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Interactions of Coinage-Group Cations with the Tetraselenotungstate Anion: Multinuclear NMR Spectroscopic Results and Crystal Structures of (μ-WSe$_4$)[(PMe$_2$Ph)$_2$Cu]$_2$, (μ-WSe$_4$)[(PMePh$_2$)Au]$_2$, and (μ_3-Cl)(μ_3-WSe$_4$)[(PPh$_3$)Cu]$_3$

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Reaction of a CH$_3$CN solution of [NPr$_4$]$_2$[WSe$_4$] with 2 equivalents of Cu$^+$, Ag$^+$, or Au$^+$ in the presence of excess PMe$_2$Ph affords (μ-WSe$_4$)[(PMe$_2$Ph)$_2$M]$_2$ (M = Cu (**1**), Ag (**2**), or Au (**3**)). (μ-WSe$_4$)[(PMe$_2$Ph)$_2$Cu]$_2$ crystallizes with four formula units in the monoclinic space group C_{2h}^6–$C2/c$ in a cell of dimensions a = 19.315 (7) Å, b = 15.575 (4) Å, c = 16.829 (7) Å, and β = 127.99 (1)° (T = 113 K). Full anisotropic refinement of the structure led to a value of $R(F)$ = 0.032 ($R_w(F)$ = 0.042) for 196 variables and 4047 unique reflections. The molecule possesses a crystallographic 2-fold axis; the W center is tetrahedrally coordinated to four Se atoms that bridge to the Cu atoms; coordination of each Cu atom to two P atoms completes the distorted tetrahedral geometry about each Cu atom. Substitution of PMePh$_2$ for PMe$_2$Ph with M = Au$^+$ affords (μ-WSe$_4$)[(PMePh$_2$)Au]$_2$ (**4**). This compound crystallizes with four molecules in the monoclinic space group $P2_1/c$ in a cell of dimensions a = 14.647 (5) Å, b = 14.161 (5) Å, c = 15.319 (6) Å, and β = 106.65 (1)° (T = 113 K). A value of $R(F)$ = 0.088 ($R_w(F)$ = 0.081) for 186 variables and 5859 unique reflections was obtained from anisotropic refinement of the heavy atoms. The structure is similar to that of **1**, except that the geometry around the Au atoms is distorted trigonal planar. The ^{77}Se NMR spectra of solutions of **1**–**4** exhibit a single peak; for **1**–**3** this peak shifts to lower field with increasing atomic number of the coinage metal. The ^{31}P NMR spectra also consist of a single resonance. Reaction of [NPr$_4$]$_2$[WSe$_4$] with [(PPh$_3$)$_2$Cu(BH$_3$)(CN)]$_2$ in CH$_2$Cl$_2$ in the presence of NH$_4$Cl affords the cubane-like compound (μ_3-Cl)(μ_3-WSe$_4$)-[(PPh$_3$)Cu]$_3$ (**5**). Its structure, which has analogues in the MoSe$_4^{2-}$ and the WS$_4^{2-}$ systems, is that of a cubane in which each Cu center is bonded tetrahedrally to a P atom, a Cl atom, and two Se atoms and the W center is bonded tetrahedrally to four Se atoms. Consistent with this solid-state structure, the ^{77}Se NMR spectrum of a solution of **5** displays two resonances at δ 1651 and 1232 ppm. The compound crystallizes with four molecules in the orthorhombic space group D_2^4-$P2_12_12_1$ in a cell of dimensions a = 12.88 (1) Å, b = 17.72 (1) Å, and c = 22.59 (1) Å (T = 113 K). The structure has been refined anisotropically to a value of $R(F)$ = 0.063 ($R_w(F)$ = 0.069) for 570 variables and 8950 observations.

