



Synthesis and spectroscopic characterization of eleven mixed-ligand diorganotellurium(IV) compounds containing dithiocarbamate and dithiophosphate ligands

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ABSTRACT

Eleven mixed-ligand organotellurium(IV) compounds of composition $R_2Te(dtc)(dtp)$ have been prepared employing two different dithiocarbamate (dtc) and dithiophosphate (dtp) ligands: **1**, $R_2 = C_4H_8$, $dtc = S_2CNEt_2$, $dtp = S_2P(OCH_2)_2CtEt_2$; **2**, $R_2 = C_8H_8$, $dtc = S_2CNEt_2$, $dtp = S_2P(OCH_2)_2CtEt_2$; **3**, $R_2 = C_4H_8O$, $dtc = S_2CNEt_2$, $dtp = S_2P(OCH_2)_2CtEt_2$; **4**, $R_2 = C_5H_{10}$, $dtc = S_2CNEt_2$, $dtp = S_2P(OCH_2)_2CtEt_2$; **5**, $R_2 = C_4H_8$, $dtc = S_2CN(CH_2)_4$, $dtp = S_2P(OCH_2)_2CtEt_2$; **6**, $R_2 = C_8H_8$, $dtc = S_2CN(CH_2)_4$, $dtp = S_2P(OCH_2)_2CtEt_2$; **7**, $R_2 = C_4H_8O$, $dtc = S_2CN(CH_2)_4$, $dtp = S_2P(OCH_2)_2CtEt_2$; **8**, $R_2 = C_5H_{10}$, $dtc = S_2CN(CH_2)_4$, $dtp = S_2P(OCH_2)_2CtEt_2$; **9**, $R_2 = C_4H_8$, $dtc = S_2CN(CH_2)_4$, $dtp = S_2P(OCH_2)_2CMe^nPr$; **10**, $R_2 = C_8H_8$, $dtc = S_2CN(CH_2)_4$, $dtp = S_2P(OCH_2)_2CMe^nPr$; **11**, $R_2 = C_4H_8O$, $dtc = S_2CN(CH_2)_4$, $dtp = S_2P(OCH_2)_2CMe^nPr$. **1–11** were characterized by mass spectrometry, IR spectroscopy and multinuclear NMR (1H , ^{13}C , ^{31}P , ^{125}Te) spectroscopy. The molecular structures of **2**, **4** and **6**, of which **2** crystallized in form of two different polymorphs (**2a** and **2b**), were analyzed by single-crystal X-ray diffraction analysis. This analysis showed that the coordination mode of both ligand types is anisobidentate. When considering only covalent $Te-C$ and $Te-S$ bonds, the coordination geometry of the tellurium atoms is distorted Ψ -trigonal-bipyramidal, since the lone pair is stereochemically active and occupies an equatorial position together with the carbon atoms of the tellurocycles. If secondary $Te \cdots S$ interactions are considered also, the coordination sphere around tellurium is best described as bicapped Ψ -trigonal-bipyramidal for the complexes with two intramolecular $Te \cdots S$ secondary bonds and monomeric molecular structures, and pentagonal-bipyramidal for the complexes in which neighboring molecules in the crystal lattice are linked through additional weak intermolecular $Te \cdots S$ secondary bonds to form dimeric supramolecular aggregates.

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1. Introduction

Organotellurium(IV) fragments have been combined with a variety of 1,1-dithiolate ligands, and the resulting complexes exhibit a large structural diversity due to the strong tendency to form intra- and intermolecular secondary $Te \cdots S$ interactions, which in the second case give rise to supramolecular associations. With bidentate ligands the ligand bonding is usually anisobidentate (unsymmetrical bidentate) and, generally, the lone pair at the tellurium center is

stereochemically active [1]. So far, relatively few derivatives containing mixed ligands have been prepared [2–6], but it seems that the use of two different ligand types reduces the tendency for intermolecular association. We now report on the synthesis of eleven organotellurium(IV) compounds, in which the tellurium atom is bound to two different types of 1,1-dithiolates, one dtc and one dtp ligand. All compounds have been characterized by mass spectrometry, IR spectroscopy and NMR (1H , ^{13}C , ^{31}P , ^{125}Te) spectroscopy. Single-crystals suitable for X-ray diffraction analysis were obtained for three complexes, of which one crystallized in form of two different polymorphs from the same solution, and allowed to analyze the coordination geometry at the tellurium center and the supramolecular interactions with more detail.

