

Solvothermal synthesis, molecular structures and spectroscopic characterization of the cluster compounds $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]$ and $\text{Cs}[\text{HFe}_3\text{Te}(\text{CO})_9]$

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Abstract

The iron carbonyl tellurido cluster $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]$ (**1**) has been synthesized at 80°C in moderate yield by heating a mixture of $\text{Fe}_3(\text{CO})_{12}$, Na_2Te_2 , and Ph_4PBr in a 2:1:6 molar ratio in a sealed Pyrex tube containing 0.4 ml of methanol. Another cluster, $\text{Cs}[\text{HFe}_3\text{Te}(\text{CO})_9]$ (**2**) has been prepared similarly by allowing $\text{Fe}_3(\text{CO})_{12}$ to react with Cs_2Te_3 (4:1 molar ratio) in 0.2 ml of H_2O at 130°C. Compound **1** crystallizes in the monoclinic space group $C2/c$ (No. 15) with $a = 23.324(3)$ Å, $b = 11.793(2)$ Å, $c = 23.499(5)$ Å, $\beta = 102.02(1)^\circ$, $V = 6322(2)$ Å³, $Z = 4$. A central $[\text{Fe}_2(\mu_3\text{-Te})_2(\text{CO})_6]$ butterfly unit remains connected to two $\text{Fe}(\text{CO})_4$ fragments through the tellurium atoms in the anion of **1**. Compound **2** crystallizes in the orthorhombic space group $Pbca$ (No. 61) with $a = 9.672(2)$ Å, $b = 15.816(4)$ Å, $c = 21.430(5)$ Å, $V = 3278(2)$ Å³, $Z = 8$. In the anion of this compound, a Te^{2-} ligand caps a triiron triangle to form an approximate tetrahedron, with a hydride ligand bridging one of the Fe–Fe bonds. Both compounds have been characterized by solid state and solution infrared spectroscopy and ¹²⁵Te NMR spectroscopy.

Keywords: Iron; Tellurium; Metal clusters; Metal carbonyls; Chalcogenides; Hydrothermal synthesis

1. Introduction

We have been investigating the solvothermal synthesis of metal carbonyl cluster compounds containing telluride ligands. Several novel tellurium-rich cluster anions, including $[\text{M}_6\text{Te}_{14}(\text{CO})_{12}]^{2-}$ ($\text{M} = \text{Ru}$ [1], Fe [2]), $[\text{M}_4\text{Te}_6(\text{TeMe})_2(\text{CO})_8]^{2-}$ ($\text{M} = \text{Ru}, \text{Fe}$) [3], and $[\text{Fe}_3\text{W}_2\text{Te}_8(\text{TeMe})(\text{CO})_{12}]^{3-}$ [4] have been prepared using this route. The chemistry of iron in this area is particularly rich, as has been demonstrated by several groups [5]. Indeed, on further investigation of the reactions between $\text{Fe}_3(\text{CO})_{12}$ and soluble polychalcogenide anions such as Te_x^{2-} , we have been able to prepare relatively tellurium-poor compounds also using the solvothermal technique. In this paper we report two

such compounds, $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]$ (**1**) and $\text{Cs}[\text{HFe}_3\text{Te}(\text{CO})_9]$ (**2**) prepared by methanothermal and hydrothermal reactions respectively.

2. Experimental section

Solids were handled in a glove-box under a nitrogen atmosphere. Na_2Te_2 and Cs_2Te_3 were prepared by reacting stoichiometric amounts of the elements in liquid ammonia. $\text{Fe}_3(\text{CO})_{12}$ was used as received from a commercial source.

