

# Application of the Hydro(solvento)thermal Technique to the Synthesis of Metal Carbonyl Chalcogenide Clusters. 2. Synthesis and X-ray Structures of $[(\text{Fe}_4\text{Te}_4(\text{CO})_{10})_2(\text{Te}_2)]^{2-}$ and $[(\text{Fe}_2\text{Se}(\text{CO})_6)_2(\text{Se}_2)]^{2-}$ †

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The hydrothermal reaction of  $\text{Fe}(\text{CO})_5$  with  $\text{Na}_2\text{Te}_2$  in the presence of  $\text{Ph}_4\text{PCl}$  at 110 °C forms  $(\text{Ph}_4\text{P})_2[(\text{Fe}_4\text{Te}_4(\text{CO})_{10})_2(\text{Te}_2)]$  (I) while the reaction of  $\text{Fe}(\text{CO})_5$  with  $\text{Na}_2\text{Se}_2$  in superheated methanol at 80 °C results in  $(\text{Ph}_4\text{P})_2[(\text{Fe}_2\text{Se}(\text{CO})_6)_2(\text{Se}_2)]$  (II). The structures of (I) and (II) were determined by X-ray single-crystal analysis. (I) crystallizes in the space group  $P\bar{1}$ , and (II) in the space group  $P2_1/n$ . The cell parameters are  $a = 14.930(4)$  Å,  $b = 24.070(3)$  Å,  $c = 13.045(2)$  Å,  $\alpha = 93.19(1)^\circ$ ,  $\beta = 113.36(1)^\circ$ ,  $\gamma = 76.61(2)^\circ$ ,  $V = 4183(3)$  Å<sup>3</sup>, and  $Z = 2$  at 23 °C for (I) and  $a = 10.561(6)$  Å,  $b = 14.021(5)$  Å,  $c = 20.46(1)$  Å,  $\beta = 91.89(4)^\circ$ ,  $V = 3028(2)$  Å<sup>3</sup>, and  $Z = 4$  at -100 °C for (II). The  $[(\text{Fe}_4\text{Te}_4(\text{CO})_{10})_2(\text{Te}_2)]^{2-}$  anion in (I) forms a ditelluride,  $\text{Te}_2^{2-}$ , bridged double cubane-like structure with eight iron atoms in two  $\text{Fe}_4\text{Te}_4$  cubes being octahedrally-coordinated by bridging tellurium ligands and terminal CO groups. The  $[(\text{Fe}_2\text{Se}(\text{CO})_6)_2(\text{Se}_2)]^{2-}$  molecule in (II) adopts a double "butterfly" conformation caused by an intramolecular Se–Se linkage between two  $\text{Fe}_2\text{Se}_2(\text{CO})_6$  units. All iron atoms in this structure have a distorted octahedral geometry achieved by selenium ligands, CO groups, and a Fe–Fe single bond. The average Fe–Te bond distance is 2.619(4) Å, and Fe–Se = 2.386(17) Å.

## Introduction

The incorporation of main group elements into transition metal clusters often introduces unique structural features and unusual reactivities, thus providing new opportunities for studies of structural principles and new chemical reactions.<sup>1–3</sup> One particular area of current interest is the preparation of chalcogen-containing metal carbonyl clusters.<sup>4–7</sup> Syntheses designed to produce novel metal carbonyl clusters containing chalcogens have imposed a great challenge to the cluster chemist and still occupy a prominent position in this research area.<sup>3–7</sup> A common approach to obtaining large clusters is to react a chalcogen-containing cluster either with a complex having labile groups or with a coordinatively unsaturated species generated in-situ by UV irradiation.<sup>8</sup> This has been particularly successful in the syntheses of many sulfur-containing metal clusters.<sup>3,4b,8b–c</sup> However, such reactions often suffer low yields and require lengthy separation procedures.

† For part 1, see ref 10.

‡ A. P. Sloan Fellow 1991–1993.

- (1) See, for example: (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds; Pergamon: Oxford, England, 1982; Vol. 6, Chapters 41–43, pp 879–1043. (b) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169–208.
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- (8) For recent examples, see: (a) Mathur, P.; Chakrabarty, D.; Hossain, Md. M.; Rashid, R. S. *J. Organomet. Chem.* **1991**, *420*, 79–86. (b) Adams, R. D.; Babin, J. E.; Wang, J.-G.; Wu, W. *Inorg. Chem.* **1989**, *28*, 703–709. (c) Adams, R. D.; Babin, J. E.; Estrada, J.; Wang, J.-G.; Wang, M. B.; Low, A. A. *Polyhedron* **1989**, *8*, 1885–1890.

Table I. Data for Crystal Structure Analysis of  $(\text{Ph}_4\text{P})_2[(\text{Fe}_4\text{Te}_4(\text{CO})_{10})_2(\text{Te}_2)]$  (I) and  $(\text{Ph}_4\text{P})_2[(\text{Fe}_2\text{Se}(\text{CO})_6)_2(\text{Se}_2)]$  (II)

	compd	
	I	II
formula	$\text{C}_{68}\text{H}_{40}\text{O}_{20}\text{P}_2\text{Fe}_8\text{Te}_{10}$	$\text{C}_{60}\text{H}_{40}\text{P}_2\text{O}_{12}\text{Fe}_4\text{Se}_4$
$a$ , Å	14.930(4)	10.561(6)
$b$ , Å	24.070(3)	14.021(5)
$c$ , Å	13.045(2)	20.46(1)
$\alpha$ , deg	93.19(1)	90.00
$\beta$ , deg	113.36(1)	91.89(4)
$\gamma$ , deg	76.61(2)	90.00
$Z$ ; $V$ , Å <sup>3</sup>	2, 4183(3)	4, 3028(2)
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
$D_{\text{calc}}$ , g/cm <sup>3</sup>	2.35	1.71
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	48.8	34.3
cryst size, mm	0.13 × 0.19 × 0.37	0.09 × 0.11 × 0.20
$2\theta_{\text{max}}$ , deg	50.0	45.0
temp, °C	23	-100
no. of data colld	15 332	4422
no. of data used	8757	1273
$(F_o^2 > 3\sigma(F_o^2))$		
min, max abs cor	0.76, 1.11	0.79, 1.17
no. of variables	973	220
no. of atoms per asym unit (including H)	148	61
final $R/R_w$ , %	4.3/5.7	6.0/7.0

