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Crystal and molecular structure of bis(μ_3-tellurido)-decacarbonyltriiron, [$Fe_3(CO)_{10}Te_2$]

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Abstract

The tellurium complex [$Fe_3(CO)_9Te_2$] reacts with CO to give [$Fe_3(CO)_{10}Te_2$]. The reaction occurs via attack of CO on a peripheral iron atom of the open triangle of [$Fe_3(CO)_9Te_2$] with consequent rupture of an iron–iron bond. The complex lies on a crystallographic two-fold axis and contains an iron–iron bond between two Fe atoms each linked to three terminal carbonyl groups: a third Fe atom, linked to four terminal CO groups, is connected to the Fe_2 unit by two bridging Te atoms.

Introduction

Several papers [1–5] describe the structures and the reactivity [6–12] of [$Fe_3(CO)_9X_2$] (X = S, Se or Te) and their derivatives. Particular attention was paid to explaining the reactions of the Te complexes upon addition of a molecule, L, to form [$Fe_3(CO)_9LTe_2$] and to relating them to the corresponding sulphur and selenium derivatives [6b].

With L = CO [$Fe_3(CO)_9Te_2$] forms [$Fe_3(CO)_{10}Te_2$]. This is the simplest derivative obtained in the addition reaction, and was characterized spectroscopically in 1968 [8]. Here the X-ray structural study of this complex is reported, and a comparison with the parent [$Fe_3(CO)_9Te_2$] and with the related [$Fe_3(CO)_9\{P(C_6H_5)_3\}Te_2$] is made.

Results and discussion

The bond lengths and angles for [$Fe_3(CO)_{10}Te_2$] are in Table 1; Table 2 lists the fractional atomic coordinates.

The [$Fe_3(CO)_{10}Te_2$] molecule (Fig. 1) lies on a crystallographic two-fold axis passing through Fe(2) and the mid-point of the Fe(1)–Fe(1a) bond. Fe(1) and

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Table 1

Bond lengths (Å) and angles (°) in [$Fe_3(CO)_{10}Te_2$]

Te–Fe(1)	2.571(1)	Te–Fe(2)	2.675(1)
Te ··· Te(a)	3.111(1)	Te–Fe(1a)	2.561(1)
Fe(1) ··· Fe(2)	3.972(1)	Fe(1)–C(11)	1.788(4)
Fe(1)–C(12)	1.793(4)	Fe(1)–C(13)	1.770(4)
Fe(1)–Fe(1a)	2.582(1)	Fe(2)–C(21)	1.820(4)
Fe(2)–C(22)	1.820(4)	C(11)–O(11)	1.141(5)
C(12)–O(12)	1.137(4)	C(13)–O(13)	1.142(5)
C(21)–O(21)	1.134(5)	C(22)–O(22)	1.133(5)
Fe(1)–Te–Fe(2)	98.4(1)	Fe(1)–Te–Te(a)	52.5(1)
Fe(2)–Te–Te(a)	54.4(1)	Fe(1)–Te–Fe(1a)	60.4(1)
Fe(2)–Te–Fe(1a)	98.7(1)	Te(a)–Te–Fe(1a)	52.8(1)
Te–Fe(1)–C(11)	155.8(1)	Te–Fe(1)–C(12)	105.2(1)
C(11)–Fe(1)–C(12)	97.1(2)	Te–Fe(1)–C(13)	92.6(1)
C(11)–Fe(1)–C(13)	94.7(2)	C(12)–Fe(1)–C(13)	95.9(2)
Te–Fe(1)–Te(a)	74.6(1)	C(11)–Fe(1)–Te(a)	90.3(1)
C(12)–Fe(1)–Te(a)	105.8(1)	C(13)–Fe(1)–Te(a)	157.1(1)
Te–Fe(1)–Fe(1a)	59.6(1)	C(11)–Fe(1)–Fe(1a)	96.5(1)
C(12)–Fe(1)–Fe(1a)	160.3(1)	C(13)–Fe(1)–Fe(1a)	97.2(1)
Te(a)–Fe(1)–Fe(1a)	60.0(1)	Te–Fe(2)–C(21)	94.5(1)
Te–Fe(2)–C(22)	86.3(1)	C(21)–Fe(2)–C(22)	91.4(2)
Te–Fe(2)–Te(a)	71.1(1)	C(21)–Fe(2)–Te(a)	165.5(1)
C(22)–Fe(2)–Te(a)	89.6(1)	Te–Fe(2)–C(21a)	165.5(1)
C(21)–Fe(2)–C(21a)	100.0(2)	C(22)–Fe(2)–C(21a)	91.8(2)
C(22)–Fe(2)–C(22a)	175.0(2)	Fe(1)–C(11)–O(11)	178.8(4)
Fe(1)–C(12)–O(12)	175.4(4)	Fe(1)–C(13)–O(13)	177.2(4)
Fe(2)–C(21)–O(21)	178.9(3)	Fe(2)–C(22)–O(22)	176.5(3)