Infrared (IR) spectra were recorded on a Nicolet IR/42 spectrometer. Solution IR spectra were obtained using a cell with NaCl windows. UV-visible spectra were obtained on a Hitachi U-2000 spectrophotometer. A Varian VXR-300 NMR spectrometer was used to obtain the ¹H NMR spectrum. ¹²⁵Te NMR spectra were obtained on a Varian VXR-500 spectrometer operating at ca. 157.9 MHz for ¹²⁵Te resonances. Spectra data were

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referenced to a signal for TeCl_4 , dissolved in $\text{D}_2\text{O}/\text{HCl}$, at 1237 ppm with respect to Me_2Te at 0.0 ppm. Elemental analysis for the heavy atoms was performed by energy dispersive spectroscopy (EDS) of X-rays using a JEOL JSM-6400V scanning electron microscope equipped with a TN 5500 EDS detector.

2.1. Preparation of $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]$ (**1**)

A 100 mg amount of $\text{Fe}_3(\text{CO})_{12}$ (0.2 mmol) was thoroughly mixed with 30 mg of Na_2Te_2 (0.1 mmol) and 250 mg of Ph_4PBr (0.6 mmol) and the mixture was loaded into a thick-walled Pyrex tube of 9 mm outer diameter. The tube was sealed under vacuum (volume after sealing ca. 4 ml) after introducing 0.4 ml of MeOH. The sealed tube was opened after 24 h of heating at 80°C . The solid product was washed with MeOH to obtain 72 mg of dark brown crystals. Yield 31% (based on Fe). EDS analysis for P, Fe, and Te carried out on a few randomly selected crystals showed the average P:Fe:Te ratio of 1:1.9:1. IR data: (a) (ν_{CO} , cm^{-1} ; KBr pellet) 2033(m), 2000(s), 1991(s), 1975(s), 1947(sh), 1937(s), 1917(s), 1908(s), 1896(s); (b) (ν_{CO} , cm^{-1} ; CH_2Cl_2 solution) 2035(m), 2000(s), 1983(s), 1938(s), 1904(s, br). UV-vis spectral data in CH_2Cl_2 solution: $\lambda_{\text{max}} = 306$ nm (poorly defined peak). ^{125}Te NMR data: -195 ppm (in CD_2Cl_2).

2.2. Preparation of $\text{Cs}[\text{HFe}_3\text{Te}(\text{CO})_9]$ (**2**)

A 100 mg amount of $\text{Fe}_3(\text{CO})_{12}$ (0.2 mmol) was mixed with 32 mg of Cs_2Te_3 (0.05 mmol) and the mixture was heated at 130°C for 15 h in a vacuum-sealed tube containing 0.2 ml of water. The crystalline solid product was washed with ca. 20 ml of water on a filtering frit in air and dried in vacuo over P_4O_{10} . The red-brown solid was extracted with diethyl ether in an inert atmosphere and the resulting solution was evaporated to dryness to obtain 45 mg of red-brown powder. Yield 33% (based on Fe). EDS analysis gave an average Cs:Fe:Te ratio of 1:3.6:1.2. IR data: (a) (ν_{CO} , cm^{-1} ; KBr pellet) 2044(m), 2024(sh), 2008(s), 1984(s), 1976(s), 1957(sh), 1932(s), 1921(s), 1879(sh), 1871(m); (b) (ν_{CO} , cm^{-1} ; acetone solution) 2047(s), 2027(m), 2008(s), 1984(s), 1975(s), 1959(s, br), 1910(m); (c) (ν_{CO} , cm^{-1} ; DMF solution) 2047(w), 2027(w), 2003(s), 1977(s), 1937(sh), 1921(s), 1896(m), 1869(w). UV-vis spectral data in DMF solution: $\lambda_{\text{max}} = 347$ nm ($\epsilon = 9800 \text{ M}^{-1} \text{ cm}^{-1}$). ^{125}Te NMR data: 262 ppm (in acetone- d_6); 270 ppm (in CD_3CN).