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2. Experimental section

2.1. Instrumental

Mass spectra determinations were performed on a JEOL JMS-WSX 102A instrument by electron impact (EI) at 70 eV. IR spectra were recorded in the region of 4000–500 cm^{-1} as KBr pellets using a Bruker Vector 22 FT spectrophotometer. ^1H , ^{13}C , ^{31}P and ^{125}Te NMR spectra were recorded on Varian Gemini 200 and Varian Inova 400 equipments at room temperature in CDCl_3 . The chemical shifts are relative to internal Me_4Si (^1H and ^{13}C), external 85% H_3PO_4 (^{31}P) and 1,1-diiodotellurothane, $\text{C}_4\text{H}_8\text{TeI}_2$ (^{125}Te).

2.2. X-ray crystallography

X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$, monochromator: graphite). Frames were collected at $T = 293 \text{ K}$ (compounds **2a**, **2b** and **4**) and $T = 100 \text{ K}$ (compound **6**) via ω - and φ -rotation at 10 s per frame (SMART) [7a]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [7b]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [7c and d]. Non hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. For compound **6** only weakly diffracting crystals could be grown. The CH_2Cl_2 molecules in the crystal lattice of this compound are disordered over a crystallographic inversion center ($\text{occ} = 0.50$).

2.3. Preparative part

All reagents were of commercial grade and were used as received. The starting $\text{R}_2\text{Te}(\text{dtc})$ complexes and the sodium salts of the cyclic dithiophosphates were synthesized as reported previously [8–11]. For the preparation of compounds **1–11**, the monosubstituted diorganotellurium(IV) dithiocarbamates $\text{R}_2\text{Te}(\text{dtc})$ were dissolved in methanol (30 ml), whereupon the sodium salt of the corresponding dithiophosphate ligand was added in a 1:1 molar ratio. The solutions were stirred for 5 h (for **6–8**, **10** and **11**) or 24 h (for **1–5** and **9**). The residues obtained after evaporation to dryness were subsequently dissolved in dichloromethane. After filtration to separate NaI, the solutions were evaporated and the resulting solids recrystallized from a dichloromethane-*n*-hexane mixture.

2.4. $\text{C}_4\text{H}_8\text{Te}[\text{S}_2\text{CNET}_2][\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (**1**)

This compound was prepared in the form of a pale-yellow solid by reaction of $\text{C}_4\text{H}_8\text{Te}[\text{S}_2\text{CNET}_2]$ (0.350 g, 0.763 mmol) with $\text{Na}[\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (0.189 g, 0.763 mmol). M.p. 123–125 °C. Yield 0.333 g (82%). MS (EI, 70 eV) m/z 283 (CNPS_3Te^+ , 100%), 278 ($\text{C}_5\text{H}_{10}\text{NS}_2\text{Te}^+$, 5%), 186 ($\text{C}_4\text{H}_8\text{Te}^+$, <5%), 148 ($\text{S}_2\text{CNC}_4\text{H}_{10}$, 10%), 116 ($\text{C}_5\text{H}_{10}\text{NS}^+$, 65%). IR (KBr, cm^{-1}) ν 2968m, 2928m, 2874m, 1483m, 1452m, 1414m, 1353m 1270m, 1198w, 1137w, 1068m, 992s, 933m, 798s, 677s, 526 m. ^1H NMR (CDCl_3): δ 0.86 (t, 6H, CCH_2CH_3), 1.29 (t, 6H, NCH_2CH_3), 1.49 (q, 4H, CCH_2CH_3), 2.76 (bs, 4H, $\text{CH}_2\text{CH}_2\text{Te}$), 3.37 (t, 4H, $\text{CH}_2\text{CH}_2\text{Te}$), 3.86 (q, 4H, NCH_2CH_3), 4.12 (d, 4H, $^3J_{\text{P-H}} = 15.8 \text{ Hz}$, POCH_2). ^{13}C NMR (CDCl_3): δ 7.2 (s, CCH_2CH_3), 12.3 (s, NCH_2CH_3), 23.1 (s, CCH_2CH_3), 33.2 (s, $\text{CH}_2\text{CH}_2\text{Te}$), 37.4 (d, $^3J_{\text{C-P}} = 6.1 \text{ Hz}$, POCH_2C), 41.9 (s, $\text{CH}_2\text{CH}_2\text{Te}$), 49.2 (s, NCH_2CH_3), 72.8 (d, $^2J_{\text{C-P}} = 9.2 \text{ Hz}$, POCH_2), 193.9 (s, NCS_2). ^{31}P NMR (CDCl_3): δ 99.7 ($^3J_{\text{P-H}} = 15.8 \text{ Hz}$). ^{125}Te NMR (CDCl_3): δ 806.

