Articles

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Chemistry of High-Valent Transition-Metal Polytellurides: Preparation and Structure of Oxy Tellurides and Ditellurolenes of Molybdenum and Tungsten

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The high-valent halides $MoCl_5$ and WCl_6 react readily with a solution of polytelluride anions (Te_3^{2-}, Te_4^{2-}, Te_5^{2-}) in DMF to form $[O{=}Mo(Te_4)_2]^{2-}$ (Ia) and $[O{=}W(Te_4)_2]^{2-}$ (Ib), respectively, in good yield. The origin of the oxygen atom of the oxy group is not known. The compounds can be isolated as their $[(C_6H_5)_4P]^+$ salts and have been characterized by IR and ^{125}Te NMR spectroscopy and single-crystal X-ray diffraction. Crystal data for $[(C_6H_5)_4P]_2[O{=}Mo(Te_4)_2]$: monoclinic, $C2/c$, $Z = 4$, $a = 24.328\ (12)$ Å, $b = 13.308\ (4)$ Å, $c = 19.325\ (10)$ Å, $\beta = 106.66\ (4)°$, $V = 5994.3\ (4.6)$ Å^3, $R = 0.0645$ for 2103 observed reflections. Crystal data for $[(C_6H_5)_4P]_2[O{=}W(Te_4)_2]$: monoclinic, $C2/c$, $Z = 4$, $a = 24.318\ (15)$ Å, $b = 13.278\ (7)$ Å, $c = 19.315\ (10)$ Å, $\beta = 106.47\ (4)°$, $V = 5980.8\ (33)$ Å^3, $R = 0.0553$ for 2600 observed reflections. The structures each contain a transition metal in a square-pyramidal coordination environment, with the basal sites occupied by chelating Te_4^{2-} rings and an oxo group in the apical position. The ^{125}Te NMR spectra each display two peaks whose shifts are comparable to those previously assigned to the corresponding metal oxy selenide clusters. The downfield resonance is assigned to the tellurium atoms adjacent to the metal and the other to the ring tellurium atoms. Reaction of the molybdenum oxy telluride cluster with 2 equiv of dimethyl acetylenedicarboxylate results in addition of the acetylene group across both tellurium rings, with formation of the novel bis(ditellurolene) complex $[(C_6H_5)_4P]_2[O{=}Mo(Te_2C_2(CO_2CH_3)_2)_2]\cdot THF$ ($[C_6H_5)_4P]_2$(II)), which has also been characterized by IR and ^{125}Te NMR spectroscopy and single-crystal X-ray diffraction. Crystal data for II: triclinic, $P\bar{1}$, $Z = 2$, $a = 11.469\ (4)$ Å, $b = 12.841\ (5)$ Å, $c = 22.365\ (7)$ Å, $\alpha = 85.03\ (3)°$, $\beta = 89.28\ (3)°$, $\gamma = 76.29\ (3)°$, $V = 3187.9\ (19)$ Å^3, $R = 0.0396$ for 6242 observed reflections.

Introduction

The chemistry of soluble molybdenum and tungsten sulfides is very extensive[1] due to their significance in biology[2] and catalysis.[3] The chemistry of the selenides is less well studied,[4] and that of tellurium is almost unknown. The various metal polysulfides are traditionally prepared by the reaction of tetrathiometalates with sulfur-transfer reagents.[5] The corresponding tellurium compounds are not yet available, which impedes the progress of metal telluride chemistry. We[6] and others[7] have recently developed a general route to molecular transition-metal tellurides and selenides using soluble polychalcogenides extracted from alkali-metal salts of selenium and tellurium. Thus, we have been able to prepare a variety of novel metal chalcogen complexes. In this paper we report the extension of this reaction to high-valent metal halides, leading to the formation of molybdenum and tungsten oxy tellurides in good yield.

It is well-known that sulfur rings coordinated to a metal center will react with activated acetylenes to form coordinated dithiolenes in a variety of coordination environments.[1c,8,9] This is a potentially useful reaction because previous work has shown that halophilic metal centers will readily transfer coordinated dithiolenes to carbon halide complexes, forming organic dithiolenes. Dithiolenes are well-known and have attracted a great deal of interest as potential low-dimensional conductors.[10] However, tellurium-containing rings are not so well-known.[11]

The polytelluride complexes described here can be used to lead to a significant extension of organotellurium coordination chemistry. We report the reaction of an activated acetylene with an inorganic polytelluride complex to form a novel metal ditellurolene. This is a rare class of compound and the first made by this method.[12] The coordination chemistry of organotellurides is slightly more developed[13] than that of purely inorganic tellurides,[14] but it is still quite primitive compared to metal thiolate and thiolene chemistry.[15] However, these new ditellurolene complexes may also serve as group-transfer reagents to form unsaturated tellurium-containing rings.

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(1) (a) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. (b) Müller, A. *Polyhedron* **1986**, *5*, 323. (c) Coucouvanis, D.; Hadjikyriacou, A. I.; Draganjac, M.; Kanatzidis, M. G.; Ileperama, O. *Polyhedron* **1986**, *5*, 349. (d) Harmer, M. A.; Halbert, T. R.; Pan, W.-H.; Coyle, C. L.; Cohen, S. A.; Stiefel, E. I. *Polyhedron* **1986**, *5*, 341.

