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Reaction of Dimethyl Acetylenedicarboxylate with WSe_9^{2-} and $W_2Se_{10}^{2-}$: Synthesis and Characterization of the $[W(Se_2C_2(COOCH_3)_2)_3]^{2-}$ and $[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]^{2-}$ Anions

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The reaction of dimethyl acetylenedicarboxylate (DMA) with WSe_9^{2-} and $W_2Se_{10}^{2-}$ affords the new soluble anions $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ and $W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$, respectively. $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot{}^1/_2DMF$ crystallizes with eight formula units in the monoclinic space group C^6_{2h}-$C2/c$ in a cell of dimensions $a = 23.21$ (3) Å, $b = 14.77$ (2) Å, $c = 43.33$ (5) Å, and $\beta = 94.46$ (4)°. Three chelating diselenene ligands provide trigonal-prismatic coordination about the W^{IV} center. $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$ crystallizes with one formula unit in the triclinic space group C^1_i-$P\bar{1}$ in a cell of dimensions $a = 13.036$ (3) Å, $b = 13.506$ (3) Å, $c = 13.683$ (3) Å, $\alpha = 104.86$ (1)°, $\beta = 110.24$ (1)°, and $\gamma = 97.60$ (1)°. The anion possesses a center of symmetry. The W^V center is in a distorted-octahedral geometry. ^{77}Se NMR spectroscopy of $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ shows the expected one resonance at $\delta = 839$ ppm (relative to Me_2Se), while $W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$ shows two lines at $\delta = 1360$ (bridging) ppm and $\delta = 874$ (diselenene) ppm. Variable-temperature studies show that the resonance at 874 ppm broadens as the sample is cooled, collapses by −40 °C, and returns as two peaks at $\delta = 754$ and 967 ppm by −90 °C. The resonance at 1360 ppm and that of $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ show no temperature dependence.

Introduction

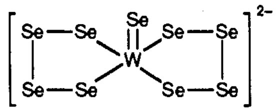
Recent synthetic efforts have produced a number of new, soluble transition-metal selenide anions[1-8] and telluride anions,[9] which extend the soluble metal–chalcogenide chemistry from the well-known sulfur anions.[10-15] While the reactivities of these new complexes have been little explored as yet,[16] the sulfur complexes are known to undergo a wide range of reactions with both electrophiles and nucleophiles.[16-24] Reactions with electrophiles such as CS_2 and activated acetylenes have been studied as models for hydrodesulfurization catalysis.[18]

Sulfur in these soluble sulfides displays three distinct modes of bonding: bridging two (or more) metals, binding terminally to one metal (as can oxygen), and forming MS_n rings. CS_2 will add to an MS_2 ring to form the chelating perthiocarbonate (CS_4^{2-}) ligand;[22] CS_2 will also add to an MS_4 ring with elimination of sulfur to form the CS_4^{2-} ion.[21-23] The reactions of activated acetylenes, R—C≡C—R (e.g., R = $COOCH_3$, CF_3),[16-21,24] with MS_2 or MS_4 rings are more complex. As a function of ring size, metal (Mo, W), and terminal chalcogen atom (O or S), activated acetylenes form either the symmetric S,S-chelating dithiolene ligand[16-19,21,24] or, less commonly, the asymmetric S,C-chelating vinyl disulfide ligand.[20] Activated acetylenes will react with terminal sulfur atoms as well as with MS_n rings (n = 2, 4, 5). Thus, a metal atom that is in an MS_n ring and is bound to a terminal sulfur atom is coordinated to not one but two dithiolene ligands after reaction with an acetylene.[17,18] While mechanisms have been proposed for the formation of dithiolene from the reaction of acetylene with an MS_n ring,[15,18] none has been proposed to explain the inclusion of a terminal sulfur atom in a dithiolene ligand. The reaction of an alkyne with a bridging sulfur atom has not been reported.

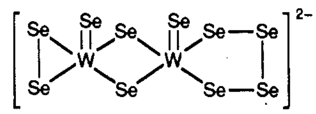
Here we report the reactions of an activated acetylene with the MSe_n (n = 2–4) rings in some of the new, soluble transition-metal selenides we have prepared[1-5] and the characterization of the resultant new products, chiefly by ^{77}Se NMR spectroscopic and single-crystal X-ray diffraction techniques.

Experimental Section

All reactions were carried out under an atmosphere of dry dinitrogen with the use of standard Schlenk techniques. Solvents were dried and distilled before use. The WSe_9^{2-} anion[4] (A) as $[AsPh_4]_2[WSe_9]$ and the



A



B

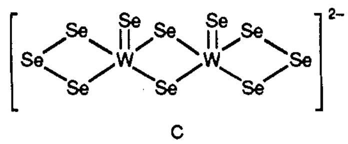


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Table I. Crystallographic Details

compd	$[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$	$[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot {}^1/_2DMF$
formula	$C_{78}H_{78}N_2O_{18}P_2Se_{10}W_2$	$C_{74.5}H_{69.5}As_2N_{0.5}O_{12.5}Se_6W$
fw	2551	1979
a, Å	13.036 (3)	23.21 (3)
b, Å	13.506 (3)	14.77 (2)
c, Å	13.683 (3)	43.33 (5)
α, deg	104.86 (1)	90
β, deg	110.24 (1)	94.46 (4)
γ, deg	97.60 (1)	90
vol, Å^3	2119	14815
Z	1	8
d(calcd), g cm^{-3}	1.999	1.784
space group	C_i^1-$P\bar{1}$	C_{2h}^6-$C2/c$
T, °C	−150	−150
λ, Å	0.7093 (Mo $K\alpha_1$)	
μ, cm^{-1}	71.2	54.4
transmissn coeff	0.480–0.673	0.406–0.505
$R(F_o^2)$	0.055	0.127
$R_w(F_o^2)$	0.089	0.155
$R(F_o)$ $(F_o^2 > 3\sigma(F_o^2))$	0.030	0.056
$R_w(F_o)$ $(F_o^2 > 3\sigma(F_o^2))$	0.035	0.061

$W_2Se_{10}^{2-}$ anions[3] (B, C) as $[PPh_4]_2[W_2Se_{10}]$ were synthesized by literature methods. Dimethyl acetylenedicarboxylate (DMA) was used as purchased from Alfa Chemicals, Denver, CO. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Electronic absorption (UV–vis) and infrared spectra were recorded on a Perkin-Elmer 330 UV–vis spectrophotometer and Perkin-Elmer 283 IR spectrometer, respectively. ^{77}Se NMR spectra were obtained on a Varian XLA-400 spectrometer equipped with a 10-mm broad-band tunable probe.[3] All resonances are referenced to Me_2Se ($\delta = 0$ ppm) as a standard.

