</sub> 8) Solvent composed of mixture of liquid SO<sub>2</sub>/C<sub>2</sub>N<sub>2</sub>.

# $Te_4[AsF_6]_2 \cdot SO_2(3)$

Finely powdered tellurium (500 mg, 3.92 mmol) was loaded in an argon filled glove-box into the evacuated arm of an H-shaped vessel. AsF<sub>5</sub> (520 mg, 3.06 mmol) and anhydrous SO<sub>2</sub> (40 mL) were condensed onto the tellurium using a cooling bath (-140 °C). The reactants were stirred at -30 °C for 2 h and afterwards for 5 h at 20 °C. The dark red solution containing Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub> was filtered to the other side of the H-shaped vessel and the volatiles SO<sub>2</sub> and AsF<sub>5</sub> were distilled back to the other side onto the remaining amount of tellurium to complete the reaction. The formed light red solution was filtered again and combined with the red precipitate of (3) in the second compartment. The solvent was concentrated and decanted by a stainless steel cannula yielding a red powder together with a large number of red crystals. The Raman spectra of the red solids were in full agreement with the spectra reported for  $Te_4[AsF_6]_2$  [6]. The compound was dissolved and stored in anhydrous sulfur dioxide (40 mL).

# $Te_6[AsF_6]_4 \cdot 2SO_2(4)$

Analogously to the synthesis of 3, tellurium (70.4 mg, 0.550 mmol), a 10-fold excess of AsF<sub>5</sub> (920 mg, 5.50 mmol) and liquid SO<sub>2</sub> (40 mL) were used. On warming the mixture to room temperature and stirring, a deep red color, caused by the emergence of the  $Te_4^{2+}$ cation appeared, which changed to red-brown after one hour. After two days, this solution was filtered through the glass frit into the second compartment of the reaction vessel and left standing for two weeks. The solution gained finally a light orange-brown color and some dark red crystals precipitated when the solvent volume was reduced in vacuo until crystallization started. After standing an additional week, large dark red crystals settled and the color of the solution turned yellow-red. Afterwards, the solvent was concentrated and decanted by the stainless steel cannula technique. The Raman spectrum of the solid was in agreement with literature data for Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·2SO<sub>2</sub> [7]. Dark red, prismatic crystals of 4 were isolated and stored in anhydrous SO<sub>2</sub> (40 mL). Because 4 has an inverse temperature gradient of the solubility in liquid SO<sub>2</sub>, the solution must be stirred at -70 °C for two minutes before transferring by cannula from the calibrated vessel.

## $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$ (1)

In a typical experiment a freshly prepared solution of 4 (20 mL), cooled to -70 °C, was added through a stainless steel cannula, by applying an argon pressure gradient, onto a frozen mixture of cyanogen (3 mL, 54.8 mmol) and SO<sub>2</sub> (15 mL) kept at -140 °C, using the technique described in Figure 1. The red solution was stirred at -30 °C for 1 h and afterwards another hour at 20 °C. Subsequently, the solvent volume was reduced to one third of its original volume by distillation. Keeping the concentrated red solution by a water bath at 20 °C, red crystals of 1 deposited in quantitative yield. Raman spectra of the solid, taken from different regions of the solid material showed only the presence of 1.

# $Te_4[AsF_6]_2 \cdot C_2N_2$ (2)

In a typical experiment as described in Figure 1, a freshly prepared solution of **3** (20 mL), cooled to -70 °C, was added by a stainless steel cannula onto a frozen mixture of (3 mL, 54.8 mmol) cyanogen and SO<sub>2</sub> (15 mL) at -140 °C. The red solution was stirred at -30 °C for 1 h and subsequently another hour at 20 °C. After-

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**Table 1.** Crystallographic data and details of the structure refinement for  $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$  and  $Te_4[AsF_6]_2 \cdot C_2N_2$ . Standard deviations given in brackets refer to the last significant digit.

