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Isolation and Characterization of $Fe_2(\mu\text{-}Te_2)(CO)_6$ and Its Conversion to $Fe_3(\mu_3\text{-}Te)_2(CO)_x$ (x = 9, 10)

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Using a modified version of the original synthesis for $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ (**1**), we have isolated $Fe_2(\mu\text{-}Te_2)(CO)_6$ (**2**), a molecular complex of Te_2. Compound **2** is a thermally labile compound which was isolated by gel permeation chromatography and characterized by IR, mass spectrometry, and ^{125}Te NMR. In the presence of base or Me_3NO, **2** reacts with $Fe(CO)_5$ to afford **1**. In the base-promoted reaction $Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$ (**3**) was also isolated and shown to be an intermediate in the Hieber synthesis. The unusual reactivity of these tellurium compounds is most likely due to the strain inherent in small closed clusters that contain large nonmetal atoms.

Introduction

The coordination chemistry of the dichalcogenides E_2 (E = S, Se) is currently receiving considerable attention since chalcogenide-rich metal complexes exhibit unusual structural and reactivity patterns. As a result of recent work, complexes of the S_2 ligand are now relatively common.[1] Fewer diselenium compounds are known, and with few exceptions (vide infra) they are all prepared via the oxidative addition of $c\text{-}Se_8$ with low-valent group 8 metal complexes.[2] There also exist several tetra- and pentasulfide and -selenide derivatives of the transition metals.[3] However, no examples of discrete metal complexes that contain a Te_x ($x > 1$) ligand are known.[4]

The reaction of the oxyanions of sulfur(IV), selenium(IV), and tellurium(IV) with basic iron carbonyl solutions was reported in 1958 to afford both $Fe_2(\mu\text{-}E_2)(CO)_6$ (E = S, Se) and $Fe_3(\mu_3\text{-}E)_2(CO)_9$ (E = S, Se, Te).[5] In the case of sulfur and selenium compounds, the di- and triiron derivatives can be effectively separated by fractional sublimation. The formulation of these compounds as ($\mu\text{-}E_2$) or $(\mu_3\text{-}E)_3$ emphasizes the presence or absence of a direct chalcogenide bonding interaction as substantiated crystallographically by Dahl and coworkers.[6] The synthetic route of Hieber and Gruber distinguishes itself in assembling the dichalcogenide ligands from monochalcogenide precursors, an important consideration in the present case. We have reexamined this reaction where E = Te and have succeeded in isolating a diiron complex of the elusive Te_2 molecule.[7] In addition to demonstrating the existence of the title complex, this project has resulted in the implementation of some novel techniques of somewhat greater generality and the elucidation of selected mechanistic features of the synthesis developed by Hieber and Gruber.

Scheme I

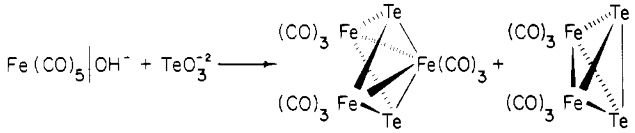

Table I. Infrared Spectroscopic Data (Cyclohexane Solution), cm^{-1}

$Fe_2(\mu\text{-}S_2)(CO)_6$	2085, 2045, 2008
$Fe_2(\mu\text{-}Se_2)(CO)_6$	2078, 2038, 2002
$Fe_2(\mu\text{-}Te_2)(CO)_6$	2067, 2028, 1995
$Fe_3(\mu_3\text{-}S)_2(CO)_9$	2062, 2045, 2024
$Fe_3(\mu_3\text{-}Se)_2(CO)_9$	2057, 2038, 2017
$Fe_3(\mu_3\text{-}Te)_2(CO)_9$	2045, 2025, 2004
$Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$	2104, 2054, 2049, 2038 2019, 1994, 1984, 1972

