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New Mixed-Metal Carbonyl Tellurido Clusters from Solvothermal Synthesis

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Mixed-metal carbonyl telluride clusters $(Ph_4P)_2[Fe_2MTe_3(CO)_{11}]$ (M = Mo, (**1**), W, (**2**)) and $Na(Et_4N)_2[Fe_3W_2Te_8(TeMe)(CO)_{12}]\cdot 2H_2O$ (**3**) have been synthesized methanothermally at 80 °C using mixtures of $Fe_3(CO)_{12}$, $M(CO)_6$ (M = Mo, W), and Na_2Te_2 with Ph_4PBr, or $Et_4NCl\cdot H_2O$, in a sealed Pyrex tube. Compound **1** crystallizes in the monoclinic space group $C2/c$ with $a = 20.379(4)$ Å, $b = 14.724(3)$ Å, $c = 39.298(6)$ Å, $\beta = 95.22(1)°$, $V = 11742(7)$ Å^3, and $Z = 8$. In the anionic $[Fe_2Mo(Te_2)(Te)(CO)_{11}]^{2-}$ cluster of **1**, a $[Fe_2(Te_2)(Te)(CO)_6]^{2-}$ unit is joined to an $Mo(CO)_5$ moiety by its Te_2^{2-} ligand. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.636(3)$ Å, $b = 13.385(4)$ Å, $c = 20.804(7)$ Å, $\alpha = 73.30(3)°$, $\beta = 87.24(3)°$, $\gamma = 65.40(2)°$, $V = 3054(4)$ Å^3, and $Z = 2$. In the $[Fe_3W_2(Te_2)_3(Te)_2(TeMe)(CO)_{12}]^{3-}$ anion of **3**, a W−W unit is connected to the rest of the cluster through telluride ligands to form an unsymmetrical cagelike structure. ^{125}Te NMR spectral data for **1**−**3** and $(Ph_4P)_2[Fe_2(Te_2)(Te)(CO)_6]$ have been obtained in DMSO-d_6. Clusters **1**, **2**, and $(Ph_4P)_2[Fe_2(Te_2)(Te)(CO)_6]$ display three-line spectra, while seven singlets are observed for **3**, corresponding to seven different environments for the tellurium atoms in **3**.

Introduction

The chemistry of metal carbonyl telluride clusters has drawn considerable current interest.[1,2] Our group has focused on the use of hydro(solvo)thermal technique for the synthesis of compounds of this class, and several cluster anions, including $[M_6Te_{14}(CO)_{12}]^{2-}$ (M = Ru,[3] Fe[4]), $[Fe_8Te_{10}(CO)_{20}]^{2-}$,[5] and $[M_4Te_6(TeMe)_2(CO)_8]^{2-}$ (M = Ru, Fe),[6] have been made via this route. In addition to the synthesis of these and other[7] homometallic cluster compounds, there has also been a fair amount of recent activity in the preparation of mixed-metal carbonyl telluride clusters, and compounds such as $Fe_2WTe_2(CO)_{10}$,[8] $Fe_2Ru_2Te_2(CO)_{11}$,[9] and $(C_5H_5)_2Mo_2Fe_xTe_2(CO)_7$ (x = 1, 2)[10] have been reported. Studies on mixed-metal chalcogenide clusters have also been performed from the bioinorganic point of view.[11] Heterometallic cluster compounds, on the other hand, have been shown to be important in the field of catalysis.[12] Encouraged by the facile and clean synthesis of novel homometallic carbonyl chalcogenide clusters using the solvothermal method, we have now extended it to obtain corresponding mixed-metal carbonyl clusters. Herein, we report on the compounds $(Ph_4P)_2[Fe_2MoTe_3(CO)_{11}]$ (**1**), $(Ph_4P)_2[Fe_2WTe_3(CO)_{11}]$ (**2**), and $Na(Et_4N)_2[Fe_3W_2Te_8(TeMe)(CO)_{12}]\cdot 2H_2O$ (**3**), which derive from solvothermal oxidative decarbonylation reactions. In contrast to other known heterometallic clusters which are neutral,[8−10] these are the first examples of anionic mixed-metal carbonyl telluride clusters.

Experimental Section

Solids were handled in a glovebox under nitrogen atmosphere. Na_2Te_2 and Cs_2Te_3 were prepared by reacting stoichiometric amounts of the elements in liquid ammonia. $Fe_3(CO)_{12}$ 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, and UV−visible spectra were obtained on a Hitachi U-2000 spectrophotometer. A Varian VXR-300 NMR spectrometer was used to obtain the ^{1}H NMR spectrum, and ^{125}Te NMR spectra were obtained on a Varian VXR-500 spectrometer operating at ca. 157.9 MHz for ^{125}Te resonances. Spectral data were referenced to a signal for $TeCl_4$, dissolved in D_2O/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.