Introduction

While the chemistry of the MoS$_4^{2-}$ and WS$_4^{2-}$ ions has been extensively investigated, the chemistry of the corresponding selenide anions MoSe$_4^{2-}$ and WSe$_4^{2-}$ has not. Interactions of MoS$_4^{2-}$ and WS$_4^{2-}$ with the coinage-metal cations Cu$^+$, Ag$^+$, and Au$^+$ have been studied and have afforded some interesting chemistry.[1] In the Cu/MoS$_4$ system, complexes having the general structure L$_{1,2}$Cu(μ-S)$_2$M(μ-S)$_2$CuL$_{1,2}$ (Figure 1a–c) have been reported that contain Cu and phosphine ligands,[2] single cyano ligands,[3] or single benzenethiolate ligands.[4] In the Cu/WS$_4$ system, complexes are known in which Cu is ligated to phenanthroline,[5] thiocyanate,[6] or chloride.[7,8] Two coinage-metal complexes of WSe$_4$ have also been reported.[9,10] In addition, the syntheses of Mo and W/Cu/chalcogenide cubanes have been probed[3,10,11] (Figure 1d). The present synthetic, NMR spectroscopic, and crystallographic study is concerned with the interactions of these coinage-metal cations with the WSe$_4^{2-}$ anion. Some of this chemistry parallels that of the sulfides.

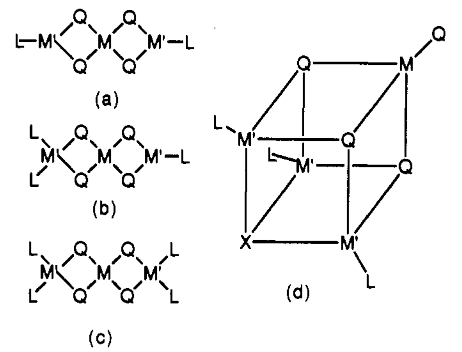

Figure 1. Sketches of known structures that contain the MQ$_4^{2-}$ core (Q = S or Se; M = Mo or W; M′ = Cu, Ag, or Au; L = ligand; X = Cl or Br).

Experimental Section

Syntheses. All syntheses and manipulations were performed in oven-dried glassware under purified N$_2$ with the use of standard inert-atmosphere techniques.[12] *N,N*-Dimethylformamide (DMF) was used as purchased from Baxter Healthcare Corp., Muskegon, MI. Other solvents

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were distilled over appropriate drying agents[13] prior to use. Microanalysis of **1** was performed by Analytical Laboratories, Elbach, Engelskirchen, Germany; microanalyses of **2**–**4** were performed by Oneida Research Services, Whitesboro, NY; microanalysis of **5** was performed by Galbraith Laboratories, Inc., Knoxville, TN. $[NPr_4]_2[WSe_4]$ was prepared by modifications of the literature method.[14] Other reagents were used as received from Aldrich Chemical Co., Milwaukee, WI.

$(\mu$-$WSe_4)[(PMe_2Ph)_2Cu]_2$ (1). A suspension of CuCl (0.038 g, 0.38 mmol) in CH_3CN (5 mL) was added with stirring to a solution of $[NPr_4]_2[WSe_4]$ (0.168 g, 0.19 mmol) in CH_3CN (5 mL). A red solid rapidly precipitated. Upon addition of excess PMe_2Ph (0.2 mL), the precipitate redissolved. The resultant solution was stirred for about 30 min and then filtered to afford an orange-red filtrate. Slow addition of Et_2O produced after 1 day X-ray-quality crystals of $(\mu$-$WSe_4)[(PMe_2Ph)_2Cu]_2$ (**1**) (0.153 g, 68% yield) as red blocks. Anal. Calcd: C, 32.8; H, 3.3; Cu, 10.8; W, 15.7. Found: C, 34.4; H, 3.9; Cu, 11.3; W, 16.3. UV–vis (DMF) [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: 323 (17 070), 485 (2850). IR (KBr): 300, 285, 280 cm^{-1}. ^{31}P NMR (CH_3CN): δ −40.1. ^{77}Se NMR (DMF): δ 1044.