Results and Discussion

Using the method reported by Hieber and Gruber, treatment of a basic solution of $Fe(CO)_5$ with K_2TeO_3 gave a black mixture composed primarily of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ (**1**) and $FeTe_x$.[5] Sublimation of the crude product afforded a very small amount of black film, whose IR spectrum was consistent with its being an approximately equimolar mixture of **1** and $Fe_2(\mu\text{-}Te_2)(CO)_6$ (**2**) (Scheme I). Inasmuch as this purification process was very inefficient, we attempted the separation of **1** from **2** using adsorption chromatography but with no success. The behavior of our impure sample clearly indicated that **2** was a very labile compound, and this consideration precluded most conventional purification methods. We solved our problem by resorting to nonaqueous gel permeation

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(4) The Te_2^{2-} moiety is known to function as an η^1-ligand in the solid state for compounds of the formula MTe_2 which possess the pyrite and marcasite structures: Vaughan, D. J.; Craig, R. C. "Mineral Chemistry of Metal Sulfides"; Cambridge University Press: Cambridge, 1978.

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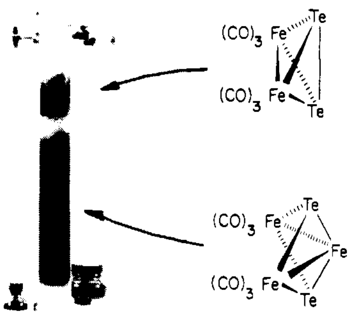


Figure 1. Separation of $Fe_2(\mu\text{-}Te_2)(CO)_6$ (top) and $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ on 8% cross-linked polystyrene gel (bottom).

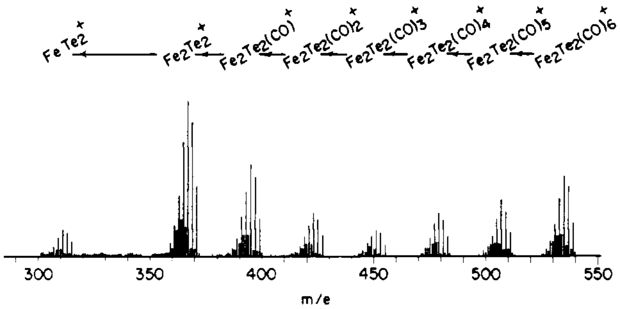


Figure 2. 70-eV mass spectrum of $Fe_2(\mu\text{-}Te_2)(CO)_6$.

Table II. ^{125}Te NMR Chemical Shift Data Measured at 31.57 MHz in $CDCl_3$ in Ppm[a]

$TeCl_4$	1138[b]	Me_2Te (neat)	0
$Fe_3(\mu_3\text{-}Te)_2(CO)_9$	1123	Me_2Te (1.37 M)	−18.6
Ph_2Te_2	423[c]	$Fe_2(\mu\text{-}Te_2)(CO)_6$	−733

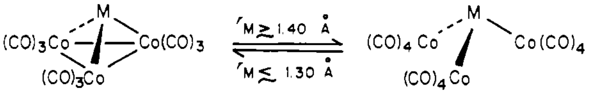
[a] Upfield shifts are negative. [b] Reference 10. [c] Reported[10] 422 ppm.

chromatography employing 8% cross-linked polystyrene as the inert but highly effective stationary phase. As a consequence of the considerable difference between the molecular volumes of **1** and **2** the separation was facile (Figure 1). Using this method, we have now optimized the yield of **2** to ca. 4% based on starting $Fe(CO)_5$. Furthermore, we have found that this chromatographic technique is of some general usefulness in the separation of other polynuclear organometallic complexes of differing nuclearity.