Preparation of $(Ph_4P)_2[Fe_2MoTe_3(CO)_{11}]$ (1). A mixture of $Fe_3(CO)_{12}$ (25 mg, 0.05 mmol), $Mo(CO)_6$ (26 mg, 0.1 mmol), Na_2Te_2 (75 mg, 0.25 mmol), and Ph_4PBr (170 mg, 0.4 mmol) was loaded into a Pyrex tube, which was sealed under vacuum after the addition of 0.5 mL MeOH. The tube, having an inner volume of ca. 4 mL, was heated for 7 h at 80 °C. The product was washed three times with 20 mL portions of MeOH and finally with diethyl ether to obtain 105 mg of dark brown solid. About 40% of it consisted of chunky crystals of **1**, and these were separated from the rest of the product under a microscope. Various other reactant ratios (also varying the reaction time and temperature) used in an effort to prepare this compound in the pure form did not give the desired result. Elemental analysis carried out on several randomly selected crystals using energy dispersive spectroscopy (EDS) of X-rays on an SEM showed P:Fe:Mo:Te ratios close to the expected values. IR data: (a) (ν_{CO}, cm^{-1}; KBr pellet) 2043-

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Table 1. Positional Parameters and *B*(eq) Values for $(Ph_4P)_2[Fe_2MoTe_3(CO)_{11}]$ (**1**)

atom	*x*	*y*	*z*	*B*(eq), Å^2	atom	*x*	*y*	*z*	*B*(eq), Å^2
Te(1)	0.39049(9)	0.0774(1)	0.62599(5)	3.8(1)	C(21)	0.296(1)	−0.706(2)	0.4453(7)	4.3(6)
Te(2)	0.49052(9)	−0.0863(1)	0.63549(5)	3.7(1)	C(22)	0.328(1)	−0.728(2)	0.4762(7)	3.8(6)
Te(3)	0.5943(1)	−0.2006(1)	0.62415(7)	6.5(1)	C(23)	0.332(1)	−0.667(2)	0.5043(6)	2.6(5)
Mo(1)	0.5518(2)	−0.3632(2)	0.65420(8)	6.0(2)	C(24)	0.243(1)	−0.428(2)	0.5304(6)	2.6(5)
Fe(1)	0.5169(2)	0.0781(3)	0.6226(1)	3.3(2)	C(25)	0.182(1)	−0.466(2)	0.5236(7)	4.0(6)
Fe(2)	0.4397(2)	−0.0194(3)	0.5796(1)	3.7(2)	C(26)	0.124(1)	−0.416(2)	0.5239(6)	4.1(6)
P(1)	0.3169(3)	−0.4965(4)	0.5316(2)	2.9(4)	C(27)	0.131(1)	−0.322(2)	0.5299(7)	4.8(7)
P(2)	0.7555(4)	0.2912(6)	0.7127(2)	5.1(5)	C(28)	0.189(2)	−0.280(2)	0.5345(8)	6.9(8)
O(1)	0.514(1)	−0.542(2)	0.6892(7)	10.1(7)	C(29)	0.251(2)	−0.334(2)	0.5355(8)	6.2(8)
O(2)	0.558(1)	−0.465(1)	0.5830(6)	7.3(6)	C(30)	0.390(1)	−0.425(2)	0.5246(7)	3.5(5)
O(3)	0.400(1)	−0.321(1)	0.6335(6)	7.6(6)	C(31)	0.415(1)	−0.436(1)	0.4941(6)	2.7(5)
O(4)	0.535(1)	−0.240(2)	0.7170(7)	10.8(8)	C(32)	0.472(1)	−0.379(2)	0.4882(7)	4.9(7)
O(5)	0.696(2)	−0.399(3)	0.677(1)	19(1)	C(33)	0.495(1)	−0.317(2)	0.5142(8)	5.0(7)
O(6)	0.5022(8)	0.237(1)	0.5777(5)	4.5(4)	C(34)	0.465(2)	−0.308(2)	0.5454(9)	6.9(8)
O(7)	0.548(1)	0.168(1)	0.6885(6)	6.5(5)	C(35)	0.410(2)	−0.369(2)	0.5514(8)	6.5(8)
O(8)	0.652(1)	0.040(1)	0.6087(5)	5.7(5)	C(36)	0.717(2)	0.338(2)	0.671(1)	7.3(9)
O(9)	0.537(1)	−0.096(1)	0.5392(5)	6.1(5)	C(37)	0.657(4)	0.324(4)	0.661(2)	18(1)
O(10)	0.334(1)	−0.148(1)	0.5638(5)	5.5(5)	C(38)	0.630(2)	0.345(3)	0.627(1)	12(1)
O(11)	0.399(1)	0.123(1)	0.5322(5)	6.7(5)	C(39)	0.668(3)	0.381(3)	0.606(1)	13(1)
C(1)	0.533(2)	−0.477(3)	0.677(1)	8(1)	C(40)	0.717(3)	0.426(4)	0.619(2)	16(1)
C(2)	0.559(2)	−0.430(2)	0.6097(9)	6.6(8)	C(41)	0.749(2)	0.396(3)	0.652(1)	12(1)
C(3)	0.456(2)	−0.334(2)	0.6401(8)	5.2(7)	C(42)	0.815(1)	0.371(2)	0.7327(7)	3.3(6)
C(4)	0.545(2)	−0.291(2)	0.695(1)	6.9(9)	C(43)	0.865(2)	0.392(3)	0.712(1)	10(1)
C(5)	0.654(3)	−0.390(4)	0.671(2)	16(1)	C(44)	0.912(2)	0.459(3)	0.728(1)	11(1)
C(6)	0.507(1)	0.174(2)	0.5956(7)	3.4(6)	C(45)	0.908(2)	0.493(2)	0.762(1)	6.2(8)
C(7)	0.533(1)	0.127(2)	0.6628(8)	5.3(7)	C(46)	0.862(2)	0.460(2)	0.7794(8)	6.2(8)
C(8)	0.597(1)	0.052(2)	0.6134(7)	4.3(7)	C(47)	0.812(2)	0.404(2)	0.766(1)	7.6(9)
C(9)	0.499(1)	−0.063(2)	0.5562(7)	4.8(7)	C(48)	0.793(2)	0.185(2)	0.708(1)	7.5(9)
C(10)	0.377(1)	−0.098(2)	0.5708(7)	4.7(7)	C(49)	0.849(2)	0.161(3)	0.725(1)	10(1)
C(11)	0.417(1)	0.064(2)	0.5517(8)	5.9(8)	C(50)	0.891(3)	0.079(4)	0.721(1)	14(1)
C(12)	0.331(1)	−0.551(2)	0.5723(6)	3.4(6)	C(51)	0.849(3)	0.019(4)	0.703(1)	14(1)
C(13)	0.277(1)	−0.578(2)	0.5873(7)	4.0(6)	C(52)	0.795(2)	0.047(3)	0.676(1)	11(1)
C(14)	0.286(2)	−0.632(2)	0.6191(8)	6.2(8)	C(53)	0.759(2)	0.137(3)	0.675(1)	12(1)
C(15)	0.355(2)	−0.652(2)	0.6308(9)	7.4(9)	C(54)	0.686(1)	0.277(2)	0.7390(8)	4.8(7)
C(16)	0.411(2)	−0.618(2)	0.6154(9)	7.1(9)	C(55)	0.636(2)	0.338(3)	0.737(1)	9(1)
C(17)	0.400(1)	−0.568(2)	0.5851(8)	5.8(7)	C(56)	0.584(2)	0.326(3)	0.761(1)	10(1)
C(18)	0.307(1)	−0.579(2)	0.4984(6)	2.8(5)	C(57)	0.591(2)	0.254(2)	0.7795(9)	6.4(8)
C(19)	0.272(1)	−0.553(2)	0.4659(8)	5.3(7)	C(58)	0.634(2)	0.195(3)	0.783(1)	9(1)
C(20)	0.271(1)	−0.616(2)	0.4386(7)	4.9(7)	C(59)	0.693(2)	0.204(3)	0.762(1)	9(1)

