End-on bonding of a Te_3^{2-} polytelluride chain to a transition-metal fragment: synthesis and structure of $[K(2,2,2\text{-crypt})]_2[Cr(CO)_5Te_3]\cdot 0.5C_2N_2H_8$ and $[K(2,2,2\text{-crypt})]_2[\{Cr(CO)_5\}_2Te_2]$

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The reaction of K_2Te_4 with different stoichiometries of $[Cr(CO)_6]$ and 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) in en (ethylenediamine) gives dark brown plates of $[K(2,2,2\text{-crypt})]_2[Cr(CO)_5Te_3]\cdot 0.5C_2N_2H_8$ and orange needles of $[K(2,2,2\text{-crypt})]_2[\{Cr(CO)_5\}_2Te_2]$ which are characterized by X-ray crystallography and IR spectroscopy.

The chemistry of compounds containing inorganic Zintl anions ligated to organometallic fragments has been expanding very rapidly in the last few years. Among these compounds are cagelike structures with homoatomic pnicogen anions ligated to transition-metal atoms as found in $[E_7Mo(CO)_3]^{3-}$,[1] mixed chalcogen–pnicogen clusters as in $[Mo(CO)_2(As_3Se_3)_2]^{2-}$ [2] or complexes with chalcogen chains chelating transition-metal centres.[3] The template synthesis of $[Cr(en)_3][Te_6]$,[4] a polytelluride with a framework structure, whose pores contain $[Cr(en)_3]^{3+}$ cations, raised questions concerning the reaction mechanism. In this context we were interested in the first reaction steps of the oxidative decarbonylation of $[Cr(CO)_6]$ in the presence of polytelluride solutions in en. In analogy to the synthesis of $[Cr(en)_3][Te_6]$, which was prepared from barium polytelluride and $[Cr(CO)_6]$ in en under solvothermal conditions we extended our investigations to the reactions of polytellurides with $[Cr(CO)_6]$ in en under ambient conditions.

Here we describe the synthesis† and characterization of $[K(2,2,2\text{-crypt})]_2[Cr(CO)_5Te_3]\cdot 0.5en$ **1** (2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) containing the $[Cr(CO)_5Te_3]^{2-}$ anion **2** and $[K(2,2,2\text{-crypt})]_2[\{Cr(CO)_5\}_2Te_2]$ **3** containing the $[\{Cr(CO)_5\}_2Te_2]^{2-}$ anion **4**. Both compounds were characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction.

The title compounds were obtained from reactions of solutions of K_2Te_4, $[Cr(CO)_6]$ and 2,2,2-crypt in en in different ratios. A $[Cr(CO)_6]:K_2Te_4$ ratio of 1 : 1 yields **1** whereas a reactant ratio of 4 : 1 yields **3**. A still greater excess of $[Cr(CO)_6]$ leads to the formation of the $[\{Cr(CO)_5\}_3Te]^{2-}$ anion.[5] Compound **1** can be prepared by the following procedure: K_2Te_4 (0.1176 g, 0.2 mmol) was dissolved in 10 ml of en. The solution was filtered and solid $[Cr(CO)_6]$ (0.044 g, 0.2 mmol) and 2,2,2-crypt (0.15 g, 0.4 mmol) were added. The reaction mixture was diluted with an additional 10 ml of en and stored at room temperature overnight. After slow evaporation of the solvent dark brown plates of $[K(2,2,2\text{-crypt})]_2[Cr(CO)_5Te_3]\cdot 0.5en$ were isolated (yield 49 mg, 18%). Compound **3** can be prepared in the following way: K_2Te_4 (0. 1176 g, 0.2 mmol) was dissolved in 10 ml of en. After addition of solid $[Cr(CO)]_6$ (0.176 g, 0.8 mmol) and 2,2,2-crypt (0.15 g, 0.4 mmol) the reaction mixture was diluted with 10 ml of en and stored at room temperature overnight. After solvent evaporation, orange needles of $[K(2,2,2\text{-crypt})]_2[\{Cr(CO)_5\}_2Te_2]$ were isolated (yield 191 mg, 65%).‡