Fe(1a) link three nearly eclipsed CO groups. The Fe(2) atom is bonded to two equatorial CO groups lying almost exactly on the Fe_3 plane and to two CO groups axial with respect to the same plane.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for [$Fe_3(CO)_{10}Te_2$]

Atom	x	y	z	U_{eq}
Te	1201(1)	2105(1)	3717(1)	39(1)
Fe(1)	1262(1)	2977(1)	2062(1)	42(1)
Fe(2)	0	904(1)	2500	41(1)
C(11)	418(4)	3622(3)	949(3)	61(1)
O(11)	−110(4)	4044(2)	252(3)	86(1)
C(12)	2930(3)	2644(3)	1509(3)	54(1)
O(12)	4019(3)	2481(3)	1153(2)	80(1)
C(13)	2472(4)	3642(3)	2984(3)	63(1)
O(13)	3256(4)	4088(2)	3541(3)	94(2)
C(21)	1013(4)	259(2)	3611(3)	56(1)
O(21)	1642(4)	−152(2)	4291(3)	80(1)
C(22)	1855(4)	949(2)	1966(3)	55(1)
O(22)	3034(3)	943(2)	1658(3)	87(1)

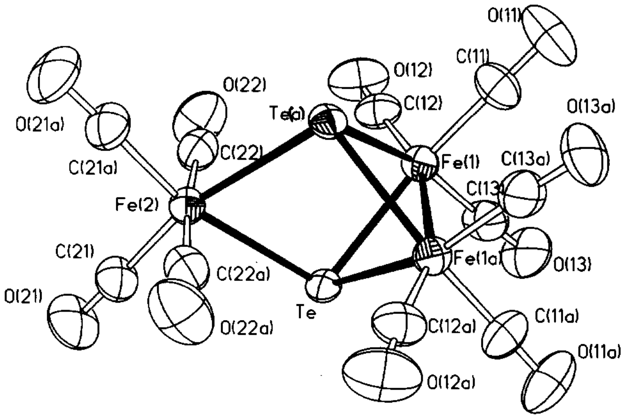

Fig. 1. View of the molecule of [$Fe_3(CO)_{10}Te_2$] showing the thermal ellipsoids (50% probability) and the atom-labelling scheme. The label "a" refers to atom generated by the crystallographic two-fold axis.

Table 3 shows related bond lengths and angles of [$Fe_3(CO)_9Te_2$] and [$Fe_3(CO)_{10}Te_2$], and of the analogous complex [$Fe_3(CO)_9\{P(C_6H_5)_3\}Te_2$]. It is clear from the Table that the geometries of the CO and PPh_3 complexes are quite similar. Comparison of the parent compound [$Fe_3(CO)_9Te_2$] and [$Fe_3(CO)_{10}Te_2$] shows considerable shortening of the Fe(1)–Fe(1a) bond of $Fe_3(CO)_{10}Te_2$ with respect to the average Fe–Fe distance in the triangle in [$Fe_3(CO)_9Te_2$], a small elongation of the Fe(1,1a)–Te bonds and a great lengthening of the Fe_{unique}–Te

Table 3

Selected interatomic distances (Å) and bond angles for [$Fe_3(CO)_9Te_2$], [$Fe_3(CO)_{10}Te_2$], and [$Fe_3(CO)_9\{P(C_6H_5)_3\}Te_2$]