(m), 2009(m), 1966(s), 1938(s, sh), 1911(s, br), 1839(m, br); (b) (ν_{CO}, cm^{-1}; in DMF) 2044(w), 2012(m), 1973(s), 1932(sh), 1919(s), 1856-(m, br). UV−vis spectral data (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); in DMF): 335(sh), 414 (15 200), 509 (7590). ^{125}Te NMR data (δ, ppm; in DMSO-d_6): 159, −600, −703.

Preparation of $(Ph_4P)_2[Fe_2WTe_3(CO)_{11}]$ (2). A mixture of $Fe_3(CO)_{12}$ (50 mg, 0.1 mmol), $W(CO)_6$ (53 mg, 0.15 mmol), Na_2Te_2 (75 mg, 0.25 mmol), and Ph_4PBr (170 mg, 0.4 mmol) was heated with 0.5 mL of MeOH as above for 18 h. An amount of 160 mg of dark brown, single-phase, crystalline material was obtained in 73% yield (based on W). IR data: (a) (ν_{CO}, cm^{-1}; KBr pellet) 2042(m), 2010(s), 1967(s), 1939(s), 1901(s, br), 1831(m, br);. (b) (ν_{CO}, cm^{-1}; in DMF) 2043(w), 2012(m), 1975(s), 1928(sh), 1910(s), 1852(m, br). UV−vis spectral data (λ_{max}, nm (ϵ, M^{-1} cm^{-1}); in DMF): 335(sh), 420 (12 090), 509 (6460). ^{125}Te NMR data (δ, ppm; in DMSO-d_6): 149, −635, −712.

