Telluride Alkylation and Formation of Novel Metal Carbonyl Polytelluride Clusters in Superheated Alcohols. Isolation of the Complexes $[M_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$ (M = Fe, Ru)

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Metal carbonyl polychalcogenide anions display unusual structures and interesting reactivity patterns.[1−3] Several approaches using a variety of chalcogen sources have been used for the synthesis of these compounds.[4−7] Some examples of clusters made by solution routes are $[Fe_3Se(CO)_9]^{2-}$,[4] $[Fe_3Te(CO)_{12}]^{2-}$,[4] $[Fe_8Te_{10}(CO)_{20}]^{2-}$,[2] $[Fe_8Te_6(CO)_{24}]^{2-}$,[5] $[Fe_2Te_3(CO)_6]^{2-}$,[6] and $[W_6Te_8(CO)_{18}]^{2-}$.[7] A novel development in this area has been the emergence of the hydro(solvo)thermal technique as a successful, straightforward route to these carbonyl compounds.[8] This technique often leads to highly pure, crystalline products in excellent yield. We showed previously that, under hydrothermal conditions, polytelluride anions oxidatively decarbonylate both $Fe(CO)_5$[8a] and $Ru_3(CO)_{12}$[8b] and form the interesting multinuclear cluster anions $[Fe_8Te_{10}(CO)_{20}]^{2-}$ and $[Ru_6Te_{14}(CO)_{12}]^{2-}$ crystallized in pure form as their Ph_4P^+ salts. These promising results which were obtained with water as the solvent led us to explore possible solvent effects on the outcome of these reactions. Herein we report preliminary results on methanothermal reactions between $M_3(CO)_{12}$ (M = Fe, Ru) and Na_2Te_2 which lead to the novel clusters $[M_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$. These complexes feature an interesting but unanticipated solvent-derived methylation of Te^{2-} ions and demonstrate a dramatic influence of the solvent on this chemistry.

Using a small volume of methanol as the solvent, the cluster compound $(Me_4N)_2[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**1**) is made at 110 °C by reacting $Fe_3(CO)_{12}$ with Na_2Te_2 and Me_4NBr in a 1:5:6 molar ratio in a sealed Pyrex tube.[9] The compound $(Ph_4P)_2[Ru_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**2**) forms similarly at 80−130 °C from $Ru_3(CO)_{12}$, Na_2Te_2, and Ph_4PBr.[10] The anions in both compounds have the same structure;[11] see Figure 1. The structures consist of a planar M_4 rectangle with an inversion center in the midst. The shorter arms of the rectangle are bridged by μ_2-Te^{2-} ligands while the longer ones are bridged by two μ_2-$TeMe^-$ ligands. Then two ditelluride ligands, one above and the other below the M_4 rectangle, bridge all four metal atoms in a μ_2,μ_2-η^1,η^1 fashion. All transition metal atoms in these molecules feature an octahedral coordination. The idealized symmetry of this cluster is D_{2h}. Both anions have normal M−Te as well as Te−Te (Te_2^{2-}) distances. The structural motif of the anions in **1** and **2** can be thought of as originating from the fusion of two $[Fe_2Te_3(CO)_6]^{2-}$ anions.[6] In $[Fe_2Te_3(CO)_6]^{2-}$ the metal atoms are held together by μ_2-Te^- and μ_2,η^1-Te_2^{2-} ligands. The two dimeric anions approach each other in a centrosymmetric fashion so that the dangling tellurium atom belonging to the ditelluride ligand of one $[Fe_2Te_3(CO)_6]^{2-}$ anion forms two new Fe−Te bonds with the Fe atoms of the other anion transforming the ditelluride to a μ_2,μ_2-η^1,η^1-Te_2^{2-} ligand. A carbonyl ligand on each of the metal atoms of $[Fe_2Te_3(CO)_6]^{2-}$ may now be putatively assumed to have been replaced by incoming μ_2,η^1-$TeMe^-$ ligands. The above proposal is reasonable because we do isolate $(Ph_4P)_2[Fe_2Te_3(CO)_6]$ in the early stages of these reactions.[12] In fact, $(Ph_4P)_2[Fe_2Te_3(CO)_6]$ converts to $(Ph_4P)_2[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**3**), a compound containing the same anion as **1**, upon heating in MeOH with Na_2Te_2 at 110 °C, suggesting that it is an intermediate in the formation of the tetramers.