The IR spectrum of the chromatographically purified sample of **2** was similar to that for the analogous S_2 and Se_2 complexes (Table I) and indicated a complete absence of **1**. Nonetheless, **2** proved to be too unstable to isolate as a pure solid. Evaporation of hexane solutions of **2** under a stream of Ar or CO resulted in substantial decomposition to an insoluble black compound which contained carbonyls but gave variable combustion analyses. We suspect that this product was impure $Fe_4(\mu_3\text{-}Te)_4(CO)_{12}$, analogous to the known $Co_4(\mu_3\text{-}Sb)_4(CO)_{12}$ which is also insoluble and nonvolatile.[8]

The electron-impact mass spectrum of **2** (Figure 2) substantiates its structure, and the high-resolution measurement confirmed its formulation. Peaks for all of the possible $Fe_2(\mu\text{-}Te_2)(CO)_x$ (x = 0–6) were observed, including the 100% peak corresponding to the $Fe_2Te_2^+$ ion. Dahl and co-workers have previously noted that the 100% peak for the isoelectronic $Co_2(\mu\text{-}As_2)(CO)_6$ corresponds to that for the ionized Co_2As_2 core.[9]

Scheme II



M = R_3NB, RC,
Al, RSi, P,
S, RGe, Se

M = Sb, RSn, Bi, RPb

Finally, complex **1** was characterized by ^{125}Te Fourier transform NMR. These data dramatically distinguish **2** from **1** and other reference compounds (Table II). Few ^{125}Te NMR measurements have been made on transition-metal derivatives, and it is interesting to note that the chemical shift differences between two superficially similar compounds, **1** and **2**, almost bracket the known ^{125}Te NMR chemical shift scale for divalent tellurium.[10] The paramagnetic contribution to the nuclear shielding precludes detailed correlation of the chemical shift data with conventional ground-state inductive effects.[11] Nonetheless, the observed trend of the chemical shifts is qualitatively consistent with the notion that a μ_3-Te would be substantially more deshielded than two-coordinate tellurium compounds (Me_2Te, Ph_2Te_2) and a bridging Te_2 moiety. In fact, chemical shifts greater than 1000 ppm downfield of Me_2Te are unknown for any Te(II) compounds (e.g., R_2Te, R_3Te^+, or R_2Te_2) but are normal for Te(IV) derivatives (e.g., $TeCl_4$). Upfield chemical shifts are known only for $(Me_3Sn)_2Te$ (−1214 ppm).[10] The observed chemical shift scale parallels that found for the ^{77}Se NMR of a number of transition-metal complexes containing elementary selenium ligands.[12]

The instability of **2** is easily rationalized upon recognition of the considerable strain imposed by the tetrahedral framework on the Fe–Te–Fe and Fe–Te–Fe angles. Schmid has recently reviewed the structural chemistry of the geometrically similar tetrahedral nonmetal–tricobalt carbonyl clusters $MCo_3(CO)_x$.[13] It is found that when the covalent radius of M is 1.30 Å or less, $MCo_3(CO)_x$ adopts a closed nonacarbonyl structure; with larger ($r \gtrsim 1.40$ Å) tethering nonmetals, the open structure prevails (Scheme II). Assuming similar arguments apply to compounds of the formula $M_2M'_2(CO)_6$, we arrive at the conclusion that $Fe_2(\mu\text{-}E_2)(CO)_6$ (E = S, r = 1.02 Å; E = Se, r = 1.16 Å) and $Co_2(\mu\text{-}E_2)(CO)_6$ (E = P, r = 1.06 Å; E = As, r = 1.20 Å) would be stable as closed tetrahedra but that $Co_2(\mu\text{-}Sb_2)(CO)_6$ (r_{Sb} = 1.40 Å) would not. Consistent with this proposal, the $Co_2(\mu\text{-}E_2)(CO)_6$ synthesis when applied to antimony affords the cubane cluster exclusively.[8] Interestingly the covalent radius of Te at 1.36 Å is intermediate between Schmid's extremes of 1.30 and 1.40 Å. Thus closed tetrahedral Te clusters are on the brink of instability and may be expected to exhibit enhanced reactivity relative to the less strained analogues.