(2) (a) *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1986. (b) Averill, B. A. *Struct. Bonding* **1983**, *53*, 59. (c) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455.

(3) (a) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 361. (b) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265.

(4) (a) Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 1710. (b) Wardle, R. W. M.; Chau, C.-N.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1859. (c) Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747. (d) O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971.

(5) (a) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201. (b) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenzinger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321. (c) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

(6) (a) Flomer, W. A.; O'Neal, S. C.; Jeter, D.; Cordes, A. W.; Kolis, J. W. *Inorg. Chem.* **1988**, *27*, 969. (b) Flomer, W. A.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 3682. (c) Flomer, W. A.; O'Neal, S. C.; Pennington, W. T.; Jeter, D.; Cordes, A. W.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1702.

(7) (a) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 433. (b) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 432. (c) Haushalter, R. C. *Inorg. Chim. Acta* **1985**, *102*, L37. (d) Eichhorn, B. W.; Haushalter, R. C.; Cotton, F. A.; Wilson, B. *Inorg. Chem.* **1988**, *27*, 4084.

(8) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

(9) (a) Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139. (b) Kanatzidis, M. G.; Coucouvanis, D. *Inorg. Chem.* **1984**, *23*, 403.

(10) (a) Williams, J. M. *Prog. Inorg. Chem.* **1985**, *33*, 183. (b) Becker, J. Y., Bernstein, J., Bittner, S., Eds. The Chemistry of Organic Conductors. *Isr. J. Chem.* **1986**, *27*, 289.

(11) Cowan, D.; Kini, A. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1987; Vol. 2, p 463.

(12) (a) Giolondo, D. M.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 1636. (b) Köpf, H.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1192. (c) Meunier, P.; Gautheron, B.; Mazouz, A. *J. Organomet. Chem.* **1987**, *320*, C39.

(13) Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1986; p 679.

(14) (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. (b) Böttcher, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 759.

(15) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.

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Table I. Crystallographic Data for Structures of Ia, Ib, and II

	$[(C_6H_5)_4P]_2$(Ia)	$[(C_6H_5)_4P]_2$(Ib)	$[(C_6H_5)_4P]_2$(II)
chem formula	$C_{48}H_{40}OP_2MoTe_8$	$C_{48}H_{40}OP_2WTe_8$	$C_{64}H_{60}O_{10}P_2MoTe_4$
FW	1811.49	1899.4	1657.5
a, Å	24.328 (11)	24.318 (15)	11.469 (4)
b, Å	13.308 (4)	13.278 (7)	12.841 (5)
c, Å	19.325 (10)	19.315 (10)	22.365 (6)
α, deg			85.03 (3)
β, deg	106.66 (4)	106.47 (4)	89.28 (3)
δ, deg			76.29 (3)
V, Å^3	5994.3 (46)	5980.8 (33)	3187.9 (19)
Z	4	4	2
space group	$C2/c$	$C2/c$	$P\bar{1}$
size, mm	0.2 × 0.2 × 0.4	0.2 × 0.2 × 0.4	0.1 × 0.3 × 0.4
T, °C	25	25	25
λ, Å	0.71073	0.71073	0.71073
ρ, g cm^{-3}	2.01	2.11	1.73
μ, cm^{-1}	164.65	192.33	21.02
R	0.0645	0.0553	0.0396
R_w	0.0689	0.0608	0.0445
collecn range	$h,k,\pm l$	$h,k,\pm l$	$-h,\pm k,\pm l$
no. of measd reflns	4565	4258	12759
no. of obsd reflns	2103 $[F_o > 3\sigma(F_o)]$	2600 $[F_o > 3\sigma(F_o)]$	6242 $[F_o > 3\sigma(F_o)]$
no. of params	273	273	707
final resid chem, e	1.56	2.17	1.17

Experimental Section

Unless otherwise specified, all work was done in a drybox or with standard Schlenk techniques, under an atmosphere of purified argon, as the polytellurides are extremely air sensitive. Solvents were Aldrich Gold Label and were thoroughly degassed and stored over sieves before use. All reagents were purchased from Strem Chemical and used as received. The starting material K_2Te_2 was prepared by reacting elemental potassium with elemental tellurium in liquid ammonia in the correct ratio, as previously described.[6a] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or Atlantic Microlabs, Atlanta, GA.[16]

Preparation of $[(C_6H_5)_4P]_2[O{=}Mo(Te_4)_2]$ ($[C_6H_5)_4P]_2$(Ia)). A flask was charged with 488 mg (1.464 mmol) of K_2Te_2, 110 mg (0.403 mmol) of $MoCl_5$, and 307 mg (0.773 mmol) of $(C_6H_5)_4PBr$. To this flask was added 10 mL of dimethylformamide (DMF) and the reaction mixture stirred for 4 h at 25 °C. The deep brown solution was filtered, 10 mL of THF slowly added to form a layer, and the solution stored at 4 °C for 48 h. After initial crystallization, 285 mg (43% yield) of black crystals was isolated and washed with THF. The volume of the mother liquor was reduced to 10 mL under vacuum and another layer of THF added. A second crop of black crystals was harvested in the same fashion (total yield 557 mg, 84%). IR (Nujol mull): 936 (m) cm^{-1}. ^{125}Te NMR (relative to $Te(OH)_6$, in H_2O): 89, 717 ppm. Anal. Calcd: C, 31.80; H, 2.22. Found: C, 29.90; H, 2.40.