$(\mu$-$WSe_4)[(PMe_2Ph)_2Ag]_2$ (2). AgSCN (0.089 g, 0.54 mmol) suspended in CH_3CN (10 mL) was added to a solution of $[NPr_4]_2[WSe_4]$ (0.235 g, 0.27 mmol) in CH_3CN (5 mL). An excess of PMe_2Ph (0.1 mL) was added to bring the resulting red precipitate back into solution. The reaction was stirred for 30 min, and then the volume was reduced by about one-third to induce rapid precipitation of purple-red crystalline blocks of $(\mu$-$WSe_4)[(PMe_2Ph)_2Ag]_2$ (**2**) (0.108 g, 38% yield). Anal. Calcd: C, 30.31; H, 3.50; W, 14.50; Se, 24.91; Ag, 17.01. Found: C, 30.76; H, 3.12; W, 15.15; Se, 24.90; Ag, 16.95. UV–vis (DMF) [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: 455 (19 910), 470 (sh), 510 (sh). IR (KBr): 325, 315 cm^{-1}. ^{31}P NMR (CH_3CN): δ −36.0. ^{77}Se NMR (DMF): δ 1092.

$(\mu$-$WSe_4)[(PMe_2Ph)_2Au]_2$ (3). AuCN (0.078 g, 0.36 mmol) in CH_3CN (5 mL) was added with stirring to a CH_3CN (10 mL) solution of $[NPr_4]_2[WSe_4]$ (0.153 g, 0.18 mmol). This precipitate was brought back into solution by the addition of excess PMe_2Ph (0.1 mL). The resultant solution was stirred for 30 min and then filtered to yield a red filtrate. Addition of Et_2O produced red blocks (0.175 g, 74% yield) of $(\mu$-$WSe_4)[(PMe_2Ph)_2Au]_2$ (**3**). Anal. Calcd: C, 26.6; H, 3.1; P, 8.6; Se, 21.8; W, 12.7. Found: C, 26.7; H, 3.2; P, 7.5; Se, 20.2; W, 12.4. UV–vis (CH_3CN) [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: 340 (5150), 375 (1560), 420 (870), 475 (2361). IR (KBr): 305, 295 cm^{-1}. ^{31}P NMR (CH_3CN): δ −34.3. ^{77}Se NMR (DMF): δ 1234.

$(\mu$-$WSe_4)[(PMePh_2)Au]_2$ (4). AuCN (0.089 g, 0.40 mmol) in CH_3CN (10 mL) was added with stirring to $[NPr_4]_2[WSe_4]$ (0.174 g, 0.20 mmol) in CH_3CN (5 mL). Dropwise addition of $PMePh_2$ (0.1 mL) dissolved the resulting red precipitate. Filtration of the solution after 30 min of stirring yielded a red solution. Slow addition of Et_2O induced the crystallization of $(\mu$-$WSe_4)[(PMePh_2)Au]_2$ (**4**) as red needles marginally suitable for X-ray analysis (0.197 g, 76% yield). Anal. Calcd: C, 24.13; H, 2.03. Found: C, 24.59; H, 3.23. UV–vis (DMF) [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: 310 (7530), 435 (3110), 458 (sh), 468 (3760), 485 (sh). IR (KBr): 310, 300 cm^{-1}. ^{31}P NMR (CH_3CN): δ −20.5. ^{77}Se NMR (CH_3CN): δ 1244.