The structure§ of **1** contains, in addition to **2** two crystallographically independent $[K(2,2,2\text{-crypt})]^+$ cations and one solvent molecule which loosely links two $[K(2,2,2\text{-crypt})]^+$ cations. The anion contains a $[Cr(CO)_5]$ fragment bonded to a Te_3^{2-} chain in an end-on fashion as shown in Fig. 1(*a*). To our knowledge, **2** is the first example of a complex containing an η^1-bonded Te_3^{2-} ligand. η^1-Bonded chalcogenide chains are very rare; in $[K(2,2,2\text{-crypt})]_2[Mo_4(Te_2)_5(Te_3)_2(en)_4]$,[6] $[K(2,2,2\text{-crypt})]_2[Fe_2Te_3(CO)_6]\cdot 0.5en$,[7] and $[Cp_2Cr_2(\mu\text{-}S_2)_2(\mu\text{-}S)]$[8] dichalcogenide groups are bonded to the metal in a μ_2-η^1 mode while $KAuSe_{13}$[9] represents the only example of a μ_1-η^1 bonded polychalcogenide chain. Here the polymeric structure is stabilized by electrostatic interactions between the terminal atoms of the Se_5^{2-} chains and the potassium cations. The structure of **2** is reminiscent of the structure of the $[Cr(CO)_4Te_4]^{2-}$ anion,[10] where a five-membered metallacycle is formed by the Te_4^{2-} chain and the metal centre of the

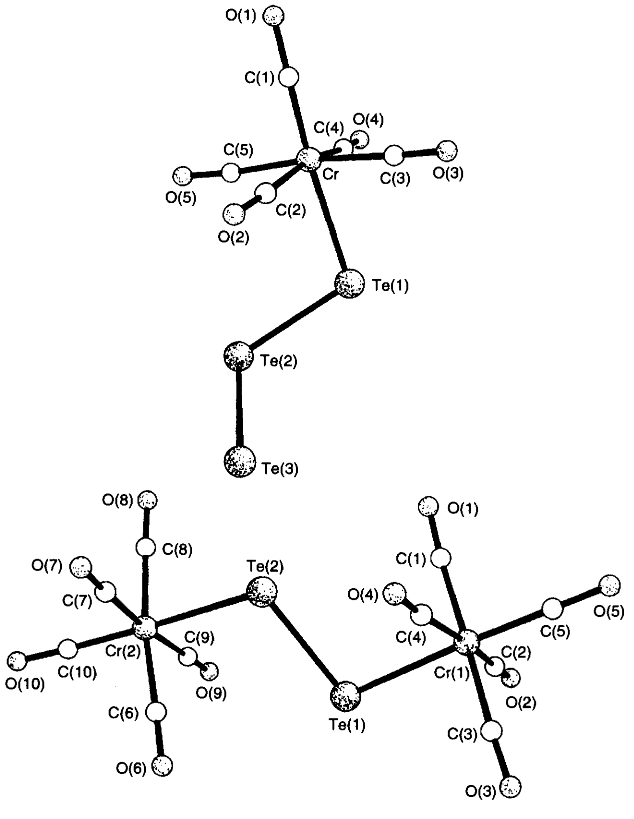

Fig. 1 (*a*) Structure of the anion of $[K(2,2,2\text{-crypt})]_2[Cr(CO)_5Te_3]\cdot 0.5en$ with atom labelling. Selected bond lengths (Å) and angles (°): Te(1)–Cr 2.754(5), Te(1)–Te(2) 2.728(3), Te(2)–Te(3) 2.690(3), Cr–C(mean) 1.831; Te(2)–Te(1)–Cr(1) 105.0(1), Te(1)–Te(2)–Te(3) 110.5(1). (*b*) Structure of the anion of $[K(2,2,2\text{-crypt})]_2[\{Cr(CO)_5\}_2Te_2]$ with atom labelling. Selected bond lengths (Å) and angles (°): Te(1)–Te(2) 2.736(1), Te(1)–Cr(1) 2.756(2), Te(2)–Cr(2) 2.722(2), Cr–C(mean) 1.859; Te(2)–Te(1)–Cr(1) 98.1(1), Te(1)–Te(2)–Cr(2) 105.8(1).

$[Cr(CO)_4]$ fragment. Although a few examples of smaller rings containing three-membered chalcogenide chains exist,[11] the ring closure in **2** remains incomplete, possibly due to steric demands of the puckered ring. Typically, ring formation of the trichalcogenide ligand is favoured compared to open-chain bonding as examples such as $[ME_3(\eta\text{-}C_5Me_5)]$[¶] (M = Ti, Zr, Hf; E = S, Se or Te) show. Ring formation in a hypothetical cyclo-$[Cr(CO)_4Te_3]^{2-}$ seems to be hindered by the mutually exclusive bonding requirements of the metal and tellurium atoms. Generally, smaller ME_n rings with $n \leqslant 3$ require bond angles smaller than 90° for the E–M–E angle.[13] Therefore the η^2-E_n complexes with octahedral coordination around the metal are only formed with $n \geqslant 4$. A d^6-ML_5 fragment like $[Cr(CO)_5]$ is isolobal with zerovalent Te[14] and so **2** and **4** can be viewed as organometallically substituted Te_4^{2-} chains or considering the isolobal series $Te \leftrightarrow CH_2 \leftrightarrow CH_3^+ \leftrightarrow Cr(CO)_5$ as organometallic butane analogues.