$[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot {}^1/_2DMF$. $[AsPh_4]_2[WSe_9]$ (200 mg, ~0.1 mmol) was dissolved in DMF (10.0 mL), and excess DMA (0.2 mL) was added. An instantaneous color change from dark brown to purple was observed. After the solution was stirred for 15 min, it was filtered and 40 mL of toluene was added. When the mixture stood overnight at −40 °C, black-purple diffraction-quality crystals formed; these contain both a toluene and half a DMF molecule per anion as solvents of crystallization, as determined in the X-ray diffraction study (118 mg, ~60% yield). Anal. Calcd for $C_{66}H_{58}As_2O_{12}Se_6W$ (solvent free): C, 42.84; H, 3.16; As, 8.10. Found: C, 43.68; H, 3.45; As, 8.07. Despite repeated attempts satisfactory analyses for W and Se could not be obtained. Electronic absorption (UV–vis) spectrum (DMF; λ_{max}, nm (ϵ_M)): 350 (17 500), 480 sh, 585 (5500), 670 (4000). IR spectrum (KBr; cm^{-1}): 1710, 1690 (ν_{CO}); 1440 ($\nu_{C=C}$); 350 (br). ^{77}Se NMR spectrum (DMF; ppm): δ 839 (^{183}W satellites; $^1J_{W-Se} = 34$ Hz).

$[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$. $[PPh_4][W_2Se_{10}]$ (184 mg, ~0.1 mmol) was dissolved in DMF (10 mL), and DMA (0.5 mL) was added. The color of the solution changed immediately from red-brown to purple. After the solution was stirred for 10 min, it was filtered and toluene (15 mL) was added to the filtrate. At room temperature over a 24-h period the product separated as needle-shaped purple crystals; these contain two DMF molecules per anion as solvents of crystallization, as a subsequent X-ray structure determination showed; yield 140 mg (~55%). Anal. Calcd for $C_{78}H_{78}N_2O_{18}P_2Se_{10}W_2$: C, 36.7; H, 3.1; P, 2.4; Se, 31.0; W, 14.4. Found: C, 36.4; H, 3.1; P, 2.7, Se, 29.9; W, 15.6. Absorption spectrum (DMF; λ_{max}, nm (ϵ_M)): 550 (16 000), 440 sh, 360 (29 500), 295 (33 500). IR spectrum (KBr; cm^{-1}): 1720, 1690 (ν_{CO}); 1435 ($\nu_{C=C}$). ^{77}Se NMR (DMF, 20 °C; ppm): δ 1360 (^{183}W satellites; $^1J_{W-Se} = 38$ Hz), 874.

Crystallographic Studies. For both $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot {}^1/_2DMF$ and $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$ a crystal suitable for diffraction studies was mounted on a glass fiber and placed in the cold stream (−150 °C)[25] of an Enraf-Nonius CAD4 diffractometer. In each case a unit cell was determined from 25 automatically centered reflections, at which point each crystal was transferred to the cold stream (−150 °C) of a Picker FACS-1 diffractometer. Data collection proceeded on the FACS-1 for both crystals, and for each the intensities of six standard reflections monitored every 100 reflections were found to be constant within counting statistics. Some crystallographic details are summarized in Table I; more information is available in Table IS.[26]

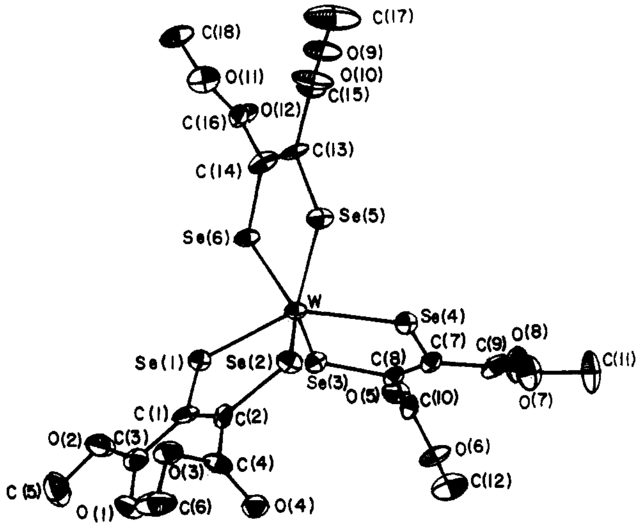


Figure 1. Structure of the $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ ion. Here and in Figure 2 the 50% probability ellipsoids are shown.

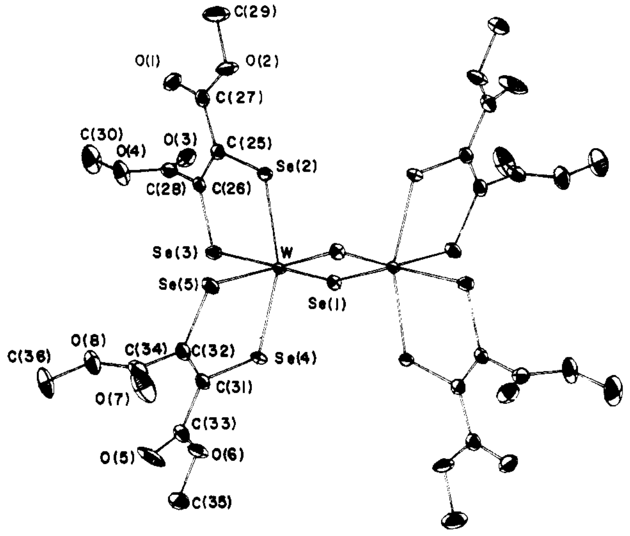
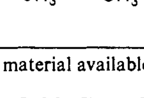


Figure 2. Structure of the $W_2Se_2(Se_2C_2(COOCH_3)_2)_3^{2-}$ ion. The ion possesses a crystallographically imposed center of symmetry.

The reflection conditions *hkl* ($h + k = 2n$) and *h*0*l* ($h, l = 2n$) were met for $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot {}^1/_2DMF$. This indicates either the centrosymmetric space group $C2/c$ (C_{2h}^6) or the noncentrosymmetric space group Cc (C_s^4). The centrosymmetric group was chosen. For $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$ a triclinic cell was found and the centric space group C_i^1-$P\bar{1}$ was chosen. For each structure, the successful refinement in the chosen space group confirms the appropriateness of the choice.

The solution and refinement of each structure involved procedures standard in this laboratory.[27] Both structures were solved by a combination of Patterson and Fourier synthesis techniques. Refinement was by full-matrix least-squares methods.

In $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot {}^1/_2DMF$, there is an ordered toluene solvent molecule. In addition, a DMF



$HC(=O)N(CH_3)_2$

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[25] The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. I. de Vic, 31320 Castanet-Tolosan, France.

[26] For the supplementary material available, see the paragraph at the end of this paper.