Preparation of $Na(Et_4N)_2[Fe_3W_2Te_8(TeMe)(CO)_{12}]\cdot 2H_2O$ (3). A mixture of $Fe_3(CO)_{12}$ (50 mg, 0.1 mmol), $W(CO)_6$ (70 mg, 0.2 mmol), Na_2Te_2 (180 mg, 0.6 mmol), and $Et_4NCl\cdot H_2O$ (110 mg, 0.6 mmol) was heated with 0.5 mL of MeOH for 72 h to afford 150 mg of pure dark brown crystalline product of **3** in 64% yield (based on W). Satisfactory elemental analysis was obtained. IR data: (a) (ν_{CO}, cm^{-1}; KBr pellet) 1968(sh), 1942(sh), 1921(s, br), 1897(sh), 1858(sh), 1831-(sh), 1808(sh); (b) (ν_{CO}, cm^{-1}; in DMF) 1982(sh), 1969(w), 1921(sh), 1914(s), 1901(sh), 1873(s), 1844(m), 1816(sh). ^{1}H NMR data (δ, ppm; in DMSO-d_6): 3.20(q, 16H), 2.16(s, 3H), 1.14(t, 24H). ^{125}Te NMR data (δ, ppm; in DMSO-d_6): 1368, 1114, 590, 428, 273, 169, −527.

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 on a Nicolet P3/V diffractometer using Mo Kα radiation (λ = 0.7107 Å). 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.

Crystal data for $(Ph_4P)_2[Fe_2MoTe_3(CO)_{11}]$ (1): monoclinic *C*2/*c*, $Z = 8$, $a = 20.379(4)$ Å, $b = 14.724(3)$ Å, $c = 39.298(6)$ Å, $\beta = 95.22(1)°$, $V = 11742(7)$ Å^3, data collection temperature = −86 °C, $2\theta_{max}$ (Mo Kα) = 45°, scan technique = ω, unique reflections 7714 , 2766 with $F_o^2 > 3\sigma(F_o^2)$. The structure was solved by direct methods (SHELXS-86) and was refined by full-matrix least-squares techniques using the TEXSAN crystallographic software package [TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, Molecular Structure Corp., The Woodlands, TX]. An absorption correction based on DIFABS [Walker, N.; Stuart, D. Acta Crystallogr. **1983**, *A39*, 158] was applied; μ = 22.7 cm^{-1}. Minimum and maximum absorption corrections were 0.7396 and 1.1715, respectively. Final $R = R_w$ = 6.7%.

Crystal data for $Na(Et_4N)_2[Fe_3W_2Te_8(TeMe)(CO)_{12}]\cdot 2H_2O$ (3): triclinic $P\bar{1}$, $Z = 2$, $a = 12.636(3)$ Å, $b = 13.385(4)$ Å, $c = 20.804(7)$ Å, $\alpha = 73.30(3)°$, $\beta = 87.24(3)°$, $\gamma = 65.40(2)°$, $V = 3054(4)$ Å^3, data collection temperature = −86 °C, $2\theta_{max}$ (Mo Kα) = 45°, scan technique = $\theta/2\theta$; unique reflections 8063, 5741 with $F_o^2 > 3\sigma(F_o^2)$. The structure was solved and refined as above. The data were corrected for absorption with DIFABS; μ = 88.1 cm^{-1}. Minimum and maximum absorption corrections were 0.7133 and 1.2982, respectively. Final *R* = 5.7%, R_w = 7.2%. The Na$^+$ ions lying on two centers of symmetry were refined with partial occupation factors because of underlying disorder with two other positions. Four oxygen atoms of 0.5 occupancy were located near the Na$^+$ ions. There were signs of disorder in the regions of the Et$_4$N$^+$ cations also. The highest electron density of ca. 2 e/Å^3 in the final difference Fourier map lay 1.25 Å from Te(9).

All carbon atoms and oxygen atoms were isotropically refined. Hydrogen atom positions were calculated but not refined. The hydrogen atoms could not be located, and their positions were calculated. The final atomic coordinates and equivalent isotropic thermal parameters