Formula	$Te_6[AsF_6]_4 \cdot 1.5C_2N_2$	$Te_4[AsF_6]_2 \cdot C_2N_2$
Crystal system	monoclinic	monoclinic
Space group	C2/m	$P2_1/n$
Lattice constants /Å	a = 14.6165(3)	a = 6.7896(9)
	b = 9.7841(2)	b = 10.458(1)
	c = 19.5286(4)	c = 11.901(1)
	$\beta = 107.21(10)^{\circ}$	$\beta = 96.668(7)^{\circ}$
Unit cell volume /Å <sup>3</sup>	2667.8(8)	839.3(2)
Number of formula units $Z$	4	2
Calculated density $/g \cdot cm^{-3}$	3.982	3.721
Absorption coefficient /mm <sup>-1</sup>	11.571	10.904
Range of data collection	$8.9^\circ < 2\theta < 55.0^\circ$	$6.6^{\circ} < 2\theta < 55.0$
Number of independent	3217	1614
reflections		
Number of refined parameters	206	101
Ratio reflections / parameters	15.6	16.0
$R_{\rm int}$ on averaging reflections	0.023	0.027
Crystal size /mm	0.3  imes 0.2  imes 0.35	$0.2 \times 0.3 \times 0.3$
Absorption correction	semi-empirical [18]	semi-empirical [18]
$R( F )$ for $F_{o} > 4\sigma(F_{o})$	0.028	0.052
R( F ) for all reflections	0.034	0.083
$R_{\rm w}(F^2)$	0.079	0.1163
max. and min. electron density $/e \cdot \mathring{A}^{-3}$	1.26 / -1.34	1.89 / -0.82

wards, the solvent volume was reduced to one third of its original volume by distillation. Keeping the temperature of the concentrated solution constant at 20 °C by a water bath, red crystals of **2** deposited in quantitative yield. Raman spectra of the solid taken from different regions of the crystalline material showed only the presence of **2**.

#### **Crystal Structure Determinations**

Crystals of both compounds are very sensitive towards oxidation, hydrolysis and the loss of  $C_2N_2$ . So crystals were selected at -50 °C under inert oil (Fromblin, Aldrich Inc.) and transferred into the cold nitrogen stream of the crystal cooling device of a Bruker-Nonius Kappa-CCD diffractometer equipped with graphite monochromatized Mo- $K_{\alpha}$  radiation. Data collections were performed in all cases at -150 °C (123 K). Both crystal structures were solved by direct methods and refined based on  $F^2$  with anisotropic displacement parameters for all atoms [17]. A semiempirical absorption correction was applied to all data sets [18]. Table 1 contains the crystallographic data and details of the structure determinations, Table 2 and Table 3 the positional parameters of the atoms. Further crystallographic data like coefficients of the anisotropic temperature factors have been deposited [19]. Graphical representations were made using the program DIAMOND [20].

#### Raman Spectra

FT-Raman spectra on solid samples of **1** and **2** and of liquid  $C_2N_2$  were recorded with a Bruker FT Raman spectrometer RFS100. The excitation was provided by a Nd:YAG laser of 1064 nm output. The data for both compounds (resolution 4 cm<sup>-1</sup>, 1000 scans, laser power 25 mW, 20 °C) and for the liquid (resolution 4 cm<sup>-1</sup>, 500 scans, 200 mW, 20 °C) were obtained in the 180° backscattering geometry. Since both investigated solid compounds are very sensitive against air and moisture, samples were irradiated inside the

