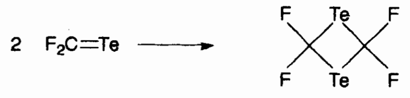
Synthesis and Characterization of 2,2,4,4-Tetrafluoro-1,3-ditelluretane and -1-selena-3-telluretane *via* the Intermediate Difluorotelluroketone

Roland Boese,[b] Alois Haas*[a] and Christian Limberg[a]

[a] *Lehrstuhl für Anorganische Chemie II der Ruhr-Universität Bochum, Postfach 102148, D-4630 Bochum 1, Germany*
[b] *Institut für Anorganische Chemie der Universität-G.H., Universitätsstraße 3-5, D-4300 Essen, Germany*

Difluorotelluroketone is made by reacting $Hg(TeCF_3)_2$ with Et_2AlI and is characterized by its dimerization product $F_2\overline{CTeCF_2Te}$ as well as by cocondensation with F_2CSe to $F_2\overline{CTeCF_2Se}$; preliminary X-ray data for $F_2\overline{CTeCF_2Te}$ are provided.

Compounds containing a Te=C group are, because of their instability, almost unknown.[1] So far few telluro-esters[2] and -amides[3] stabilized by resonance delocalization have been described. It is also possible to coordinate tellurocarbonyl compounds to transition metals.[4] No free telluroaldehydes and ketones have been isolated.[5,6] Examples, described so far, have been generated *in situ* and characterized by [4 + 2] cycloadditions to dienes.[5,6] With the exception of the cyclic dimeric telluroadamantanone, characterized by its mass spectrum, no other 1,3-ditelluretanes have been mentioned.[6]



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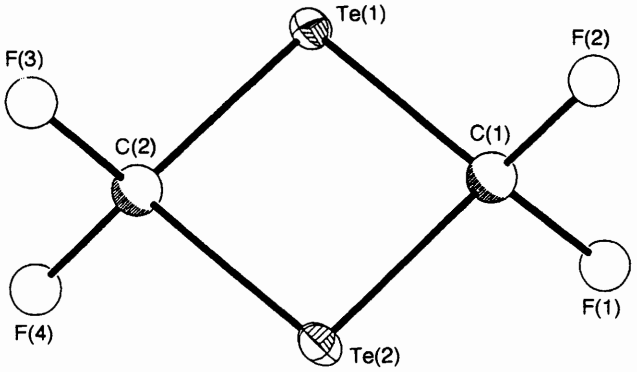

Fig. 1 The crystal structure of **2**. Average bond lengths (in Å over two independent molecules in the unit cell): C–F 1.359(10), Te–C 2.191(11); angles (°): C–Te–C 78.9(4), Te–C–Te 101.2(4), F–C–F 105.3(10), Te–C–F 112.7(5).

3

We report the first synthesis of difluorotelluroketone **1**, its cyclic dimer F_2CTeCF_2Te **2** and F_2CTeCF_2Se **3**. As the $R_fCF{=}Se$ derivatives[8] are synthesized according to reaction (1); it was of interest to study comparable reactions with $Hg(TeCF_3)_2$, prepared from $CF_3TeTeCF_3$ and mercury.[9] By reacting $Hg(TeCF_3)_2$ (1.2 g = 2.1 mmol) with Et_2AlI (1 ml = 7.5 mmol) at 20 °C 5×10^{-3} Torr without solvent, **1** condenses in about 10% yield into a trap, cooled with liquid nitrogen as a deep violet, transient, amorphous material, which is thermally very unstable [eqn. (2)].

$$Hg(SeCF_2R_f)_2 + 2\,R_2AlI \rightarrow 2\,R_fCFSe + HgI_2 + 2\,R_2AlF$$
$$R_f = F, CF_3, C_2F_5 \quad R = I, Et \qquad (1)$$

$$Hg(TeCF_3)_2 + 2\,Et_2AlI \rightarrow HgI_2 + 2\,Et_2AlF + 2\,\underset{\mathbf{1}}{Te{=}CF_2} \qquad (2)$$

As the reaction is highly exothermic, some of the $Hg(TeCF_3)_2$ decomposes to mercury and $(CF_3)_2Te_2$,[9] which can be recovered in a trap cooled at −40 °C. If the Dewar vessel with liquid nitrogen is removed slowly, an almost quantitative dimerization to dark-red coloured **2** is observed, which can be easily crystallized by sublimation. It is very sensitive to air and light but stable for a few hours at room temperature.

