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An Unusual Mixed Tellurium–Iron Carbonylate: Synthesis, Structure, and Reactivity of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$

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The coordination chemistry of chalcogen-containing complexes is currently receiving considerable attention since chalcogenide-rich metal compounds exhibit unusual structural and reactivity patterns.[1,2] Of the mixed tellurium–iron complexes, $Te_2Fe_3(CO)_9$ and $Te_2Fe_2(CO)_6$ have been used as good starting materials for the preparation of mixed metal clusters.[3,4] $Te_2Fe_3(CO)_9$ was first reported by Hieber and Gruber from the reaction of TeO_3^{2-} with basic iron carbonyl solution followed by acidification,[5] and $Te_2Fe_2(CO)_6$ was later isolated as a minor product by Rauchfuss and co-workers.[6] Although some mechanistic information for the formation of $Te_2Fe_3(CO)_9$ and $Te_2Fe_2(CO)_6$ was proposed,[6] the anionic intermediate species in the reaction remained unknown, which plagued the understanding of the chemical transformations of this system. Here we report the isolation and characterization of a highly unusual tellurium–iron carbonylate, $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ (**1**), as the intermediate in the reaction. This molecule illustrates interesting bonding patterns and aids in understanding the formation and chemical transformations of $Te_2Fe_2(CO)_6$ and $Te_2Fe_3(CO)_9$.

The reaction of K_2TeO_3 with $Fe(CO)_5$/KOH in methanol forms deep red solutions whose infrared data indicate the existence of an anionic carbonyl species.[7] The unstable species decomposes slowly in solution and can be isolated as the $[PhCH_2NMe_3]^+$ salt (**1**). On the basis of analyses, spectroscopic data, and X-ray analysis, **1** is shown to be $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$.[8,9] The core geometry of **1** can be viewed as two $Te_2Fe_3(CO)_9$ clusters asymmetrically attached each to the two Te atoms of the anion $[Te_2Fe_2(CO)_6]^{2-}$, in which Te(1) and Te(1)′ are nonbonded ($d_{Te-Te} = 3.267(2)$ Å). The dianion of **1** is located on the crystallographic 2-fold axis which passes through the centers of Fe(1)–Fe(1)′ and Te(1)–Te(1)′, respectively. The ORTEP diagram of the dianion of **1** is shown in Figure 1. An X-ray diffraction study of crystals of a minor product showed it to be the recently reported $[Te_4Fe_5(CO)_{14}]^{2-}$.[10]

In **1**, the Te(2)–Te(3) distance of 3.123(2) Å is within the known range of 3.06–3.14 Å for significant Te–Te bonding interaction[11] and is comparable to those in other related clusters such as $Cp_2Mo_2FeTe_2(CO)_7$ (3.142 Å),[11] $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe$-

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(7) IR (ν_{CO}, MeOH): 2026 s, 2004 vs, 1956 m (br) cm^{-1}.

(8) To a solution of 10.00 g (36.79 mmol) of $K_2TeO_3 \cdot H_2O$ in 50 mL of deionized H_2O was added a solution prepared from 1.33 mL (9.98 mmol) of $Fe(CO)_5$, 3.33 mL of 50% aqueous KOH, and 10 mL of MeOH. After being stirred for 2 h at room temperature, the solution was filtered and an aqueous solution of 6.83 g (36.79 mmol) of $[PhCH_2NMe_3]Cl$ added dropwise, precipitating the dark red product. This was collected by filtration, washed with H_2O, and dried under vacuum. Recrystallization from CH_2Cl_2 gave 2.6 g (19.4% based on Te) of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ (**1**). IR (ν_{CO}, CH_2Cl_2) for **1**: 2026 s, 2004 vs, 1956 m (br) cm^{-1}. Anal. Calcd (found) for **1**: C, 23.52 (24.12); H, 1.55 (1.47); N, 1.19 (1.28). Crystals were grown from CH_2Cl_2 solution.

(9) X-ray crystal data for **1**: $Te_6Fe_8C_{44}H_{32}O_{24}N_2$, fw = 2185.12, monoclinic, $C2/c$ (No. 15), $a = 20.694(7)$ Å, $b = 14.649(4)$ Å, $c = 22.813(7)$ Å, $\beta = 101.45(3)°$, $V = 6778(4)$ Å^3, $Z = 4$, $2\theta_{max} = 45°$, $T = 25$ °C, $R = 0.050$, $R_w = 0.060$ for $I > 2\sigma(I)$, Nonius (CAD-4), Mo Kα radiation. All data reduction and structural refinement were performed using the NRCC-SDP-VAX packages.