 $U_{eq}$  $\overline{Z}$ x v Te(1) 6743(1) 1588(1)3520(1) 17(1)Te(2) 8477(1) 1605(1)3295(1) 17(1)6871(1) 1605(1) Te(3) 2161(1) 19(1) As(1)4086(1)0 2423(1)17(1)As(2) 5000 0 5000 17(1)1992(1) As(3) 17(1)0 18(1)As(4)5000 0 0 22(1)As(5)1358(1) 0 4550(1) 15(1)F(1) 4969(3) 0 2000(2)26(1)F(2) 3268(3) 0 2891(3) 29(1)1230(3) 4749(2) 3015(2) 23(1)F(3) 3475(2) 1261(4) F(4) 1881(2)32(1)1761(3) 3818(2) F(5) 0 25(1)F(6) 992(3) 0 5314(2) 23(1)2179(2) -1245(3)4935(2) 27(1)F(7) F(8) 525(2) 1250(4)4176(2) 27(1)F(9) 109(3) 1236(4) 2643(2) 33(1)F(10) -1201(3)1863(3) 36(1) 0 F(11) 1231(3) 2174(3) 37(1) 0 1251(4) F(12) -88(3)1367(2)39(1) F(13) 5780(4) 0 873(3) 39(1) F(14) 4031(3) 327(3) 37(1)0 5000 1741(6) 0 F(15) 52(2)4447(2) F(16) 5739(3) 0 27(1)F(17) 4300(2) 1250(4) 4481(2) 30(1) 33(2) C(1) -488(6)-112(5)291(5) N(1) 1303(6) 0 44(2)C(2) 7473(4) 2251(6) 328(3) 28(1)7405(4) 1844(6) 857(3) N(2) 34(1)

**Table 3.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters /Å<sup>2</sup> × 10<sup>3</sup> for Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub>·C<sub>2</sub>N<sub>2</sub> (**2**).  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ii}$  tensor.

	x	У	Ζ	$U_{eq}$
Te(1)	962(1)	1548(1)	4453(1)	30(1)
Te(2)	1321(2)	-926(1)	955(1)	33(1)
As(1)	-327(2)	5539(1)	2888(1)	29(1)
F(1)	168(13)	6207(7)	4214(6)	38(2)
F(2)	1626(15)	6421(8)	2461(7)	50(2)
F(3)	1337(15)	4331(8)	3272(7)	51(2)
F(4)	-729(14)	4901(8)	1561(7)	50(2)
F(5)	-2191(15)	4669(9)	3319(8)	59(3)
F(6)	-1845(16)	6789(8)	2521(8)	62(3)
C(1)	-4890(20)	4364(14)	5093(14)	45(4)
N(1)	4880(20)	6746(13)	4810(13)	65(4)

reaction vessel under  $SO_2/C_2N_2$  gas pressure. The FT-Raman spectra were taken from red crystals adherent at the inner wall of a compartment of the "H-shaped" vessel.

### **Results and Discussion**

#### **Synthesis**

It is well known that  $AsF_5$  in liquid  $SO_2$  dissolves elemental tellurium under oxidation to  $Te_6^{4+}$  or  $Te_4^{2+}$  polycationic clusters, depending on the molar amount of  $AsF_5$  used. The ionic compounds  $Te_6[AsF_6]_4 \cdot 2SO_2$  and  $Te_4[AsF_6]_2 \cdot SO_2$  can

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters  $/\text{Å}^2 \times 10^3$  for Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·1.5C<sub>2</sub>N<sub>2</sub> (1).  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

be isolated from such solutions on distilling off the solvent [7, 21]. The use of a mixture of  $C_2N_2$  and  $SO_2$  gives the same polycationic clusters and solvate containing crystals are obtained, which do not contain  $SO_2$  but only  $C_2N_2$ . In these reactions, as a side product a dark brown amorphous solid is precipitated, which could not be characterized, but represents probably the polymer of cyanogen, beside other unknown cyanogen containing products. The polymerization of C<sub>2</sub>N<sub>2</sub> is apparently initiated by the strong Lewis acidic AsF<sub>5</sub>. This disadvantageous course of the reactions can be overcome by the use of stock solutions, which contain the respective tellurium clusters as the  $[AsF_6]^-$  salts in liquid SO<sub>2</sub> without the presence of excess AsF<sub>5</sub>. Adding these solutions to mixtures of SO<sub>2</sub>/C<sub>2</sub>N<sub>2</sub> gives on slow distilling off the solvents  $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$  (1) and  $Te_4[AsF_6]_2 \cdot C_2N_2$  (2) as dark red, hydrolytically unstable crystals in quantitative yield. Cyanogen turnes out to be a markedly stronger ligand towards the polycationic clusters in comparison to SO<sub>2</sub>, since even in the presence of an excess, SO<sub>2</sub> is completely replaced in all reaction products by  $C_2N_2$ . According to equations (I) and (II) the  $C_2N_2$  adducts are obtained by ligand exchange of SO<sub>2</sub> against C<sub>2</sub>N<sub>2</sub>.

