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A New Synthetic Route to Se_2NCl_3 Leading to a New Modification of This Chloride Nitride of Trivalent Selenium

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ABSTRACT

Se_2NCl_3 was prepared in 58% yield by the reaction of $SeCl_4$ with $Se_2[N(SiMe_3)_2]_2$. This method provides a new and convenient one-day and one-pot synthesis for the preparation of this neutral chloronitride of trivalent selenium. The low-temperature structure was determined by a single-crystal X-ray diffraction analysis. The compound crystallizes in the monoclinic space group $P\,2_1/a$ with $Z = 4$ and unit cell dimensions $a = 7.605(3)$, $b = 8.7643(20)$, $c = 8.966(3)$ Å, and $\beta = 93.23(3)°$. The structure is made up of essentially planar Se_2NCl_3 molecules (C_{2v} symmetry) that are packed in a coplanar fashion to form one-dimensional chains. There are strong intermolecular interactions with short intermolecular Se···Se distances of 3.82 Å, which is significantly shorter than the sum of the covalent radii (4.0 Å). This explains the golden color and the metallic luster of this compound. Se_2NCl_3 was first reported in 1992 by K. Dehnicke et al. to form transparent red crystals (orthorhombic, space group P bca, $a = 12.290(6)$, $b = 8.046(4)$, $c = 24.336(12)$ Å) without significant intermolecular interactions (Se···Se, 4.10 Å). Therefore, Se_2NCl_3 is polymorphic, crystallizing either in the orthorhombic or in the monoclinic system.

INTRODUCTION

During the last 5 to 7 years, significant advances have been made in the area of selenium-nitrogen chemistry, as indicated by the number of recent reviews covering various aspects of the subject [1–8]. The impetus for such studies has, in part, been derived from the possibility that the polymer $(SeN)_x$ may exhibit even more unusual properties than those of the metallic superconductor $(SN)_x$ [7]. Since the only known binary Se–N compound is the highly explosive cage molecule Se_4N_4 [9,10], ternary selenium–nitrogen–chlorine compounds are of great interest as building blocks in preparative Se–N chemistry. Several Se–N chlorides that are potential sources of the SeNSe unit have been synthesized for

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Dedicated to Professor Kurt Dehnicke on the occasion of his sixty-fifth birthday.

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the first time recently: Se_2NCl_3 [11], $[(SeCl)_2N]^+$ [11–14], $[(SeCl_2)_2N]^+$ [15,16], and $[Se_3N_2Cl]^+$ [17,18]. However, Se_2NCl_3 represents the only known neutral selenium chloride nitride. This compound was first prepared by Dehnicke et al. by the action of *tris*(trimethylsilyl)amine on a suspension of selenium tetrachloride in boiling dichloromethane (Equation 1) [11].

$$2\ SeCl_4 + N(SiMe_3)_3 \rightarrow \underset{\mathbf{1}}{Se_2NCl_3} + 3\ ClSiMe_3 + Cl_2 \qquad (1)$$

Diseleniumtrichloride nitride (1) has proven to be a very reactive and suitable synthetic reagent that, for example, by treatment with suitable Lewis acids (e.g., $GaCl_3$, $FeCl_3$, and $SbCl_5$), can easily be transformed into the corresponding cation $[(SeCl)_2N]^+$ [11–14].

Originally, Se_2NCl_3 was recrystallized from dichloromethane, and the crystals, when viewed against light, appeared red; but when viewed against a background, they appeared shiny, metallic green [11]. This crystalline form of diseleniumtrichloride nitride was characterized by X-ray diffraction analysis and was shown to be orthorhombic. In this article, we report a new convenient one-pot reaction to give Se_2NCl_3. This route does not require a recrystallization procedure and produces 1 in 58% yield as a microcrystalline material with a golden, metallic luster. Furthermore, Se_2NCl_3 was shown by X-ray analysis to exist in two polymorphic forms, orthorhombic and monoclinic, which are very close in energy.

EXPERIMENTAL

Materials and Methods. $SeCl_4$ [19] and $Se_2[N(SiMe_3)_2]_2$ [20] were prepared by standard procedures according to the literature. $N(SiMe_3)_3$ (Aldrich) was used as supplied. SO_2 (Air Products) and CH_2Cl_2 (Merck) were dried over CaH_2 or P_4O_{10}, respectively, and distilled prior to use. General reaction conditions were as described previously [13]. Conductivity measurements were performed on single crystals under nitrogen using an Extech 380925 instrument.

Preparation of Se_2NCl_3 (1). A solution of $Se_2[N(SiMe_3)_2]_2$ (1.6 g, 3.34 mmol) in SO_2 (10 mL) was added to a suspension of $SeCl_4$ (2.1 g, 10 mmol) in 10 mL of SO_2 and stirred at 10°C. After 12 hours, the precipitated golden, microcrystalline solid was separated by filtration, washed twice with 3 mL of cold SO_2 and dried in vacuum (yield 1.62 g, 58%, based on $SeCl_4$, rapid decomposition at room temperature, slow decomposition at 0°C, stable at −18°C). IR spectra: Nujol mull, KBr plates, Perkin Elmer 580 B (cm^{-1}): 830 s (ν_{as}-SeNSe), 558 s (δ-SeNSe), 350 s, sh (ν-SeCl).