Preparation of $[(C_6H_5)_4P]_2[O{=}W(Te_4)_2]$ ($[C_6H_5)_4P]_2$(Ib)). A procedure similar to that described above was followed for the tungsten compound, with 110 mg (0.277 mmol) of WCl_6, 336 mg (1.008 mmol) of K_2Te_2, and 211 mg (0.504 mmol) of $(C_6H_5)_4PBr$. The reaction mixture was worked up as described above, except the solution was olive green. The resulting crop of black crystalline solid was washed with THF and dried (yield 196 mg, 41%). A second crop of crystals could be isolated as above (total yield 370 mg, 75%). Use of WCl_4O or WCl_4 instead of WCl_6 as the starting material gave the same product, but with a somewhat lower yield. IR (Nujol mull): 948 (m) cm^{-1}. ^{125}Te NMR (relative to $Te(OH)_6$, in H_2O): +120, +903 ppm. Anal. Calcd for $C_{48}H_{40}OWP_2Te_8$: C, 30.35; H, 2.12. Found: C, 29.66; H, 2.13.

Preparation of $[(C_6H_5)_4P]_2[O{=}Mo(Te_2C_2(CO_2CH_3)_2)]\cdot THF$ ($[C_6H_5)_4P]_2$(II)). To a solution of 300 mg of $[(C_6H_5)_4P]_2[O{=}Mo(Te_4)_2]$ in 5 mL of DMF was added 1 mL of 0.5 M $CH_3O_2CC{\equiv}CCO_2CH_3$ (DMAD) in acetonitrile. The solution was stirred at 25 °C for 24 h and filtered through a glass frit. The solvent was removed under vacuum and the brown oil dissolved in 5 mL of acetone. Hexane (4 mL) was added as a layer and the solution stored at 4 °C for 3 days. Clear orange crystalline solid could be isolated (yield 90 mg, 26%). IR (Nujol mull): 1700 (s), 1219 (s), 919 (m) cm^{-1}. ^{125}Te NMR (relative to $Te(OH)_6$, in H_2O): 71 ppm. Anal. Calcd for $C_{64}H_{60}O_{10}MoP_2Te_4$: C, 46.38; H, 3.65. Found: C, 45.33; H, 3.70.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[(C_6H_5)_4P]_2[MoOTe_8]$

	x	y	z	U(eq)[a]
Mo(1)	0	1604 (2)	2500	63 (1)
Te(1)	910 (1)	2299 (1)	2091 (1)	75 (1)
Te(2)	1847 (1)	1537 (1)	3128 (1)	84 (1)
Te(3)	1661 (1)	2349 (2)	4314 (1)	97 (1)
Te(4)	449 (1)	2142 (1)	3883 (1)	85 (1)
P(1)	1838 (2)	8032 (4)	3459 (3)	61 (2)
O(1)	0	343 (15)	2500	84 (9)
C(11)	1375 (10)	8245 (16)	4047 (9)	69 (8)
C(12)	1300 (10)	7442 (15)	4468 (12)	72 (9)
C(13)	970 (12)	7671 (22)	4943 (12)	96 (12)
C(14)	693 (11)	8534 (20)	4956 (12)	83 (10)
C(15)	802 (11)	9311 (20)	4552 (12)	87 (10)
C(16)	1147 (11)	9147 (15)	4076 (11)	75 (9)
C(21)	1459 (9)	8250 (14)	2526 (9)	56 (7)
C(22)	1025 (12)	8892 (16)	2318 (11)	83 (10)
C(23)	760 (12)	9109 (20)	1583 (13)	98 (11)
C(24)	916 (13)	8579 (18)	1076 (11)	90 (11)
C(25)	1364 (12)	7928 (17)	1310 (14)	88 (12)
C(26)	1650 (10)	7753 (17)	2016 (9)	75 (9)
C(31)	2440 (10)	8864 (14)	3733 (9)	63 (8)
C(32)	2813 (13)	9037 (18)	3315 (13)	92 (12)
C(33)	3301 (11)	9610 (19)	3551 (13)	86 (10)
C(34)	3376 (11)	10107 (16)	4180 (13)	81 (10)
C(35)	3032 (12)	9960 (17)	4627 (12)	83 (10)
C(36)	2555 (10)	9345 (16)	4396 (11)	73 (9)
C(41)	2103 (11)	6764 (15)	3520 (10)	74 (9)
C(42)	2670 (11)	6526 (17)	3780 (12)	77 (9)
C(43)	2833 (13)	5520 (22)	3817 (13)	99 (12)
C(44)	2425 (16)	4784 (23)	3609 (15)	102 (14)
C(45)	1847 (14)	4972 (17)	3378 (13)	92 (13)
C(46)	1676 (10)	5987 (17)	3312 (12)	78 (9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^{125}Te NMR Spectra. Samples were run in nondeuterated DMF and prepared as concentrated as possible by stirring excess solid with DMF for 24 h at room temperature. The solutions were sealed in 10-mm tubes under vacuum. Spectra were recorded on an IBM 200AT spectrometer at 63.135 MHz and referenced by using $Te(OH)_6$ in H_2O as an external standard. Due to the wide sweep width necessary to scan the entire tellurium spectrum, the data were collected by successively scanning 20000-Hz increments over the entire range of known ^{125}Te shifts. The scans were performed with a pulse width of 12 μs and a relaxation delay of 4 s. The T_1 values of this class of compounds are completely unknown, but other tellurium compounds generally have T_1 values between 0.5 and 2 s.[17] These parameters were selected because they appeared to give the best signal to noise ratio. Approximately 8000 scans were used in each case.