 $Te_{6}[AsF_{6}]_{4} \cdot 2SO_{2} + 1.5 C_{2}N_{2} \rightarrow Te_{6}[AsF_{6}]_{4} \cdot 1.5C_{2}N_{2} + 2 SO_{2} (I)$ 

 $Te_{4}[AsF_{6}]_{2} \cdot SO_{2} + C_{2}N_{2} \rightarrow Te_{4}[AsF_{6}]_{2} \cdot C_{2}N_{2} + SO_{2} (II)$ 

In an atmosphere of  $C_2N_2$  both compounds are thermally stable at ambient temperature. By collecting repeatedly Raman spectra from identical solid samples and comparing these, no signs of degradation could be detected and series of identical spectra were obtained.



**Figure 2.** The atoms of the asymmetric unit of the structure of  $\text{Te}_{6}[\text{AsF}_{6}]_{4} \cdot 1.5\text{C}_{2}\text{N}_{2}$  (1). Thermal ellipsoids are drawn at 50 % probability level; symmetry operations: I: x, -y, z, II: 0.5+x, 0.5+y, z, III: 0.5-x, 0.5+y, -z, IV: 1.5-x, 0.5-y, -z; selected bond lengths /Å: Te(1)-Te(2) 2.6966(4), Te(1)-Te(3) 2.7139(4), Te(2)-Te(3) 2.7078(4), Te(1)-Te(1)^{I} 3.1067(6), Te(2)-Te(2)^{I} 3.1413(6), Te(3)-Te(3)^{I} 3.1399(7), Te(3)-N(2) 2.886(6), C(1)-N(1) 1.138(12), C(1)-C(1)^{II} 1.362(18), C(2)-N(2) 1.138(12), C(2)-C(2)^{IV} 1.396(11).



**Figure 3.** The structure of  $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$  (1) depicted as the unit cell (top) in a view slightly inclined to the *b*-axis.  $[AsF_6]^-$  anions are shown as filled octahedra,  $Te_6^{4+}$  cations as filled trigonal prisms. Cyanogen molecules are drawn as ball and stick models. On bottom a section of the structure is shown illustrating the connection of  $Te_6^{4+}$  clusters by the coordinated cyanogen molecules to a zig-zag chain.

# Crystal Structure of $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$ (1)

The crystal structure of  $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$  is made up of trigonal prismatic Te<sub>6</sub><sup>4+</sup> clusters, almost regular octahedral  $[AsF_6]^-$  anions and cyanogen molecules. Figure 2 shows the molecular entities of the asymmetric unit with the atomic numbering and Figure 3 the unit cell. The trigonal prismatic  $Te_6^{4+}$  cation has crystallographic  $C_s$  symmetry and is defined by three independent tellurium atoms forming one triangular face of the cluster. The Te<sub>6</sub><sup>4+</sup> polycation is very close to the ideal  $D_{3h}$  symmetry. The bonds within the triangular faces range from 2.697 to 2.714 Å with an average of 2.706 Å. The long bonds along the edges parallel to the threefold symmetry axis of the prism range from 3.107 to 3.141 Å with an average of 3.129 Å. The interplanar angle between the triangular faces is less than 1°. The mirror plane, which bisects the cluster through the center of gravity perpendicular to the threefold axis presupposes that there is no twist between both triangular faces. The  $Te_6^{4+}$  cluster in the structure of 1 has the typical structural features as already observed for the analogous clusters in Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·2AsF<sub>3</sub> [22], Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·2SO<sub>2</sub> [7, 21],  $(Te_6)(Se_8)[AsF_6]_6 \cdot SO_2$  [23].