[27] For example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277. All data were collected with Mo $K\alpha$ radiation on a Picker FACS-1 diffractometer operated under the Vanderbilt disk-oriented system: Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570. The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. An analytical absorption correction was applied to each crystal: de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot{}^1/_2DMF$

atom	x	y	z	B_{eq}, Å^2	atom	x	y	z	B_{eq}, Å^2
W(1)	0.018676 (25)	0.978718 (38)	0.380952 (12)	1.42 (1)	C(29)	0.11988 (79)	0.2882 (11)	0.33798 (33)	3.4 (5)
Se(1)	−0.044433 (63)	0.953267 (91)	0.332179 (31)	1.78 (4)	C(30)	0.11993 (61)	0.37075 (91)	0.32211 (29)	1.8 (4)
Se(2)	−0.030877 (65)	0.839268 (95)	0.397099 (31)	1.90 (4)	C(31)	0.23826 (61)	0.53444 (84)	0.27323 (29)	1.8 (4)
Se(3)	0.094684 (60)	0.98032 (10)	0.343101 (30)	1.82 (3)	C(32)	0.27571 (57)	0.54628 (97)	0.29995 (30)	2.1 (4)
Se(4)	0.102766 (64)	0.922843 (94)	0.415713 (31)	1.83 (4)	C(33)	0.33062 (64)	0.5785 (10)	0.29786 (34)	2.7 (4)
Se(5)	−0.009174 (64)	1.037534 (90)	0.432009 (30)	1.87 (4)	C(34)	0.35064 (67)	0.5977 (11)	0.26822 (34)	3.3 (4)
Se(6)	0.000940 (65)	1.138799 (93)	0.364910 (31)	1.88 (4)	C(35)	0.31346 (65)	0.58096 (99)	0.24241 (31)	2.3 (4)
As(1)	0.161585 (65)	0.492835 (93)	0.278052 (31)	1.81 (4)	C(36)	0.25815 (66)	0.5505 (10)	0.24426 (33)	2.3 (4)
As(2)	0.171761 (67)	0.425839 (97)	0.466652 (31)	1.84 (4)	C(37)	0.11776 (65)	0.58789 (90)	0.29462 (32)	1.9 (4)
O(1)	−0.12368 (47)	0.71930 (66)	0.30385 (21)	2.6 (3)	C(38)	0.05783 (69)	0.5903 (11)	0.28837 (40)	3.5 (5)
O(2)	−0.12081 (53)	0.85860 (70)	0.28439 (23)	3.5 (3)	C(39)	0.02690 (71)	0.6590 (11)	0.30069 (45)	4.1 (5)
O(3)	−0.15499 (44)	0.69809 (64)	0.36702 (22)	2.4 (3)	C(40)	0.05353 (73)	0.7271 (12)	0.31792 (43)	3.9 (5)
O(4)	−0.06641 (43)	0.63347 (67)	0.36910 (22)	2.4 (3)	C(41)	0.11421 (72)	0.72223 (87)	0.32393 (32)	2.3 (4)
O(5)	0.22844 (44)	0.99712 (62)	0.32716 (21)	2.5 (3)	C(42)	0.14642 (76)	0.65602 (97)	0.31165 (31)	2.5 (4)
O(6)	0.23605 (46)	0.85280 (72)	0.34154 (25)	3.0 (3)	C(43)	0.13316 (63)	0.51601 (95)	0.44143 (30)	2.0 (4)
O(7)	0.22222 (50)	0.84242 (81)	0.43447 (24)	3.3 (3)	C(44)	0.09001 (61)	0.4916 (11)	0.41896 (30)	2.3 (4)
O(8)	0.27113 (47)	0.92868 (81)	0.40413 (26)	3.6 (3)	C(45)	0.06032 (71)	0.5544 (11)	0.40103 (34)	2.8 (4)
O(9)	−0.00383 (52)	1.29424 (71)	0.46087 (24)	3.1 (3)	C(46)	0.07574 (75)	0.6469 (10)	0.40537 (37)	3.2 (5)
O(10)	−0.05548 (52)	1.17574 (70)	0.47637 (23)	3.2 (3)	C(47)	0.11838 (84)	0.67054 (94)	0.42812 (39)	3.9 (5)
O(11)	−0.07460 (47)	1.32953 (69)	0.40313 (24)	3.0 (3)	C(48)	0.14886 (75)	0.60745 (98)	0.44658 (36)	2.8 (5)
O(12)	0.00901 (40)	1.35165 (62)	0.38248 (22)	1.9 (3)	C(49)	0.24587 (65)	0.46702 (82)	0.47906 (27)	2.0 (4)
C(1)	−0.07956 (66)	0.83931 (91)	0.33526 (29)	2.1 (4)	C(50)	0.28151 (69)	0.5057 (10)	0.45762 (31)	2.6 (4)
C(2)	−0.07354 (54)	0.79266 (86)	0.36232 (31)	1.7 (3)	C(51)	0.33901 (63)	0.5252 (12)	0.46613 (35)	3.0 (4)
C(3)	−0.11075 (61)	0.7984 (10)	0.30722 (31)	2.2 (4)	C(52)	0.36429 (73)	0.5012 (10)	0.49407 (33)	2.7 (4)
C(4)	−0.09697 (60)	0.6996 (10)	0.36598 (29)	2.1 (4)	C(53)	0.33231 (78)	0.4617 (10)	0.51550 (36)	3.4 (5)
C(5)	−0.14503 (80)	0.8211 (12)	0.25521 (34)	4.2 (5)	C(54)	0.27362 (73)	0.44332 (98)	0.50818 (35)	2.6 (4)
C(6)	−0.17950 (73)	0.6091 (11)	0.36710 (44)	3.9 (5)	C(55)	0.18029 (57)	0.31637 (89)	0.44482 (28)	1.4 (3)
C(7)	0.16852 (69)	0.9178 (11)	0.39238 (32)	1.3 (4)	C(56)	0.23526 (64)	0.28657 (96)	0.43872 (31)	1.9 (4)
C(8)	0.16456 (60)	0.94155 (92)	0.36320 (34)	1.8 (4)	C(57)	0.24143 (64)	0.20620 (95)	0.42252 (28)	2.0 (4)
C(9)	0.22535 (66)	0.8986 (11)	0.40972 (39)	2.7 (4)	C(58)	0.19416 (64)	0.15664 (95)	0.41266 (28)	1.9 (4)
C(10)	0.21409 (61)	0.93561 (97)	0.34273 (33)	2.0 (4)	C(59)	0.13822 (69)	0.18432 (89)	0.41968 (32)	2.3 (4)
C(11)	0.27380 (71)	0.8279 (14)	0.45359 (40)	4.3 (6)	C(60)	0.13165 (71)	0.26369 (95)	0.43544 (31)	2.4 (4)
C(12)	0.28333 (70)	0.8411 (11)	0.33206 (38)	4.0 (5)	C(61)	0.12740 (63)	0.40282 (89)	0.50017 (28)	1.9 (4)
C(13)	−0.01553 (65)	1.16587 (85)	0.42823 (31)	2.0 (4)	C(62)	0.13335 (67)	0.31903 (98)	0.51614 (32)	2.4 (4)
C(14)	−0.01375 (67)	1.20471 (97)	0.40028 (35)	2.2 (4)	C(63)	0.09956 (67)	0.3017 (11)	0.54050 (32)	2.6 (4)
C(15)	−0.02313 (62)	1.22093 (87)	0.45616 (29)	1.8 (3)	C(64)	0.05948 (76)	0.3646 (13)	0.54849 (36)	3.5 (5)
C(16)	−0.02331 (64)	1.3029 (11)	0.39468 (36)	2.2 (4)	C(65)	0.05400 (77)	0.4469 (11)	0.53393 (32)	3.4 (5)
C(17)	−0.06150 (96)	1.2246 (12)	0.50486 (37)	5.7 (6)	C(66)	0.08738 (69)	0.4644 (12)	0.50916 (29)	3.0 (4)
C(18)	−0.08919 (79)	1.4230 (10)	0.39738 (39)	3.5 (5)	C(67)	0.17348 (78)	0.0138 (13)	0.11810 (34)	3.6 (5)
C(19)	0.12221 (58)	0.4536 (10)	0.24052 (29)	1.8 (4)	C(68)	0.20489 (78)	−0.0663 (12)	0.12079 (32)	3.3 (5)
C(20)	0.10810 (53)	0.51570 (98)	0.21697 (29)	1.9 (3)	C(69)	0.26493 (80)	−0.0553 (12)	0.12409 (33)	3.2 (5)
C(21)	0.07564 (65)	0.4871 (10)	0.19025 (30)	2.8 (4)	C(70)	0.29158 (75)	0.0254 (14)	0.12374 (31)	3.4 (5)
C(22)	0.05734 (85)	0.3996 (13)	0.18786 (35)	4.4 (6)	C(71)	0.26072 (77)	0.1029 (14)	0.12095 (34)	3.6 (6)
C(23)	0.07103 (88)	0.3375 (12)	0.21056 (38)	4.9 (6)	C(72)	0.20105 (78)	0.0985 (12)	0.11823 (34)	3.5 (5)
C(24)	0.10358 (80)	0.3657 (10)	0.23759 (38)	3.9 (5)	C(73)	0.16508 (79)	0.1828 (12)	0.11357 (39)	4.4 (5)
C(25)	0.16399 (63)	0.38837 (89)	0.30429 (29)	1.7 (4)	N(1)	0	0.0731 (13)	$^1/_4$	5.0 (7)
C(26)	0.21138 (75)	0.3321 (10)	0.30301 (33)	2.8 (4)	C(74)	0	−0.0274 (22)	$^1/_4$	5.0 (1)
C(27)	0.21229 (84)	0.2502 (11)	0.31851 (35)	3.5 (5)	C(75)	0.02963 (75)	0.1182 (14)	0.27578 (38)	4.3 (5)
C(28)	0.16708 (74)	0.2296 (10)	0.33573 (32)	3.1 (4)	O(13)	0.0295 (11)	0.2032 (18)	0.26941 (51)	4.8 (8)