There are several unusually short Te···Te contacts between the Te^{2-} and Te_2^{2-} ligands inside the "$M_4(Te_2)_2(Te)_2(TeMe)_2$" core. The relatively short Te(2)−Te(3) distance of 3.282(1) Å in **1** and the Te(3)−Te(4) as well as Te(2)′−Te(4) distances of 3.394(1) and 3.418(1) Å, respectively, in **2** are significantly shorter than the corresponding van der Waals distance of ~4 Å. Although the Te···Te distances are considerably longer than the ~2.8 Å distance of a normal Te−Te single bond, weak bonding interactions may exist in these molecules. However, there is no consensus on what is considered a bond when it comes to such Te···Te contacts. A similar Te−Te separation of 3.23(2) Å in the $[Fe_2Te_3(CO)_6]^{2-}$ anion was considered to be nonbonding,[6] but a Te−Te separation of 3.261(1) Å in Fe$_2$-

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(9) A mixture of $Fe_3(CO)_{12}$ (50 mg, 0.1 mmol), Na_2Te_2 (150 mg, 0.5 mmol), and Me_4NBr (90 mg, 0.6 mmol) was loaded into a Pyrex tube containing 0.5 mL of MeOH. The tube (~4 mL inner volume) was flame-sealed under vacuum and heated at 110 °C for 12 h. The contents of the tube were filtered and the solid was washed first with methanol and then with water, followed by methanol and diethyl ether to obtain 94 mg of dark green crystals of $(Me_4N)_2[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**1**). Yield: 77% based on Fe. IR data: (a) (ν_{CO}, KBr pellet) 1942 (s), 1905 (s), 1872 (sh) cm^{-1}; (b) (ν_{CO}, DMF solution, NaCl cell) 1971 (w), 1941 (m), 1908 (s), 1877 (sh) cm^{-1}. ^1H NMR (in DMSO-d_6; δ, ppm): 2.2 (s, 1H), 3.1 (s, 4H).

(10) A mixture of $Ru_3(CO)_{12}$ (32 mg, 0.05 mmol), Na_2Te_2 (75 mg, 0.25 mmol), and Ph_4PBr (125 mg, 0.3 mmol) was loaded into a Pyrex tube containing 0.5 mL of MeOH. The tube (~4 mL inner volume) was flame-sealed under vacuum and was heated at 80 °C for 8 h. The product was washed with methanol and diethyl ether to obtain 140 mg of dark brown material of $(Ph_4P)_2[Ru_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**2**). Yield: 79% based on Ru. IR data: (a) (ν_{CO}, KBr pellet) 1981 (s), 1970 (sh), 1920 (sh), 1914 (s) cm^{-1}; (b) (ν_{CO}, DMF solution) 1983 (s), 1928 (s) cm^{-1}. ^1H NMR (in DMSO-d_6; δ, ppm) 1.8 (s, 1H), 7.5−8.0 (m, 8H). Single crystals were obtained from an analogous reaction carried out at 130 °C.

(11) (a) Crystal data for $(Me_4N)_2[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**1**): monoclinic $C2/m$, $Z = 2$, $a = 18.770(3)$ Å, $b = 12.188(3)$ Å, $c = 9.299(2)$ Å, $\beta = 114.87(2)°$, $V = 1930(1)$ Å^3, temperature = 20 °C, $2\theta_{max}$(Mo Kα) = 55°, $d_{calc} = 2.833$ g/cm^3. Out of 2325 independent reflections measured, 1923 with $F_o^2 > 3\sigma(F_o^2)$ were used for the solution and refinement of the structure. The number of variables refined was 99. $\mu = 74.59$ cm^{-1}. Minimum and maximum absorption corrections were 0.97 and 1.05, respectively. Final $R = 3.0\%$ and $R_w = 3.7\%$. (b) Crystal data for $(Ph_4P)_2[Ru_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**2**): monoclinic $P2_1/n$, $Z = 2$, $a = 11.753(4)$ Å, $b = 18.202(6)$ Å, $c = 15.515(3)$ Å, $\beta = 95.16(2)°$, $V = 3306(1)$ Å^3, temperature = −96 °C, $2\theta_{max}$(Mo K$_\alpha$) = 45°, $d_{calc} = 2.369$ g/cm^3. Out of the 4489 independent reflections measured, 3449 with $F_o^2 > 3\sigma(F_o^2)$ were used. The number of variables refined was 241. The structure was solved and refined as in **1**. The data were corrected for absorption with DIFABS; $\mu = 44.47$ cm^{-1}. Minimum and maximum absorption corrections were 0.79 and 1.27, respectively. Final $R = 4.6\%$, $R_w = 5.7\%$. A graphite beam monochomator was used in all cases. A $\theta/2\theta$ scan technique was used. Octants collected: $h,k,\pm l$. Other structure solution details and related information regarding data collection can be found elswhere; see ref 8a.