Table 2. Positional Parameters and *B*(eq) Values for $Na(Et_4N)_2[Fe_3W_2Te_8(TeMe)(CO)_{12}]\cdot 2H_2O$ (**3**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
W(1)	0.37805(8)	0.21007(8)	0.73918(4)	2.96(8)
W(2)	0.52498(8)	0.26530(8)	0.82660(5)	3.20(8)
Te(1)	0.4168(1)	0.1230(1)	0.87655(8)	3.8(1)
Te(2)	0.4875(1)	0.3537(1)	0.68755(7)	3.2(1)
Te(3)	0.1514(1)	0.5718(1)	0.64343(8)	3.5(1)
Te(4)	0.3188(1)	0.6364(1)	0.73995(8)	3.8(1)
Te(5)	0.2237(2)	0.2412(2)	0.93542(8)	4.6(2)
Te(6)	0.1591(1)	0.3848(1)	0.75077(7)	3.2(1)
Te(7)	0.0104(1)	0.6619(1)	0.79273(9)	4.2(1)
Te(8)	0.3371(1)	0.4548(1)	0.85368(7)	3.3(1)
Te(9)	0.2154(2)	0.7918(1)	0.58551(9)	4.8(2)
Fe(1)	0.1017(3)	0.7442(3)	0.6913(2)	4.2(3)
Fe(2)	0.3592(3)	0.5690(3)	0.6331(2)	3.6(3)
Fe(3)	0.1297(3)	0.4509(3)	0.8598(2)	3.7(3)
Na(1)	$^1/_2$	0	$^1/_2$	5(2)
Na(2)	1.0000	0	1.0000	9(5)
Na(3)	0.449(6)	0.126(6)	0.501(3)	7(1)
Na(4)	0.996(5)	0.111(5)	1.009(3)	9(1)
O(1)	0.604(1)	0.018(1)	0.7074(8)	4.5(3)
O(2)	0.280(1)	0.291(1)	0.5899(8)	4.9(4)
O(3)	0.270(2)	0.033(2)	0.7560(8)	5.3(4)
O(4)	0.619(2)	0.179(2)	0.979(1)	7.5(5)
O(5)	0.657(2)	0.427(2)	0.801(1)	9.0(6)
O(6)	0.758(2)	0.066(2)	0.8116(9)	5.9(4)
O(7)	0.092(2)	0.933(2)	0.740(1)	6.6(5)
O(8)	−0.123(2)	0.871(2)	0.611(1)	6.9(5)
O(9)	0.561(2)	0.615(2)	0.620(1)	6.1(4)
O(10)	0.371(2)	0.520(1)	0.5071(9)	5.3(4)
O(11)	0.112(2)	0.519(1)	0.9834(9)	5.3(4)
O(12)	−0.093(2)	0.430(2)	0.8643(9)	5.7(4)
O(13)	0.594(3)	0.031(3)	0.390(1)	4.1(6)
O(14)	0.546(3)	0.143(3)	0.539(2)	5.3(8)
O(15)	0.871(5)	0.216(5)	0.977(3)	10(1)
O(16)	1.032(7)	0.035(7)	0.892(4)	17(3)
N(1)	0.414(2)	0.287(2)	0.1391(9)	3.4(4)
N(2)	0.913(2)	0.268(2)	0.623(1)	6.6(6)
C(1)	0.517(2)	0.093(2)	0.722(1)	3.3(4)
C(2)	0.315(2)	0.266(2)	0.644(1)	3.5(4)
C(3)	0.306(2)	0.103(2)	0.750(1)	3.6(5)
C(4)	0.578(2)	0.215(2)	0.924(1)	5.3(6)
C(5)	0.608(2)	0.362(2)	0.812(1)	5.4(6)
C(6)	0.669(2)	0.138(2)	0.816(1)	4.3(5)
C(7)	0.095(2)	0.855(2)	0.719(1)	5.3(6)
C(8)	−0.035(3)	0.819(2)	0.644(1)	5.3(6)
C(9)	0.479(2)	0.598(2)	0.625(1)	4.6(5)
C(10)	0.367(2)	0.538(2)	0.559(1)	4.4(5)
C(11)	0.120(2)	0.491(2)	0.934(1)	4.7(5)
C(12)	−0.000(2)	0.434(2)	0.860(1)	4.7(5)
C(13)	0.437(6)	0.183(6)	0.138(3)	17(2)
C(14)	0.302(2)	0.165(2)	0.134(1)	4.9(5)
C(15)	0.378(4)	0.355(4)	0.065(2)	5(1)
C(15′)	0.405(5)	0.419(4)	0.127(3)	3(1)
C(16)	0.373(3)	0.486(2)	0.049(1)	5.6(6
C(17)	0.308(6)	0.338(5)	0.173(3)	17(2)
C(18)	0.336(3)	0.288(3)	0.258(2)	6.4(7)
C(19)	0.532(5)	0.273(4)	0.164(3)	13(1)
C(20)	0.629(3)	0.236(2)	0.119(1)	5.8(6)
C(21)	0.810(4)	0.245(4)	0.604(2)	11(1)
C(22)	0.833(5)	0.142(5)	0.644(3)	14(2)
C(23)	0.973(3)	0.252(3)	0.691(2)	8.3(9)
C(24)	0.836(5)	0.346(4)	0.714(2)	13(2)
C(25)	0.869(5)	0.399(5)	0.574(3)	14(2)
C(26)	0.997(7)	0.425(6)	0.582(4)	22(3)
C(27)	1.050(4)	0.190(4)	0.602(2)	12(1)
C(28)	1.046(4)	0.159(4)	0.545(2)	13(1)
C(29)	0.000(3)	0.757(3)	0.872(1)	6.1(6)

for atoms in the anion of **1** and all the atoms of **3** are listed in Tables 1 and 2, respectively.