2.5. $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{CNET}_2][\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (**2**)

This compound was prepared in the form of a pale-yellow solid by reaction of $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{CNET}_2]$ (0.250 g, 0.493 mmol) with $\text{Na}[\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (0.122 g, 0.493 mmol). Mp 150–152 °C. Yield 0.287 g (96%). Single-crystals suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into a solution of **2** in ethanol at room temperature. The crystalline sample contained crystals of different shape, which were separated manually. Single-crystal X-ray diffraction analysis showed that these solids were polymorphs. The crystals with the shape of elongated rectangular prisms correspond to compound **2a** and the block-shaped crystals to compound **2b**. Anal. Calc. for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{NPS}_4\text{Te}$: 39.70 C, 5.33 H, 2.31 N; found 39.44 C, 5.21 H y 2.27 N. MS (EI, 70 eV) m/z 278 ($\text{C}_5\text{H}_{10}\text{NS}_2\text{Te}^+$, <5%), 234 ($\text{C}_8\text{H}_8\text{Te}^+$, >10%), 225 ($\text{C}_7\text{H}_{14}\text{PO}_2\text{S}_2^+$, 5%), 148 ($\text{C}_5\text{H}_{10}\text{NS}_2^+$, >10%), 116 ($\text{C}_5\text{H}_{10}\text{NS}^+$, 100%). IR (KBr, cm^{-1}) 2969m, 2872w, 1489s, 1452m, 1422m, 1382w, 1272m, 1200m, 1140w, 1067m, 1067m, 991s, 929m, 795s, 679s, 523m. ^1H NMR (CDCl_3): δ 0.85 (t, 6H, CCH_2CH_3), 1.27 (t, 6H, NCH_2CH_3), 1.47 (q, 4H, CCH_2CH_3), 3.83 (q, 4H, NCH_2CH_3), 4.09 (d, 4H, $^3J_{\text{P-H}} = 16.2 \text{ Hz}$, POCH_2), 4.56 (d, 2H, $J_{\text{gem}} = 15.0 \text{ Hz}$, $\text{CH}_{\text{ec}}\text{Te}$), 4.66 (d, 2H, $J_{\text{gem}} = 15.0 \text{ Hz}$, $\text{CH}_{\text{ax}}\text{Te}$), 7.19 (m, 4H, aromatic). ^{13}C NMR (CDCl_3): δ 7.5 (s, CCH_2CH_3), 12.5 (s, NCH_2CH_3), 23.3 (s, CCH_2CH_3), 37.7 (d, $^3J_{\text{C-P}} = 4.6 \text{ Hz}$, POCH_2C), 45.7 (s, $\text{CH}_2\text{CH}_2\text{Te}$), 49.4 (s, NCH_2CH_3), 73.2 (d, $^2J_{\text{C-P}} = 9.2 \text{ Hz}$, POCH_2), 127.5 (s, $\text{C}\beta\text{CH}_2\text{Te}$), 130.1 (s, $\text{C}\gamma\text{CH}_2\text{Te}$), 139.5 (s, $\text{C}\alpha\text{CH}_2\text{Te}$), 194.5 (s, NCS_2). ^{31}P NMR (CDCl_3): δ 99.6 ($^3J_{\text{P-H}} = 15.8 \text{ Hz}$). ^{125}Te NMR (CDCl_3): δ 710.

2.6. $\text{C}_4\text{H}_8\text{OTe}[\text{S}_2\text{CNET}_2][\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (**3**)