Oxidative decarbonylation of metal carbonyls by polychalcogenide ligands  $\text{Q}_n^{2-}$  ( $\text{Q} = \text{S}, \text{Se}$  and  $\text{Te}$ ;  $n = 2–6$ ) provides a convenient route for introducing chalcogen-atoms into metal clusters, resulting in CO-containing metal polychalcogenide complexes  $[(\text{CO})_n\text{M}(\text{Q}_x)_m]^{q-}$ .<sup>9</sup> We have discovered that under the hydro(solvento)thermal conditions such reactions can undertake different pathways, often leading to the formation of chalcogen/carbonyl metal clusters.<sup>10,11</sup> Here we report the synthesis and X-ray structures of  $(\text{Ph}_4\text{P})_2[(\text{Fe}_4\text{Te}_4(\text{CO})_{10})_2(\text{Te}_2)]$  (I) and

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**Table II.** Positional Parameters and Equivalent Isotropic Displacement Values ( $\text{\AA}^2$ )<sup>a</sup> for  $(\text{Ph}_4\text{P})_2\{[\text{Fe}_4\text{Te}_4(\text{CO})_{10}]_2(\text{Te}_2)\}$  with Estimated Standard Deviations in Parentheses

atom	x	y	z	B(eq)	atom	x	y	z	B(eq)
Te(1)	0.83884(9)	0.14517(5)	0.6933(1)	3.38(2)	O(12)	0.434(1)	0.4135(7)	0.629(1)	6.2(4)
Te(2)	1.0802(1)	0.12779(6)	0.8830(1)	3.69(3)	O(13)	0.534(1)	0.1635(7)	1.014(1)	6.9(4)
Te(3)	0.9892(1)	0.22024(6)	0.6450(1)	3.97(3)	O(14)	0.832(1)	0.1803(7)	1.212(1)	7.8(4)
Te(4)	0.9222(1)	0.26140(6)	0.8621(1)	3.43(2)	O(15)	0.339(1)	0.2808(7)	1.018(1)	7.6(4)
Te(5)	0.50660(9)	0.29658(5)	0.8536(1)	3.08(2)	O(16)	0.271(1)	0.4175(7)	0.763(1)	6.6(4)
Te(6)	0.59418(9)	0.31440(5)	1.1378(1)	3.33(2)	O(17)	0.375(1)	0.4533(6)	1.121(1)	5.1(3)
Te(7)	0.55077(8)	0.42672(5)	0.9540(1)	2.93(2)	O(18)	0.802(1)	0.4714(6)	1.111(1)	5.8(3)
Te(8)	0.75456(8)	0.31635(5)	1.00937(9)	2.88(2)	O(19)	0.870(1)	0.3238(7)	1.332(1)	7.9(4)
Te(9)	0.65689(8)	0.27355(5)	0.70384(9)	2.99(2)	O(20)	0.607(1)	0.4658(6)	1.280(1)	5.7(3)
Te(10)	0.72194(9)	0.18640(5)	0.8714(1)	3.04(2)	C(1')	0.804(2)	0.327(1)	0.630(2)	6.7(6)
Fe(1)	0.8143(2)	0.2552(1)	0.6526(2)	3.45(5)	C(2')	0.750(2)	0.247(1)	0.512(2)	5.8(5)
Fe(2)	0.9129(2)	0.1594(1)	0.9092(2)	3.20(5)	C(3')	0.914(2)	0.088(1)	0.942(2)	5.0(5)
Fe(3)	1.0091(2)	0.1100(1)	0.6668(2)	4.07(6)	C(4')	0.965(1)	0.1764(9)	1.046(2)	4.5(4)
Fe(4)	1.1027(2)	0.2300(1)	0.8561(2)	4.10(6)	C(5')	1.017(2)	0.037(1)	0.699(2)	5.4(5)
Fe(5)	0.6126(2)	0.3606(1)	0.8200(2)	2.83(5)	C(6')	0.937(2)	0.104(1)	0.525(2)	7.1(6)
Fe(6)	0.6612(2)	0.2390(1)	1.0195(2)	3.20(5)	C(7')	1.128(2)	0.100(1)	0.658(2)	5.1(5)
Fe(7)	0.4306(2)	0.3679(1)	0.9737(2)	3.25(5)	C(8')	1.101(2)	0.297(1)	0.820(2)	6.3(6)
Fe(8)	0.6994(2)	0.3891(1)	1.1442(2)	3.28(5)	C(9')	1.157(2)	0.236(1)	1.003(2)	5.5(5)
O(1)	0.800(1)	0.3735(8)	0.612(1)	8.9(5)	C(10')	1.216(2)	0.199(1)	0.840(2)	5.7(5)
O(2)	0.706(1)	0.2387(7)	0.417(1)	7.7(4)	C(11')	0.690(1)	0.4018(8)	0.808(1)	3.8(4)
O(3)	0.913(1)	0.0431(7)	0.967(1)	6.9(4)	C(12')	0.508(1)	0.3887(9)	0.707(2)	4.6(4)
O(4)	1.000(1)	0.1914(7)	1.139(1)	6.9(4)	C(13')	0.586(2)	0.194(1)	1.018(2)	5.0(5)
O(5)	1.029(1)	-0.0087(8)	0.726(1)	7.9(4)	C(14')	0.762(1)	0.2050(9)	1.134(2)	4.3(4)
O(6)	0.890(1)	0.1050(7)	0.428(1)	7.6(4)	C(15')	0.374(2)	0.316(1)	0.995(2)	5.5(5)
O(7)	1.202(1)	0.0928(7)	0.647(1)	6.3(4)	C(16')	0.335(1)	0.3975(9)	0.847(2)	4.2(4)
O(8)	1.108(1)	0.3443(8)	0.798(1)	7.5(4)	C(17')	0.399(1)	0.4168(9)	1.066(2)	4.3(4)
O(9)	1.192(1)	0.2384(7)	1.101(1)	7.8(4)	C(18')	0.761(1)	0.4406(8)	1.126(1)	4.0(4)
O(10)	1.291(1)	0.1812(8)	0.831(1)	9.2(5)	C(19')	0.800(2)	0.348(1)	1.256(2)	4.9(5)
O(11)	0.742(1)	0.4297(7)	0.802(1)	6.2(4)	C(20')	0.641(1)	0.4385(9)	1.222(2)	4.4(4)