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The five symmetrically independent  $[AsF_6]^-$  anions all occupy special positions in the mirror plane for As(1), As(3), As(5) or in the 2/m center for As(2), As(4) and have therefore  $C_s$  and  $C_{2h}$  symmetry, respectively. Only slight deviations from ideal octahedral symmetry are found, indicated by As-F bonds, which span the narrow range between 1.698 and 1.750 Å and F-As-F angles between 86.9 and 93.2°, and 176.4 and 180.0°.

There are two different cyanogen molecules in the structure of which the non coordinating molecule, defined by the atoms C(1) and N(1), is centered at the special position 2/m giving the molecule  $C_{2h}$  symmetry. The second  $C_2N_2$ molecule, defined by the atoms C(2) and N(2), is located in an inversion center giving it  $C_i$  symmetry. The C–C and C–N bonds of both molecules are identical within standard deviations. The C=N bond lengths of 1.138 Å are slightly increased in comparison to 1.127 Å found for the respective bonds in crystalline cyanogen [24]. The N=C–C angles of 179° [N(1)–C(1)–C(1)<sup>II</sup>] and 178° [N(2)–C(2)–C(2)<sup>III</sup>] deviate only slightly from that in crystalline cyanogen [179.6(2)°] [24]. Comparable bond lengths and angles for the coordinated C<sub>2</sub>N<sub>2</sub> molecule were found in the recently presented [Zn(NCCN)<sub>6</sub>][AsF<sub>6</sub>]<sub>2</sub> [12].

Within a sphere of 3 Å radius around each tellurium atom of the  $Te_6^{4+}$  cation nine fluorine atoms and two nitrogen atoms are coordinated with the shortest Te-F and Te···N contacts found at 2.809 and 2.886 Å. Expanding the coordination sphere to a radius of 3.5 Å, a total of 40 fluorine atoms but still two nitrogen atoms N(2) are coordinated to the six tellurium atoms of the cluster. This coordination pattern of Te<sub>6</sub><sup>4+</sup> clusters by the fluorine atoms of fluoridometallate counterions is comparable with those known in the literature. As expected, the displacement ellipsoids of the atoms of the non-coordinating cyanogen are significant more voluminous than for the coordinating cyanogen. The Te(3)...N(2) distances are uniformly 2.886(6) Å and the Te(3)...N(2)  $\equiv$  C(2) angles of 161.5(5)° deviate considerably from linearity. The  $C_2N_2$  molecules act as N,N'-bridging ligands between each two trigonal prismatic  $Te_6^{4+}$  cations resulting in one-dimensional zigzag shaped chains -Te<sub>6</sub>-NCCN-Te<sub>6</sub>-NCCN- running along the crystallographic *b*-axis (Figure 3).

#### Crystal Structure of $Te_4[AsF_6]_2 \cdot C_2N_2$ (2)

The crystal structure of  $Te_4[AsF_6]_2 \cdot C_2N_2$  is made up of square-planar  $Te_4^{2+}$  cations, almost regular octahedral  $[AsF_6]^-$  anions and cyanogen molecules. Figure 4 shows the molecular entities of the asymmetric unit with the atomic numbering and Figure 6 the unit cell. The  $Te_4^{2+}$  ion is located at an inversion center giving it crystallographic *Ci* symmetry and is generated by two independent tellurium atoms. The Te–Te bonds lengths within the cluster cation are 2.671(1) and 2.664(1) Å and the Te–Te–Te angles are 90.18(3) and 89.82(4)°, which compares well with other compounds containing the  $Te_4^{2+}$  cation [1]. The one crystallographically independent [AsF\_6]<sup>-</sup> anion is located on a

general position. The AsF<sub>6</sub> octahedron is almost regular, the F-As-F angles deviate maximally by  $1.8^{\circ}$  from rectangularity and the As-F distances vary between 1.687(9)and 1.739(9) Å. Comparable bond lengths are found in other compounds with hexafluorido arsenate(V) ions [1].