2.3. X-ray crystallography

Single crystals used for X-ray crystal structure analysis were chosen from the product formed during the

solvothermal reactions. Intensity data for **1** and **2** were measured at room temperature on Rigaku AFC6S and Nicolet P3/V diffractometers respectively using Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$). Crystals were mounted inside sealed glass capillaries of suitable diameter. Intensities of three standard reflections were measured repeatedly (every 150 reflections) to monitor any decay and movement of crystal during the data collection. No crystal decay was observed. Data for **1** were corrected for absorption using the empirical method based on azimuthal ψ scans as well as DIFABS [6]. For **2**, only a correction using DIFABS was used. Structures were solved by direct methods (SHELXS-86) and refined on a VAXstation 3100 computer by full-matrix least-squares techniques using the TEXSAN crystallographic software package [7]. Table 1 presents the relevant crystallographic and structure solution data. For **1**, all non-hydrogen atoms other than the carbon atoms belonging to the phenyl groups in the cation were anisotropically refined. Hydrogen atom positions were calculated but not refined. For **2**, all atoms were anisotropically refined. The hydrogen atom could not be located. The final atomic coordinates and equivalent isotropic thermal parameters for atoms in the anion of **1** and all the atoms of **2** are listed in Tables 2 and 3, respectively. Selected bond distances and angles for **1** and **2** are given in Tables 4 and 5 respectively.

Table 1
Crystal data for $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]$ (**1**) and $\text{Cs}[\text{HFe}_3\text{Te}(\text{CO})_9]$ (**2**)

	1	2
Formula	$\text{C}_{62}\text{H}_{40}\text{O}_{14}\text{Fe}_4\text{Te}_2$	$\text{C}_9\text{HO}_9\text{Fe}_3\text{TeCs}$
A (\AA)	23.324(3)	9.672(2)
b (\AA)	11.793(2)	15.816(4)
c (\AA)	23.499(5)	21.430(5)
α ($^\circ$)	90	90
β ($^\circ$)	102.02(1)	90
γ ($^\circ$)	90	90
$Z; V$ (\AA^3)	4; 6322(2)	8; 3278(2)
Space group	$C2/c$ (No. 15)	$Pbca$ (No. 61)
D_{calc} (g cm^{-3})	1.628	2.760
μ (Mo K α) (cm^{-1})	19.166	65.842
Crystal size (mm^3)	$0.2 \times 0.2 \times 0.0$	$0.3 \times 0.2 \times 0.1$
$2\theta_{\text{max}}$ ($^\circ$)	45	55
Temperature ($^\circ\text{C}$)	23	23
No. of data collected (independent)	4969	3772
No. of data used ($F^2 > 3\sigma F_0^2$)	2123	2114
No. of variables	259	208
Min, max abs. corr.	0.742, 1.647	0.852, 1.466
Final R/R_w ^a	0.059/0.066	0.066/0.077
Goodness of fit ^b	2.118	1.974

^a $R = \sum(|F_0| - |F_c|) / \sum|F_0|$; $R_w = \{\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2\}^{1/2}$.

^b $\{\sum(|F_0| - |F_c|) / \sigma\} / (n - m)$ for n reflections and m variables.

3. Results and discussion

3.1. Synthesis of compounds

Complex **1** was prepared by reacting two equivalents of $\text{Fe}_3(\text{CO})_{12}$ with one equivalent of Na_2Te_2 in 0.4 ml of MeOH. Formation of $(\text{Ph}_4\text{P})_2[\text{Fe}_3\text{Te}(\text{CO})_9]$ [8,9] in small amounts has also been observed occasionally along with **1**, particularly when reaction times longer than a day were used. Use of longer reaction times coupled with reactant ratios lower than 2:1 also resulted in product contamination with yet another known cluster compound, $(\text{Ph}_4\text{P})_2[\text{Fe}_5\text{Te}_4(\text{CO})_{14}]$ [10]. The orange plate-like crystals of $(\text{Ph}_4\text{P})_2[\text{Fe}_3\text{Te}(\text{CO})_9]$ are removed by repeated washing with small volumes of methanol. Alternatively, compound **1** can be recrystallized from CH_2Cl_2 /hexane free of contamination. The IR spectra of carbonyl stretching vibrations of the samples prepared in either of the two ways are identical. The crystalline solid of **1** is moderately stable in air. Though sparingly soluble in methanol, it dissolves readily in solvents such as acetone, dichloromethane, and dimethylformamide (DMF), giving air-sensitive solutions of reddish–brown color.