molecule lies with an N–Me bond on a crystallographic 2-fold axis with the formyl group and the other methyl carbon atom disordered. In $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$, the DMF solvent molecule in the asymmetric unit has one methyl carbon atom and the formyl group disordered about the N–(other Me) bond. Refinement of the site occupancy of the O atom indicates that the disorder is, within estimated error, evenly distributed.

The final refinement for each structure was carried out on F_o^2. Prior to this final refinement, H atoms were included at calculated positions (C–H = 0.95 Å). Methyl H atoms were located in each case in difference electron density maps and their positions idealized. Each hydrogen atom was given an isotropic thermal parameter 1 Å^2 greater than its attached carbon atom. No hydrogen atoms were included in the model for either disordered DMF molecule.

The results of the refinements are given in Table I. The final positional parameters and equivalent isotropic thermal parameters are given in Tables II and III for $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot{}^1/_2DMF$[28] and $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$, respectively. Additional crystallographic details are given in the supplementary material.[26] The $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ anion is illustrated in Figure 1, and the $W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$ anion is shown in Figure 2.

Structures

It is interesting that the tungsten center has gone from tetrahedral in WSe_4^{2-} (W^{VI}) to square pyramidal in both WSe_9^{2-} (W^{IV}) and $W_2Se_{10}^{2-}$ (W^V) to trigonal prismatic (W^{IV}) (Figure 1) and distorted octahedral (W^V) (Figure 2) in the present complexes. $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot{}^1/_2DMF$ and $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$ have structures close to those of $[PPh_4]_2[Mo(S_2C_2(COOCH_3)_2)_3]\cdot C_6H_6\cdot DMF$[17] and $[PPh_4]_2[Mo_2S_2(S_2C_2(COOCH_3)_2)_4]$,[18] respectively.

In the $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ anion (Figure 1 and Table IV) the W^{IV} center is in a slightly distorted trigonal prism formed from three bidentate diselenene ligands. The angles between the least-squares planes (Table IIS)[26] defined by the three sets of four edge Se atoms (1, 2, 3, 4; 3, 4, 5, 6; 1, 2, 5, 6) are 120.4, 119.9, and 119.7° (ideal angle 120°), while the interplanar angle between the two triangular faces (Se atoms: 1, 3, 6; 2, 4, 5) is 1.8° (ideal angle 0°). The edges of the trigonal prism (Se–Se) range from 3.225 (4) to 3.381 (3) Å and average 3.26 (6) Å. The W–Se distances range from 2.486 (3) to 2.511 (3) Å. For each diselenene ligand one W–Se distance is slightly longer (~0.015 Å) than the other. The average W–Se value of 2.50 (1) Å is comparable to the average W–Se bond length in $W(S)(Se_4)_2^{2-}$ of 2.47 (3) Å.[4] The Se–W–Se average angles are similar to the S–Mo–S angles in $Mo(S_2C_2(COOCH_3)_2)_3^{2-}$,[17] with an intraligand angle of 81.9

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[28] Atom C(7) has β_{22} = −6.0 (8.6) × 10^{-4} and is formally, but not significantly, nonpositive definite.