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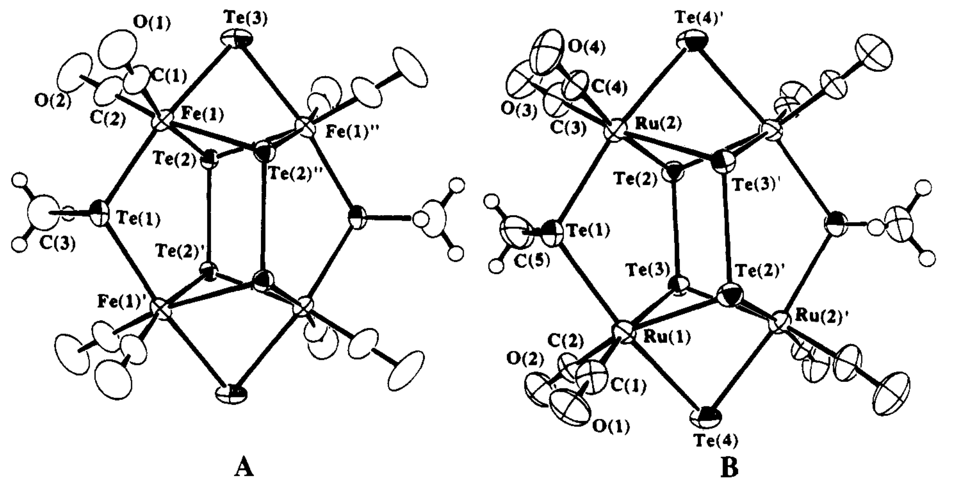

Figure 1. (A) View of $[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$ (**1**). Selected bond distances (Å) and angles (deg): Fe1(1)−Te(1) = 2.580(1), Fe(1)−Te(2) = 2.607(1), Fe(1)−Te(3) = 2.650(1), Fe(1)−C(1) = 1.744(7), Fe(1)−C(2) = 1.726(7), Te(2)−Te(2)′ = 2.818(1), Te(2)···Te(3) = 3.282(1), Te(1)−C(3) = 2.16(1), Fe(1)···Fe(1)′ = 4.329(2), Fe(1)··· Fe(1)′ = 3.482(2); Te(1)−Fe(1)−Te(2) = 96.55(3), Te(1)−Fe(1)−Te(3) = 171.87(4), Te(2)−Fe(1)−Te(2)′ = 86.56(3), Te(2)−Fe(1)−Te(3) = 77.27(3), C(1)−Fe(1)−C(2) = 93.4(3), Fe(1)−Te(1)−Fe(1)′ = 114.07(4), Fe(1)−Te(3)−Fe(1)′ = 82.15(4). (B) View of $[Ru_4(Te_2)_2(Te)_2(TeMe)_2\text{-}(CO)_8]^{2-}$ (**2**). Selected bond distances (Å) and angles (deg): Ru(1)−Te(1) = 2.676(1), Ru(1)−Te(2)′ = 2.724(2), Ru(1)−Te(3) = 2.729(1), Ru(1)−Te(4) = 2.710(1), Ru(2)−Te(1) = 2.679(1), Ru(2)−Te(2) = 2.722(2), Ru(2)−Te(3)′ = 2.727(2), Ru(2)−Te(4)′ = 2.725(1), Ru−C = 1.87(1), Te(2)−Te(3) = 2.807(1), Te(3)···Te(4) = 3.394(1), Te(2)′···Te(4) = 3.418(1), Te(1)−C(5) = 2.14(2), Ru(1)···Ru(2) = 4.460(2), Ru(1)···Ru(2)′ = 3.630(2), Te(3)−Ru(1)−Te(2)′ = 85.64(4), Te(1)−Ru(1)−Te(4) = 171.26(5), C(1)−Ru(1)−C(2) = 94.0(6), C(3)−Ru(2)−C(4) = 89.7(6), Ru(1)−Te(1)−Ru(2) = 113.54(4), Ru(1)−Te(4)−Ru(2)′ = 83.83(4).