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

$(\text{Ph}_4\text{P})_2\{[\text{Fe}_2\text{Se}(\text{CO})_6]_2(\text{Se}_2)\}$  (II), two chalcogen-containing metal carbonyl clusters prepared by hydro(methano)thermal technique. During the preparation of this manuscript, we have learned that (I) has also been prepared by the conventional solution method.<sup>12</sup>

### Experimental Section

All manipulations were carried out in a glove-box under nitrogen atmosphere.  $\text{Na}_2\text{Te}_2$  and  $\text{Na}_2\text{Se}_2$  were prepared by dissolving the stoichiometric amount of the elements in liquid ammonia.  $\text{Fe}(\text{CO})_5$  was used as obtained.

**Preparation of  $(\text{Ph}_4\text{P})_2\{[\text{Fe}_4\text{Te}_4(\text{CO})_{10}]_2(\text{Te}_2)\}$  (I).** 120 mg  $\text{Na}_2\text{Te}_2$  (0.4 mmol) and 220 mg  $\text{Ph}_4\text{PCl}$  (0.6 mmol) were thoroughly mixed and loaded into a 10-in. long thick-walled Pyrex tube (9 mm in diameter) in which 0.15 ml (1.14 mmol)  $\text{Fe}(\text{CO})_5$  had already been added. After 0.5 ml  $\text{H}_2\text{O}$  was syringed in, the tube was frozen with liquid  $\text{N}_2$ , then evacuated and sealed (the total volume is  $\sim 4$  ml after sealing). Continuous heating of the tube at 110 °C for 60 h resulted in large plate-like black crystals. Successive washing of the product with MeOH and ether afforded 100 mg analytically pure single crystals (67% yield based on  $\text{Na}_2\text{Te}_2$ ).

**Preparation of  $(\text{Ph}_4\text{P})_2\{[\text{Fe}_2\text{Se}(\text{CO})_6]_2(\text{Se}_2)\}$  (II).** This compound is prepared in a similar manner as above, except that the sealed tube contained 0.15 ml  $\text{Fe}(\text{CO})_5$  (1.14 mmol), 82 mg (0.4 mmol)  $\text{Na}_2\text{Se}_2$ , 220  $\text{Ph}_4\text{PCl}$  (0.6 mmol) and 0.8 ml MeOH. The reaction was carried out at 80 °C for 96 h. During this time, the tube had been taken out and shaken three times in a  $\sim 24$  h interval to homogenize the tube content. 117 mg needle-like black crystals were obtained (75% yield based on  $\text{Na}_2\text{Se}_2$ ).

Each product was subject to X-ray powder diffraction (XRD) studies for phase identification. The observed XRD patterns of (I) and (II) match well with those calculated from the corresponding X-ray single crystal data, confirming the homogeneity of the products.

**Crystallographic Studies.** The crystallographic data sets of compound (I) and (II) were collected on a Rigaku AFC6S four-circle diffractometer using  $\omega$ - $2\theta$  scan techniques and Mo  $K\alpha$  radiation. A crystal of (I) was mounted in a glass capillary and sealed. A crystal of (II) was affixed to the tip of a glass fiber, and the intensity data were measured at  $-100$

**Table III.** Positional Parameters and Equivalent Isotropic Displacement Values ( $\text{\AA}^2$ )<sup>a</sup> for  $(\text{Ph}_4\text{P})_2\{[\text{Fe}_2\text{Se}(\text{CO})_6]_2(\text{Se}_2)\}$  with Estimated Standard Deviations in Parentheses

atom	x	y	z	B(eq)
Se(1)	0.0374(3)	0.4205(2)	0.4834(1)	2.8(2)
Se(2)	0.1013(3)	0.2696(2)	0.3975(1)	3.0(2)
Fe(1)	-0.0719(4)	0.3812(3)	0.3850(2)	2.8(2)
Fe(2)	0.1590(4)	0.4359(3)	0.3894(2)	2.6(2)
O(1)	-0.301(2)	0.316(2)	0.449(1)	6(1)
O(2)	-0.100(2)	0.297(2)	0.254(1)	6(1)
O(3)	-0.166(2)	0.574(2)	0.347(1)	5(1)
O(4)	0.422(2)	0.432(1)	0.440(1)	5(1)
O(5)	0.197(2)	0.401(1)	0.251(1)	4(1)
O(6)	0.148(2)	0.646(2)	0.3784(9)	4(1)
C(1')	-0.215(3)	0.340(2)	0.426(2)	4.0(9)
C(2')	-0.091(3)	0.329(2)	0.307(2)	4.3(8)
C(3')	-0.132(3)	0.498(2)	0.364(1)	3.4(7)
C(4')	0.318(3)	0.433(2)	0.420(1)	2.7(6)
C(5')	0.184(3)	0.414(3)	0.305(2)	4.9(9)
C(6')	0.147(3)	0.563(2)	0.384(1)	3.0(7)