Illustrative of the reactivity inherent in the μ-Te_2 functional group, treatment of **2** with $Fe(CO)_5$ in the presence of Me_3NO is found to result in the formation of **1** (eq 1) (**2** does not react

$$Fe_2(\mu\text{-}Te_2)(CO)_6 + Fe(CO)_5 + 2Me_3NO \rightarrow Fe_3(\mu_3\text{-}Te)_2(CO)_9 + 2CO_2 + 2Me_3N \quad (1)$$

with $Fe(CO)_5$ in the absence of the decarbonylation reagent). This process suggested to us that a similar Fe_2Te_2 + Fe pathway operates in the procedure developed by Hieber and

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Scheme III

$$HFe(CO)_4^- + TeO_3^{2-} \xrightarrow{\text{several steps}} Fe_2(\mu\text{-}Te_2)(CO)_6$$

$$Fe_2(\mu\text{-}Te_2)(CO)_6 + HFe(CO)_4^- \longrightarrow HFe_3(\mu_3\text{-}Te)_2(CO)_{10}^-$$

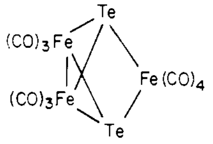
$$HFe(\mu_3\text{-}Te)_2(CO)_{10}^- + H^+ \longrightarrow H_2 + Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$$

$$Fe_3(\mu_3\text{-}Te)_2(CO)_{10} \longrightarrow Fe_3(\mu_3\text{-}Te)_2(CO)_9 + CO$$

Gruber, which affords both $Fe_3(\mu_3\text{-}E)_2(CO)_9$ and $Fe_2(\mu\text{-}E_2)(CO)_6$.

An operational test of this idea confirmed our suspicion. Treatment of **2** with a basic methanol solution of $Fe(CO)_5$, followed by acidic workup, afforded **1**, together with another compound, **3**, which we have identified as $Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$.[14] Since it is well-known that $Fe(CO)_5$ is converted to $HFe(CO)_4^-$ under basic conditions (eq 2),[15] this highly nucleophilic intermediate is presumably capable of oxidatively adding across the Te–Te bond of **2**. The combination of the *hexa*carbonyl, **2**, with the hydrido*tetra*carbonylferrate serves to afford the *deca*carbonyl, **3**. We found that compound **3** was readily decarbonylated thermally or chemically (with Me_3NO) to *cleanly* afford **1**. We are certain that the structure of **3** is comparable to that for $Fe_2Pt(\mu_3\text{-}Te)_2(CO)_6(PPh_3)_2$,[16] and contains only one iron–iron bond.[17]

$$Fe(CO)_5 + OH^- \rightarrow HFe(CO)_4^- + CO_2 \qquad (2)$$



3

Having collected this mechanistic information, we implemented a revised procedure for the preparation of **3** from the ingredients used by Hieber and Gruber. Thus we found that treatment of a well-stirred mixture of CH_2Cl_2 and aqueous K_2TeO_3 with methanolic $KHFe(CO)_4$ at 0 °C resulted in the formation of a dark brown coloration primarily in the aqueous phase. Acidification, again at 0 °C, resulted in a color change to dark red-orange and transfer of all of the color to the organic phase; workup provided **3** in 70% yield. Inasmuch as **3** is unstable with respect to **1** in the absence of CO, its isolation in good yield requires it to be an intermediate in the formation of **1**. These results are summarized in Scheme III.

Experimental Section

The Bio-Beads resin was obtained from Bio-Rad Laboratories. K_2TeO_3 was either prepared from KOH and TeO_2 (Alfa) or purchased from Alfa. Reactions were carried out in an efficient hood under argon; workups were done aerobically.