The by-product trimethylsilyl chloride was unambiguously identified by its ^1H NMR spectrum. $SeCl_2$, however, could not be detected unambiguously presumably because of subsequent reaction. Subsequent reaction of 1 with $SbCl_5$ afforded $[(SeCl)_2N]^+[SbCl_6]^-$ in high yield (cf. Refs. [12,21]).

Preparation of X-ray Samples. The microcrystalline, golden material obtained from the reaction of $Se_2[N(SiMe_3)_2]_2$ and $SeCl_4$ in SO_2 was recrystallized from 50 mL of CH_2Cl_2 at −35°C, affording crystals large enough to be suitable for X-ray crystallography.

In another experiment, we prepared 1 from $SeCl_4$ and $N(SiMe_3)_3$, exactly following the method described in the literature [11]. However, prior to recrystallization, we added one golden seed crystal obtained from the reaction of $Se_2[N(SiMe_3)_2]_2$ with $SeCl_4$. The following recrystallization then afforded golden crystals of 1 (yield 55%) that were shown by an independent low-temperature X-ray analysis to consist of monoclinic Se_2NCl_3 [21].

Crystal Data. Diseleniumtrichloride nitride (1), Se_2NCl_3, prepared from $Se_2[N(SiMe_3)_2]_2$ and $SeCl_4$, $M = 278.28$, monoclinic, $a = 7.605(3)$, $b = 8.7643(20)$, $c = 8.966(3)$ Å, and $\beta = 93.23(3)°$; $U = 596.6(3)$ Å^3, space group $P\,2_1/a$, $Z = 4$, $D_c = 3.098$ g cm^{-3}. Crystal dimensions 0.65 × 0.50 × 0.40 mm. μ(Mo–K$_\alpha$) = 13.49 mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 504.77$.

Data Collection and Processing. Rigaku AFC6S diffractometer, −170°C, $\theta/2\theta$ scan mode, $2\theta_{max} = 50.0°$, graphite monochromated Mo–K$_\alpha$ radiation, 1052 independent measured reflections, 846 observed $[I_{net} > 2.5\ \sigma\ I_{net}]$.

Structure Analysis and Refinement. The structure was solved by direct methods, and all atoms were refined anisotropically. Refinement was by block-cascade full-matrix least-squares to $R_F = 0.14$, ($R_F = \Sigma[F_o - F_c]/\Sigma[F_o]$), $R_W = 0.17$, ($R_W = \text{Sqrt.}[\Sigma(w[F_o - F_c]^2)/\Sigma\ (wF_o^2)]$); for all reflections: $R_F = 0.16$, $R_w = 0.18$. In the last D-map, the deepest hole was −5.800 e Å^{-3}, and the highest peak was 4.970 e Å^{-3}. Computations were carried out using the NRCVAX program system and published scattering factors [22–24].

Further details of the crystal structure determination are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wis-

TABLE 1 Crystallographic Data for Orthorhombic [11] and Monoclinic Se_2NCl_3

	Orthorhombic	*Monoclinic*
M_r	278.28	278.28
Space group	$P\,bca$	$P\,2_1/a$
a/Å	12.290(6)	7.605(3)
b/Å	8.046(4)	8.7643(20)
c/Å	24.336(12)	8.966(3)
β/°		93.23(3)
V/Å³	2406.5	596.6(3)
Z	16	4

TABLE 2 Selected Bond Lengths (Å) and Angles (°) for Orthorhombic [11] and Monoclinic Se_2NCl_3 (see Figure 1 for Atom Labels)

	Orthorhombic	*Monoclinic*
Se1–N1	1.742(5)	1.79(3)
Se2–N1	1.733(5)	1.73(3)
Se1–Cl1	2.269(2)	2.166(9)
Se2–Cl2	2.198(2)	2.196(9)
Se1–Cl3	2.519(2)	2.759(8)
Se2–Cl3	2.676(2)	2.682(9)
Se1–Cl3–Se2	70.7(1)	67.75(21)
Se1–N1–Se2	119.9(3)	119.4(17)
Cl1–Se1–N1	91.4(2)	95.9(9)
Cl2–Se2–N1	93.0(2)	93.4(11)
Cl3–Se1–N1	87.1(2)	84.6(9)
Cl3–Se2–N1	82.4(2)	88.1(11)
Se···Se	4.10	3.82

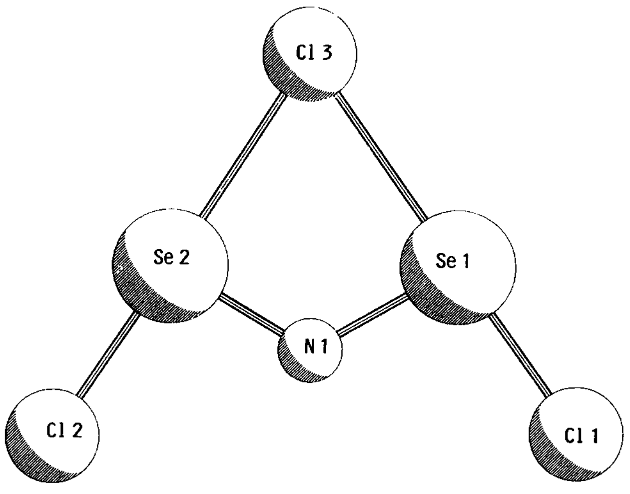

FIGURE 1 Molecular structure of **1** in the crystal.