**Figure 4.** The atoms of the asymmetric unit of the structure of  $\text{Te}_4[\text{AsF}_{6]_2} \cdot \text{C}_2\text{N}_2$  (2). Thermal ellipsoids are drawn at 50 % probability level; symmetry operations: I: -x, -y, 1-z, II: 1-x, 1-y, 1-z; selected bond lengths /Å and angles /°: Te(1)-Te(2) 2.671(1), Te(1)-Te(2)^I 2.664(1), Te(1)-N(1)^{II} 3.369(13), C(1)-N(1) 1.166(19), C(1)-C(1)^{II} 1.35(3), Te(1)-Te(2)-Te(1)^I 90.18(3), Te(2)-Te(1)-Te(2)^I 89.82(4), N(1)-C(1)-C(1)^{II} 174.(2).

A common feature of all structures with square planar  $E_4^{2+}$  (E = S, Se, Te) cations is the environment around the polycation. Generally, the shortest contacts are found by atoms located in the plane and over the edges of the  $E_4$ square unit. The next short contacts are made up by atoms which are located along the extension of the diagonals of the square. In the structure of  $Te_4[AsF_6]_2 \cdot C_2N_2$  there is one fluorine atom bridging each edge of the square planar tetratellurium cation with deviation from the plane of the ring of maximally 0.21 Å. There are several close charge transfer contacts between (Te42+)...F and (Te42+)...N, creating the coordination environment as shown in Figure 5. The shortest contacts Te···F are found as expected in the plane of the  $Te_4^{2+}$  polycation, capping the edges of the square and the shortest contacts Te····N are found along the extension of the diagonals of the cation. The cyanogen molecules act as N,N'-bridging ligands, each coordinated to four Te<sub>4</sub><sup>2+</sup> clusters, making up a two-dimensional polymeric network



Figure 5. View of the coordination sphere of the  $Te_4^{2+}$  cation the structure of  $Te_4[AsF_6]_2 \cdot C_2N_2$  (2) with all Te···F and Te···N contacts up to 3.5 Å.



spread out in the crystallographic *a*-*b*-plane (Figure 6). The arrangement of the molecules in this structure can be derived from the *anti*-CaF<sub>2</sub> or Li<sub>2</sub>O type. The  $[AsF_6]^-$  anions make up a distorted cubic net, in which the  $Te_4^{2+}$  cations and the  $C_2N_2$  molecules occupy alternatingly the cubic-shaped holes.



**Figure 6.** The structure of of  $Te_4[AsF_6]_2 \cdot C_2N_2$  (2). On top the unit cell is shown.  $[AsF_6]^-$  anions are depicted as filled octahedra,  $Te_4^{2+}$  cations and cyanogen molecules as ball and stick models. On bottom the two-dimensional net made up by  $Te_4^{2+}$  cations and coordinating cyanogen molecules is shown.

#### Raman Spectroscopy

The Raman spectra of solid Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>  $\cdot$  1.5C<sub>2</sub>N<sub>2</sub> (1) and Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub>  $\cdot$  C<sub>2</sub>N<sub>2</sub> (2) are characterized by the most intense bands at 2349 cm<sup>-1</sup> for 1 and 2331 cm<sup>-1</sup> for 2, which originate from the stretching vibration  $\nu$ (C=N). The existence of a significant  $\sigma$  donor interaction between the lone pair of the CN groups of cyanogen and the Te atoms of the cationic clusters Te<sub>6</sub><sup>4+</sup> and Te<sub>4</sub><sup>2+</sup> is indicated by the vibrational frequencies of the symmetric C=N stretching mode, since these modes were found to be shifted to higher wave numbers by 22 cm<sup>-1</sup> for 1 and 4 cm<sup>-1</sup> for (2) with respect to uncoordinated liquid cyanogen (Figure 7). The symmetrical "end-on" dihapto bonding mode of cyanogen present in the crystal structures is consistent with the Raman spectra. The frequency shift is much more pro-