X-ray Crystallographic Measurements. All crystallographic data sets were collected in a similar manner. Crystals were embedded in epoxy resin on the tip of a glass capillary and mounted on a Nicolet R3 dif-

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(16) Repeated analysis of many samples by several analytical houses consistently yielded values that were slightly low in carbon, even for highly crystalline samples that were spectroscopically clean.

(17) Granger, P.; Chapelle, S. *J. Magn. Reson.* **1980**, *39*, 329.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(C_6H_5)_4P]_2[WOTe_8]$

	x	*y*	*z*	*U*(eq)[a]
W(1)	5000	1629 (1)	2500	66 (2)
O(1)	5000	351 (12)	2500	95 (10)
Te(1)	4089 (1)	2274 (1)	2914 (1)	77 (1)
Te(2)	3141 (1)	1537 (1)	1865 (1)	87 (1)
Te(3)	3326 (1)	2331 (1)	675 (1)	97 (1)
Te(4)	4547 (1)	2163 (1)	1123 (1)	86 (1)
P(1)	3164 (2)	1974 (3)	6534 (2)	62 (2)
C(11)	2907 (9)	3253 (14)	6473 (9)	68 (7)
C(12)	2334 (10)	3504 (17)	6239 (12)	88 (9)
C(13)	2160 (10)	4498 (18)	6171 (12)	91 (9)
C(14)	2553 (12)	5233 (17)	6357 (12)	97 (11)
C(15)	3106 (12)	5006 (16)	6616 (11)	91 (10)
C(16)	3313 (10)	4027 (14)	6677 (10)	75 (8)
C(21)	3628 (8)	1767 (15)	5938 (10)	72 (7)
C(22)	3839 (9)	826 (15)	5887 (10)	75 (8)
C(23)	4161 (10)	663 (17)	5451 (11)	92 (10)
C(24)	4258 (10)	1441 (16)	5025 (12)	85 (9)
C(25)	4038 (9)	2397 (17)	5051 (12)	90 (10)
C(26)	3708 (9)	2540 (15)	5517 (9)	73 (7)
C(31)	2553 (8)	1147 (13)	6257 (10)	66 (7)
C(32)	2442 (9)	658 (16)	5606 (12)	88 (9)
C(33)	1972 (11)	54 (17)	5382 (11)	93 (9)
C(34)	1612 (10)	−110 (15)	5838 (13)	89 (10)
C(35)	1715 (9)	362 (18)	6485 (12)	87 (9)
C(36)	2193 (10)	1010 (16)	6715 (11)	89 (10)
C(41)	3546 (8)	1752 (15)	7456 (9)	68 (7)
C(42)	4012 (8)	1092 (15)	7692 (11)	74 (8)
C(43)	4264 (9)	934 (18)	8396 (11)	86 (8)
C(44)	4112 (11)	1413 (19)	8917 (13)	99 (10)
C(45)	3637 (12)	2053 (20)	8702 (11)	98 (10)
C(46)	3361 (8)	2240 (17)	7990 (11)	89 (9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

fractometer. Rotation photographs were used to assess crystal quality and obtain initial space group information. The unit cells were determined from 30 well-centered reflections with $15° < 2\theta < 28°$. Data were collected at room temperature for $3° < 2\theta < 45°$. The data were all corrected for absorption by the ψ-scan technique, with use of six strong reflections at high χ angles. The structures were solved by using the direct-methods programs and refined by using the program package of SHELXTL. For all structures, reflections were considered observed at $F_o^2 > 3\sigma(F_o^2)$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed. In each case, the final difference Fourier map had peaks of less than two electrons, always in the vicinity of the heavy atoms. Individual structure solution information is given in Table I. Refined atomic coordinates for Ia, Ib, and II are given in Tables II–IV, respectively.

Results

Reactions. The oxy telluride complexes Ia and Ib are prepared in good yield by the reaction of a polytelluride solution with either $MoCl_5$ or WCl_6 in DMF, followed by addition of PPh_4Br and precipitation with THF. The polytelluride solution is a complex mixture of polytelluride anions formed by dissolving a compound of nominal composition K_2Te_2 in DMF. The source of the oxygen atom is not clear. It may be derived from adventitious water in the DMF, or it may come from the DMF itself. Alternatively, it may come from hydrolysis of terminal telluride in solution. This has been previously postulated with metal sulfide[5b] and selenide complexes.[18] These complexes are the favored product in this system, as extensive experimentation with solvents and conditions failed to yield any other observable product in our hands. The reaction involves a reduction of the metal to 4+ in each case, and the electrons are presumably supplied by some of the polytellurides in solution.