<sup>a</sup>  $B(\text{iso})$  is defined as  $4/3[a^2\beta_{22} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

°C. The stability of the experimental setup and crystal integrity for each data collection was monitored by measuring three representative reflections periodically (every 150). No crystal decay was detected. Empirical absorption corrections based on  $\psi$  scans of three strong reflections with  $\chi \sim 90^\circ$  were applied to each data set. The structures were solved with direct methods and refined with full-matrix least squares techniques. DIFABS corrections after isotropic refinement of all atoms were then applied.<sup>13</sup> The calculations were performed on a VAXstation 3100 computer using the TEXSAN crystallographic software package of Molecular Structure Corporation.<sup>14</sup> Table I gives crystal data and details for structure analysis of two compounds. All non-hydrogen atoms were refined either isotropically or anisotropically. The hydrogen positions were calculated but not refined. The final coordinates and average temperature factors ( $B_{\text{iso}}$ ) of the atoms in the anions of (I) and (II) are given in Tables II and III.

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(14) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0. Molecular Structure Corp.: The Woodlands, TX.

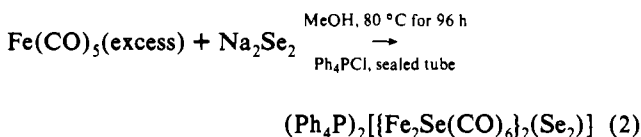
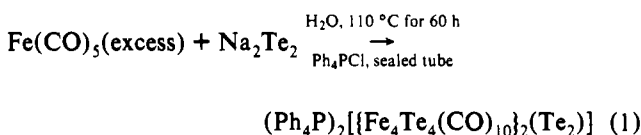
**Table IV.** Selected Geometric Data for  $(\text{Ph}_4\text{P})_2\{[\text{Fe}_4\text{Te}_4(\text{CO})_{10}\}_2(\text{Te}_2)\}^a$ 

Bond Distances (Å)			
Te(9)–Te(10)	2.829(2)	Fe–C (mean)	1.78(7)
Fe(1)–Te(1)	2.642(3)	Fe(1)–Te(3)	2.590(2)
Fe(1)–Te(4)	2.585(2)	Fe(1)–Te(9)	2.628(2)
Fe(2)–Te(1)	2.623(2)	Fe(2)–Te(2)	2.589(2)
Fe(2)–Te(4)	2.612(3)	Fe(2)–Te(10)	2.620(2)
Fe(3)–Te(1)	2.641(2)	Fe(3)–Te(2)	2.640(2)
Fe(3)–Te(3)	2.620(3)	Fe(4)–Te(2)	2.620(3)
Fe(4)–Te(3)	2.632(3)	Fe(4)–Te(4)	2.657(2)
Fe(5)–Te(5)	2.615(2)	Fe(5)–Te(7)	2.595(2)
Fe(5)–Te(8)	2.613(2)	Fe(5)–Te(9)	2.633(2)
Fe(6)–Te(5)	2.614(2)	Fe(6)–Te(6)	2.598(2)
Fe(6)–Te(8)	2.612(2)	Fe(6)–Te(10)	2.599(2)
Fe(7)–Te(5)	2.625(2)	Fe(7)–Te(6)	2.627(2)
Fe(7)–Te(7)	2.622(2)	Fe(8)–Te(6)	2.625(3)
Fe(8)–Te(7)	2.619(2)	Fe(8)–Te(8)	2.641(2)
Fe–Te (mean)	2.619(4)		
Bond Angles (deg)			
Fe(1)–Te(1)–Fe(2)	90.97(7)	Fe(1)–Te(1)–Fe(3)	96.98(8)
Fe(2)–Te(1)–Fe(3)	98.39(7)	Fe(2)–Te(2)–Fe(3)	99.29(7)
Fe(2)–Te(2)–Fe(4)	97.41(8)	Fe(3)–Te(2)–Fe(4)	93.78(8)
Fe(1)–Te(3)–Fe(3)	98.80(8)	Fe(1)–Te(3)–Fe(4)	99.40(8)
Fe(3)–Te(3)–Fe(4)	93.95(8)	Fe(1)–Te(4)–Fe(2)	92.52(8)
Fe(1)–Te(4)–Fe(4)	98.90(8)	Fe(2)–Te(4)–Fe(4)	95.94(8)
Fe(5)–Te(5)–Fe(6)	92.52(7)	Fe(5)–Te(5)–Fe(7)	97.42(7)
Fe(6)–Te(5)–Fe(7)	97.28(7)	Fe(6)–Te(6)–Fe(7)	97.61(7)
Fe(6)–Te(6)–Fe(8)	98.28(7)	Fe(7)–Te(6)–Fe(8)	95.26(7)
Fe(5)–Te(7)–Fe(7)	98.00(7)	Fe(5)–Te(7)–Fe(8)	99.29(7)
Fe(7)–Te(7)–Fe(8)	95.52(7)	Fe(5)–Te(8)–Fe(6)	92.60(7)
Fe(5)–Te(8)–Fe(8)	98.26(7)	Fe(6)–Te(8)–Fe(8)	97.51(7)
Fe–Te–Fe (mean)	96.5(5)		
Fe(1)–Te(9)–Fe(5)	122.94(8)	Fe(2)–Te(10)–Fe(6)	120.47(7)
Te(1)–Fe(1)–Te(3)	82.17(7)	Te(1)–Fe(1)–Te(4)	87.15(7)
Te(1)–Fe(1)–Te(9)	87.60(8)	Te(1)–Fe(2)–Te(2)	81.77(7)
Te(1)–Fe(2)–Te(4)	87.01(7)	Te(1)–Fe(2)–Te(10)	80.94(7)
Te(1)–Fe(3)–Te(2)	80.49(7)	Te(1)–Fe(3)–Te(3)	81.64(8)
Te(2)–Fe(3)–Te(3)	84.32(8)	Te(2)–Fe(4)–Te(3)	84.48(8)
Te(2)–Fe(4)–Te(4)	82.31(7)	Te(3)–Fe(4)–Te(4)	79.74(7)
Te(5)–Fe(5)–Te(7)	82.41(6)	Te(5)–Fe(5)–Te(8)	86.40(7)
Te(5)–Fe(5)–Te(9)	82.39(7)	Te(5)–Fe(6)–Te(6)	82.79(7)
Te(5)–Fe(6)–Te(8)	86.47(7)	Te(5)–Fe(6)–Te(10)	87.34(7)
Te(5)–Fe(7)–Te(6)	82.01(7)	Te(5)–Fe(7)–Te(7)	81.72(7)
Te(6)–Fe(7)–Te(7)	83.23(7)	Te(6)–Fe(8)–Te(7)	83.34(7)
Te(6)–Fe(8)–Te(8)	81.37(7)	Te(7)–Fe(8)–Te(8)	80.57(6)
Te–Fe–Te (mean)	83.3(5)	C–Fe–C (mean)	97(6)