$(\mu_3$-$Cl)(\mu_3$-$WSe_4)[(PPh_3)Cu]_3$ (5). $[(PPh_3)_2CuBH_3(CN)]_2$ (1.191 g, 0.95 mmol) in CH_2Cl_2 (10 mL) was added to a CH_2Cl_2 solution (15 mL) of $[NPr_4]_2[WSe_4]$ (0.550 g, 0.63 mmol) and NH_4Cl (0.034 g, 0.63 mmol). The resulting red solution was stirred for 30 min and subsequently filtered to afford an orange precipitate. Block-shaped orange crystals of $(\mu_3$-$Cl)(\mu_3$-$WSe_4)[(PPh_3)Cu]_3$ (**5**) (0.384 g, 40% yield) suitable for X-ray crystallographic analysis were obtained overnight by layering the filtrate with THF. Anal. Calcd: C, 42.9; H, 3.0. Found: C, 44.8; H, 3.1. UV–vis (CH_2Cl_2) [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: 338 (660), 490 (sh). IR (KBr): 320, 305, 295 cm^{-1}. ^{31}P NMR (CH_2Cl_2): δ 24.8. ^{77}Se NMR (DMF): δ 1232, 1651.

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer 330 double-beam UV–vis spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 283 infrared spectrophotometer with the use of pressed KBr pellets. The ^{77}Se NMR spectra were recorded on a Varian XLA-400 spectrometer equipped with a tunable probe and a deuterium lock. Chemical shifts were referenced to the secondary standard PhSeSePh at $\delta = 460$ ppm. The chemical shift scale was based on $(CH_3)_2Se$ at $\delta = 0$ ppm. Detailed experimental procedures have been described previously.[15] ^{31}P NMR spectra were obtained on a Gemini 300 spectrometer with automatic tuning capabilities and a deuterium lock. Chemical shifts were referenced to 85% H_3PO_4 at $\delta = 0$ ppm. All ^{31}P NMR spectra were obtained from samples in 5-mm round-bottom NMR tubes, while 10-mm NMR tubes were employed for ^{77}Se NMR spectroscopy. A scanning frequency of 121 MHz, a delay time of 2 s, a pulse width of 4 μs, and an acquisition time of 0.400 s were employed for the collection of ^{31}P NMR spectra.

Table I. Crystal Details for $(\mu$-$WSe_4)[(PMe_2Ph)_2Cu]_2$ (**1**), $(\mu$-$WSe_4)[(PMePh_2)Au]_2$ (**4**), and $(\mu_3$-$Cl)(\mu_3$-$WSe_4)[(PPh_3)Cu]_3$ (**5**)

	1	**4**	**5**
formula	$C_{32}H_{44}Cu_2P_4Se_4W$	$C_{26}H_{26}Au_2P_2Se_4W$	$C_{54}H_{45}ClCu_3P_3Se_4W$
fw	1179	1294	1513
a, Å	19.315 (7)	14.647 (5)	12.88 (1)
b, Å	15.575 (4)	14.161 (5)	17.72 (1)
c, Å	16.829 (7)	15.319 (6)	22.59 (1)
β, deg	127.99 (1)	106.65 (2)	90
V, Å^3	3990	3045	5281
space group	C^6_{2h}-$C2/c$	C^5_{2h}-$P2_1/c$	D^2_4-$P2_12_12_1$
Z	4	4	4
μ(Mo Kα), cm^{-1}	77.9	183.2	58.3
R on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.032	0.088	0.063
R_w on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.042	0.081	0.069

Crystallographic Studies. Unit cells of suitable crystals of **1** and **5** and a marginally suitable crystal of **4** were obtained at 113 K from the setting angles of 25 reflections that had been centered on an Enraf-Nonius CAD4 diffractometer. In each instance, the crystal was then transferred for data collection onto a Picker FACS-1 diffractometer that was also equipped with a cold stream. For each data collection, the intensities of six standard reflections remained constant within counting statistics. Some crystallographic details are listed in Table I; more are available in Table SI.[16]