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$

atom	x	y	z	B_{eq}, Å^2
W(1)	−0.021 111 (20)	−0.048 940 (18)	0.079 743 (20)	0.892 (8)
Se(1)	0.016 269 (50)	0.138 432 (44)	0.097 402 (48)	1.18 (2)
Se(2)	0.155 615 (48)	−0.110 335 (45)	0.138 943 (49)	1.20 (2)
Se(3)	0.032 546 (51)	0.019 814 (49)	0.289 183 (49)	1.44 (2)
Se(4)	−0.202 360 (48)	−0.007 229 (46)	0.079 793 (50)	1.26 (2)
Se(5)	−0.126 609 (52)	−0.234 101 (46)	0.056 552 (54)	1.55 (2)
P(1)	0.738 39 (14)	0.355 19 (12)	0.398 98 (14)	1.40 (5)
C(1)	0.748 68 (53)	0.487 50 (45)	0.478 90 (51)	1.5 (2)
C(2)	0.852 23 (52)	0.547 67 (49)	0.561 18 (55)	1.9 (2)
C(3)	0.863 57 (60)	0.652 44 (52)	0.618 61 (60)	2.5 (2)
C(4)	0.772 16 (68)	0.695 53 (52)	0.590 32 (59)	2.7 (3)
C(5)	0.669 56 (72)	0.637 90 (58)	0.510 33 (65)	3.2 (3)
C(6)	0.656 80 (59)	0.532 22 (52)	0.453 88 (57)	2.3 (2)
C(7)	0.595 85 (51)	0.278 01 (46)	0.343 73 (49)	1.5 (2)
C(8)	0.514 74 (56)	0.291 35 (51)	0.253 30 (53)	2.0 (2)
C(9)	0.403 10 (56)	0.237 92 (54)	0.216 60 (55)	2.3 (2)
C(10)	0.372 01 (53)	0.170 30 (51)	0.267 60 (55)	2.1 (2)
C(11)	0.453 34 (59)	0.157 70 (49)	0.358 20 (55)	2.1 (2)
C(12)	0.565 05 (55)	0.210 61 (49)	0.396 06 (52)	1.9 (2)
C(13)	0.776 94 (49)	0.361 59 (46)	0.286 73 (49)	1.4 (2)
C(14)	0.834 41 (58)	0.455 83 (50)	0.287 72 (53)	2.1 (2)
C(15)	0.866 52 (63)	0.459 02 (55)	0.201 96 (59)	2.7 (3)
C(16)	0.840 85 (59)	0.367 03 (56)	0.114 90 (56)	2.4 (2)
C(17)	0.781 43 (59)	0.273 31 (53)	0.113 12 (58)	2.4 (2)
C(18)	0.748 78 (58)	0.269 67 (49)	0.197 22 (58)	2.2 (2)
C(19)	0.837 53 (52)	0.303 55 (44)	0.489 47 (50)	1.4 (2)
C(20)	0.838 51 (57)	0.313 25 (49)	0.593 91 (54)	2.0 (2)
C(21)	0.919 02 (57)	0.281 75 (49)	0.666 90 (53)	2.0 (2)
C(22)	1.000 69 (58)	0.243 06 (49)	0.636 75 (56)	2.2 (2)
C(23)	1.000 39 (61)	0.233 47 (53)	0.534 23 (60)	2.4 (3)
C(24)	0.918 40 (55)	0.263 14 (48)	0.459 34 (54)	1.9 (2)
C(25)	0.219 77 (49)	−0.066 42 (44)	0.295 77 (49)	1.2 (2)
C(26)	0.169 50 (49)	−0.011 56 (46)	0.353 74 (49)	1.3 (2)
C(27)	0.325 44 (52)	−0.093 16 (46)	0.352 00 (52)	1.5 (2)
C(28)	0.220 58 (52)	0.037 59 (51)	0.476 98 (52)	1.7 (2)
C(29)	0.476 20 (64)	−0.162 95 (68)	0.332 53 (64)	3.4 (3)
C(30)	0.234 29 (69)	0.016 09 (70)	0.645 23 (58)	3.8 (3)
C(31)	−0.294 14 (50)	−0.128 92 (47)	0.079 58 (49)	1.4 (2)
C(32)	−0.260 33 (51)	−0.219 13 (48)	0.070 96 (50)	1.6 (2)
C(33)	−0.404 22 (55)	−0.122 72 (53)	0.085 75 (54)	1.9 (2)
C(34)	−0.331 93 (55)	−0.320 56 (52)	0.064 02 (59)	2.0 (2)
C(35)	−0.521 43 (60)	−0.013 61 (62)	0.122 47 (62)	2.8 (3)
C(36)	−0.395 79 (73)	−0.411 84 (70)	0.162 89 (79)	4.4 (4)
C(37)	0.276 39 (94)	−0.402 85 (94)	0.149 7 (11)	7.8 (6)
C(38)	0.311 81 (93)	−0.520 6 (10)	0.257 62 (93)	6.3 (5)
C(39)	0.117 94 (77)	−0.530 93 (76)	0.144 81 (81)	5.0 (4)
O(1)	0.370 45 (37)	−0.073 84 (34)	0.449 17 (37)	2.0 (2)
O(2)	0.367 27 (37)	−0.141 37 (37)	0.280 61 (36)	2.3 (2)
O(3)	0.282 29 (37)	0.124 16 (34)	0.523 04 (37)	2.1 (2)
O(4)	0.186 00 (38)	−0.025 55 (36)	0.525 37 (34)	2.4 (2)
O(5)	−0.477 12 (41)	−0.198 10 (41)	0.067 18 (52)	3.9 (2)
O(6)	−0.415 18 (35)	−0.023 52 (35)	0.114 92 (36)	2.0 (2)
O(7)	−0.385 62 (46)	−0.391 41 (39)	−0.021 24 (45)	3.6 (2)
O(8)	−0.323 70 (41)	−0.320 48 (39)	0.162 30 (42)	2.9 (2)
O(9)	0.049 01 (96)	−0.480 68 (89)	0.084 65 (93)	4.1 (5)
O(9)′	0.420 23 (94)	−0.455 93 (95)	0.311 2 (10)	4.3 (5)
N(1)	0.234 38 (55)	−0.485 21 (48)	0.186 40 (50)	3.1 (2)

Table IV. Selected Bond Distances (Å) and Angles (deg) for the $[W(Se_2C_2(COOCH_3)_2)_3]^{2-}$ Anion in $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot {}^1/_2DMF$

W–Se(1)	2.505 (3)	Se(1)–C(1)	1.880 (14)
W–Se(2)	2.486 (3)	Se(2)–C(2)	1.869 (13)
W–Se(3)	2.501 (3)	Se(3)–C(8)	1.870 (14)
W–Se(4)	2.511 (3)	Se(4)–C(7)	1.897 (15)
W–Se(5)	2.508 (3)	Se(5)–C(13)	1.908 (13)
W–Se(6)	2.490 (3)	Se(6)–C(14)	1.870 (15)
Se(1)–W–Se(2)	81.95 (7)	Se(2)–W–Se(6)	142.69 (7)
Se(1)–W–Se(3)	81.04 (10)	Se(3)–W–Se(4)	80.87 (10)
Se(1)–W–Se(4)	146.45 (6)	Se(3)–W–Se(5)	144.95 (6)
Se(1)–W–Se(5)	128.49 (8)	Se(3)–W–Se(6)	85.28 (6)
Se(1)–W–Se(6)	80.43 (6)	Se(4)–W–Se(5)	80.00 (9)
Se(2)–W–Se(3)	123.90 (7)	Se(4)–W–Se(6)	125.71 (5)
Se(2)–W–Se(4)	85.06 (8)	Se(5)–W–Se(6)	82.47 (7)
Se(2)–W–Se(5)	83.24 (7)		

Table V. Selected Bond Distances (Å) and Angles (deg) for the $[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]^{2-}$ Anion in $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]\cdot 2DMF$