$(CO)_6(TeMe)_2$ was also judged well outside the normal bonding range.[13] An analogous distance, however, of 3.1 Å in CuTe was shown by theoretical calculations to be bonding with a bond order 0.5.[14] Theoretical studies on Te···Te contacts present in the family MTe_2 (M = Nb, Ta, Rh, Co, Ni, Pd, Pt) similar in magnitude to the ones found in our compound were shown to be definitely bonding.[15] We agree with the conclusions of these studies and believe the same bonding interactions exist in **1**. The inclination for bonding is probably electronic in nature, as limited electron transfer from the electron-rich Te_x^{2-} ligands to the electron-withdrawing CO ligands (mediated by metal) results in partial oxidation and tendency to catenate.

The surprising result in this work is the methylation of the Te^{2-} anion which gives rise to the $Me-Te^-$ ligands. Hydrothermal reactions of $Fe(CO)_5$ as well as $Ru_3(CO)_{12}$ with Na_2Te_2 in the presence of organic countercations do not lead to such methylated species.[8] Similarly, a hydrothermal reaction between $Fe_3(CO)_{12}$ and Na_2Te_2, under the same conditions that provide $[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$ in MeOH, yields $[Fe_6(Te_2)_7(CO)_{12}]^{2-}$, which is isostructural[16] with $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$.[8b] The methyl groups most likely come from methanol which was used as the solvent and not from CO or the organic counterion. This is strongly supported by the isolation of $(Ph_4P)_2[Fe_4(Te_2)_2(Te)_2(TeEt)_2(CO)_8]$ (**4**)[17] as the product when the reaction is carried out in ethanol and also by the fact that neither **1** nor **2** can be made in the absence of methanol.

These air-sensitive, solids slowly turn yellow in air. Both **1** and **2** are moderately soluble in acetone, acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), giving yellowish green and orange-brown solutions, respectively. DMF solutions of **1** show an absorption maximum at 580 nm (ϵ, 5470 M^{-1} cm^{-1}) in its UV−vis spectrum. The spectrum for **2** in DMF is featureless. The solid state IR spectrum for **1** (KBr disc) in the carbonyl region appears as a doublet (at 1942 and 1905 cm^{-1}), as expected. The spectrum for **2** is similar, though each of the bands appears to be split, probably due to the presence of two crystallographically independent Ru(II) centers in the solid state. Similar features are observed for **3** also. In DMF solution, the IR spectrum in the carbonyl stretching vibration region of **2** appears as two bands of equal intensity (at 1983 and 1928 cm^{-1}), but the corresponding spectrum of **1** gives rise to three bands at 1971, 1941 and 1908 cm^{-1}. Reprecipitation by addition of ether yields solids with IR spectra different from those of the starting compounds **1** and **2**, which suggests that neither cluster remains intact in solution. The ^{125}Te NMR spectrum[18] for **1** supports this view, showing four singlets at 351, −519, −657, and −795 ppm, instead of the three signals which are expected on the basis of the cluster structure.

The alkylation of telluride ions, under the conditions described here, adds a new dimension to the already interesting approach of applying solvothermal conditions to oxidative decarbonylation. The clean and reproducible nature of such reactions should lead to interesting new mixed-ligand metal/Te/RTe clusters that may be inaccessible by other means. Recent results on the Mn and Re systems show that this is indeed the case.[19] Further work on the characterization of the species present in solution and the identification of new clusters formed under solvothermal conditions in the $M_3(CO)_{12}/Te_x^{2-}$ system is in progress.

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Supplementary Material Available: Tables of crystal structure analysis, atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all non-hydrogen atoms, and bond distances and angles for $(Me_4N)_2[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**1**) and $(Ph_4P)_2[Ru_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]$ (**2**), Fourier transform IR spectra (solid state and solution) for **1** and **2**, and ^{125}Te NMR spectra for **1** (16 pages). Ordering information is given on any current masthead page.

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(17) $(Ph_4P)_2[Fe_4(Te_2)_2(Te)_2(TeEt)_2(CO)_8]$ (**4**): a = 13.010(5)Å, b = 13.647(4)Å, c = 11.466(5)Å, α = 114.79(3)°, β = 112.29(3)°, γ = 80.57(3)°, V = 1710(1) Å^3; $P\bar{1}$ (No. 2). Final R = 4.5%, R_w = 5.3%.

(18) Recorded in DMSO-d_6 and referenced to δ = 1237 ppm for $TeCl_4$ in D_2O/HCl.

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