The structures of **1** and **5** were solved and refined with the use of programs and procedures standard to this laboratory.[17] After heavy-atom positions were determined by Patterson methods, successive difference electron density maps were used to determine the positions of the remaining atoms. Prior to the final least-squares cycles on F_o, hydrogen atoms were included but not varied: phenyl hydrogen atoms were at calculated positions and methyl hydrogen positions were determined from a difference electron density map and idealized (C–H = 0.95 Å). For $(\mu$-$WSe_4)[(PMe_2Ph)_2Cu]_2$ the final cycle of least-squares refinement converged to $R(F_o) = 0.032$ for 4047 reflections and 196 variables; for $(\mu_3$-$Cl)(\mu_3$-$WSe_4)[(PPh_3)Cu]_3$ (**5**) the final cycle converged to $R(F_o) = 0.063$ for 8950 reflections and 570 variables. Final positional parameters are given in Tables II and III; hydrogen atom positions and anisotropic thermal parameters of all non-hydrogen atoms are provided in Tables SII and SIII.[16]

Intensity data for **4** were processed by methods standard to this laboratory.[17] The structure was solved with the direct methods program SHELXTL.PC.[18] The positions of all non-hydrogen atoms, with the exception of carbon atoms C(2)–C(7) and C(20)–C(25), were obtained from successive difference electron density maps obtained from isotropic, full-matrix least-squares refinement.[18] One phenyl ring that exhibited disorder was fixed as an idealized rigid group. Hydrogen atoms were placed at calculated positions after an absorption correction had been applied as described previously.[17] Heavy atoms were then refined anisotropically although, in view of the poor quality of the crystal and the observed disorder in one of the phenyl rings, the resultant thermal parameters may not be too meaningful. The final refinement on F_o for 5393 observations and 186 variables led to R and R_w values of 0.088 and 0.081, respectively. No unusual features were observed in a final difference electron density map. Final positional parameters for $(\mu$-$WSe_4)[(PMePh_2)Au]_2$ are given in Table IV; anisotropic thermal parameters of all heavy atoms are provided in Table SVI;[16] hydrogen atom positions may be found in Table SVII.[16]

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Table II. Positional Parameters and B_{eq} Values (Å^2) for (μ-WSe_4)[$(PMe_2Ph)_2Cu$]$_2$

atom	x	y	z	B_{eq}
W	$^1/_2$	0.113 659 (28)	$^1/_4$	1.16 (2)
Se(1)	0.460 360 (53)	0.200 277 (50)	0.115 180 (56)	1.81 (4)
Se(2)	0.382 358 (48)	0.027 157 (49)	0.201 745 (57)	1.71 (3)
Cu(1)	$^1/_2$	0.297 799 (80)	$^1/_4$	1.42 (5)
Cu(2)	$^1/_2$	−0.071 044 (82)	$^1/_4$	1.40 (6)
P(11)	0.370 08 (13)	0.357 38 (13)	0.188 54 (14)	1.55 (8)
P(21)	0.472 97 (13)	−0.133 88 (12)	0.113 54 (14)	1.42 (8)
C(111)	0.304 52 (57)	0.390 12 (57)	0.058 67 (65)	2.8 (4)
C(112)	0.297 92 (51)	0.282 93 (52)	0.184 72 (60)	2.2 (4)
C(113)	0.368 87 (52)	0.450 48 (48)	0.252 35 (59)	1.9 (4)
C(114)	0.291 58 (54)	0.488 43 (50)	0.225 28 (64)	2.3 (4)
C(115)	0.293 04 (61)	0.558 97 (55)	0.273 95 (73)	2.9 (5)
C(116)	0.371 25 (74)	0.594 16 (57)	0.350 91 (86)	4.0 (6)
C(117)	0.448 67 (71)	0.560 22 (75)	0.379 25 (91)	5.9 (6)
C(118)	0.446 36 (64)	0.488 30 (68)	0.328 16 (89)	4.8 (5)
C(211)	0.571 32 (55)	−0.161 58 (54)	0.129 74 (59)	2.3 (4)
C(212)	0.418 25 (55)	−0.062 28 (53)	0.006 62 (61)	2.4 (4)
C(213)	0.407 14 (46)	−0.230 28 (45)	0.063 27 (54)	1.3 (3)
C(214)	0.384 37 (56)	−0.270 76 (52)	0.115 80 (59)	2.3 (4)
C(215)	0.331 72 (61)	−0.345 14 (60)	0.078 28 (69)	3.2 (5)
C(216)	0.301 99 (56)	−0.376 95 (55)	−0.012 36 (62)	2.9 (4)
C(217)	0.325 48 (60)	−0.337 97 (59)	−0.067 15 (64)	3.2 (4)
C(218)	0.377 00 (58)	−0.265 94 (54)	−0.029 00 (61)	2.6 (4)