<sup>a</sup> The estimated standard deviations in the mean bond lengths and the mean bond angles are calculated by the equation  $\sigma_l = \{\sum_n (l_n - l)^2 / n(n-1)\}^{1/2}$ , where  $l_n$  is the length (angle) of the  $n$ th bond,  $l$  the mean length (angle), and  $n$  the number of bonds.

## Results and Discussion

The one-step assembly of two iron carbonyl/polychalcogenide clusters is readily accomplished through oxidative decarbonylation of  $\text{Fe}(\text{CO})_5$  by  $\text{Na}_2\text{Q}_2$  ( $\text{Q} = \text{Te}$  or  $\text{Se}$ ) under hydro(methano)-thermal conditions:



The most intriguing feature of these reactions is the concomitant growth of single crystals of the products. Under hydro(solvo)-thermal conditions the chemical reaction is combined with a transport process leading directly to crystal growth. This implies that even  $\text{Ph}_4\text{P}^+$  salts of large clusters can be slightly soluble in hot methanol or water, which under “normal” conditions do not

**Table V.** Selected Geometric Data for  $(\text{Ph}_4\text{P})_2\{[\text{Fe}_2\text{Se}(\text{CO})_6\}_2(\text{Se}_2)\}^a$ 

Bond Distances (Å)			
Fe(1)–Fe(2)	2.555(6)	Se(1)–Se(1)	2.467(7)
Fe–C (mean)	1.80(1)	Fe(1)–Se(1)	2.354(5)
Fe(1)–Se(2)	2.415(5)	Fe(2)–Se(1)	2.358(5)
Fe(2)–Se(2)	2.417(5)	Fe–Se (mean)	2.386(17)
Se(1)–Se(2)	2.847(5)		
Bond Angles (deg)			
Fe(1)–Se(1)–Fe(2)	65.7(2)	Fe(1)–Se(2)–Fe(2)	63.8(2)
Se(1)–Se(1)–Fe(1)	107.1(2)	Se(1)–Se(1)–Fe(2)	109.2(2)
Se(1)–Fe(1)–Se(2)	73.3(2)	Se(1)–Fe(2)–Se(2)	73.2(2)
Se(1)–Fe(1)–C(1)'	94(1)	Se(1)–Fe(1)–C(2)'	156(1)
Se(1)–Fe(1)–C(3)'	98.5(9)	Se(1)–Fe(2)–C(4)'	104.0(8)
Se(1)–Fe(2)–C(5)'	151(1)	Se(1)–Fe(2)–C(6)'	96.1(9)
Se(2)–Fe(1)–C(1)'	112(1)	Se(2)–Fe(1)–C(2)'	84(1)
Se(2)–Fe(1)–C(3)'	151(1)	Se(2)–Fe(2)–C(4)'	101(1)
Se(2)–Fe(2)–C(5)'	87(1)	Se(2)–Fe(2)–C(6)'	161(1)
Fe(2)–Fe(1)–C(1)'	112(1)	Fe(2)–Fe(1)–C(2)'	84(1)
Fe(2)–Fe(1)–C(3)'	151(1)	Fe(1)–Fe(2)–C(4)'	153.8(9)
Fe(1)–Fe(2)–C(5)'	95(1)	Fe(1)–Fe(2)–C(6)'	103.5(9)
C(1)′–Fe(1)–C(2)′	102(1)	C(1)′–Fe(1)–C(3)′	96(1)
C(2)′–Fe(1)–C(3)′	98(1)	C(4)′–Fe(2)–C(5)′	100(1)
C(4)′–Fe(2)–C(6)′	96(1)	C(5)′–Fe(2)–C(6)′	97(1)

<sup>a</sup> See footnote *a* of Table IV.

dissolve them. Generally, both solubility and crystallization in a hydrothermal reaction are improved by the presence of a complexing agent—a “mineralizer” in geological terminology. In the above reactions, dichalcogenide ligands act as reagents as well as mineralizers.