nounced in the case of the higher charged  $\text{Te}_6^{4+}$  in comparison to  $\text{Te}_4^{2+}$ . Accordingly, the respective shortest Te···N distances in the crystals of 2.886 for 1 and 3.369 Å for 2 differ strongly. The effect of the increase of the frequency of the stretching vibration  $v(C \equiv N)$  for coordinated nitriles is known and has for example been observed with  $\text{SbCl}_5 \cdot \text{C}_2\text{N}_2 \cdot \text{SbCl}_5$  [8], { $[\text{Ag}(\text{NCCN})_2][\text{AsF}_6]_n$  [9],  $[\text{Cd}\{(\text{CN})_2\}_n\text{SO}_2][\text{AsF}_6]_2$  [10],  $[\text{Zn}(\text{NCCN})_6][\text{AsF}_6]_2$  [12], [Ni(NCCN)<sub>x</sub>][AsF<sub>6</sub>]\_2 [12], and other nitrile complexes [25].



Figure 7. Section of the superposed FT-Raman spectra in the C=N bond stretching region of  $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$  (1),  $Te_4[AsF_6]_2 \cdot C_2N_2$  (2), and liquid cyanogen ( $C_2N_2$ ).



Figure 8. Section of the superposed FT-Raman spectra in the region between 700 and  $90 \text{ cm}^{-1}$  of  $\text{Te}_6[\text{As}F_6]_4 \cdot 1.5\text{C}_2\text{N}_2$  (1),  $\text{Te}_4[\text{As}F_6]_2 \cdot \text{C}_2\text{N}_2$  (2), and liquid cyanogen (C<sub>2</sub>N<sub>2</sub>).

Further strong bands occur in the region between 250 and 90 cm<sup>-1</sup> and represent the cluster modes of Te<sub>6</sub><sup>4+</sup> and Te<sub>4</sub><sup>2+</sup> (Figure 8). For an isolated trigonal prismatic Te<sub>6</sub><sup>4+</sup> system with ideal  $D_{3h}$  symmetry twelve fundamental vibrations are expected which are classified as  $\Gamma_{vib} = 2A'_1 + A''_1 + A''_2 + 2E' + 2E''$ . A'<sub>1</sub> and E'' are only Raman active modes, whereas  $A''_1$  is inactive in both Raman and IR, and E' is active in both Raman and IR. The bands at 246 and 130 cm<sup>-1</sup> are related to the A'<sub>1</sub> mode. The lower point symmetry ( $C_s$ ) of the cluster cation in the solid state causes a splitting of the band normally located at 179 cm<sup>-1</sup> into 181 and 176 cm<sup>-1</sup> (assigned as E' mode). We suggest this band splitting and the large numbers of isotopes of moderately

high abundance for tellurium causes a band-broadening which covers the weak E" mode. The remaining bands in the spectrum of 1 at 119 and 96 cm<sup>-1</sup> can be assigned to a lattice mode and to the second E' mode, respectively. The bands at 678 and 367 cm<sup>-1</sup> can be assigned to the stretching and deformation modes of the  $[AsF_6]^-$  anions. The lower point symmetry of the anion compared to the ideal octahedral symmetry causes a splitting of bands which is seen in the spectrum of 1 by a broadening of bands. The band at 506 cm<sup>-1</sup> is identified as deformation mode  $\delta(NC-CN)$  by comparison with the spectrum of liquid cyanogen. Weak and moderate resolved bands at 889, 864 and 852 cm<sup>-1</sup> can be assigned to the v(C-C) stretching mode of coordinated and solvate cyanogen.

For an isolated square planar Te<sub>4</sub><sup>2+</sup> unit with ideal  $D_{4h}$  symmetry six fundamental vibrations are expected which are classified as  $\Gamma_{\rm vib} = A_{1g} + B_{1g} + B_{2g} + B_{2u} + E_u$ . The molecule has an inversion center and so the mutual exclusion rule is valid. A<sub>1g</sub>, B<sub>1g</sub> and B<sub>2g</sub> are only Raman active modes, E<sub>u</sub> is only IR active, and B<sub>2u</sub> is inactive. The A<sub>1g</sub> mode is identified at 216 cm<sup>-1</sup> and the band at 187 cm<sup>-1</sup> is assumed to be the B<sub>2g</sub> mode or a lattice vibration. The band at 106 cm<sup>-1</sup> in the low frequencies region can be assigned to the Symmetrical stretching and deformation modes of the [AsF<sub>6</sub>]<sup>-</sup> anions. Weak bands at 853 and 506 cm<sup>-1</sup> are assigned to the stretching and deformation vibrations of  $\nu$ (C–C),  $\delta$ (C–C) of cyanogen by comparison with the spectrum of liquid cyanogen.