Preparation of $Fe_2(\mu\text{-}Te_2)(CO)_6$ and $Fe_3(\mu_3\text{-}Te)_2(CO)_9$. A solution of K_2TeO_3, 33 g (130 mmol), in 180 mL of H_2O was added to a 1-L flask containing an ice-cooled solution prepared from 4.4 mL (33 mmol) of $Fe(CO)_5$, 11 mL of 50% aqueous KOH, and 30 mL of MeOH. After being stirred for 30 min at room temperature, the solution was cooled to 0 °C and *cautiously* acidified with 6 M HCl. The resulting black precipitate was filtered in air, washed with H_2O, and dried in vacuo (25 °C) for 8 h. The solid was then extracted with four 75-mL portions of CH_2Cl_2. The combined extracts were filtered and carefully evaporated to a small volume in vacuo (evaporation to dryness resulted in considerable decomposition). The CH_2Cl_2 concentrate was then applied to a 2 × 40 cm column packed with Bio-Beads SX-8 resin swelled with CH_2Cl_2. Elution with CH_2Cl_2 afforded a large, dark purple band of **1** followed by an orange band of **2**. The yields of **1** and **2** were 4.3 g (58%) and 0.35 g (4.3%), respectively. The yield of **2** was determined by measuring percent Fe in solution (ϵ at 345 nm is 1.15×10^4). Solutions of **2** were stable in air at room temperature but were routinely stored at −20 °C under argon. EI mass spectrum (70 eV): calculated for $C_6{}^{56}Fe_2O_6{}^{128}Te^{130}Te$ 537.6499, found 537.6500.

Preparation of $Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$. A solution containing 2.0 mL (15 mmol) of $Fe(CO)_5$ and 6 mL of 50% aqeuous KOH in 50 mL of MeOH was slowly added to a stirred, ice-cooled mixture of $K_2TeO_3{\cdot}H_2O$ (8.0 g, 29 mmol), 100 mL of H_2O, and 250 mL of CH_2Cl_2. Immediately after the addition was complete, the solution was acidified with 6 M HCl. The CH_2Cl_2 layer was separated, washed with H_2O, and then dried over $MgSO_4$. MeOH was added and the solution was evaporated to a small volume to give greenish black crystals, yield 2.4 g (70%). The identity of **3** was verified by IR.[15]

Reactions of $Fe_2(\mu\text{-}Te_2)(CO)_6$ with $Fe(CO)_5$. I. Excess $Me_3NO{\cdot}2H_2O$ was added to a CH_2Cl_2 solution equimolar in **2** and $Fe(CO)_5$. After being stirred for 45 min at room temperature, the solution was filtered through silica gel and evaporated to a small volume with added MeOH. **1** was isolated in 20% yield and identified by IR.

II. Excess 50% aqueous KOH was added to a MeOH solution equimolar in **2** and $Fe(CO)_5$. After being stirred for 10 min at room temperature, the mixture was acidified with 6 M HCl and diluted with H_2O. Extraction with CH_2Cl_2 gave a solution from which equal amounts of **1** and **3** were isolated in ~50% yield by crystallization with MeOH.

Conversions of $Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$ to $Fe_3(\mu_3\text{-}Te)_2(CO)_9$. I. Reaction of equimolar amounts of **3** and $Me_3NO{\cdot}2H_2O$ in CH_2Cl_2 at room temperature for 15 min afforded a solution from which **1** was isolated in 49% yield by crystallization with MeOH.

II. Compound **3** was quantitatively converted to **1** by refluxing in hexane for 30 min.

^{125}Te NMR. ^{125}Te NMR spectra were obtained on a Varian XL-100 spectrometer operating in the Fourier transform mode at 31.570 MHz. Spectra were routinely obtained by collecting data at ±25 kHz (792 ppm) of the operating frequency; absorptions beyond this range were referenced to a signal produced by a frequency synthesizer (±0.1 Hz). Operating parameters included a pulse width of 30 μs, an acquisition delay of 250 μs, and a pulse delay of 1 s. Normally spectra were collected over a 1-h period. Field frequency lock was effected by using deuterated solvents. All chemical shifts were referenced to a *neat* solution of Me_2Te, upfield shifts being negative. Spectra were measured on $CDCl_3$ solutions in 12-mm thin-walled glass sample tubes. Chemical shifts are reproducible with 1% accuracy.

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Registry No. 1, 22587-70-8; 2, 76185-27-8; 3, 78624-80-3; $Fe(CO)_5$, 13463-40-6; K_2TeO_3, 10049-23-7.

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(17) Compound **3** is strictly comparable with $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$, which we have characterized by X-ray crystallography.

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