The ultimate molar ratio of the reactants in each synthesis was determined by optimizing the synthetic yield, and/or avoiding the formation of polychalcogenide/elemental chalcogen crystals. In synthetic reactions that involve  $\text{Na}_2\text{Se}_2$ ,  $\text{H}_2\text{O}$  is found to cause decomposition of the ligand, affording single crystals of elemental selenium. The use of  $\text{MeOH}$  gave satisfactory results. In general, the products obtained from such hydrothermal conditions are the most kinetically stable, as they are “arrested” and removed from solution during crystal growth.

The structure of (I) comprises of  $\text{Ph}_4\text{P}^+$  cations and  $\{[\text{Fe}_4\text{Te}_4(\text{CO})_{10}\}_2(\text{Te}_2)\}^{2-}$  anions in the lattice. The  $\{[\text{Fe}_4\text{Te}_4(\text{CO})_{10}\}_2(\text{Te}_2)\}^{2-}$  anion contains two  $\text{Fe}_4\text{Te}_4$  cubane-like cages bridged by a  $\text{Te}_2^{2-}$  unit (Figure 1). The latter acts overall as a  $\mu_4$ -type ligand. These cages can be each described as being formed by the interpenetrating tetrahedral arrays of four iron and tellurium atoms. Such a structure is an almost omnipresent theme in iron–sulfur chemistry.<sup>15</sup> However, the octahedral coordination geometry of all the iron atoms, being completed by terminal CO groups, differs from many iron–sulfur cubanes.<sup>15</sup> The Te–Te distance in the bridging unit is 2.829(2) Å, and can be considered a normal single bond.<sup>16</sup> Other compounds containing such a  $\mu_4$  type  $\text{Te}_2^{2-}$  ligand are  $[\text{K}(\text{-crypt})]_2\text{Mo}_4\text{Te}_{16}(\text{en})_4$ <sup>17a</sup> and  $(\text{Bu}_4\text{N})_4[\text{Hg}_4\text{Te}_{12}]$ .<sup>17b</sup> The Fe–Te bond distances, ranging from 2.585(2) Å to 2.657(2) Å (average 2.619(4) Å), are rather uniform, and comparable with those found in  $\text{Cs}_7[\text{Fe}_4\text{Te}_4(\text{Te})_4]$ <sup>18a</sup> and a number of iron–telluride–telluroate complexes having cubane-like cores.<sup>18b,c</sup> Other selected bond distances and bond angles are given in Table IV. If the charge of both the ditelluride and the monotelluride ligands in this structure is taken as 2–, the

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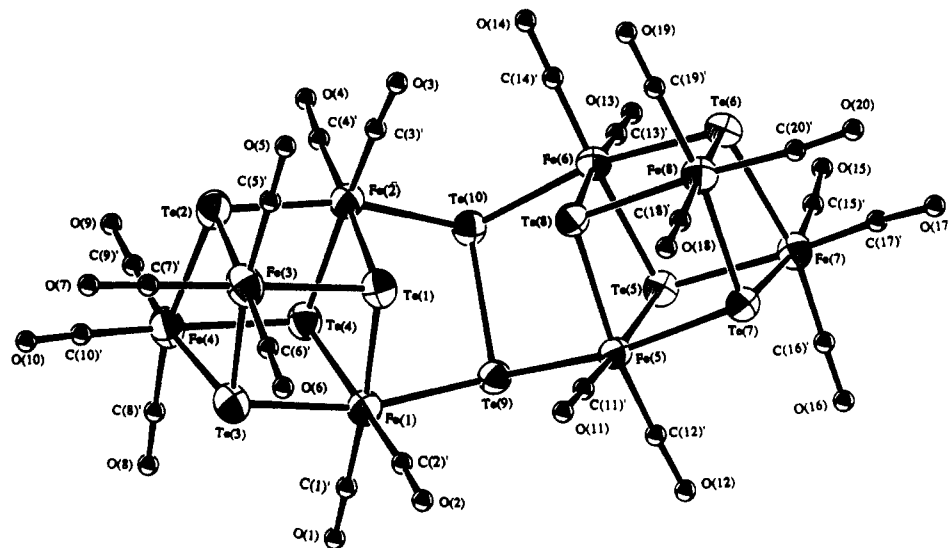


Figure 1. Structure of  $[\{\text{Fe}_4\text{Te}_4(\text{CO})_{10}\}_2(\text{Te}_2)]^{2-}$  with the atom-labeling scheme.

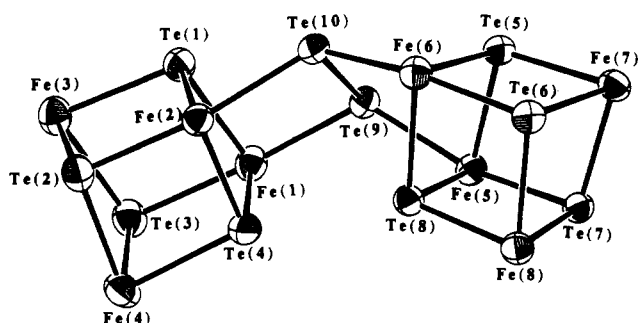


Figure 2. Structure of  $[\{\text{Fe}_4\text{Te}_4(\text{CO})_{10}\}_2(\text{Te}_2)]^{2-}$  with CO groups omitted, emphasizing the two  $\text{Fe}_4\text{Te}_4$  cores and their coupling via the  $\text{Te}_2^{2-}$  ligand.

