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Homoleptic Selenium Cyanides: Attempted Preparation of $Se(CN)_4$ and Redetermination of the Crystal Structure of $Se(CN)_2$

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The preparation of $Se(CN)_4$ was attempted by the reaction of SeF_4 with Me_3SiCN at low temperatures. However, selenium tetracyanide could not be detected by NMR spectroscopy; instead, the decomposition product $Se(CN)_2$ was isolated and its crystal structure was redetermined. In the structure of $Se(CN)_2$, layers are present with secondary $Se\cdots N$ interactions. The structure of $Se(CN)_4$ and its reductive decomposition reaction has been calculated at the MP2 level of theory.

Introduction

To the best of our knowledge, the only known homoleptic pseudohalogenides of selenium and tellurium in the +IV oxidation state are the binary tetraazides $Te(N_3)_4$ and $Se(N_3)_4$,[1] as well as the tellurium(IV) tetracyanide $Te(CN)_4$.[2] A number of reports, dealing with low-valent chalcogen dicyanides in the oxidation state +II, $E(CN)_2$ (E = S, Se, Te) exist,[3] and crystal structures have been elucidated more than 40 years ago for $S(CN)_2$[4] and $Se(CN)_2$[4d,5] and more recently for $Te(CN)_2$.[2b] The dicyanide of the lightest homologue, $O(CN)_2$, probably only exists as an intermediate.[6] Among other chalcogen compounds, selenium dicyanide was discussed recently in the course of the σ-hole concept, and the positive potential on the outer surface of the selenium atom was investigated, explaining noncovalent interactions with neighboring molecules.[7]

Experimental Section

General Procedures. All manipulation of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels or oven-dried plastic equipment and Schlenk techniques.[8] The selenium tetrafluoride was handled in PFA vessels (perfluoralkoxy-copolymer) due to the extreme sensitivity toward glass. For all NMR measurements of those compounds, a 4 mm PFA tube was used, which was placed into a standard 5 mm NMR glass tube. The solvent dichloromethane was dried by standard methods and freshly distilled prior to use. The compounds SeF_4 (Galaxy Chemicals) and trimethylsilyl cyanide (Sigma Aldrich) were used as received. Raman spectra were recorded on a PerkinElmer 2000 NIR FT spectrometer fitted with a Nd:YAG laser (1064 nm) as neat solids. NMR spectra were recorded on a JEOL Eclipse 400 instrument, and chemical shifts were determined with respect to external Me_4Si (^{13}C, 100.5 MHz), $MeNO_2$ (^{14}N, 28.9 MHz), and Me_2Se (^{77}Se, 76.3 MHz).

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X-ray Crystallography. For $\mathrm{Se(CN)_2}$,[9] an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo Kα radiation (λ = 0.71073 Å). The structure was solved using direct methods (*SIR97*[10]) and refined by full-matrix least-squares on F^2 (*SHELXL*[11]). All non-hydrogen atoms were refined anisotropically. *ORTEP* plots are shown with thermal ellipsoids at the 50% probability level.

Caution! *The proposed selenium tetracyanide is expected to be potentially hazardous. For safety precautions please see ref 1a.*

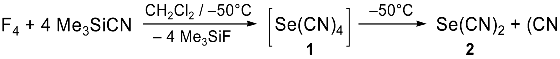
Attempted Preparation of $\mathbf{Se(CN)_4}$. A solution of $\mathrm{SeF_4}$ (274 mg, 1.77 mmol) in $\mathrm{CH_2Cl_2}$ (1 mL) was treated with $\mathrm{Me_3SiCN}$ (710 mg, 7.16 mmol) at −50 °C. Upon dropwise addition of $\mathrm{Me_3SiCN}$, a fizzling noise was noticeable. After 15 min stirring, a sample for NMR spectroscopy was prepared and the spectrum was recorded at −30 °C. In the ^{77}Se NMR spectrum, no evidence was found for **1**, only the resonance for one of the decomposition products $\mathrm{Se(CN)_2}$ (**2**) was found. **2**: ^{13}C NMR ($\mathrm{CH_2Cl_2}$, −30 °C) δ 92.8. ^{77}Se NMR ($\mathrm{CH_2Cl_2}$, −30 °C) δ 292. Raman: ν = 2327 (86), 2310 (24), 550 (12), 534 (5), 443 (7), 359 (2), 112 (24) cm^{-1}.