Reaction of unsaturated electrophiles with coordinated sulfur and selenium rings is known. These result in formation of unsaturated five-membered rings and elimination of elemental chalcogen. We have extended this reaction to telluride rings for the first time. Reaction of 2 equiv of dimethyl acetylenedicarboxylate (DMAD) results in formation of complex II, containing two coordinated ditellurolene rings:

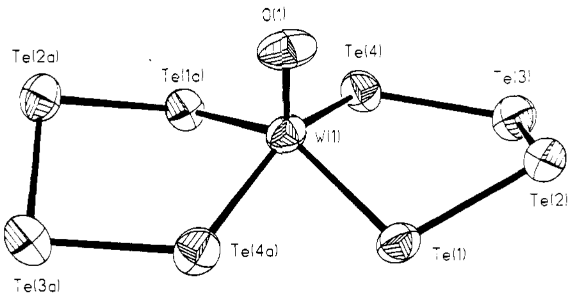


Figure 1. ORTEP view of $[O{=}W(Te_4)_2]^{2-}$ (Ib) with 40% probability ellipsoids.

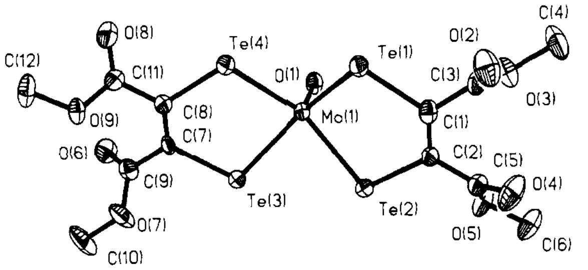
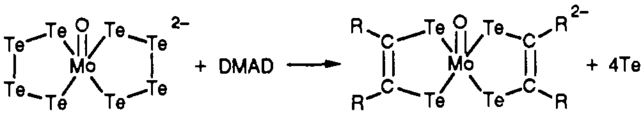


Figure 2. Top ORTEP view of $[O{=}Mo(Te_2C_2(CO_2CH_3)_2)_2]^{2-}$ (II) with 40% probability ellipsoids.



This is analogous to the corresponding sulfide reaction.[1c] This reaction presumably occurs by attack of the electrophilic acetylene upon the electron-rich tellurium ring, resulting in elimination of the tellurium atoms not directly bonded to the metal center. Precipitation of elemental tellurium is observed. However, the reaction is undoubtedly more complex than that. Chromatography of the reaction mixture results in isolation of the tetrafunctionalized tellurophene, suggesting that further, more complicated reactions are taking place.[19]

Structures of $[(C_6H_5)_4P]_2[O{=}M(Te_4)_2]$ (M = Mo, W). The overall structures of anions Ia and Ib are similar to those of the corresponding $O{=}M(E_4)_2^{2-}$ compounds, where E represents sulfur[5b] or selenium.[18] The metal is in a square-pyramidal coordination environment with an apical oxo group and two Te_4^{2-} groups chelated to the four basal sites (see Figure 1). The molecule contains a 2-fold rotation axis along the M=O vector, and the five-membered metal polytelluride ring is in the envelope configuration. This appears to be a general structural type for the metal nonachalcogens, as the isostructural MoS_9^{2-},[5a] $MoSe_9^{2-}$,[4b] $WSSe_8^{2-}$,[18] and ReS_9^{-} [20] are also known. In many of the metal polychalcogenide complexes, the formation of a five-membered ring seems to be a thermodynamically favored process.[9a]

There are few Mo–Te or W–Te complexes that have been structurally characterized;[6a,7d,21] however, the bond distances observed in these complexes appear normal (see Tables V andVI). The Mo–Te distances are slightly longer than the W–Te distances (average 2.697 versus 2.685 Å), but they are significantly shorter than the distances in $(CO)_4WTe_4^{2-}$ (2.83 Å average). This is reasonable as the carbonyl complex contains a formally zerovalent metal versus M^{4+} in the current complexes. The Te–Te distances

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(18) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790.

(19) Flomer, W. A.; Pennington, W. T.; Kolis, J. W. Manuscript in preparation.

(20) (a) Müller, A.; Krickemeyer, E.; Bögge, H. *Z. Anorg. Allg. Chem.* **1987**, *554*, 61. (b) Cotton, F. A.; Kibala, P. A.; Matusz, M. *Polyhedron* **1988**, *8*, 83.

(21) Faggiani, R.; Gillespie, R. J.; Campana, C.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* **1987**, 485.

Table IV. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(C_6H_5)_4P]_2[O{=}Mo(Te_2C_2R_2)_2]$