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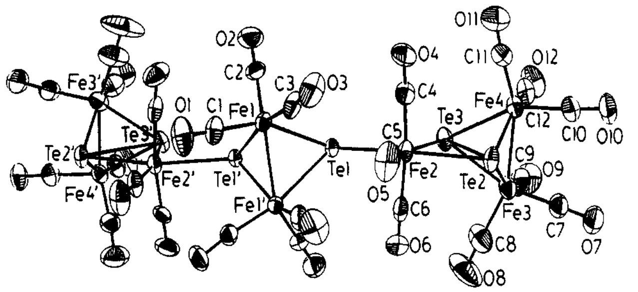

Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion of **1**. Selected bond distances (Å) and angles (deg): Te(1)-Te(1)' = 3.267(2), Te(1)-Fe(1) = 2.552(3), Te(1)-Fe(1)' = 2.583(3), Te(1)-Fe(2) = 2.637(3), Te(2)-Te(3) = 3.123(2), Te(2)-Fe(2) = 2.633(3), Te(2)-Fe(3) = 2.563(3), Te(2)-Fe(4) = 2.564(3), Te(3)-Fe(2) = 2.639(3), Te(3)-Fe(3) = 2.572(3), Te(3)-Fe(4) = 2.569(3), Fe(3)-Fe(4) = 2.577(4), Fe(1)-Fe(1)' = 2.625(5); Te(1)-Fe(1)-Te(1)' = 79.02(8), Te(2)-Fe(4)-Te(3) = 74.96(8), Te(1)-Fe(2)-Te(2) = 162.92(11), Te(1)-Fe(2)-Te(3) = 91.08(8), Te(2)-Fe(2)-Te(3) = 72.67(7), Te(2)-Fe(3)-Te(3) = 74.94(9).

$(CO)_3PPh_3$ (3.14 Å),[12] and $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$ (3.114 Å).[13] On the basis of the structural feature, the hypervalency of Te(2) and Te(3) atoms in **1** is evident. It is reminiscent of the bonding situation observed in the above-mentioned compounds.

The Te_2Fe_2 skeletons of **1** are similar to the class of compounds of the general formula $E_2Fe_2(CO)_6$ (E = S, Se).[14,15] The average Fe–Fe bond and Te–Fe bond in **1** are normal.[11] In **1**, the Te(1)–Fe(1)–Te(1)′ angle in the central open-tetrahedron is 79.02° and the Te(3)–Fe(4)–Te(2) and Te(3)–Fe(3)–Te(2) angles in the terminal tetrahedron average 74.95°. These angles are much larger than E–Fe–E angles in the *closo*-tetrahedral $E_2Fe_2(CO)_6$ (E = S, Se; 53.53°, 58.05°) and are close to the 75° found in $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$, 75° in $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe(CO)_3PPh_3$, and 79° in $Fe_2Te_2(CO)_6Ru_3(CO)_{11}$,[4a] which is consistent with some degree of opening of the $TeFe_2Te$ "tetrahedron" to accumulate the iron carbonyl groups.

Treatment of **1** with the mild oxidant $[Cu(CH_3CN)_4]BF_4$ or dilute HCl produces $Te_2Fe_3(CO)_9$ as a major product in good yield.[16] Conversely, the reduction of $Te_2Fe_3(CO)_9$ with 2 molar equiv of $CoCp_2$ yields the anion of **1**.[17] Compound **1** can be converted slowly to the cluster anion $[Te_4Fe_5(CO)_{14}]^{2-}$ in MeOH/CH_2Cl_2 solution by loss of $Te_2Fe_2(CO)_6$ and iron carbonyl groups. Interestingly, we found that **1** could react with refluxing CH_2Cl_2 to form the previously reported complex[18] $Fe_2(CO)_6(\mu\text{-}TeCH_2\text{-}Te)$.[13] The oxidative addition across Te–Te bonds in compound **1** may explain the formation of this methylene-bridged complex due to the TeFeTe strain. This is similar to that found in the methylenation of $Te_2Fe_2(CO)_6$.[13b]

It is well known that $Te_2Fe_3(CO)_9$ can add ligands to the $Fe(CO)_3$ fragment bridging the Te–Te bond in $Te_2Fe_2(CO)_6$ clusters.[12] The oxidation of **1** is therefore believed to proceed via Te–Te and Fe–Fe bond formation and Te–Fe bond breakage to give $Te_2Fe_3(CO)_9$ and $Te_2Fe_2(CO)_6$.

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Supplementary Material Available: A complete listing of crystallographic data, atomic positional parameters, table of bond distances and angles, and anisotropic thermal parameters for **1** (7 pages). Ordering information is given on any current masthead page.

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(16) To a solution of 2.6 g (1.19 mmol) of **1** in 60 mL of CH_2Cl_2 was added 3.63 g (11.56 mmol) of $[Cu(CH_3CN)_4]BF_4$. The mixed solution was allowed to stir at room temperature overnight, and the solution was filtered and the solvent removed under vacuum. The residue was then extracted into several portions of 20 mL of hexane, and the extracts were chromatographed to give 1.27 g (1.88 mmol) of $Te_2Fe_3(CO)_9$ (53% based on Te) and very small amount of $Te_2Fe_2(CO)_6$.

(17) To a mixture of 0.5 g (0.74 mmol) of $Te_2Fe_3(CO)_9$ and 0.3 g (1.6 mmol) of $CoCp_2$ was added 50 mL of THF. The solution was allowed to stir at room temperature for 7 days. The infrared spectrum of the THF solution showed IR bands corresponding to $[Te_6Fe_8(CO)_{24}]^{2-}$. The following workup gave 0.2 g (0.088 mmol) of $[CoCp_2]_2[Te_6Fe_8(CO)_{24}]$ (35% based on Te).

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