Compound **2** has been synthesized by allowing four equivalents of $\text{Fe}_3(\text{CO})_{12}$ to react with one equivalent of Cs_2Te_3 under hydrothermal conditions at 130°C. The product was found to be mixed with a brownish–orange powder that does not dissolve in common organic solvents and water. Crystals of **2** are partially soluble in water and, during initial washing with water, formation of an orange–brown filtrate was observed. Taking advantage of the fact that compound **2** is highly soluble in diethyl ether, a red–brown powder of **2** can be isolated

Table 2

Positional parameters and equivalent isotropic displacement values (\AA^2)^a for the $[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]^{2-}$ anion in **1** with esds in parentheses

Atom	x	y	z	B_{eq}
Te(1)	0.06981(4)	0.1907(1)	0.27520(5)	4.25(5)
Fe(1)	0.1815(1)	0.2199(2)	0.3206(1)	4.0(1)
Fe(2)	0.0092(1)	0.3191(2)	0.1964(1)	4.5(1)
O(1)	0.1928(6)	0.043(1)	0.2343(6)	8.0(8)
O(2)	0.3075(5)	0.210(1)	0.3635(6)	9.5(9)
O(3)	0.1569(7)	0.150(1)	0.4325(6)	9(1)
O(4)	0.1868(6)	0.467(1)	0.3057(6)	7.0(8)
O(5)	–0.0036(7)	0.209(2)	0.0831(7)	11(1)
O(6)	0.1116(6)	0.452(1)	0.1835(6)	8.1(8)
O(7)	–0.0668(5)	0.517(1)	0.1729(7)	8.5(8)
C(1)	0.1885(7)	0.116(2)	0.2670(9)	5(1)
C(2)	0.2566(7)	0.215(2)	0.3458(8)	6(1)
C(3)	0.1662(7)	0.176(2)	0.3872(8)	5.1(9)
C(4)	0.1815(7)	0.369(2)	0.3068(8)	5(1)
C(5)	0.0021(9)	0.251(2)	0.1295(9)	7(1)
C(6)	0.0708(8)	0.400(1)	0.1923(7)	4.7(9)
C(7)	–0.0384(7)	0.434(1)	0.1792(7)	4.4(8)

^a $B_{\text{iso,eq}}$ is defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$

Table 3

Positional parameters and equivalent isotropic displacement values (\AA^2)^a for $\text{Cs}[\text{HF}_3\text{Te}(\text{CO})_9]$ (**2**) with esds in parentheses

Atom	x	y	z	B_{eq}
Cs(1)	0.2224(1)	0.7522(1)	0.40931(5)	3.08(5)
Te(1)	0.0533(1)	0.47529(8)	0.14514(5)	2.22(4)
Fe(1)	0.2125(3)	0.5425(2)	0.0681(1)	1.8(1)
Fe(2)	0.2139(3)	0.5868(2)	0.1863(1)	1.9(1)
Fe(3)	0.2998(3)	0.4294(2)	0.1502(1)	2.1(1)
O(1)	0.033(2)	0.673(1)	0.0193(7)	4.2(8)
O(2)	0.475(2)	0.624(1)	0.0413(8)	4.8(9)
O(3)	0.214(1)	0.434(1)	–0.0416(6)	3.3(6)
O(4)	0.196(2)	0.584(1)	0.3237(5)	4.8(8)
O(5)	–0.003(2)	0.711(1)	0.1694(7)	4.1(8)
O(6)	0.440(2)	0.706(1)	0.1743(7)	4.2(8)
O(7)	0.590(2)	0.426(1)	0.1146(9)	6(1)
O(8)	0.238(2)	0.293(1)	0.0619(6)	3.8(7)
O(9)	0.302(2)	0.330(1)	0.2659(6)	4.7(8)
C(1)	0.104(2)	0.621(1)	0.0388(8)	2.2(7)
C(2)	0.376(2)	0.592(1)	0.0534(8)	2.7(8)
C(3)	0.211(2)	0.475(1)	0.0010(8)	2.3(7)
C(4)	0.196(2)	0.583(1)	0.271(1)	3.2(9)
C(5)	0.085(2)	0.663(1)	0.1753(8)	2.5(8)
C(6)	0.352(2)	0.659(1)	0.1775(8)	2.2(7)
C(7)	0.479(2)	0.427(1)	0.129(1)	3(1)
C(8)	0.260(2)	0.347(1)	0.0949(8)	2.9(8)
C(9)	0.302(2)	0.371(1)	0.2210(8)	2.9(8)