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Te(1)	1647 (1)	9446 (1)	8222 (1)	45 (1)	C(26)	8853 (8)	2898 (7)	5476 (4)	50 (3)
Te(2)	1055 (1)	10378 (1)	6653 (1)	47 (1)	C(27)	9120 (9)	2017 (7)	5140 (4)	61 (4)
Te(3)	4163 (1)	9164 (1)	6295 (1)	43 (1)	C(28)	8465 (9)	1988 (8)	4632 (5)	66 (4)
Te(4)	4727 (1)	8398 (1)	7881 (1)	47 (1)	C(29)	7541 (9)	2837 (7)	4456 (4)	60 (4)
Mo(1)	2735 (1)	8781 (1)	7205 (1)	36 (1)	C(30)	7252 (8)	3731 (7)	4781 (4)	54 (3)
P(1)	7543	4948 (2)	5700 (1)	38 (1)	C(31)	7226 (7)	6079 (6)	5146 (4)	42 (3)
P(2)	2800 (2)	3792 (2)	10054 (1)	43 (1)	C(32)	6175 (8)	6863 (7)	5148 (4)	51 (3)
O(1)	2404 (4)	7603 (4)	7094 (3)	46 (2)	C(33)	5981 (9)	7726 (7)	4713 (5)	64 (4)
O(2)	−965 (6)	10985 (6)	8825 (3)	82 (3)	C(34)	6833 (10)	7763 (8)	4277 (5)	64 (4)
O(3)	−1831 (5)	10025 (5)	8274 (3)	63 (3)	C(35)	7855 (9)	7003 (7)	4257 (4)	59 (4)
O(4)	−2087 (6)	12097 (6)	7395 (4)	91 (3)	C(36)	8054 (9)	6147 (7)	4712 (4)	58 (4)
O(5)	−1869 (5)	11064 (5)	6644 (3)	69 (3)	C(37)	1759 (7)	2955 (7)	10122 (4)	45 (3)
O(6)	7563 (6)	7601 (5)	6128 (3)	64 (3)	C(38)	1000 (8)	2954 (7)	10615 (4)	55 (4)
O(7)	6942 (6)	9362 (5)	5899 (3)	79 (3)	C(39)	222 (9)	2282 (8)	10666 (5)	71 (4)
O(8)	7608 (7)	7299 (9)	7947 (5)	162 (6)	C(40)	189 (9)	1616 (8)	10239 (6)	73 (5)
O(9)	8156 (5)	8338 (5)	7240 (3)	60 (3)	C(41)	931 (10)	1594 (8)	9749 (5)	72 (5)
C(1)	−62 (7)	10393 (6)	7902 (4)	43 (3)	C(42)	1744 (9)	2243 (7)	9700 (4)	60 (4)
C(2)	−298 (7)	10731 (6)	7331 (4)	40 (3)	C(43)	2652 (7)	4648 (6)	10658 (4)	45 (3)
C(3)	−990 (7)	10528 (7)	8390 (4)	46 (3)	C(44)	3390 (10)	4367 (8)	11159 (4)	68 (4)
C(4)	−2793 (9)	10082 (11)	8711 (5)	93 (6)	C(45)	3232 (12)	5038 (10)	11615 (5)	83 (5)
C(5)	−1483 (7)	11347 (7)	7130 (4)	48 (3)	C(46)	2347 (12)	5959 (10)	11575 (5)	85 (6)
C(6)	−3090 (9)	11572 (9)	6456 (5)	83 (5)	C(47)	1618 (12)	6228 (10)	11107 (6)	95 (6)
C(7)	5946 (6)	8561 (6)	6675 (4)	40 (3)	C(48)	1741 (10)	5576 (8)	10637 (5)	75 (5)
C(8)	6138 (7)	8305 (7)	7251 (4)	46 (3)	C(49)	4273 (8)	2924 (7)	10054 (4)	52 (4)
C(9)	6904 (8)	8437 (7)	6210 (4)	46 (3)	C(50)	5143 (10)	3146 (9)	9650 (6)	89 (6)
C(10)	7890 (11)	9322 (10)	5464 (6)	102 (6)	C(51)	6280 (12)	2438 (14)	9683 (8)	128 (8)
C(11)	7346 (8)	7918 (8)	7508 (5)	63 (4)	C(52)	6508 (12)	1516 (12)	10103 (7)	105 (7)
C(12)	9377 (8)	7914 (8)	7417 (5)	75 (5)	C(53)	5657 (13)	1332 (13)	10412 (6)	120 (7)
C(13)	8752 (7)	4966 (7)	6189 (4)	42 (3)	C(54)	4534 (10)	2029 (11)	10395 (6)	99 (6)
C(14)	9521 (8)	5645 (7)	6069 (4)	50 (3)	C(55)	2494 (8)	4665 (8)	9374 (4)	56 (4)
C(15)	10471 (9)	5590 (9)	6451 (5)	70 (5)	C(56)	3121 (10)	5458 (10)	9245 (5)	91 (5)
C(16)	10677 (9)	4854 (11)	6937 (6)	81 (5)	C(57)	2918 (12)	6108 (11)	8721 (6)	111 (7)
C(17)	9911 (9)	4190 (9)	7063 (4)	74 (5)	C(58)	2042 (12)	6053 (9)	8353 (5)	88 (6)
C(18)	8942 (8)	4251 (8)	6686 (4)	60 (4)	C(59)	1318 (10)	5393 (9)	8503 (4)	70 (4)
C(19)	6237 (7)	4964 (6)	6138 (3)	38 (3)	C(60)	1553 (9)	4690 (7)	9010 (4)	58 (4)
C(20)	5453 (8)	4356 (7)	6042 (4)	51 (3)	C(61)	4523 (30)	1894 (28)	7662 (16)	276 (15)
C(21)	4412 (8)	4444 (8)	6380 (5)	59 (4)	C(62)	4264 (27)	3025 (25)	8051 (14)	256 (12)
C(22)	4166 (8)	5178 (8)	6798 (4)	61 (4)	C(63)	3639 (25)	2207 (23)	8455 (13)	231 (11)
C(23)	4937 (8)	5787 (7)	6905 (4)	56 (4)	C(64)	2681 (28)	2678 (26)	7971 (16)	271 (14)
C(24)	6006 (8)	5695 (7)	6588 (4)	49 (3)	C(65)	3485 (30)	2104 (25)	7474 (14)	243 (13)
C(25)	7917 (7)	3761 (6)	5297 (4)	42 (3)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Lengths (Å) and Angles (deg) for $[(C_6H_5)_4P]_2[MoOTe_8]$ (Ia)