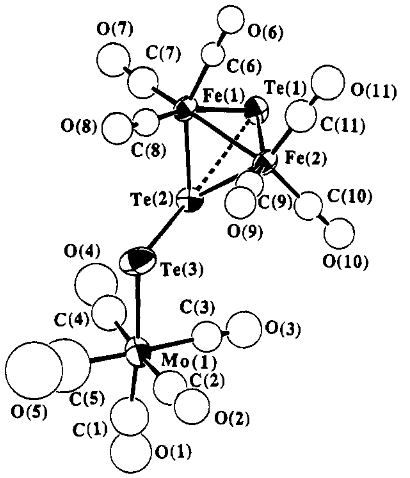

Figure 1. Structure of $[Fe_2MoTe_3(CO)_{11}]^{2-}$ with labeling scheme. Important bond distances (Å) and angles (deg): Fe(1)−Fe(2) = 2.628(5), Fe(1)−Te(1) = 2.591(4), Fe(2)−Te(1) = 2.586(4), Fe(1)−Te(2) = 2.541(4), Fe(2)−Te(2) = 2.539(5), Te(1)−Te(2) = 3.157(3), Te(2)−Te(3) = 2.769(3), Mo(1)−Te(3) = 2.839(4), Te(1)−Te(2)−Te(3) = 159.87(9), Te(2)−Te(3)−Mo(1) = 100.3(1).

Results and Discussion

All three compounds have been prepared by heating a sealed tube containing a mixture of $Fe_3(CO)_{12}$, $M(CO)_6$ (M = Mo, W), and Na_2Te_2 with the appropriate organic salt in 0.5 mL of MeOH at 80 °C. While compounds **2** and **3** could be obtained as pure crystalline solids, large chunky crystals of **1** having rhombic faces were found to consist of ~40% of the total product. These crystals are large enough to be manually separated from the rest of product. Infrared spectroscopy shows that the remaining product contains more of **1** mixed with some other unidentified compound.

The molecular structures of **1** and **3** were determined by X-ray crystal structure analysis. Figure 1 shows the structure of the $[Fe_2MoTe_3(CO)_{11}]^{2-}$ anion. Its tungsten analog, compound **2**, is X-ray isomorphous. All the metal centers in this structure are found to have an approximate octahedral coordination. A monotelluride ligand bridges the Fe centers which are in turn connected to the Mo center through a μ_3-η^2-Te_2^{2-} ligand. This cluster can be thought of as a CO-substitution adduct of the known cluster anion $[Fe_2Te_3(CO)_6]^{2-}$ [13] and $Mo(CO)_6$. The $[Fe_2Te_3(CO)_6]^{2-}$ dimer acts as a ligand via the terminal tellurium atom (Te(3) in Figure 1) of the ditelluride. The Fe atoms in $[Fe_2(Te_2)(Te)(CO)_6]^{2-}$ and **1** are present in the +1 oxidation state while the Mo atom is still in the zero oxidation state. Though reactions between metal carbonyls and soluble polytellurides commonly lead to partial oxidative decarbonylation, in the present instance there is no net oxidation of the Mo atom. Such a situation was also observed for the compound $(Ph_4P)_2[Mo(Te_4)(CO)_4]$, which was prepared from $Mo(CO)_6$ and K_2Te_4.[14]

In spite of the obvious relationship of $[Fe_2Te_3(CO)_6]^{2-}$ with **1**, there are some significant metric differences between the two. For example, the Fe−Fe distance is 0.02 Å shorter in **1** compared to that in $[Fe_2Te_3(CO)]_6]^{2-}$, and the Te−Te single-bond distance of the Te_2^{2-} ligand in **1** is longer by 0.03 Å. The most pronounced structural difference between the two structures is that the Te(1)- - -Te(2) distance in **1** is 0.15 Å shorter than the corresponding distance for $[Fe_2Te_3(CO_6)]^{2-}$, suggesting a considerably more bonding character.[15]

Compound **3** has a remarkable cagelike structure (Figure 2) with identifiable structural fragments found to be present in the structures of other related metal carbonyl telluride clusters. The

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(13) Eichhorn, B. W.; Haushalter, R. C.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 728.

(14) Flomer, W. A.; O'Neal, S. C.; Kolis, J. W.; Jeter, D.; Cordes, A. W. *Inorg. Chem.* **1988**, *27*, 969.