^a $B_{\text{iso,eq}}$ is defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$

in pure form by evaporating an ether extract of the crude product. In the preparation of **2**, use of $\text{Fe}_3(\text{CO})_{12}:\text{Cs}_2\text{-Te}_3$ ratios lower than 2:1 resulted in the formation of $\text{Cs}_2[\text{Fe}_5\text{Te}_4(\text{CO})_{14}]$, which is analogous to the reported [10] $(\text{Ph}_4\text{P})_2[\text{Fe}_5\text{Te}_4(\text{CO})_{14}]$ cluster, along with larger amounts of the brownish–orange powder mentioned above. Compound **2** is soluble in polar organic solvents, but is sparingly so in chloroform and dichloromethane. This compound is air-stable in the solid state, and its orange–brown solutions are also moderately stable in air.

3.2. Description of structures

The $[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]^{2-}$ anion in **1**, shown in Fig. 1, contains a crystallographic two-fold axis. The central ' $\text{Fe}_2\text{Te}_2(\text{CO})_6$ ' fragment is connected to two $\text{Fe}(\text{CO})_4$

Table 4

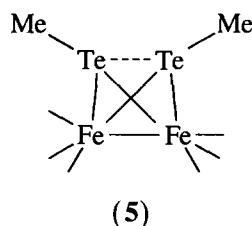
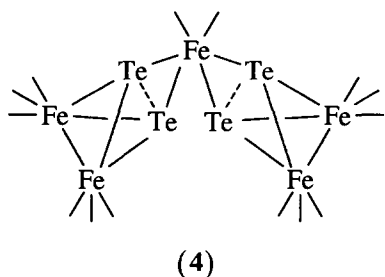
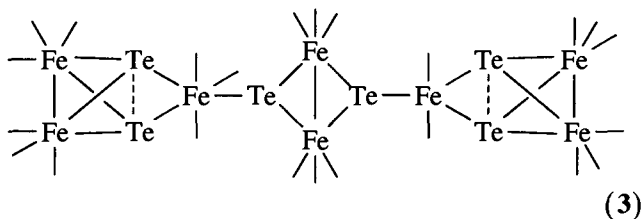
Selected geometric data for $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]$ (**1**)

Bond distances (\AA)			
Te(1)–Te(1)'	3.225(2)	Fe(1)–Te(1)	2.625(2)
Te(1)–Fe(2)	2.576(3)	Fe(2)–Fe(2)'	2.641(5)
Bond angles ($^\circ$)			
Te(1)–Te(1)–Fe(1)	172.02(6)	Te(1)–Te(1)–Fe(2)	51.29(6)
Fe(1)–Te(1)–Fe(2)	124.41(8)	Fe(2)–Te(1)–Fe(2)'	61.7(1)
Te(1)–Fe(2)–Te(1)'	77.48(8)	Te(1)–Fe(2)–Fe(2)'	59.21(8)
Fe(1)–C–O (mean)	176(2)	Fe(2)–C–O (mean)	174(2)

Table 5
Selected geometric data for $\text{Cs}[\text{HFe}_3\text{Te}(\text{CO})_9]$ (**2**)