Mo(1)–Te(1)	2.716 (2)	Mo(1)–Te(4)	2.677 (2)
Mo(1)–O(1)	1.679 (20)	Te(1)–Te(2)	2.763 (2)
Te(2)–Te(3)	2.686 (2)	Te(3)–Te(4)	2.838 (3)
Te(4)–Mo(1)–Te(1)	93.8 (1)	O(1)–Mo(1)–Te(1)	109.0 (1)
O(1)–Mo(1)–Te(4)	105.5 (1)	Te(2)–Te(1)–Mo(1)	103.61 (1)
Te(3)–Te(2)–Te(1)	99.5 (1)	Te(4)–Te(3)–Te(2)	97.2 (1)
Te(3)–Te(4)–Mo(1)	114.3 (1)		

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $[(C_6H_5)_4P]_2[WOTe_8]$ (Ib)

W(1)–O(1)	1.697 (16)	W(1)–Te(1)	2.697 (1)
W(1)–Te(4)	2.671 (1)	Te(1)–Te(2)	2.778 (2)
Te(2)–Te(3)	2.682 (2)	Te(3)–Te(4)	2.858 (2)
Te(1)–W(1)–O(1)	108.5 (1)	Te(4)–W(1)–O(1)	105.5 (1)
Te(4)–W(1)–Te(1)	93.9 (1)	Te(2)–Te(1)–W(1)	104.8 (1)
Te(3)–Te(2)–Te(1)	100.4 (1)	Te(4)–Te(3)–Te(2)	97.0 (1)
Te(3)–Te(4)–W(1)	115.0 (1)		

show a considerable variation in bond distance around the ring (2.68–2.85 Å) in each case. This phenomenon is common for four-membered chalcogen rings and has been explained in terms of repulsive overlap of lone pairs.[1c,5b] The variation observed in these complexes is somewhat large for tellurium.

The bite angle of tetratelluride chelates is 94°, which is normal for a square-pyramidal complex but somewhat smaller than that observed in $(CO)_4MTe_4^{2-}$ (98°). The W=O distance is longer than the Mo=O distance, but both are typical of high-valent metal oxo groups.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for $[(C_6H_5)_4P]_2[O{=}Mo(Te_2C_2R_2)_2]$ (II)

Te(1)–Mo(1)	2.686 (1)	Te(1)–C(1)	2.142 (7)
Te(2)–Mo(1)	2.682 (1)	Te(2)–C(2)	2.154 (8)
Te(3)–Mo(1)	2.681 (1)	Te(3)–C(7)	2.164 (7)
Te(4)–Mo(1)	2.678 (1)	Te(4)–C(8)	2.122 (8)
Mo(1)–O(1)	1.683 (6)		
Mo(1)–Te(1)–C(1)	102.5 (2)	Mo(1)–Te(2)–C(2)	103.0 (2)
Mo(1)–Te(3)–C(7)	103.1 (2)	Mo(1)–Te(4)–C(8)	104.3 (2)
Te(1)–Mo(1)–Te(2)	85.0 (1)	Te(1)–Mo(1)–Te(3)	147.0 (1)
Te(2)–Mo(1)–Te(3)	85.6 (1)	Te(1)–Mo(1)–Te(4)	83.4 (1)
Te(2)–Mo(1)–Te(4)	142.5 (1)	Te(3)–Mo(1)–Te(4)	85.0 (1)
Te(1)–Mo(1)–O(1)	107.2 (2)	Te(2)–Mo(1)–O(1)	108.4 (2)
Te(3)–Mo(1)–O(1)	105.8 (2)	Te(4)–Mo(1)–O(1)	109.1 (2)

Structure of $[(C_6H_5)_4P]_2[O{=}Mo(Te_2C_2(CO_2CH_3)_2)_2]\cdot$THF ($[(C_6H_5)_4P]_2$(II)). The molecule contains the same basic geometry as the precursor molecule, a square pyramid with an apical oxo group (see Figure 2). The structure contains two well-separated $[(C_6H_5)_4P]^+$ cations and a disordered THF molecule. However, the most interesting aspect is unquestionably the two ditellurolene groups. This is one of the very few metal ditellurolene complexes reported[12] and only the second characterized crystallographically.

The Mo–Te distances are all fairly short at 2.68 Å, and the C–Te distances are 2.145 Å on average (see Table VII). This is comparable to aryl-telluride distances (2.12 Å for $(C_6H_5)_2Te_2$)[22] but is somewhat longer than the phenyl distances in the platinum

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[22] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, England, 1975.