W–W′	2.989 (1)	W–Se(5)	2.574 (1)
W–Se(1)	2.445 (1)	Se(2)–C(25)	1.905 (6)
W–Se(1)′	2.442 (1)	Se(3)–C(26)	1.857 (6)
W–Se(2)	2.492 (1)	Se(4)–C(31)	1.899 (6)
W–Se(3)	2.577 (1)	Se(5)–C(32)	1.852 (6)
W–Se(4)	2.501 (1)		
Se(1)–W–Se(1)′	104.60 (2)	Se(1)′–W–Se(5)	83.56 (3)
Se(1)–W–Se(2)	112.20 (2)	Se(2)–W–Se(3)	82.01 (2)
Se(1)–W–Se(3)	84.27 (3)	Se(2)–W–Se(4)	158.45 (2)
Se(1)–W–Se(4)	78.76 (2)	Se(2)–W–Se(5)	86.87 (3)
Se(1)–W–Se(5)	160.26 (2)	Se(3)–W–Se(4)	80.72 (2)
Se(1)′–W–Se(2)	78.53 (2)	Se(3)–W–Se(5)	93.78 (3)
Se(1)′–W–Se(3)	166.47 (2)	Se(4)–W–Se(5)	81.53 (2)
Se(1)′–W–Se(4)	117.78 (2)		

(5)° (80.5 (5)°), a cis interligand angle of 82.6 (2.6)° (83.0 (2.0)°), and a trans interligand angle of 135 (10)° (135 (8)°). The W–Se–C angles average 107.8 (6)° (109 (1.5)°). The average carbon–carbon bond length in the diselenene ring is 1.34 (3) Å. This is consistent with a bond order reduction from 3 to 2.[29] Least-squares planes for the three WSe_2C_2 five-membered rings show only very small deviations from planarity (Table IIS).[26] The planarity of these WSe_2C_2 rings contrasts with the MSe_4 rings in $WSe(Se_4)_2^{2-}$ (A)[4] or $W_2Se_{10}^{2-}$ (B),[3] which are puckered like cyclopentane.[29]

The tetraphenylarsonium cations are unremarkable (Table IVS). The average As–C distance is 1.89 (2) Å, the average C–As–C angle is 109.5 (2.5)°, and the average C–C distance is 1.39 (2) Å. The solvent molecules are also normal.[26]

The $W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$ anion (Figure 2 and Table V) is a centrosymmetric dimer with distorted-octahedral geometry about each tungsten atom. Each W^V center is bonded to two bidentate diselenene ligands and two Se atoms that bridge the W atoms. The distorted-octahedral nature is seen in the least-squares planes (Table IIS):[26] W, Se(1), Se(1)′, Se(3), and Se(5), average deviation 0.33 Å; W, Se(1)′, Se(2), Se(3), and Se(4), average deviation 0.11 Å; W, Se(1), Se(2), Se(4), and Se(5), average deviation 0.16 Å. The interplanar angles, which ideally would be 90°, are 86.52, 83.60, and 94.90° for these three planes. The complex retains the $W_2Se_2^{6+}$ core of $W_2Se_{10}^{2-}$. Apparently this core is rigid and holds the chelating diselenene ligands in a distorted-octahedral geometry instead of allowing trigonal-prismatic coordination about the W atom. The bridging W–Se distances (W–Se(1) = 2.445 (1) Å; W–Se (1)′ = 2.442 (1) Å) are basically unchanged from those in $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ (2.45 (5) and 2.45 (4) Å).[3] The W–W′ distance of 2.989 (1) Å is longer than that in other W–Se dimers that contain a two-electron W–W bond, i.e. $W_2Se_9^{2-}$ (2.897 (2) Å) and $W_2Se_{10}^{2-}$ (2.903 (2) Å),[3] but is shorter than that in $W_3Se_9^{2-}$ or $W_3Se_8O^{2-}$ (3.037 Å),[3] which have one-electron W–W bonds. The Se(1)–W–Se(1)′ angle of 104.60 (2)° is slightly larger than comparable angles in $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ (103.28 (8) and 103.17 (9)°,[3] respectively).

The W–Se distances to the diselenene ligands range from 2.492 (1) to 2.577 (1) Å with one W–Se distance about 0.07 Å shorter than the other in a given pair. The long W–Se bonds (W–Se(3) and W–Se(5)) are trans to and coplanar with the bridging W–Se bonds (W–Se(1) and W–Se(1)′), while the short W–Se bonds (W–Se(2) and W–Se(4)) are axial to the plane containing the long-W–Se-bonded Se atoms and bridging Se atoms. The alternation in M–Se lengths is also seen in $WS(Se_4)_2^{2-}$ and $MoO(Se_4)_2^{2-}$ [4] and to a much smaller extent in $W(Se_2C_2(COOCH_3)_2)_3^{2-}$. In MQ_4 rings (Q = S, Se) this bond length alternation is thought to arise from M(dπ)–Q(dπ) interactions and extends to the Q–Q bonds.[4,30] There is an analogous, slight alternation in the Se–C distances in the diselenene rings of each

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(29) Dithiolate complexes of the type $[M(SCH_2CH_2S)_3]^-$ (M = Nb, Ta) have a single C–C bond, puckered chelate rings, and geometries intermediate between trigonal prismatic and octahedral: Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 86–87.

(30) Block, H. D.; Allmann, R. *Cryst. Struct. Commun.* **1975**, *4*, 53–56.

Table VI. Comparison of Selected Average Bond Distances (Å) and Angles (deg) for Diselenene Ligands in $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ and $W_2Se_2(Se_2C_2(COOCH_3)_2)_3^{2-}$

	n	$W(Se_2C_2R_2)_3^{2-}$	*n*	$W_2Se_2(Se_2C_2R_2)_4^{2-}$
		Distances		
C=C	3	1.339 (25)[a]	2	1.340 (8)
C—COOMe	6	1.491 (21)	4	1.489 (20)
C=O	6	1.198 (17)	4	1.199 (8)
C—OCH$_3$	6	1.348 (19)	4	1.332 (15)
O—CH$_3$	6	1.440 (19)	4	1.453 (8)
		Angles		
C=C—C	6	122.2 (1.5)	4	122.2 (1.6)
C—C=O	6	124.7 (1.6)	4	123.7 (1.0)
C—C—OMe	6	112.5 (1.3)	4	111.8 (0.9)
O—C—OMe	6	122.8 (1.9)	4	124.5 (1.7)
C—O—CH$_3$	6	115.3 (1.4)	4	114.5 (0.6)
W—Se—C	6	107.8 (6)	4	107.6 (1.0)

[a] The value in parentheses is the larger of an individual standard deviation as estimated from the inverse matrix or as estimated on the assumption that the values averaged (*n*) are from the same population.