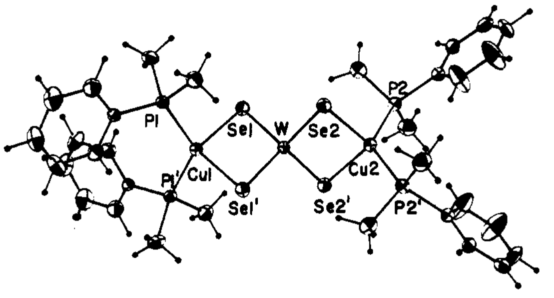

Figure 2. Structure of (μ-WSe_4)[$(PMe_2Ph)_2Cu$]$_2$ (**1**). Here and in succeeding figures the 50% probabiity ellipsoids are depicted.

Results and Discussion

Synthesis. In the present study, complexes containing the coinage metal cations M^+ coordinate to the WSe_4^{2-} anion in a M:W ratio of 2:1, but the resulting compounds are insoluble. Addition of a phosphine to the reactions causes the products to dissolve; from these reaction mixtures compounds **1**–**3**, in which a WSe_4 group bridges two $M(PMe_2Ph)_2$ groups (Figure 2), can be obtained:

$$WSe_4^{2-} + 2M^+ + PMe_2Ph\ (\text{excess}) \rightarrow (\mu\text{-}WSe_4)[(PMe_2Ph)_2M]_2 \quad (1)$$

Elemental analyses and spectroscopic results on the Ag (**2**) and Au (**3**) analogues of **1** suggest that all three molecules are similar. Substitution of a bulkier phosphine ($PMePh_2$) in the Au^+ reaction of eq 1 results in the formation of (μ-WSe_4)[$(PMePh_2)Au$]$_2$ (**4**), where the WSe_4 group bridges two $Au(PMePh_2)$ groups (Figure 3).

When a phosphine-substituted Cu^+ species is added to WSe_4^{2-} in a 3:1 Cu:W ratio in the presence of the Cl^- anion, the distorted cubane complex (**5**) (Figure 4) is obtained:

$$WSe_4^{2-} + 3CuPPh_3^{+} + Cl^- \rightarrow (\mu_3\text{-}Cl)(\mu_3\text{-}WSe_4)[(PPh_3)Cu]_3 \quad (2)$$

Structures. The structure of (μ-WSe_4)[$(PMe_2Ph)_2Cu$]$_2$ (**1**) is shown in Figure 2, and metrical data are presented in Table V. This structure has analogues in both the MS_4^{2-} [2] and MSe_4^{2-} [9,10] systems. The structure has a crystallographically imposed 2-fold axis. The W center is tetrahedral within error and is less distorted than in other MQ_4^{2-} derivatives,[2,9] except for the silver analogue.[10]

Table III. Positional Parameters and B_{eq} Values (Å^2) for (μ_3-Cl)(μ_3-WSe_4)[$(PPh_3)_3Cu$]$_3$