Bond distances			
Fe(1)–Te(1)	2.495(3)	Fe(2)–Te(1)	2.510(3)
Fe(3)–Te(1)	2.495(3)	Fe(1)–Fe(2)	2.628(3)
Fe(1)–Fe(3)	2.647(3)	Fe(2)–Fe(3)	2.736(4)
Bond angles (°)			
Fe(1)–Te(1)–Fe(2)	63.35(8)	Fe(1)–Te(1)–Fe(3)	64.09(9)
Fe(2)–Te(1)–Fe(3)	66.28(9)	Te(1)–Fe(1)–Fe(2)	58.60(8)
Te(1)–Fe(1)–Fe(3)	57.95(8)	Fe(2)–Fe(1)–Fe(3)	62.5(1)
Te(1)–Fe(2)–Fe(1)	58.05(8)	Te(1)–Fe(2)–Fe(3)	56.59(8)
Fe(1)–Fe(2)–Fe(3)	59.10(9)	Te(1)–Fe(3)–Fe(1)	57.97(8)
Te(1)–Fe(3)–Fe(2)	57.12(8)	Fe(1)–Fe(3)–Fe(2)	58.42(9)
Fe(1)–C–O (mean)	178(2)	Fe(2)–C–O (mean)	176(2)
Fe(3)–C–O (mean)	178(2)		

fragments through the two tellurium atoms. Allowing for the minor structural variations found locally, the 'Fe₂Te₂(CO)₆' fragment is similar to other such fragments commonly found in iron–telluride carbonyl cluster chemistry. In the [Fe₈Te₆(CO)₂₄]²⁻ (**3**) cluster anion, such a fragment connects two other Fe(CO)₃ fragments through the two tellurium atoms [11]. The same cluster has two other 'Fe₂Te₂(CO)₆' fragments which are bonded through the tellurium atoms as bidentate ligands to the Fe(CO)₃ fragments connected to the central unit. In [Fe₅Te₄(CO)₁₄]²⁻ (**4**) however, the same 'butterfly' unit, which appears as a tetrahedron in Fig. 1 owing to the close contact between the tellurium atoms, is chelated to another iron center through its tellurium



Scheme 1.

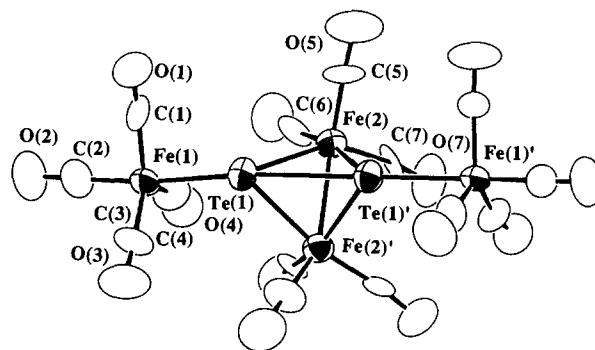


Fig. 1. An ORTEP view of the $[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]^{2-}$ anion in **1** with atom labeling scheme.

atoms [10]. In a third example, for the Fe₂(TeMe)₂(CO)₆ (**5**) cluster, the tellurium atoms are methylated; but the butterfly unit maintains its overall geometry [5c]. This diiron unit is structurally related to Fe₂Te₂(CO)₆ (**6**), in which the Te atoms are close enough to form a single bond between themselves, and are not further connected to any other moiety [12,13]. Compared with the Te–Te single bond distance of ca. 2.71 Å in **6** [13], this distance is much longer in **1** at 3.225(2) Å. The corresponding distances in **3** [11], **4** [10], and **5** [5c] are 3.267(2) Å (and 3.123(2) Å), 3.152(2) Å, and 3.261(1) Å respectively. Such short Te...Te distances have been observed in other clusters, as we reported earlier [3,4]. The van der Waals separation between two Te atoms is over 4 Å [14]. Thus, it appears likely that in the cases where the Te–Te separation is ca. 3.3 Å or less, partial bonding overlap between the relatively large Te atoms is significant. This has been extensively discussed in the literature [15].