The structure[§] of **3** contains in addition to **4** one crystallographically independent $[K(2,2,2\text{-crypt})]^+$ cation showing no remarkable features. In **4**, shown in Fig. 1(*b*), two $[Cr(CO)_5]$ fragments are connected by a ditelluride group. Thus the structure of **4** is analogous to other organometallic η^2-dichalcogenide complexes[15] and diorganoditellurides.[16] The average Cr–Te distance in both compounds is 2.743 Å and is comparable to those found in other molecular chromium tellurides.[17]

Since tellurium can act as a π-donor ligand the *trans* Cr–C bonds in both compounds are shorter than the *cis* Cr–C bonds as observed in other substituted metal carbonyl chalcogenide complexes. In both **1** and **3** the terminal ligands $\{[Cr(CO)_5]$, or Te$\}$ are bonded in a *trans* conformation to the central ditelluride group. The influence of the lone pairs at the tellurium atoms is apparent from the chain conformation. Whereas the chain in **4** is nearly planar with a torsional angle of 2.7°, we observe a torsional angle of 64.4° in the structure of **2** due to the lone-pair repulsion of the tellurium atoms. Compound **2** can be viewed as the first member of a substitutional series of the Te_4^{2-} anion, where Te atoms are replaced by organometallic fragments, **4** being a second member of this series. Compound **4** can also be viewed as an intermediate in the formation of $[\{Cr(CO)_5\}_4Te_2]^{2-}$.[17a] On the other hand, **2** is a possible intermediate in the formation of the $[Cr(CO)_4Te_4]^{2-}$ anion,[17b] where a Te_4^{2-} chain is chelating a $[Cr(CO)_4]$ fragment with both terminal atoms. Interestingly, the reaction products of group 6 carbonyls with polytellurides in en are completely different from those obtained in other solvents such as dmf. This indicates that even seemingly simple substitution reactions of metal carbonyls are strongly solvent dependent.

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Footnotes

[†] All handling procedures were carried out under dry argon.

[‡] Satisfactory elemental analyses were obtained for **1** and **3**. IR, KBr pellet (cm^{-1}) for **1**: ν(CO): ν_E 1907s, ν_{A1} 2029m; IR, KBr pellet (cm^{-1}) for **3**: ν(CO): ν_E 1927s, ν_{A1} 2031m.

[§] *Crystal data*: *for* **1**; $C_{42}H_{74}CrK_2N_4O_{17}Te_3$, M = 1436.1, monoclinic, space group $P2_1/n$ (no. 14), a = 14.800(3), b = 21.452(4), c = 18.564(4) Å, β = 92.76(3)°, U = 7588.7(2) Å^3, D_c = 1.620 g cm^{-3}, μ(Mo-Kα) = 1.858 mm^{-1}, Z = 4, $F(000)$ = 2868, T = 183 K. 8144 unique data were collected using a Siemens P4 four-circle diffractometer, Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures.[18] Final R = 0.060 and R_w = 0.039 for 2317 observations with $I \geqslant 2\sigma(I)$ (all Te, Cr, and K atoms were refined anisotropically and all C, N and O atoms isotropically).

For **2**; $C_{46}H_{72}Cr_2K_2N_4O_{22}Te_2$, M = 1466.5, monoclinic, space group $P2_1/n$ (no. 14), a = 15.371(5), b = 21.010(6), c = 19.259(5) Å, β = 90.37(3)°, U = 7621.9(3) Å^3, D_c = 1.566 g cm^{-3}, μ(Mo-Kα) = 1.475 mm^{-1}, Z = 4, $F(000)$ = 2960, T = 183 K. 13402 unique data were collected using a Siemens P4 four-circle diffractometer, Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures.[18] Final R = 0.048 and R_w = 0.040 for 6583 observations with $I \geqslant 2\sigma(I)$ (all Te, Cr, K, O, N and the C atoms of the cryptands refined anisotropically and the C and O atoms of the carbonyl groups isotropically). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/124.

[¶] Interestingly, substitution of η-C_5Me_5 ligands by the less bulky C_5H_5 groups leads to the formation of $TiE_5(\eta\text{-}C_5H_5)$ complexes with six-membered TiE_5 rings. Even with excess sulfur the reaction of $TiCl_2(\eta\text{-}C_5Me_5)$ with polysulfide yields only the four-membered ring; see ref. 12.

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