Compound **2** melts at 106 °C (decomp.) and was characterized by NMR, IR and mass spectroscopy.† An X-ray crystal structure‡ determination on single crystals of **2**, obtained by sublimation, showed the structure presented. The two independent molecules in the unit cell differ only a little in bond lengths and angles. The C–Te–C bond angle, which is about 3° smaller than its comparable Se-analogue, is striking, while the Te–C–Te angle is about 3° larger. The distance between the two Te-atoms (3.385 Å) is smaller than the sum of van der Waals radii (4.40 Å).[7]

Cocondensation of an excess of F_2CSe with F_2CTe on warming from −196 °C to 20 °C and immediate fractionation of the reaction products provides **3**, in the trap cooled to −55 °C, as an orange solid which sublimes readily and decomposes at 20 °C in a few minutes, depositing tellurium. In solution it is more stable and can be handled for about 8 hours. Compound **3** was also characterized by NMR, IR and mass spectroscopy.§

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† ^{19}F NMR (referenced to $CFCl_3$, 250 MHz, $CDCl_3$): δ −38.8 (s). ^{13}C NMR (referenced to $CDCl_3$, 250 MHz, $CDCl_3$); δ 45.3 (higher order). ^{125}Te NMR (referenced to Me_2Te, 250 MHz, $CDCl_3$): δ 2321.7 [quin, ^2J (Te–F) 122.1 Hz]. Mass spectrum: *m/z* 356 (63), (M^+): 300 (85) ($Te_2CF_2^+$); 287 (20), (Te_2CF^+); 256 (60), (Te_2^+); 180 (50), ($TeCF_2^+$); 161 (15), ($TeCF^+$); 142 (5), (TeC^+); 130 (100), (Te^+); 50 (18), (CF_2^+). IR (KBr) ν/cm⁻¹: 1017vs, br, 798w, 739m. Satisfactory elemental analyses were obtained.

‡ *Crystal data*: $C_2F_4Te_2$, M_r = 355.2, monoclinic, space group $P2_1$, T = 115 K, a = 7.053(1), b = 11.361(2), c = 7.482(1) Å, β = 91.43(1)°, V = 599.3(2) Å³, Z = 4, D_c = 3.937 g cm⁻³, Mo-Kα radiation (graphite monochromator), λ = 0.71069 Å, μ = 9.74 mm⁻¹.

Empirical absorption corrections were applied to the 1849 unique reflections; of these, 1031 having $F_o \geqslant 4\sigma(F)$ were retained for structure refinements. All calculations were carried out with the SHELXTL-PLUS programs. Anisotropic thermal parameters were applied for Te-atoms. R = 0.035 (R_w = 0.035). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ ^{19}F NMR (250 MHz, $CDCl_3$): δ −42.0 (s), ^{77}Se NMR (referenced to Me_2Se, 250 MHz, $CDCl_3$): δ 1220.1 [quin, ^2J (Se–F) 73.4 Hz], ^{125}Te NMR (250 MHz $CDCl_3$): δ 2272.8 [quin, ^2J (Te–F) 103.7 Hz]. Mass spectrum: *m/z* 308(30), (M^+); 258 (18), ($SeTeCF_2^+$); 239 (7), ($SeTeCF^+$); 208 (15), ($SeTe^+$); 180 (100), (F_2CTe^+); 161 (10), ($FCTe^+$); 149 (3), (FTe^+); 130 (70), (Te^+/F_2CSe^+); 111 (15), ($FCSe^+$); 80 (17), (Se^+); 50 (11), (CF_2^+); 43 (22), (C_2F^+); 31 (20), (CF^+). IR(gas) ν/cm⁻¹: 1265m, 1157w, 1092vs, br, 814s.