The Fe–Fe distances fall into two regions. The Fe(2)–Fe(2') distance for **1** compares well with the corresponding distances of 2.625(5) Å, 2.647(8) Å, and

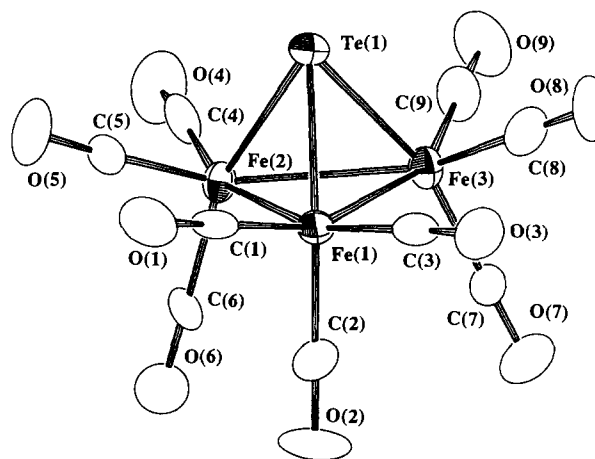


Fig. 2. An ORTEP view of the $[\text{HFe}_3\text{Te}(\text{CO})_9]^-$ anion in **2** with atom labeling scheme.

2.634(5) Å in $[\text{Fe}_8\text{Te}_6(\text{CO})_{24}]^{2-}$ [11], $\text{Fe}_2\text{Te}_2(\text{CO})_6$ [13], and $\text{Fe}_2(\text{TeMe})_2(\text{CO})_6$ [5c] respectively. In the cases where the ' $\text{Fe}_2\text{Te}_2(\text{CO})_6$ ' unit remains bonded in a chelating mode to an $\text{Fe}(\text{CO})_n$ fragment, the Fe–Fe distances are shorter than 2.6 Å. For **1**, the Te(1)–Fe(2) distance is shorter compared with the Te(1)–Fe(1) bond by ca. 0.05 Å, which is an indication of the difference in oxidation states of Fe(1) and Fe(2), the former being in the zero while the latter is in the +1 oxidation state.

The structure of the $[\text{HFe}_3\text{Te}(\text{CO})_9]^-$ cluster anion in **2** is closely related to the known $[\text{Fe}_3\text{Te}(\text{CO})_9]^{2-}$ cluster [8,9]. The tellurium atom caps a triangle of iron atoms to form an approximate tetrahedron. The Fe–Te distances of ca. 2.5 Å are comparable with the corresponding distances in $[\text{Fe}_3\text{Te}(\text{CO})_9]^{2-}$. All of the carbonyl groups are terminal, and the Fe–C–O geometries do not significantly deviate from linearity. The hydrogen atom in the cluster could not be directly located; however, a significant structural distortion in the cluster gives a reasonable clue. The three Fe–Fe distances in **2** are 2.628(3) Å, 2.647(3) Å, and 2.736(4) Å. While the first two distances are comparable in magnitude with the Fe–Fe distances for the $[\text{Fe}_3\text{Te}(\text{CO})_9]^{2-}$ cluster [8,9], the Fe(2)–Fe(3) distance of 2.736(4) Å is significantly longer. We presume that the hydrogen atom bridges this particular Fe–Fe edge of the Fe_3 triangle. Such lengthening of an Fe–Fe single bond on being bridged by a hydride ligand is a feature of common occurrence in iron carbonyl cluster chemistry [16]. The presence of a bridging hydride ligand is supported by our observation of an upfield shifted singlet at –21.8 ppm in the ^1H NMR spectrum of **2** in acetone- d_6 . In a protonation experiment with $(\text{Ph}_4\text{P})_2[\text{Fe}_3\text{Te}(\text{CO})_9]$, a singlet at nearly the same position has been reported [9]. This report also discusses the lack of reactivity of the capping Te atom in the cluster toward electrophiles. Thus, it appears highly probable that in $[\text{HFe}_3\text{Te}(\text{CO})_9]^-$ the proton does not reside on the tellurium atom, but acts as a bridge for the Fe(2)–Fe(3) bond, as supported by the structural data.