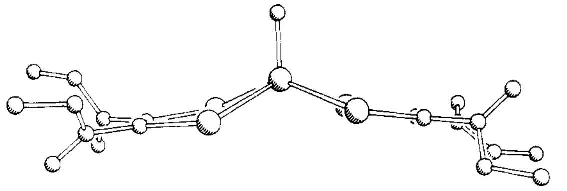

Figure 3. Side view of II showing the flattened five-membered ring and the orientation of the ester groups.

ditellurolene complex reported.[12a] The bite angle is 85°, which is considerably less than that of η^2-Te_4 complexes. This is probably due to the smaller ring size of the ditellurolene chelate. The dihedral angle of the five-membered ring is considerably less than normally expected. This results in an almost planar ring with a dihedral angle of only 13° (see Figure 3). In contrast, the five-membered ring in $Cp_2Ti(S_2C_2R_2)$ has a dihedral angle of 44°.[8] The flattened rings may be due to donation of a lone pair of electrons from each tellurium atom to the electron-poor metal center. This electron deficiency may be partly due to the presence of the oxo group.

The orientation of the ester groups deserves comment. The two ester groups on each ligand are in similar orientations. However, one of the ligands contains both groups above the square base of the pyramid and the other contains both groups below the base of the pyramid (see Figure 3). We see no obvious reason for this curiosity in the packing of the molecules in the unit cell. However, that is probably the basis for the orientation, since preliminary solution ^{125}Te NMR spectra of the complex show only one signal. This suggests that free rotation is taking place in solution at room temperature.

Spectroscopy. The IR spectrum of the oxy tellurides is distinctive with the presence of the conspicuous metal oxo stretch in the vicinity of 950 cm^{-1}. These bands are diagnostic for this class of compounds. In addition to metal oxo stretches, the ditellurolene complexes possesses the expected broad bands at 1700 and 1219 cm^{-1}, indicative of C=O and C—O stretching, respectively.

We were able to perform ^{125}Te NMR spectroscopy on both of the $O{=}M(Te_4)_2^{2-}$ complexes as well as the ditellurolene complex. The oxy telluride complexes each possess two resonances of equal intensity (see Figure 4). In both complexes, one resonance is about 800 ppm downfield of the other. The downfield resonance in each case was assigned to the tellurium bound to the metal center. This is based on previous work on the corresponding selenium complexes, which show shift differences of magnitude similar to ours.[18] The spectrum of the ditellurolene complex displays only one resonance, which is nearly unshifted with respect to the downfield resonance of $O{=}Mo(Te_4)_2^{2-}$. This is the resonance that is assigned to the tellurium atom bound to the metal center. We feel that this strengthens the assignment of the parent compounds, as the environment of the tellurium bound to the metal is not substantially altered. As the shift of heavy atoms is dominated by the paramagnetic contribution, tellurium atoms bound to metal centers with similar coordination environments and oxidation states would be expected to have similar shifts.

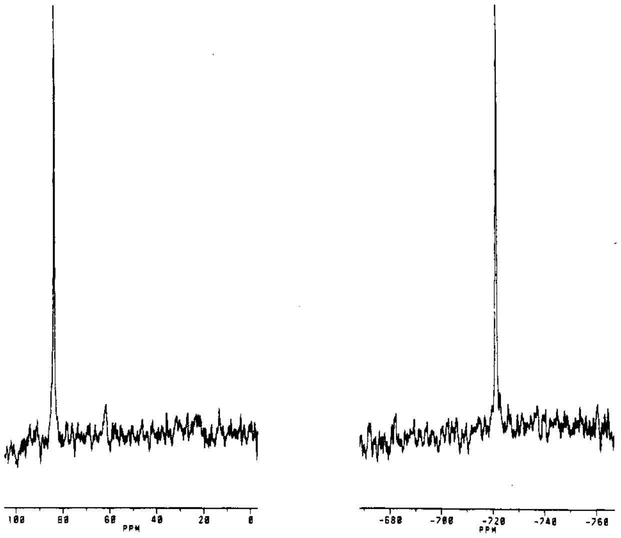

Figure 4. ^{125}Te NMR spectrum of $[O{=}Mo(Te_4)_2]^{2-}$ in DMF solution.

Conclusion

We have described a convenient synthesis of some novel metal oxy telluride complexes from soluble polytellurides and high-valent molybdenum and tungsten chlorides. These have structures that are similar to those of previously reported sulfides and selenides. However, the source of the oxygen atom is unknown at this time. These new compounds have IR and ^{125}Te NMR spectral characteristics that are in full agreement with the structures.

The molybdenum compound reacts readily with dimethyl acetylenedicarboxylate via a somewhat complicated mechanism to form a coordinated ditellurolene complex. This reaction is exciting because the presence of a hard halophilic metal center makes these complexes potentially useful as ditellurolene-transfer reagents. It has previously been shown that dithiolenes coordinated to halophilic centers are excellent reagents for dithiolene-transfer reactions. We are currently investigating these reactions.

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Registry No. Ia, 120881-69-8; Ib, 120881-71-2; II, 120881-74-5; DMAD, 762-42-5; K_2Te_2, 78547-42-9; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; Te_4^{2-}, 77835-84-8.

Supplementary Material Available: For structures of Ia, Ib, and II, complete tables of bond distances and angles, positions of hydrogen atoms, and anisotropic thermal parameters (13 pages); tables of observed and calculated structure factors (48 pages). Ordering information is given on any current masthead page.