Computational Details. The calculations were carried out using the program package *G03W*[12] at the MP2 level of theory[13] using a cc-pVTZ[14] for carbon and nitrogen and a MWB-28-ECP for selenium[15] with a (14s10p2d1f)/[3s3p2d1f] basis set.[16]

Results and Discussion

The reaction of $\mathrm{SeF_4}$ with 4 equiv of $\mathrm{Me_3SiCN}$ in dichloromethane as solvent at low temperatures did not yield the desired product, selenium(IV) tetracyanide (**1**). Instead, reductive decomposition to selenium(II) dicyanide (**2**) and cyanogen occurred, which could both be subsequently identified (Scheme 1).

Scheme 1. Reaction of $\mathrm{SeF_4}$ with $\mathrm{Me_3SiCN}$



$$\mathrm{SeF_4 + 4\,Me_3SiCN} \xrightarrow[-\,4\,\mathrm{Me_3SiF}]{\mathrm{CH_2Cl_2}\,/\,-50\,°\mathrm{C}} \underset{\mathbf{1}}{\left[\mathrm{Se(CN)_4}\right]} \xrightarrow{-50\,°\mathrm{C}} \underset{\mathbf{2}}{\mathrm{Se(CN)_2}} + \mathrm{(CN)_2}$$

Table 1. Comparison of Observed and Calculated Raman Frequencies [cm^{-1}] for $\mathrm{Se(CN)_2}$ (**2**); Raman Intensities in Parentheses are Relative Intensities for the Experimental Intensities and are Given in Units of Å^4 amu^{-1} for the Calculated Intensities; ip = in phase, oop = out of phase

mode description	calculated	observed
$\mathrm{CN}_{\text{stretch, ip}}$	2283 (125)	2327 (86)
$\mathrm{CN}_{\text{stretch, oop}}$	2270 (59)	2310 (24)
$\mathrm{CSeC}_{\text{stretch, oop}}$	540 (6)	550 (12)
$\mathrm{CSeC}_{\text{stretch, ip}}$	522 (2)	534 (5)
$\mathrm{CSeC}_{\text{bend/scissors}}$	441 (3)	443 (7)
$\mathrm{CSeC}_{\text{wag}}$	344 (2)	359 (2)
$\mathrm{CSeC}_{\text{twist}}$	327 (0.4)	
$\mathrm{SeCN}_{\text{wag}}$	288 (0.2)	
$\mathrm{SeCN}_{\text{twist}}$	105 (8)	112 (24)

On the basis of ^{77}Se NMR spectra, which were recorded after the reaction mixture was stirred for 15 min at −50 °C, no evidence for the formation of **1** was obtained. Instead, a single resonance at δ = 292 ($\mathrm{CH_2Cl_2}$) was observed, which was assigned to $\mathrm{Se(CN)_2}$ (**2**). The previously reported chemical shift of δ = 0.29 is definitely incorrect, as well as the reported chemical shift for $\mathrm{Se_2(CN)_2}$ (δ = 0.45); both values must be multiplied by the factor 1000, because these values are reported in parts per thousand, and not in parts per million, as stated.[17]

In the ^{19}F NMR spectrum of the reaction mixture, resonances corresponding to traces of $\mathrm{SeF_4}$ and $\mathrm{SeOF_2}$ (impurity in the sample of $\mathrm{SeF_4}$ used for synthesis), in addition to the major resonance corresponding to $\mathrm{Me_3SiF}$, could be detected. After removal of all volatile materials, the formation of $\mathrm{Se(CN)_2}$ was also established by Raman spectroscopy of the pale-yellow residue (Table 1). The second decomposition product, cyanogen $\mathrm{(CN)_2}$, was identified by ^{13}C NMR spectroscopy (δ = 96.3 in $\mathrm{CH_2Cl_2}$) by comparison with an authentic sample (δ = 95.2 in $\mathrm{C_6D_6}$). A broad resonance at δ = −115 ($\mathrm{CH_2Cl_2}$) is found in the ^{14}N NMR spectrum, which is assigned to cyanogen (authentic sample of cyanogen: δ = −111 in $\mathrm{C_6D_6}$; $\mathrm{Me_3SiCN}$: δ = −88 in $\mathrm{CDCl_3}$). The reported converted value of δ = −80[17] assigned for $\mathrm{Se(CN)_2}$ could not be confirmed.

The calculated structure (MP2/cc-pVTZ, Table 2) of **1** adopts a pseudo trigonal-bipyramidal arrangement with the free valence electron pair occupying one equatorial position and is shown in Figure 1.

The reductive decomposition of **1** (Scheme 1) yields an energy difference for **2** and one molecule of cyanogen of ΔE = −300.4 kJ mol^{-1}. The calculation supports our experimental findings for the instability of **1**. Compared to the value for the analogous tellurium compound (ΔE = −161.1 kJ mol^{-1}), which was shown to be feasible at low temperatures,[2] the reductive decomposition is considerably more favored in the case of **1**.