3.3. Spectroscopic data

Both compounds have been characterized by spectroscopic techniques. A poorly defined absorption maximum at 306 nm is the only absorption feature in the UV-vis spectrum of **1** in CH_2Cl_2 . The solid state IR spectrum for the carbonyl stretching vibrations of **1** in a KBr disc is quite characteristic. In CH_2Cl_2 solution, the spectrum changes somewhat, but the main absorptions remain the same. The fact that the compound can be recovered quantitatively in the form of large chunky single crystals from a CH_2Cl_2 solution suggests that this species is stable in solution. We have previously reported [3] that some metal carbonyl telluride species may not be stable in solution.

The ^{125}Te NMR spectrum for **1** has been recorded in

CD_2Cl_2 . As expected, only one singlet is seen at –195 ppm relative to Me_2Te , corresponding to a single chemical environment for tellurium in the solid state. The signal for $\text{Fe}_2\text{Te}_2(\text{CO})_6$ was found to occur at –733 ppm [17]. In this cluster, the tellurium atoms are bonded to each other by a single bond. In cluster **1**, the Te–Te separation of 3.225(2) Å is still too long for a single bond. The cluster $\text{Fe}_2(\text{TeMe})_2(\text{CO})_6$ [5c] displays its ^{125}Te signal at 20 ppm (Te–Te 3.261(1) Å). These figures are being cited in view of a previous attempt [18] to correlate ^{125}Te chemical shifts with the degree of bonding interaction between tellurium atoms in similar situations. In agreement with earlier reports [5c,19], however, the data reported here should provide additional corroboration that ^{125}Te NMR chemical shift data are not easily correlated with chemical environments of the tellurium nuclei. We have previously observed disparate chemical shifts for several compounds which are difficult to assign [1,3,4]. Further studies, including theoretical treatments, are definitely required in order to understand the factors that influence the position of tellurium resonances in the chemical shift scale.

A red–brown solution of **2** in DMF shows a moderately intense absorption band in its UV-vis spectrum. Again, the similarity of the ν_{CO} values in the solid, as well as solution IR spectra for **2**, indicates the stability of the species in solution. For this compound, the ^{125}Te signal is observed at 262 ppm in acetone- d_6 and 270 ppm in CD_3CN . For the related compound $(\text{Ph}_4\text{P})_2[\text{Fe}_3\text{Te}(\text{CO})_9]$ the signal was observed at 361 ppm in CD_3CN [9]. Considering that the environments of the tellurium atoms are nearly the same in this compound and **2**, the difference of nearly 100 ppm is quite high, and can be attributed to the effect of protonation. It appears that even minor perturbations in other parts of the molecule may also have large effects on the ^{125}Te chemical shifts.

4. Concluding remarks

Despite the numerous studies available on the iron carbonyl/alkali metal telluride system, it is remarkable that new Fe/Te/CO compounds continue to be discovered, particularly through solvothermal chemistry. Formation of **1** has not so far been reported from conventional solution conditions. Similarly, compound **2** has not been isolated in the solid state so far, and its formation in a hydrothermal reaction does not require the additional protonation step. It thus appears that the solvothermal technique provides a useful alternative method for delving into intricate synthetic chemistry.

5. Supplementary material available

Tables of crystal structure analysis data, atomic coordinates and isotropic and anisotropic thermal parameters

of all non-hydrogen atoms, full lists of bond distances and angles (12 pages), and calculated and observed structure factors (30 pages) for $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{Te}_2(\text{CO})_{14}]$ (**1**) and $\text{Cs}[\text{HFe}_3\text{Te}(\text{CO})_9]$ (**2**); Fourier transform IR spectra (solid state and solution) for **1** and **2** (5 pages); ^{125}Te NMR spectra for **1** and **2** (3 pages). Ordering information is given in any current masthead page.

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