atom	x	y	z	B_{eq}
W	0.336061 (65)	0.003874 (50)	0.023536 (35)	1.33 (2)
Se(1)	0.24352 (18)	0.02256 (11)	0.114078 (90)	1.45 (5)
Se(2)	0.26298 (18)	0.08305 (11)	−0.050523 (93)	1.55 (5)
Se(3)	0.31744 (17)	−0.12256 (12)	−0.007486 (91)	1.57 (5)
Se(4)	0.50236 (25)	0.02938 (17)	0.03398 (16)	4.7 (1)
Cu(1)	0.15083 (22)	0.07805 (15)	0.03369 (12)	2.13 (7)
Cu(2)	0.19392 (21)	−0.04396 (14)	−0.06058 (11)	1.54 (6)
Cu(3)	0.19735 (23)	−0.09738 (15)	0.07161 (12)	1.91 (7)
Cl	0.03600 (39)	−0.04899 (22)	0.00523 (20)	0.9 (1)
P(1)	0.02558 (47)	0.16173 (32)	0.03626 (25)	1.5 (1)
P(2)	0.14564 (44)	−0.09563 (30)	−0.14559 (23)	1.2 (1)
P(3)	0.13564 (47)	−0.19098 (33)	0.12680 (26)	1.6 (1)
C(11)	−0.0966 (18)	0.1262 (12)	0.06785 (96)	1.7 (5)
C(12)	−0.0963 (19)	0.0662 (13)	0.10495 (97)	2.0 (6)
C(13)	−0.1810 (23)	0.0340 (14)	0.1276 (10)	3.2 (7)
C(14)	−0.2748 (20)	0.0684 (16)	0.1115 (11)	3.8 (8)
C(15)	−0.2792 (23)	0.1286 (17)	0.0746 (11)	3.8 (8)
C(16)	−0.1896 (16)	0.1580 (12)	0.0528 (10)	2.2 (6)
C(17)	−0.0092 (17)	0.1927 (11)	−0.03677 (91)	1.6 (4)
C(18)	−0.0410 (19)	0.2693 (13)	−0.0499 (10)	2.3 (6)
C(19)	−0.0660 (18)	0.2897 (12)	−0.1073 (11)	2.2 (6)
C(110)	−0.0613 (18)	0.2366 (14)	−0.1513 (10)	2.4 (7)
C(111)	−0.0303 (20)	0.1621 (14)	−0.1409 (10)	2.3 (6)
C(112)	−0.0070 (18)	0.1395 (13)	−0.0831 (11)	2.4 (6)
C(113)	0.0548 (18)	0.2492 (13)	0.07821 (96)	2.1 (6)
C(114)	−0.0198 (16)	0.2893 (12)	0.10871 (87)	1.5 (5)
C(115)	0.0092 (21)	0.3564 (13)	0.1357 (11)	2.5 (7)
C(116)	0.1055 (21)	0.3851 (14)	0.1315 (12)	3.2 (7)
C(117)	0.1820 (19)	0.3415 (12)	0.1001 (11)	2.5 (7)
C(118)	0.1563 (21)	0.2768 (12)	0.07490 (97)	1.9 (4)
C(21)	0.0498 (16)	−0.0477 (12)	−0.18948 (93)	1.3 (5)
C(22)	−0.0506 (20)	−0.0421 (13)	−0.1644 (10)	2.4 (6)
C(23)	−0.1314 (18)	−0.0086 (16)	−0.1952 (11)	3.2 (7)
C(24)	−0.1157 (19)	0.0171 (13)	−0.2520 (12)	3.0 (7)
C(25)	−0.0209 (22)	0.0098 (11)	−0.27653 (87)	2.5 (6)
C(26)	0.0628 (18)	−0.0229 (12)	−0.24728 (95)	1.9 (6)
C(27)	0.0835 (16)	−0.1878 (11)	−0.13725 (82)	0.9 (5)
C(28)	0.0920 (17)	−0.2261 (11)	−0.08174 (92)	1.4 (4)
C(29)	0.0424 (17)	−0.2951 (11)	−0.07617 (98)	1.8 (5)
C(210)	−0.0131 (19)	−0.3260 (13)	−0.12131 (95)	2.0 (6)
C(211)	−0.0228 (18)	−0.2880 (13)	−0.1736 (10)	2.2 (6)
C(212)	0.0242 (19)	−0.2195 (12)	−0.18203 (94)	1.9 (6)
C(213)	0.2559 (19)	−0.1085 (11)	−0.19614 (92)	1.6 (5)
C(214)	0.2584 (19)	−0.1614 (14)	−0.2384 (11)	2.5 (7)
C(215)	0.3451 (25)	−0.1703 (13)	−0.2756 (11)	3.2 (7)
C(216)	0.4274 (18)	−0.1211 (14)	−0.2671 (11)	2.5 (6)
C(217)	0.4267 (26)	−0.0688 (17)	−0.2235 (14)	4.4 (7)
C(218)	0.3439 (21)	−0.0630 (13)	−0.1887 (11)	2.8 (7)
C(31)	0.1514 (21)	−0.2851 (13)	0.0969 (10)	2.8 (7)
C(32)	0.0747 (18)	−0.3402 (13)	0.1000 (11)	2.5 (6)
C(33)	0.0953 (24)	−0.4132 (15)	0.0801 (10)	3.7 (8)
C(34)	0.1962 (23)	−0.4306 (14)	0.0531 (12)	3.8 (8)
C(35)	0.2709 (20)	−0.3736 (13)	0.05019 (91)	2.3 (6)
C(36)	0.2494 (21)	−0.3023 (12)	0.0702 (10)	2.4 (6)
C(37)	−0.0018 (16)	−0.1827 (11)	0.14078 (89)	1.2 (5)
C(38)	−0.0692 (20)	−0.1858 (13)	0.0935 (10)	2.3 (6)
C(39)	−0.1756 (20)	−0.1801 (13)	0.10174 (99)	2.4 (6)
C(310)	−0.2157 (18)	−0.1660 (13)	0.1580 (11)	2.6 (6)
C(311)	−0.1520 (20)	−0.1613 (15)	0.20442 (94)	2.8 (6)
C(312)	−0.0449 (19)	−0.1703 (16)	0.1947 (12)	3.4 (7)
C(313)	0.1926 (18)	−0.1992 (11)	0.20096 (95)	1.7 (4)
C(314)	0.2230 (20)	−0.1344 (12)	0.2301 (10)	2.0 (6)
C(315)	0.2664 (20)	−0.1412 (14)	0.2884 (11)	2.7 (7)
C(316)	0.2762 (18)	−0.2109 (14)	0.31184 (91)	2.2 (6)
C(317)	0.2471 (24)	−0.2743 (13)	0.2836 (11)	3.0 (7)
C(318)	0.2060 (23)	−0.2680 (13)	0.2271 (10)	3.0 (7)