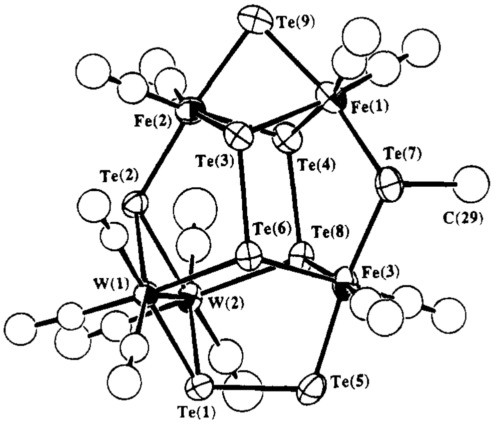
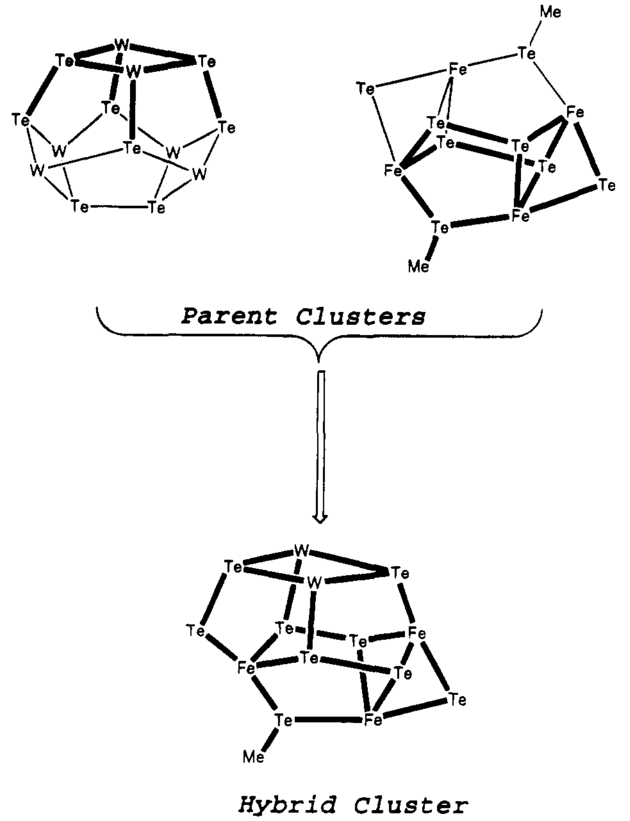


Figure 2. Structure of $[Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$ with labeling scheme. The CO ligands were not labeled for clarity. Representative bond distances (Å) and angles (deg): Fe(1)−Te(7) = 2.545(4), Fe(1)−Te(9) = 2.641(4), Fe(1)−Te(3) = 2.603(4), Fe(2)−Te(2) = 2.574(4), Fe(3)−Te(6) = 2.619(3), Fe(3)−Te(5) = 2.575(4), W(1)−Te(1) = 2.741(2), W(1)−Te(2) = 2.765(2), W(1)−W(2) = 3.089(1), Te(3)−Te(6) = 2.803(2), Te(1)−Te(5) = 2.751(3), Te(3)−Te(9) = 3.261(2), Te(7)−C(29) = 2.31(3), Fe(1)−Te(9)−Fe(2) = 83.2(1), Fe(1)−Te(7)−Fe(3) = 116.3(1), Fe(1)−Te(3)−Te(6) = 107.2(1), W(1)−Te(6)−Te(3) = 101.45(7), W(1)−Te(2)−W(2) = 67.79(5), Te(2)−W(1)−Te(1) = 111.75(6).

polyhedral cluster $[Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$ has four triangular, one rhombic, and six approximately pentagonal faces. There are four types of telluride ligands—Te(9) represents a μ_2-Te^{2-} ligand, Te(2) is a μ_3-Te^{2-} ligand, Te(3)−Te(6) and Te(4)−Te(8) constitute a pair of equivalent μ_2,μ_2-η^1,η^1-Te_2^{2-} ligands, and Te(1)−Te(5) is a μ_3-η^2-Te_2^{2-} ligand. In addition, two of the iron atoms are bridged by a Te-Me$^-$ ligand. As we have previously shown for $[Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$,[6] here too an alcohol-induced Te-alkylation reaction gives rise to this rare species. The structure of this heterometallic cluster is a beautiful example of a hybrid between two known homometallic structures, viz., $[Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$ [6] and $[W_6Te_8(CO)_{18}]^{2-}$;[7g] see Scheme 1. The structural parameters pertaining to the Fe fragment of **3** are comparable to those of $[Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$.[6] The rhombus-like face formed by the atoms W(1), Te(1), W(2), and Te(2) in **3** is similar to such a face in the $[W_6Te_8(CO)_{18}]^{2-}$ cluster.[7g] The W−W and the W−Te distances in **3** are similar to those found in $[W_6Te_8(CO)_{18}]^{2-}$. The formal oxidation states of Fe and W in **3** are +2 and +1, respectively, in accord with the corresponding oxidation states in the parent clusters $[Fe_4Te_6(TeMe)_2(CO)_8]^{2-}$ and $[W_6Te_8(CO)_{18}]^{2-}$.

The dark brown solids of **1**−**3** are moderately air-sensitive. They are soluble in polar organic solvents, although the solubility in methanol is fairly low. The reddish brown DMF solutions of **1** and **2** show two absorption maxima in the visible region, at 414 and 509 nm and at 420 and 509 nm, respectively. A pinkish solution of $(Ph_4P)_2[Fe_2Te_3(CO)_6]$ in DMF shows only a single absorption maximum at 515 nm having an extinction coefficient (7230 M^{-1} cm^{-1}) comparable to that of the band at 509 nm for **1** and **2**, suggesting that these bands might be of similar origin. Both **1** and **2** display analogous infrared spectra for the carbonyl stretching vibrations in the solid state as well as in DMF solutions. The solution and the solid state spectra are nearly the same, although there are small shifts in some of the band positions. This proves that compounds **1** and **2** remain intact in solution.