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[9] Crystallographic data for **2**: $\mathrm{C_2N_2Se}$, M_w = 130.99, orthorhombic, space group *Pbca*, a = 8.632(5) Å, b = 6.847(5) Å, c = 12.8151(7) Å, V = 757.4(7) Å^3, Z = 8, ρ_{calcd} = 2.297 g cm^{-3}, μ = 9.688 mm^{-1}, θ range 4.0−26.0°, T = 200 K, reflns collected 2804 (R_{int} = 0.0459), Final R_1 (2σ data) = 0.0334, wR_2 (all data) = 0.0949.

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Table 2. Computational Results for **1** and **2**

	Se(CN)$_2$	Se(CN)$_4$
point group	C_{2v}	C_{2v}
el. state	$^1A_1$	$^1A'$
$-E$/a.u.	194.610124	379.814761
NIMAG	0	0
zpe/kJ mol^{-1}	40.82	78.92
d(Se−C)/Å	1.842	equatorial 1.854 ax. 2.066
d(C−N)/Å	1.176	equatorial 1.178 ax. 1.180
<(CSeC)/°	94.9	eq−eq 102.5 ax−ax 167.1 ax−eq 86.0

The same tendency regarding tellurium compounds being more stable than selenium compounds with the same substituents was observed previously for the analogous binary azide species Te(N$_3$)$_4$ and Se(N$_3$)$_4$ and their anions.[1]

Because there are some ambiguities and contradictions between the previously reported structural characterizations, that is, different space group, atom distances and angles, we redetermined the crystal structure of **2**. Single crystals were grown by slow evaporation of a dichloromethane solution at ambient temperature. The compound crystallized in the space group *Pbca* with 8 molecules in the unit cell and is shown in Figure 2. Prior crystal structures of this compound Se(CN)$_2$ (**2**) have been published in 1963 by Hazell[4d] and in 1966 by Linke and Lemmer.[5] Whereas the first report suggested the wrong space group (*Cmca*), in the second one the space group *Pbca* was determined, which we can confirm. In accordance to the previously reported findings, single molecules of **2** are present, which are linked via secondary Se···N interactions (Se1···N1 2.813(9) and Se1···N2 2.835(7) Å), and are significantly below the sum of the selenium−nitrogen van der Waals radii (vdWr SeN 3.45 Å[18]).

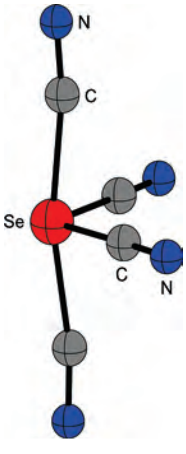

Figure 1. Calculated structure of **1** (C_{2v}) at the MP2/cc-pVTZ level of theory; selected bond lengths (Å) and angles (deg): Se−C$_{eq}$ 1.854, C$_{eq}$−N$_{eq}$ 1.178, Se−C$_{ax}$ 2.066, C$_{ax}$−N$_{ax}$ 1.180, C$_{eq}$−Se−C$_{eq}$ 102.50, C$_{ax}$−Se−C$_{ax}$ 167.17, Se−C$_{eq}$−N$_{eq}$ 177.20, Se−C$_{ax}$−N$_{ax}$ 170.60.

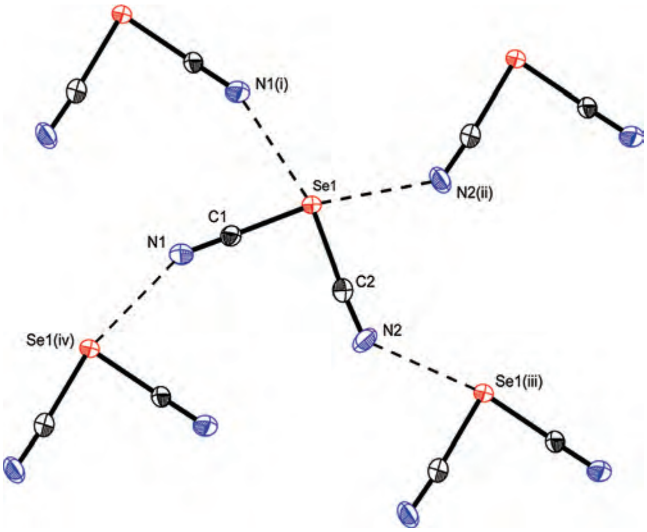

Figure 2. Molecular structure of **2**; selected bond lengths (Å) and angles (deg): Se1−C1 1.862(7), Se1−C2 1.870(7), C1−N1 1.138(8), C2−N2 1.131(8), Se1−C1−N1 179.2(7), Se1−C2−N2 176.3(6), C1−Se1−C2 91.3(3), Se1···N1(*i*)/Se1(*iv*)···N1 2.813(9), Se1···N2(*ii*)/Se1(*iii*)···N2 2.835(7), with $i = 0.5 - x, -0.5 + y, z$; $ii = 1.5 - x, -0.5 + y, z$; $iii = 1.5 - x, 0.5 + y, z$; $iv = 0.5 - x, 0.5 + y, z$.