This compound was prepared in the form of a pale-yellow solid by reaction of $\text{C}_4\text{H}_8\text{OTe}[\text{S}_2\text{CNET}_2]$ (0.200 g, 0.421 mmol) with $\text{Na}[\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (0.105 g, 0.421 mmol). Mp 140–143 °C. Yield 0.109 g (45%). MS (EI, 70 eV) m/z 225 ($\text{C}_7\text{H}_{14}\text{PO}_2\text{S}_2^+$, <15%), 202 ($\text{C}_4\text{H}_8\text{OTe}^+$, 5%), 148 ($\text{C}_5\text{H}_{10}\text{NS}_2^+$, <15%), 116 ($\text{C}_5\text{H}_{10}\text{NS}^+$, 100%). IR (KBr, cm^{-1}) 2970m, 2932m, 2872 w, 1486m, 1457m, 1421w, 1384w, 1272m, 1201w (ν C–N), 1140w, 1070m, 994s, 933m, 799s, 882w, 679s, 605w, 557w, 527m. ^1H NMR (CDCl_3): δ 0.88 (t, 6H, CCH_2CH_3), 1.31 (t, 6H, NCH_2CH_3), 1.54 (q, 4H, CCH_2CH_3), 3.25 (m, 4H, $\text{CH}_2\text{CH}_2\text{Te}$), 3.88 (q, 4H, NCH_2CH_3), 4.15 (d, 4H, $^3J_{\text{P-H}} = 15.8 \text{ Hz}$, POCH_2), 4.28 (m, 4H, $\text{OCH}_2\text{CH}_2\text{Te}$). ^{13}C NMR (CDCl_3): δ 7.5 (s, CCH_2CH_3), 12.6 (s, NCH_2CH_3), 23.3 (s, CCH_2CH_3), 28.5 (s, $\text{CH}_2\text{CH}_2\text{Te}$), 37.7 (d, $^3J_{\text{C-P}} = 6.1 \text{ Hz}$, POCH_2C), 49.4 (s, NCH_2CH_3), 66.2 (s, $\text{OCH}_2\text{CH}_2\text{Te}$), 73.3 (d, $^2J_{\text{C-P}} = 9.2 \text{ Hz}$, POCH_2), 193.7 (s, NCS_2). ^{31}P NMR (CDCl_3): δ 97.9 ($^3J_{\text{P-H}} = 15.8 \text{ Hz}$). ^{125}Te NMR (CDCl_3): δ 514.

2.7. $\text{C}_5\text{H}_{10}\text{Te}[\text{S}_2\text{CNET}_2][\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (**4**)

This compound was prepared in the form of a pale-yellow solid by reaction of $\text{C}_5\text{H}_{10}\text{Te}[\text{S}_2\text{CNET}_2]$ (0.200 g, 0.423 mmol) with $\text{Na}[\text{S}_2\text{P}(\text{OCH}_2)_2\text{CET}_2]$ (0.105 g, 0.423 mmol). Mp 133–135 °C. Yield 0.144 g (60%). Single-crystals suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into a solution of **4** in ethanol at room temperature. Anal. Calc. for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{NPS}_4\text{Te}$: 35.75 C, 5.95 H, 2.45 N; found 35.48 C, 5.98 H y 2.51 N. MS (EI, 70 eV) m/z 225 ($\text{C}_7\text{H}_{14}\text{PO}_2\text{S}_2^+$, 10%), 200 ($\text{C}_5\text{H}_{10}\text{Te}^+$, <30%), 148 ($\text{C}_5\text{H}_{10}\text{NS}_2^+$, 20%), 116 ($\text{C}_5\text{H}_{10}\text{NS}^+$, 100%). IR (KBr, cm^{-1}) 2969m, 2926m, 2873d, 1491m, 1455m, 1421m, 1383d, 1272m, 1201m, 1144d, 1068m, 994 f, 929m, 792 f, 679 f, 605d, 526m. ^1H NMR (CDCl_3): δ 0.87 (t, 6H, CCH_2CH_3), 1.31 (t, 6H, NCH_2CH_3), 1.50 (q, 4H, CCH_2CH_3), 1.78 (bs, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Te}$), 2.08 (bs, 2H, $\text{CH}_{\text{ec}}\text{CH}_2\text{Te}$), 2.27 (bs, 2H, $\text{CH}_{\text{ax}}\text{CH}_2\text{Te}$), 3.34 (t, 4H, CH_2Te), 3.88 (q, 4H, NCH_2CH_3), 4.13 (d, 4H, $^3J_{\text{P-H}} = 15.8 \text{ Hz}$, POCH_2). ^{13}C NMR (CDCl_3): δ 7.5 (s, CCH_2CH_3), 12.6 (s, NCH_2CH_3), 22.9 (s, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Te}$), 23.3 (s, CCH_2CH_3), 27.2 (s, $\text{CH}_2\text{CH}_2\text{Te}$), 31.6 (s, CH_2Te), 37.7 (d, $^3J_{\text{C-P}} = 5.4 \text{ Hz}$, POCH_2C), 49.4

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