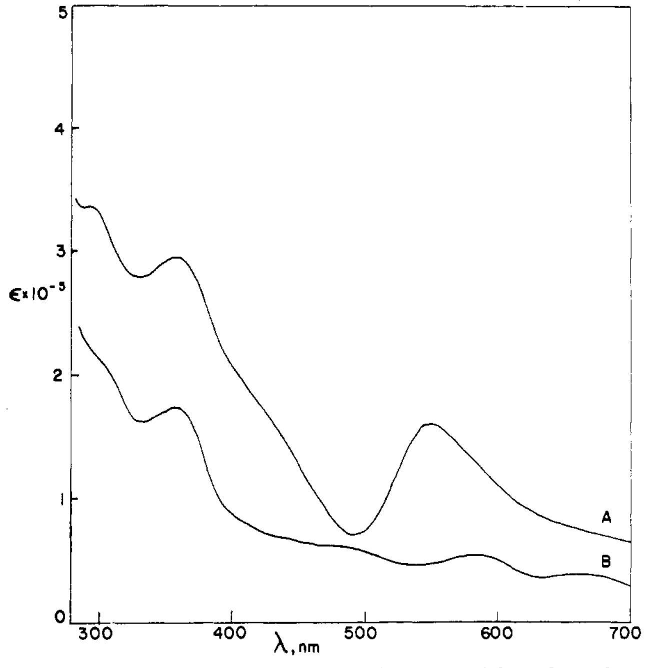

Figure 3. Electronic absorption (UV-vis) spectra of $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]$ (A) and $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]$ (B). Both are 1 × 10^{-5} M in DMF solution.

complex (Tables IV and V). In the $W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$ ion the WSe_2C_2 five-membered rings are again essentially planar (Table IIS).[26] The Se–W–Se angles in the diselenene ligands are 82.01 (2)° (Se(2)–W–Se(3)) and 81.53 (2)° (Se(4)–W–Se(5)), essentially identical with the angles in $W(Se_2C_2(COOCH_3)_2)_3^{2-}$.

Table VI compares average distances and angles for the diselenene ligands in the two complexes. There are no unexpected features.

The PPh_4^+ cation with an average P–C distance of 1.798 (7) Å, an average C–P–C angle of 109.5 (2.2)°, and an average C–C distance of 1.385 (8) Å is normal (Table VIIS).[26]

Spectroscopy

The electronic absorption (UV–vis) spectrum of each complex (Figure 3) shows several intense bands corresponding to strong ligand–metal interactions. These bands are not of the d–d type but probably arise from charge transfer. Similar dithiolene complexes and their band assignments are reported in the literature.[31]

The ^{77}Se NMR spectrum of $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ shows the expected single resonance (δ = 839 ppm, $^1J_{Se-W}$ = 34 Hz).

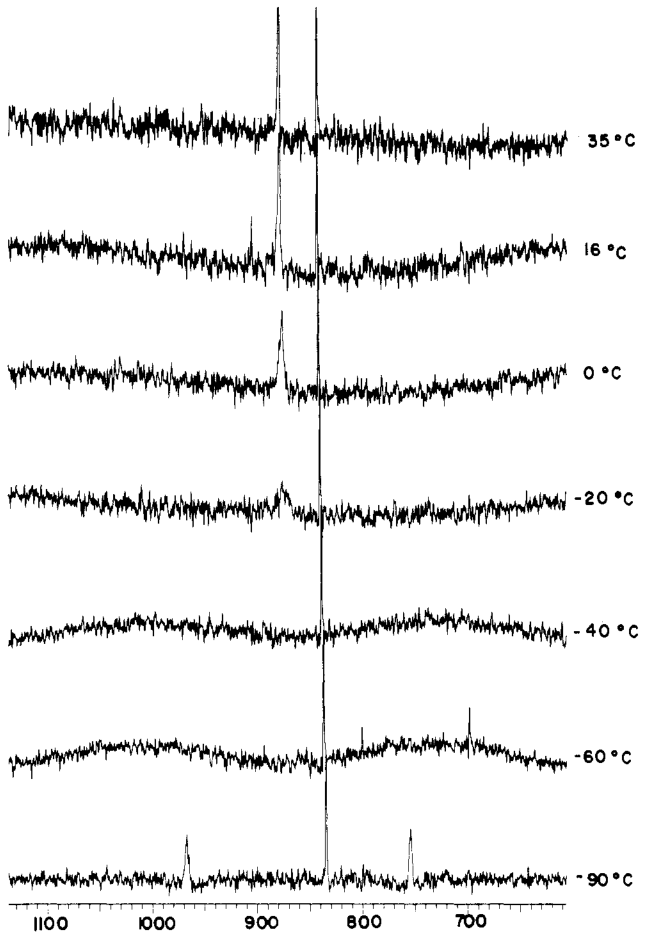

Figure 4. Variable-temperature ^{77}Se NMR spectra of the diselenene resonances of $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]$ (δ = 874 ppm at 16 °C) and $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]$ (δ = 839 ppm) in DMF/dichloromethane solution.

The resonance is in the region seen for metal-bound Se atoms of MSe_n rings.[3,4]

$W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$ shows two lines at δ = 1360 ppm ($^1J_{W-Se}$ = 38 Hz) and δ = 874 ppm. The resonance at 874 ppm is assigned to diselenene by analogy to $W(Se_2C_2(COOCH_3)_2)_3^{2-}$, and the resonance at 1360 ppm is then assigned to bridging Se atoms. This is approximately 400–500 ppm downfield from similar bridging resonances seen in $W_2Se_9^{2-}$, $W_2Se_{10}^{2-}$, and $W_3QSe_8^{2-}$ (Q = O, Se),[3] but rough integrations of the two peaks confirm this assignment (i.e. there are eight diselenene Se atoms versus two bridging Se atoms). The Se resonance from the diselenene ligand in $Cp_2Ti(Se_2C_2(COOCH_3)_2)$ (a d^0, neutral species) is at 1001 ppm.[16]

The structure of the anion, if retained in solution, would lead to a three-line spectrum (with the ratio axial diselenene Se: equatorial diselenene Se:bridging Se = 2:2:1). At room temperature only two resonances are seen: one of normal width at 1360 ppm assigned to the bridging Se atoms and another of great width (~150 Hz) at 874 ppm assigned to the diselenene ligands. Figure 4 shows the temperature dependence of this latter resonance as well as the near temperature independence of the single resonance in the $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ anion; the resonance shifts 8 ppm between 35 and −90 °C. The resonance at 1360 ppm in $W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$ (not shown) also displays virtual temperature independence. But the 874 ppm resonance in the latter anion broadens, then collapses by −40 °C, and then returns as two broad (~250 Hz) resonances of equal intensity at 754 and 967 ppm as the temperature is lowered to −90 °C. This resonance has shifted 5 ppm by −20 °C, and this continued shift as the temperature is lowered results in the average value of the two resonances at −90 °C being 860 ppm rather than 874 ppm. Since the diselenene resonance in the monomeric compound shows very little temperature dependence, it seems most likely that the tem-

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perature dependence of the 874 ppm resonance in Figure 4 results not from a dissociative process but from stereochemical nonrigidity of the diselenene ligands in the dimer. The low-temperature spectrum is consistent with the static structure in the crystal, i.e., a distorted-octahedral coordination about the W^V center.