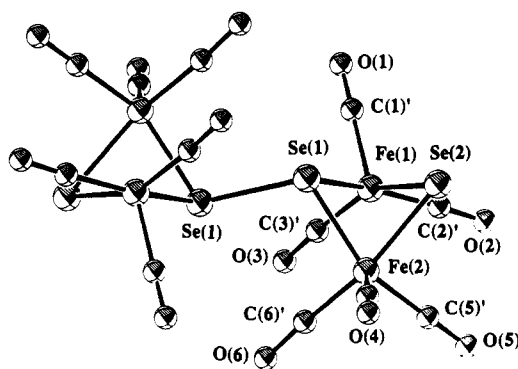


Figure 3. Structure of  $[\{\text{Fe}_2\text{Se}(\text{CO})_6\}_2(\text{Se}_2)]^{2-}$  with the atom-labeling scheme.

eight iron atoms would have a formal oxidation state  $2+$ . Consistent with this oxidation state, the observed long Fe–Fe distances in both cubanes (the shortest distance is 3.75 Å) exclude any possible M–M bonding in (I). As a result, the two  $\text{Fe}_4\text{Te}_4$  cubanes have approximate local  $T_d$  symmetry as shown in Figure 2.

Thus far, the majority of the  $[\text{Fe}_4\text{Q}_4(\text{X})_4]^{n-}$  ( $\text{Q} = \text{S}, \text{Se}$  and  $\text{Te}$ ) cubanes found in the literature are mixed-valent with extensive M–M bonding in the  $\text{Fe}_4\text{Q}_4$  cores.<sup>15,18</sup> Therefore, the formal oxidation state of iron atoms is often a non-integral value between 2 and 3. Dahl and co-workers showed that when the nitrosyl clusters  $[\text{Fe}_4\text{Q}_4(\text{NO})_4]$  ( $\text{Q} = \text{S}, \text{Se}$ ) were reacted with CO to form  $[\text{Fe}_4\text{Q}_4(\text{CO})_{12}]$  ( $\text{Q} = \text{S}, \text{Se}$ ), the Fe–Fe distances expanded from 2.65 Å to 3.47 Å (for  $\text{Q} = \text{S}$ ), or 2.71 Å to 3.62 Å (for  $\text{Q} = \text{Se}$ ).<sup>19</sup> This was in accordance with the analysis of the qualitative MO's of cubane-like  $\text{Fe}_4\text{Q}_4$  clusters ( $\text{Q} = \text{S}, \text{Se}$  and  $\text{Te}$ ), which predicted that if the 60e nitrosyl cubane cluster was to expand to a 72e cluster, the additional 12 valence electrons would have to occupy the six empty tetrairon antibonding MO's (i.e.  $t_1 + t_2$ ) of the cluster, resulting in complete breakage of the M–M bonding.<sup>20</sup> A similar argument applies in (I). Elimination of the metal–metal bonding in (I) liberates the two cubanes from severe distortion.

The lattice of (II) is made up of  $\text{Ph}_4\text{P}^+$  cations and discrete  $[\{\text{Fe}_2\text{Se}(\text{CO})_6\}_2(\text{Se}_2)]^{2-}$  anions. The latter has a known sulfur analog  $[\{\text{Fe}_2\text{S}(\text{CO})_6\}_2(\text{S}_2)]^{2-}$ .<sup>21</sup> The  $[\{\text{Fe}_2\text{Se}(\text{CO})_6\}_2(\text{Se}_2)]^{2-}$ , as depicted in Figure 3, possesses a Se–Se linkage (also a  $\mu_4$ -type ligand) between two  $\text{Fe}_2\text{Se}_2(\text{CO})_6$  units which are crystallo-

graphically related to each other by an inversion center at the midpoint of the diselenide  $\text{Se}_2^{2-}$  ligand. The asymmetric unit  $[\text{Fe}_2\text{Se}_2(\text{CO})_6]^-$  can be viewed as being formed by two square pyramids of the  $\text{FeSe}_2(\text{CO})_3$  fragments which share one edge (i.e.  $\text{Se}(1)\text{--}\text{Se}(2)$ ) of their basal planes. These basal planes are each defined by  $\text{Se}(1)/\text{Se}(2)/\text{C}(2)/\text{C}(3)$  or  $\text{Se}(1)/\text{Se}(2)/\text{C}(5)/\text{C}(6)$ , and the apexes by  $\text{C}(1)$  or  $\text{C}(4)$ , respectively.<sup>22</sup> If the charge of the diselenide and the monoselenide ligands is each taken as  $2-$ , the four iron atoms would have a formal oxidation state  $1+$ . The coordination geometry around the iron atoms is best described as distorted octahedral because, in addition to the normal chemical bonds to the corners of the square pyramids, the iron atoms are very close at 2.555(6) Å to each other. This is consistent with an Fe–Fe single bond, and comparable with that found in  $\text{Fe}_2(\text{Se}_2)(\text{CO})_6$  (2.575(2) Å)<sup>23</sup> and  $(\text{Ph}_4\text{As})_2[\{\text{Fe}_2\text{S}(\text{CO})_6\}_2(\text{S}_2)]$  (2.516(1) Å).<sup>21</sup> The short Fe–Fe bond gives rise to the non-planar conformation of two  $\text{Fe}_2\text{Se}_2$  units, hence the whole molecule looks like two butterflies joining their wings in a side-by-side fashion (Figure 4). The bond distance of the  $\text{Se}_2^{2-}$  unit in (II) (i.e.  $\text{Se}(1)\text{--}\text{Se}(1) = 2.467(7)$  Å) approaches the upper limit of a single Se–Se bond<sup>24,25</sup> while the intramolecular Se–Se distance (i.e.  $\text{Se}(1)\text{--}\text{Se}(2)$ ) of 2.847(5) is significantly

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(22)  $\text{Se}(1)$ ,  $\text{Se}(2)$ ,  $\text{C}(2)$  and  $\text{C}(3)$  deviate from the best least-squares plane by  $-0.003$ ,  $0.004$ ,  $-0.301$  and  $0.249$  Å respectively, and  $\text{Fe}(1)$  is displaced from the plane by  $-0.372$  Å.  $\text{Se}(1)$ ,  $\text{Se}(2)$ ,  $\text{C}(5)$  and  $\text{C}(6)$  deviate from the best least-squares plane by  $-0.001$ ,  $0.001$ ,  $-0.112$  and  $0.083$  Å respectively with  $\text{Fe}(2)$  lying  $0.343$  Å above it.