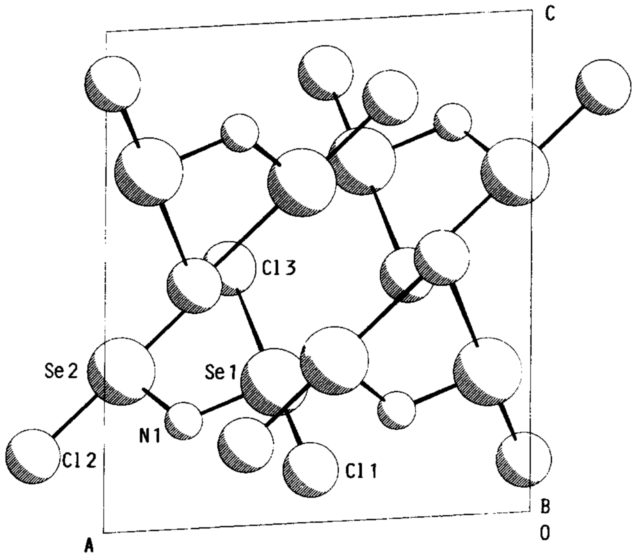

FIGURE 2 Packing diagram for **1** in the monoclinic system.

senschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-59172, the names of the authors, and the journal citation.

RESULTS AND DISCUSSION

In addition to the method described in the literature (cf. Equation 1) [11], diseleniumtrichloride nitride (**1**) can be prepared in 58% yield by the action of diselenium di[bis(trimethylsilyl)nitride] on a suspension of selenium tetrachloride in liquid sulfur dioxide (Equation 2). This new route provides a convenient one-pot reaction, since the desired product is only slightly soluble in SO_2 and can easily be separated by filtration.

$$3\,\mathrm{SeCl_4} + \mathrm{Se_2[N(SiMe_3)_2]_2} \xrightarrow{\mathrm{SO_2}} \underset{\mathbf{1}}{2\,\mathrm{Se_2NCl_3}}\downarrow + 4\,\mathrm{ClSiMe_3} + \mathrm{SeCl_2} \qquad (2)$$

In contrast to the material obtained from a reaction according to Equation 1, the reaction according to Equation 2 always led to microcrystalline **1**, which had a golden color and a metallic luster. Subsequently, the X-ray structure analysis revealed compound **1** to be polymorphic and to exist in two modifications. Whereas compound **1** was shown earlier to crystallize in an orthorhombic space group [11], in the present work, we established that there is also a monoclinic form of **1** (Table 1). Both structures are made up of discrete Se_2NCl_3 molecules, the structural parameters of which are essentially identical within experimental errors (Figure 1, Table 2). However, in the monoclinic form, there are short intermolecular Se···Se contacts of 3.82 Å, which is substantially shorter than the sum of the van-der-Waals radii of 4.00 Å [25] (Figure 2). This may well explain the golden color and the metallic luster of monoclinic **1**. In contrast, the shortest intermolecular

Se···Se distances in monoclinic 1 are 4.10 Å [11]. We subjected three different crystals of monoclinic 1 to an X-ray diffraction analysis, and all clearly confirmed the monoclinic cell parameters and the short intermolecular Se···Se distances in the solid state. We are still trying to get better crystals of monoclinic 1; however, with this compound slowly decomposing even at 0°C, this is likely not possible.

In the solid state, the monoclinic form of 1 is stable under an inert-gas atmosphere below -5°C only. At higher temperatures, 1 decomposes to give Se_2Cl_2 and other yet to be identified decomposition products.

In another experiment, we prepared 1 from $SeCl_4$ and $N(SiMe_3)_3$ exactly following the method described in the literature [11]. However, prior to recrystallization, we added one golden seed crystal obtained from the reaction of $Se_2[N(SiMe_3)_2]_2$ with $SeCl_4$. The following recrystallization then afforded golden crystals of 1 (yield 55%) that were shown by an independent low-temperature X-ray analysis to consist of monoclinic Se_2NCl_3.

The metallic luster of monoclinic 1 naturally led to an investigation of the electrical conductivity. However, due to the great air sensitivity and especially due to the instability at ambient temperature and even at 0 °C, these measurements were not easy to carry out and were performed under N_2 in a dry box with precooled samples. Two measurements on single crystals were carried out at 0 °C and at 20 °C (± 5 °C). It could be established that monoclinic 1 does not show significant electrical conductivity. The measured electrical resistivity was $>10^6$ ohm cm (at 0 °C and 20 °C). The relative high value may well be explained by partial decomposition and formation of elemental selenium (cf. electrical resistivity of elemental gray selenium at 25 °C: 10^{10} ohm cm, very dependent on purity) [26].

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