Scheme 1



Three resonances for **1** as well as **2** are easily observed in the ^{125}Te NMR spectra in DMSO-d_6 solution. These occur at 159, −600, −703 and at 149, −635, −712 ppm, respectively, and are consistent with our expectation of three ^{125}Te signals for these compounds having tellurium nuclei in three different chemical environments. The related cluster compound $(Ph_4P)_2[Fe_2Te_3(CO)_6]$ also shows (under similar conditions) three resonances, which are much broader and more difficult to observe, at 241, −32, and −613 ppm.[16] Noting that atom Te(1) in Figure 1 has a very different environment and that there is a singlet at −32 ppm for this compound, this resonance is assignable to this dangling tellurium atom. Comparing the spectra of **1** and **2**, it can be seen that the signals at −600 and −635 ppm, respectively, for **1** and **2** show the largest shift in resonance positions, relative to one another. These signals may be tentatively assigned to the tellurium atom from the μ_3-η^2-Te_2^{2-} ligand which is bonded to the Mo or W center. The latter two atoms could be expected to cause a large difference in the chemical shift for this signal. The remaining ^{125}Te signals are not easily assigned to any specific tellurium atoms in $[Fe_2(Te_2)(Te)(CO)_6]^{2-}$, $[Fe_2Mo(Te_2)(Te)(CO)_{11}]^{2-}$, or $[Fe_2W(Te_2)(Te)(CO)_{11}]^{2-}$ in the absence of other comparable chemical shift data for related compounds.

The UV−vis spectrum of **3** in DMF solution has no features other than two ill-defined shoulders at 370 and 500 nm. In comparison to the broad infrared absorptions of **3** in the solid state, the spectrum for the carbonyl stretching vibrations in DMF

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(15) (a) Canadell, E.; Jobic, S.; Brec, R.; Rouxel, J. *J. Solid State Chem.* **1992**, *98*, 59. (b) Canadell, E.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 1398. (c) Jobic, S.; Brec, R.; Rouxel, J. *J. Solid State Chem.* **1992**, *96*, 169. (d) Lee, S.; Hoistad, L. M.; Kampf, J. *New J. Chem.* **1992**, *16*, 657. (e) Mar, A.; Jobic, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 8963. (f) Whangbo, M.-H.; Canadell, E. *J. Am. Chem. Soc.* **1992**, *114*, 9587. (g) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3838. (h) Canadell, E.; Mathey, Y.; Whangbo, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 104. (i) Jobic, S.; Brec, R.; Rouxel, J. *J. Solid State Chem.* **1992**, *98*, 59. (j) Gressier, P.; Whangbo, M. H. *Inorg. Chem.* **1984**, *23*, 1228.

(16) ^{125}Te NMR chemical shifts were referenced to δ = 1237 ppm for $TeCl_4$ in D_2O/HCl [Schumann, H.; Magerstodt, M. J. *J. Organomet. Chem.* **1982**, *232*, 147].

solution is well-resolved. Even though the band positions in the solid state and solution spectra are somewhat different, it is not difficult to discern the inherent similarity of the spectra by visual inspection. Corresponding to the seven different chemical environments for the tellurium atoms of **3**, we have been able to observe seven singlets (at 1368, 1114, 590, 428, 273, 169, −527 ppm) in its ^{125}Te NMR spectrum, in DMSO-d_6.[13c] The ^{125}Te NMR data , combined with IR spectral data, thus suggest that the anion in **3** retains its structure in solution.

We have demonstrated above that the solvothermal technique is useful for the preparation of not only novel homometallic but also heterometallic carbonyl chalcogenide clusters. Synthetic possibilities for mixed-metal compounds appear quite promising. The fact that we do not obtain a mixture of the two parent homometallic clusters suggests that these reactions are entropically favored, and thus, by varying the reaction conditions, it should be possible to prepare other interesting mixed-metal clusters which may not be easily accessible through the usual ambient-pressure solution route.

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Supporting Information Available: Tables of crystal structure analysis data, atomic coordinates and isotropic and anisotropic thermal parameters of all non-hydrogen atoms for $(Ph_4P)_2[Fe_2MoTe_3(CO)_{11}]$ (**1**) and $Na(Et_4N)_2[Fe_3W_2Te_8(TeMe)(CO)_{12}]\cdot 2H_2O$ (**3**), a fully labeled ORTEP view of the $[Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$ anion in **3**, Fourier transform IR spectra (solid state and solution) for **1−3**, and ^{125}Te NMR spectra for **1−3** and $(Ph_4P)_2[Fe_2Te_3(CO)_6]$ (25 pages). Ordering information is given on any current masthead page.

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