Table 4 summarizes the observed Raman bands of crystalline Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·1.5C<sub>2</sub>N<sub>2</sub> (1), Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub>·C<sub>2</sub>N<sub>2</sub> (2), and of liquid cyanogen together with the tentative assignment which is based on literature data [25–27]. In liquid C<sub>2</sub>N<sub>2</sub> the region around 100 cm<sup>-1</sup> is dominated by a broad intensive band. Our recent low-temperature Raman measurements of solid sulfur dioxide and solid cyanogen between -35 °C and -130 °C and a group theoretical analysis based on the known orthorhombic crystal structure of C<sub>2</sub>N<sub>2</sub> [28] showed that the lattice vibrations are in the same region. So we conclude that the broad band in liquid cyanogen appreciably originates from intermolecular interactions in the condensed phase.

#### **Conclusion and Outlook**

The reaction of tellurium with arsenic pentafluoride in liquid SO<sub>2</sub> in the presence of cyanogen led to the formation of the first characterized Lewis acid-base complexes between a polynitrile and a polycationic cluster. Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·2SO<sub>2</sub> and Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub>·SO<sub>2</sub> are suitable starting compounds for ligand exchange reactions as a result of the substitutional lability of the SO<sub>2</sub> ligands. In the crystalline hexafluorido arsenates Te<sub>6</sub>[AsF<sub>6</sub>]<sub>4</sub>·1.5C<sub>2</sub>N<sub>2</sub> (1) and Te<sub>4</sub>[AsF<sub>6</sub>]<sub>2</sub>·C<sub>2</sub>N<sub>2</sub> (2) all weak coordinative Te···O-S-O bonds are replaced by stronger Te···NC-CN bonds, even if an excess of SO<sub>2</sub> is present in the reaction medium. This distinct reaction behavior underlines the higher nucleophilic

**Table 4.** FT-Raman spectra bands of  $Te_6[AsF_6]_4 \cdot 1.5C_2N_2$  (1),  $Te_4[AsF_6]_2 \cdot C_2N_2$  (2), and liquid cyanogen.

1	2	$C_2N_2$	Assignment
2349	2331	2327	$v_{\rm s}(C\equiv N)$
889	853	849	v(C-C)
864, 852 <sup>a)</sup>			v(C-C)
678	670		$v(AsF_6^-)$
506	506	505	$\delta(C-C), [\delta(SO_2)]$
367	367		$\delta(AsF_6^-)$
246			$v(Te_6^{4+})$
	216		$v(Te_4^{2+})$
	187 <sup>c)</sup>		$v(Te_4^{2+})$
181, 176			$v(Te_{6}^{4+})$
129			$v(Te_6^{4+})$
118			lattice mode
	106		$v(Te_4^{2+})$
		94 broad <sup>b)</sup>	/
96			$v({\rm Te_6}^{4+})$

a)  $\nu(C-C)$  stretching mode of solvate cyanogens. b) Intermolecular translational and rotational interactions. c)  $B_{2g}$  mode or lattice vibration.

properties of cyanogen in comparison to SO<sub>2</sub>. The existence of a significant  $\sigma$  donor interaction between the nitrile groups of the cyanogen moieties and the polycationic tellurium clusters is indicated by the vibrational frequencies of the symmetric CN stretching mode in the Raman spectra, which were found to be shifted to slightly higher wave numbers with respect to uncoordinated cyanogen.

These results became the starting point for further studies of Lewis acid-base complexes and coordination polymers between CN group bearing molecules and tellurium polycationic clusters [29]. We found that neutral polynitriles with a low lying HOMO are suitable as ligands towards the polycations, whereupon we will report in due course.

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