Synthesis

WSe_4^{2-} and elemental selenium react at ambient temperature in DMF solution to form WSe_9^{2-}[4] (A); in refluxing acetonitrile they form the two $W_2Se_{10}^{2-}$[2,3] isomers B and C. When reacted with excess DMA in DMF solution at room temperature, A yields $W(Se_2C_2(COOCH_3)_2)_3^{2-}$ within 10 min and both B and C give $W_2Se_2(Se_2C_2(COOCH_3)_2)_4^{2-}$. While A and B both have well-known Mo–S analogues[32,33] that react with DMA to give the sulfur analogues of the title compounds,[17,18] C has no corresponding sulfur analogue and its reaction is the first known between an MQ_3 ring and an activated acetylene (Q = S, Se).

The reactions with DMA of the W–Se complexes are more facile than those of the corresponding Mo–S complexes. Thus, MoS_9^{2-} must be at 60 °C in DMF to react with DMA[17] while $Mo_2S_{10}^{2-}$ must be refluxed with DMA in CH_3CN for 30 min;[18] both WSe_9^{2-} and $W_2Se_{10}^{2-}$ react essentially instantaneously at room temperature in DMF. The greater reactivity of Se vs that of S is also seen in reactions of DMA with Cp_2TiQ_5 (Q = S, Se), where Se reacts at lower temperature than S and in greater yield.[16]

Terminal selenium and sulfur atoms will also react with acetylene to form the corresponding diselenene or dithiolene ligands, but no mechanism has been proposed for this reaction. Two different mechanisms have been proposed for the reaction of activated acetylenes with MQ_n (Q = S, Se) rings: cycloaddition[18] and an associative electrophilic attack.[16,18] Electrophilic attack of one acetylenic carbon atom on one of the metal-bound chalcogen atoms as the rate-determining step seems also to be applicable to reaction with a terminal chalcogen atom, whereas a cycloaddition reaction is impossible for one atom.

The similarity of this W–Se chemistry to that of the Mo–S system perhaps results from similarities in the relative sizes and orbital overlaps of W and Se compared with those of Mo and S. We are currently investigating the reactions of $MQ(Se_4)_2^{2-}$ (M = Mo, W; Q = O, S, Se) with DMA to study the effect of the metal and terminal chalcogen on reactivity.

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Supplementary Material Available: Complete crystallographic details (Table IS) and least-squares planes (Table IIS), anisotropic thermal parameters and hydrogen atom positions (Table IIIS) and additional distances and angles (Table IVS) for $[AsPh_4]_2[W(Se_2C_2(COOCH_3)_2)_3]$, and anisotropic thermal parameters and hydrogen atom positions (Table VIS) and additional distances and angles (Table VIIS) for $[PPh_4]_2[W_2Se_2(Se_2C_2(COOCH_3)_2)_3]$ (11 pages); $10|F_o|$ vs $10|F_c|$ (Tables VS and VIIIS) (79 pages). Ordering information is given on any current masthead page.

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Spectroscopy and Linkage Isomerization Kinetics of (Chloranilato)bis(phosphine)palladium(II) Compounds

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In order to better understand the electronic and steric factors that influence the transformation of sp^3- to sp^2-hybridized carbon in the first coordination sphere of palladium(II), linkage isomerization induced by the reactions of 24 triarylphosphine (or triarylarsine), trialkylphosphine, and diphosphine ligands with $[Pd(C\text{-}CA)(CH_3CN)_2]$ ($C\text{-}CA^{2-}$ = chloranilate ligated as a dicarbanion through C–Cl carbon atoms) has been investigated. Infrared and UV–visible spectra of the $[Pd(CA)(PR_3)_2]$ products reveal that $\pi\text{-}CA^{2-}$ (chloranilate ligated as a *p*-quinone) is present in all cases. A linear correlation between ^{31}P coordination chemical shifts and Hammett σ_p substituent constants for seven compounds of the type $[Pd(\pi\text{-}CA)(P\{Ph\text{-}p\text{-}X\}_3)_2]$ (X = H, F, Cl, CH_3, CF_3, OCH_3, NMe_2) suggests that polarization of phosphorus 3p electron density toward the electrophilic Pd(II) center contributes significantly to $\Delta(^{31}P)$. Stopped-flow kinetic studies of $[Pd(\pi\text{-}CA)(P\{Ph\text{-}X\}_3)_2]$ formation (X = *m*- and *p*-CH_3, *m*- and *p*-OCH_3, *m*- and *p*-Cl, and *p*-F) from $[Pd(C\text{-}CA)(CH_3CN)_2]$ in acetonitrile solution (25 °C) support the mechanism previously suggested for X = H. Rate-limiting linkage isomerization (rate constant k_i) follows preequilibrium formation of $[Pd(C\text{-}CA)(P\{Ph\text{-}p\text{-}X\}_3)_2]$ (stepwise formation constants K_1 and K_2). Considering only those phosphines with *p*-X substituents, Hammett plots of log K_2 and log k_i vs σ_p are reasonably linear, yielding ρ constants of −3.12 and −1.32, respectively. Enhancements in k_i with increasing electron-donating power of X suggest that the polarization of phosphine electron density toward Pd(II) destabilizes the trans Pd–carbanion C bonds, forcing chloranilate to function as a weaker σ donor in the π-CA linkage isomer.

Introduction

In order to better understand the electronic and steric factors that influence the transformation of sp^3- to sp^2-hybridized carbon in the first coordination sphere of palladium(II), we have undertaken studies of linkage isomerization[1] and protonolysis[2] reactions of carbon-bonded chloranilate (*C*-CA) in $[Pd(C\text{-}CA)(CH_3CN)_2]$ and $[Pd(C\text{-}CA)Cl_2]^{2-}$, respectively. Thus, the 2,5-dioxo-3,6-dichloro-1,4-benzoquinone ligand is formally ligated as a dicarbanion in these Pd(II) complexes, with negative charges localized on the C–Cl carbon atoms. We previously reported that triphenylphosphine reacts rapidly with $[Pd(C\text{-}CA)(CH_3CN)_2]$ to give $[Pd(\pi\text{-}CA)(PPh_3)_2]$, in which chloranilate is coordinated as a *p*-quinone (Figure 1).[1] The rate constant for $C\text{-}CA^{2-}$ to $\pi\text{-}CA^{2-}$ linkage isomerization within the precursor complex $[Pd(C\text{-}CA)(PPh_3)_2]$ ($k_i = 8.44 \times 10^{-2}\ s^{-1}$; 25 °C, acetonitrile solution) reflects a predominantly enthalpic activation barrier ($\Delta H^\ddagger$ = 17.1 kcal mol^{-1}; $\Delta S^\ddagger$ = −6 eu).[1]

In this paper, we describe the synthesis and spectroscopic characterization of $[Pd(\pi\text{-}CA)(AsPh_3)_2]$ and 22 complexes of the form $[Pd(\pi\text{-}CA)L_2]$, where L represents half of a diphosphine chelating ligand or PR_3, where R = an alkyl or aryl substituent. In addition, stopped-flow kinetic studies of chloranilate linkage isomerization triggered by the reactions of para- and meta-substituted triphenylphosphines with $[Pd(C\text{-}CA)(CH_3CN)_2]$ are reported, with the objective of correlating rate parameters with the electronic and steric characteristics of the $[Pd(\pi\text{-}CA)(P\{Ph\text{-}$

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