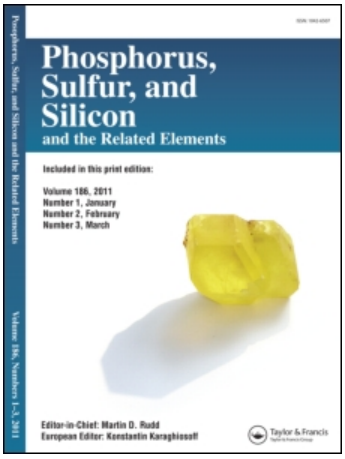

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Novel Tellurium Halides

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Tellurium reacts with SO_2Cl_2 in THF producing $[HOC_4H_8][TeCl_5(OC_4H_8)]$ **(1a)**. In CS_2 $[H_3O][Te_3Cl_{13}]\cdot SO_2$ **(2)** is formed. When Me_3SiBr or Me_2SO is added to the reaction solution of **1a**, $[HOC_4H_8][TeBr_5(OC_4H_8)]$ **(1b)** and $[(Me_2SO)_2H]_2[TeCl_6]$ **(3)** are obtained, respectively. The reaction between metallic nickel, tellurium, and SO_2Cl_2 in acetonitrile produces $[Ni(CH_3CN)_6][Te_2Cl_{10}]$ **(4)**. All products are characterized by ^{125}Te NMR spectroscopy and X-ray crystallography.

Keywords: Tellurium chloride; ^{125}Te NMR spectroscopy; X-ray crystallography

INTRODUCTION

Sulfur and selenium dichlorides are useful reagents for many synthetic applications. SCl_2 may be prepared from its elements or by chlorination of S_2Cl_2.[1, 2] For several years $SeCl_2$ was considered to be stable only in gas phase.[3-5] However, quite recently we reported that pure $SeCl_2$ can be prepared from equimolar amounts of selenium and SO_2Cl_2 in THF. No disproportionation was observed until 24 hours was elapsed.[6]

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The preparation of $TeCl_2$ was reported for the first time in 1887,[7] but only a few preparative routes are known.[8, 9] We have attempted to prepare $TeCl_2$ by the reaction between tellurium and SO_2Cl_2 in an analogous fashion to $SeCl_2$. Instead of $TeCl_2$ we obtained different tellurium-chlorine anions depending on reaction conditions.

EXPERIMENTAL

All reactions were carried out under a dry argon atmosphere that was passed through P_4O_{10} before use. The solvents were dried by fresh distillation under a dry nitrogen atmosphere. ^{125}Te NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 126.240 MHz. Diffraction data were collected on a Nonius Kappa CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) by recording 360 frames via φ-rotation ($\Delta\varphi = 10$; two times 20-40 s per frame). The structures were solved by direct methods and refined on F^2.

1a and **2** were prepared by equimolar amounts of tellurium and SO_2Cl_2 and **4** from equimolar amounts of tellurium, SO_2Cl_2, and metallic nickel. **1a** was prepared in THF, **2** in CS_2 and **4** in acetonitrile. **1b** and **3** were formed when equimolar amounts of Me_3SiBr and DMSO, respectively, were added to the reaction solutions of **1a**. In general, crystalline products were formed upon cooling the reaction solutions. **2**, however, crystallized at room temperature. ^{125}Te chemical shifts of the products are as follows: **1a** 1712 ppm, **1b** 1674 ppm, **2** 1803 ppm, **3** 1570 ppm, **4** 1669 ppm.

RESULTS AND DISCUSSION

The structures of **1a** and **1b** are similar containing a $[TeX_5(OC_4H_8)]^-$ anion where one of the octahedral sites of tellurium is occupied by THF molecule. The $[HOC_4H_8]^+$ cation is a protonated solvent molecule.

3 consists of a $[TeCl_6]^{2-}$ anion and two $[H(Me_2SO)_2]^+$ cations. In these cations two Me_2SO molecules are bridged by a proton.

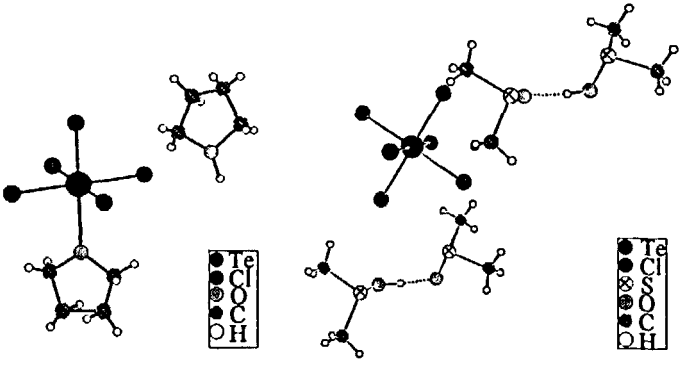

FIGURE 1 Molecular structures of **1** and **3**.

4 consist of a $[Te_2Cl_{10}]^{2-}$ anion and a relatively large $[Ni(MeCN)_6]^+$ cation. The environment of nickel atom is octahedral and the acetonitrile molecules are coordinated to nickel via nitrogen.

2 contains a novel $[Te_3Cl_{13}]^-$ anion. The structure of the anion shows a cyclic arrangement of three $TeCl_3^+$ fragments connected by three bridging Cl^- anions. One chloride ion is shared by all three tellurium atoms. The structure is similar to that of the subunit of tetrameric δ-TeI_4. The framework of $[Te_3Cl_{13}]^-$ is obtained upon

removing one TeI_3 unit from δ-TeI_4. The protons of H_3O^+ ion show close contacs to the bridging chlorine atoms. **2** also contains a disordered SO_2 molecule.

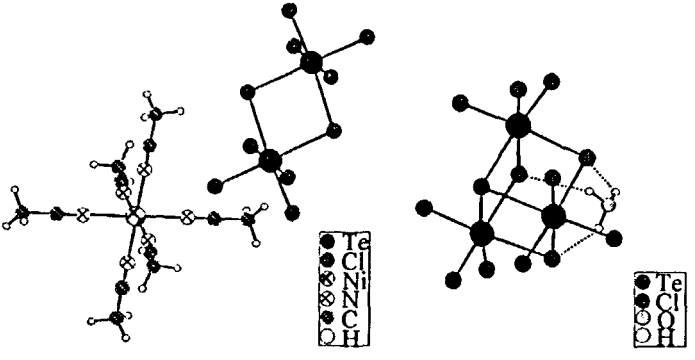

FIGURE 2 Molecular structures of **4** and **2**.

Acknowledgments
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