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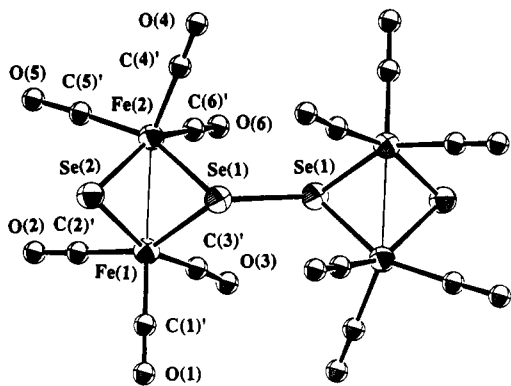


Figure 4. A different view of  $[\text{Fe}_2\text{Se}(\text{CO})_6]^{2-}$  showing the double "butterfly" conformation of the molecule.

shorter than their van der Waals contact (i.e. 4.00 Å).<sup>26</sup> This indicates that the valence electrons in the Se atoms are more or less delocalized among these four Se atoms. The same structural feature has also been observed in the sulfur analog.<sup>21</sup> It appears that Se(1) and Se(2) form a partial bond by removal of electron density from these atoms and transfer to the Se(1)–Se(1) bond and to the CO ligands. Selected bond distances and bond angles in (II) are summarized in Table V.

It has been shown that the  $\text{Fe}_2\text{Q}_2$  ( $\text{Q} = \text{S}$  or  $\text{Se}$ ) unit is a fundamental building block to a large family of iron–sulfur (–selenium) clusters,<sup>27</sup> where the  $\text{Fe}_2\text{Q}_2$  rhomb can be either planar or non-planar. However, when two iron atoms are each coordinated by three CO groups and two  $\mu_2$ -type bridging ligands acting overall as 3-electron donors, the molecule will invariably adopt a "butterfly" conformation with an Fe–Fe single bond.<sup>28</sup> This salient feature has been manifested by a variety of structurally related compounds containing amido, phosphido and thiolato ligands.<sup>29</sup> In view of its electronic structure, (II) apparently falls into this category. It is worthwhile to note that the iron–tellurium cluster  $[\text{Fe}_2(\text{Te})(\text{Te}_2)(\text{CO})_6]^{2-}$  also belongs to this group.<sup>30</sup> The unusual  $\text{Te}_2^{2-}$  acts as a  $\mu_2\text{-}\eta^1$ -ligand which bridges two iron centers using one tellurium atom while another tellurium atom assumes a terminal position. This molecule has a "butterfly" structure as well.

Both (I) and (II) show multi-peak CO absorptions in the solid-state IR spectra (KBr pellet). Four broad bands are identifiable for (I) at 2013, 1968, 1912 and 1900  $\text{cm}^{-1}$  while (II) gives three absorptions at 1994, 1919 and 1898  $\text{cm}^{-1}$ . Although complicated by the overlap of the CO absorptions from different metal centers in the crystal lattice, the overall pattern of each molecule is very characteristic of the compound and the absorption energies are consistent with the terminal ligation for all CO groups. The two compounds are moderately soluble in DMF, giving featureless UV/vis spectra in the 200–800 nm region.

In summary, two transition metal carbonyl clusters containing polychalcogenides are obtained by reactions of  $\text{Fe}(\text{CO})_5$  with  $\text{Na}_2\text{Q}_2$  ( $\text{Q} = \text{Te}$  or  $\text{Se}$ ) under hydro(methano)thermal conditions. Although these two compounds may also be accessible by conventional solution reactions as demonstrated by Kolis in the synthesis of (I)<sup>12</sup> as well as by Averill in the synthesis of the sulfur analogue of (II),<sup>21</sup> the current method provides an interesting synthetic alternative. It has been perceived that hydro(methano)thermal technique might not be suitable for the syntheses of compounds containing transition metal carbonyls. Presumably, such a process will be hindered by either the poor thermal stability of metal carbonyls, or the low solubility of both reactants and products in  $\text{H}_2\text{O}$  or  $\text{MeOH}$ . However, with the altered solvent behavior of  $\text{H}_2\text{O}/\text{MeOH}$  and the presence of polychalcogenide ligands acting as reagents as well as "mineralizers", the disadvantage of insufficient solubility of metal carbonyls and  $\text{Ph}_4\text{P}^+$  salts in these two solvents can be readily overcome. Through the successful syntheses of these two clusters, we have proven the applicability of the hydro(methano)thermal technique to the preparation of inorganic compounds involving organometallic molecules. Such a method may create new exciting synthetic opportunities for organometallic-main group compounds. Applications of this technique to organometallic synthesis should by no means be limited to metal carbonyls.

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**Supplementary Material Available:** Tables of atomic coordinates of all atoms and anisotropic and isotropic thermal parameters of all non-hydrogen atoms for (I) and (II) (10 pages). Ordering information is given on any current masthead page. Listings of calculated and observed structure factors ( $10F_o/10F_c$ ) are available on request from the authors by quoting the journal citation.

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