	[$Fe_3(CO)_9Te_2$] [a]	[$Fe_3(CO)_{10}Te_2$]	[$Fe_3(CO)_9\{P(C_6H_5)_3\}Te_2$]
Fe–Fe	2.740(1)	2.584(2)	2.585(1)
	2.754(1)		
Fe···Fe	3.774(1)	3.972(1)	3.947(1)
			3.939(1)
Fe–Te	2.541(1)	2.571(1)	2.565(1)
	2.530(1)	2.562(1)	2.577(1)
	2.532(1)		2.575(1)
	2.557(1)		2.567(1)
	2.531(1)		2.657(1)
	2.538(1)		2.668(1)
Te···Te	3.380(1)	3.111(1)	3.138(1)
Fe–Te–Fe	65.89(4)	98.4(1)	98.19(2)
	96.17(5)	98.6(1)	97.62(2)
	65.39(4)	60.5(1)	97.66(2)
	65.43(4)		97.59(2)
	96.27(5)		60.35(2)
	65.18(4)		60.36(2)

[a] The data for [$Fe_3(CO)_9Te_2$] refer to a redetermination of the structure in the triclinic space group $P\bar{1}$ with $a = 7.065(2)$, $b = 9.468(3)$, $c = 13.270(3)$ Å, $\alpha = 94.48(2)$, $\beta = 95.25(2)$, $\gamma = 110.46(2)°$, $Z = 2$, $R = 0.040$ for 4316 observed reflections

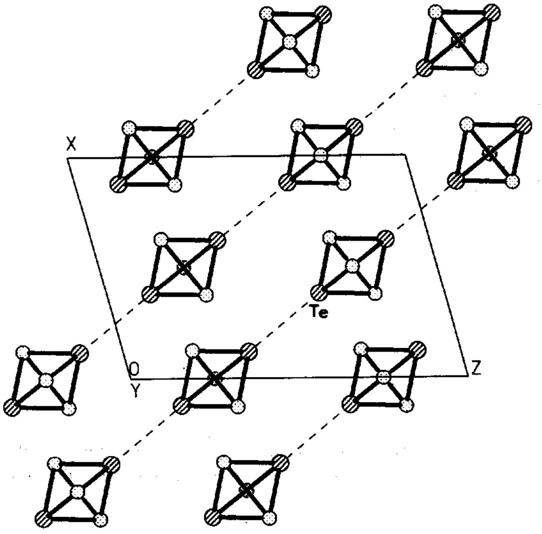

Fig. 2. Crystal packing projection of [$Fe_3(CO)_{10}Te_2$] down the *y* axis showing the intermolecular Te ··· Te contacts. The CO groups are omitted for clarity. The contacts refer to molecules at 0.5 − *x*, 0.5 − *y*, − *z* with respect to the molecule at *x*, *y*. *z*.

bond and a shortening of the Te ··· Te distance. This has the value (3.111 Å) not too different from the value (2.84 Å) found in crystalline tellurium. The shortening of the Fe–Fe bond is quite normal; in [$Fe_2(CO)_6Se_2Pt(P(C_6H_5)_3)_2$] [5], where the atomic arrangement is similar, the Fe–Fe distance (2.533 Å) is smaller than that in [$Fe_3(CO)_9Se_2$] (2.65 Å); this shortening can be rationalized by considering that in

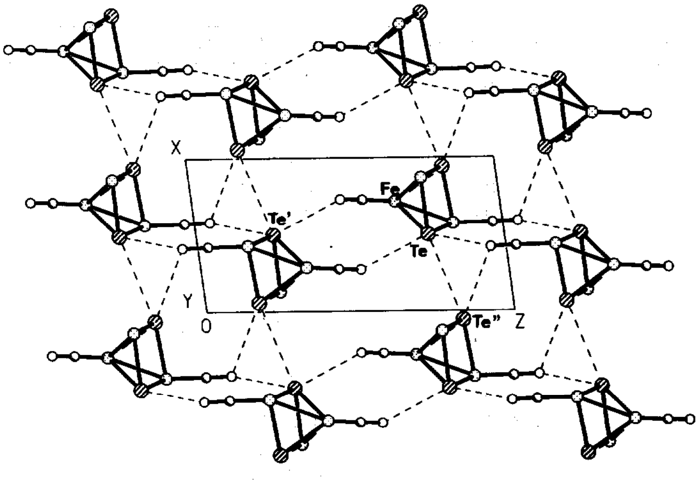

Fig. 3. Crystal packing projection of [$Fe_3(CO)_9Te_2$] down the *y* axis, showing the intermolecular Te ··· Te and Te ··· O contacts. The CO groups not involved in the contacts are omitted for clarity. The atoms designated thus (Fe, Te) relate to the molecule at *x*, *y*, *z*, those designated with a single prime (Te′) to the molecule related by a crystallographic centre of symmetry, and those with a double prime (Te″) to the molecule at 1 − *x*, *y*, *z*.