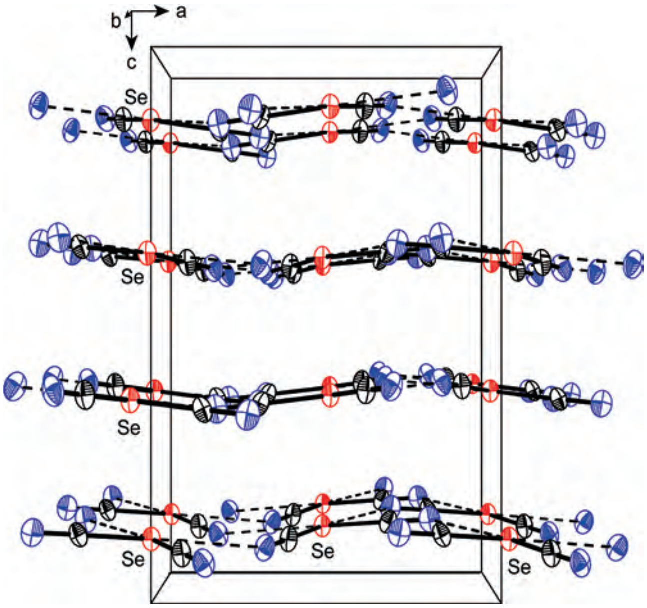

Figure 3. View of the layered structure of **2**; only selected atoms are labeled for clarity.

These interactions are somewhat comparable to the previously reported interactions of 2.81/2.74 Å[5] but significantly longer than the earlier reported value of 2.35(10) Å.[4d] A theoretical report explained those relatively strong intermolecular interactions with the σ-hole concept.[7] Regions of positive electrostatic potential on the outer surface of the selenium atom, resulting from the strong electron-withdrawing cyano groups, interact with the lone-pairs of the nitrogen atom of a neighboring cyano group creating intermolecular contacts. The Se−C distances are 1.862(7) (Se1−C1)/1.870(7) Å (Se1−C2) and comparable to the reported distance of 1.86(10) Å[4d] as well as the calculated value (1.86 Å)[17] but considerably shorter than the afterward reported values of 2.08/2.01 Å.[5] The C−N distances (C1−N1 1.138(8)/C2−N2 1.131(8) Å) lie in-between the published values (1.42(15) Å,[4d] 1.07/1.27 Å,[5] calcd: 1.16 Å[17]) and are comparable to the distances in the analogous tellurium dicyanide (1.131(7)/1.149(7) Å[2b]). The Se−C−N angles are close to linearity (Se1−C1−N1 179.2(7)°, Se1−C2−N2

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176.3(6)°) and partly in good agreement with the published values (177(6)°,[4d] 168/155°,[5] calcd: 175°[17]). Again significantly different is the C−Se−C angle (91.3(3)°), which is the smallest compared to the other published results (119(6)°,[4d] 99°,[5] calcd: 97°[17]); however, the angle is widened compared to the analogous $Te(CN)_2$ (85.4°[2b]). Taking the secondary Se···N interactions into account, the geometry around the selenium atom can be described as distorted square-planar with an N1(*i*)···Se1···N2(*ii*) angle of 114.6(2)° and the two lone-pairs of the selenium atom located above and beneath that plane, respectively. This results in slightly curled layers along the *c* axis with a distance of approximately 3.9 Å between those layers (Figure 3).

As a result of the different Se−C distances, Linke and Lemmer[4a] concluded that a selenocyan cyanide, $NC^- \ {}^+SeCN$, is formed, which they also suggested for the dicyanide of the lighter homologue, $S(CN)_2$. Our findings, with two nearly equal Se−C distances, are in strong contrast to such an ionic species, and we therefore conclude that two covalent Se−C bonds are present in **2**. The same situation with two covalent bonds is also likely to be present in the structure of $S(CN)_2$, because the S−C values published by Emerson are also nearly equal (1.736(15)/1.718(18) Å[4b]), in contrast to the values of Linke and Lemmer (1.87/2.07 Å[4a]).

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Supporting Information Available: CIF file for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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