Table 4

Crystal data for $[Fe_3(CO)_{10}Te_2]$

Empirical formula	$C_{10}Fe_3O_{10}Te_2$
Colour; habit	dark red, prismatic
Crystal size (mm)	0.20×0.25×0.30
Crystal system	monoclinic
Space group	$C2/c$
Unit-cell dimensions	
a (Å)	8.288(2)
b (Å)	18.120(4)
c (Å)	12.168(2)
β (°)	105.05(3)
Volume (Å^3)	1764.7(6)
Z	4
Formula weight	702.8
Density (calc.) (Mg m^{-3})	2.645
Absorption coefficient (mm^{-1})	5.731
$F(000)$	1288

Table 5

Experimental data for $[Fe_3(CO)_{10}Te_2]$

Diffractometer used	Siemens P4
Radiation	Mo–K_α ($\lambda = 0.71073$ Å)
Monochromator	Highly oriented graphite crystal
2θ range (°)	4.0 to 60.0
Scan type	$2\theta - \theta$
Scan speed	Variable; 4.00 to 29.00° min^{-1} in θ
Scan range (θ)	2.40° plus K_α-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 35.0% of total scan time
Standard reflections	2 measured every 50 reflections
Index ranges	$-11 \le h \le 11, 0 \le k \le 25$ $0 \le l \le 17$
Reflections collected	3492
Independent reflections	1959 ($R_{int} = 3.18\%$)
Observed reflections	1957 ($F > 4.0\sigma(F)$)
Absorption correction	Semi-empirical
Min./max. transmission	0.015/0.027
System	Siemens SHELXTL PLUS (PC Version)
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Extinction correction	$\chi = 0.00038(2)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$
Number of parameters refined	115
Final R (obs. data)	$R = 2.29\%$, $R_w = 2.82\%$
R (all data)	$R = 2.30\%$, $R_w = 2.82\%$
Goodness of fit	1.45
Largest and mean Δ/σ	0.001, 0.000
Data to parameter ratio	17.0:1
Largest difference peak (e Å^{-3})	1.93
Largest difference trough (e Å^{-3})	0.00

the $Fe_3(CO)_9Te_2$ complex there are two types of $Fe(CO)_3$ group, tri- and tetra-coordinate. The bond between them is longer than the corresponding bond in $[Fe_3(CO)_{10}Te_2]$ where both $Fe(CO)_3$ groups are three coordinate.

A similar phenomenon is observed in $[Fe_3(CO)_9S_2]$ ($Fe(CO)_3$ groups with coordination 3 and 4, Fe–Fe 2.597(1) Å) [2] with $[Fe_2(CO)_6S_2]$ ($Fe(CO)_3$ groups with coordination 3, Fe–Fe 2.54(1) Å) [1]. The lengthening of the Fe_{unique}–Te bond parallels the opening of the Fe–Te–Fe_{unique} angles (from 65° to 98°) and the closeness of the two Te atoms. Both these effects are also found in the $P(C_6H_5)_3$ adduct, but to a smaller extent.

It is clear from the packing patterns of $Fe_3(CO)_{10}Te_2$ that in the crystal the Te atom is a centre for intermolecular bonding (Fig. 2). In fact the Te ··· Te intermolecular distance of 3.596(1) Å is significantly shorter than the sum of the van der Waals radii (4.2 Å), and diagonal chains are formed (Fig. 2).

In the parent complex $[Fe_3(CO)_9Te_2]$ this function of the tellurium atom is even more evident. Short Te ··· O_{CO} contacts (3.48, 3.58 and 3.62 Å) and Te ··· Te contacts (4.043(1) Å) give rise to the extended framework shown in Fig. 3.

Experimental

Crystallography

Crystals of the complex were obtained by cooling a n-heptane solution at −12°C. The crystal data, data collection parameters and data concerning the solution and refinement of the structure are collected in Tables 4 and 5 respectively.

Tables of anisotropic thermal parameters and observed and calculated structure factors are available from the author.

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