The geometry about the Cu atoms may be described as distorted tetrahedral, with angles varying from 101.9 (1) to 131.2 (1)°. Not surprisingly, bond angles decrease in the order P–Cu–P, Se–Cu–P, and Se–Cu–Se, as seen in a variety of related compounds.[2,9,10] The W–Se bond lengths for (μ-WSe_4)[$(PMe_2Ph)_2Cu$]$_2$ (2.317 (1)–2.327 (1) Å) are perhaps slightly longer than those in the WSe_4^{2-} anion (2.307 (1)–2.310 (1) Å).[9] These correspond well with those reported in other mixed-metal systems

Table IV. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for (μ-WSe_4)[($PMePh_2$)Au]$_2$

atom	x	y	z	U_{eq}
W	0.7443 (2)	0.1585 (2)	−0.0036 (1)	0.058 (1)
Au(1)	0.6248 (2)	0.2852 (1)	−0.1319 (1)	0.068 (1)
Au(2)	0.8674 (2)	0.0404 (2)	0.1305 (1)	0.053 (1)
Se(1)	0.5770 (4)	0.1522 (3)	−0.0466 (3)	0.076 (2)
Se(2)	0.8028 (5)	0.2759 (4)	−0.0813 (3)	0.085 (3)
Se(3)	0.7909 (3)	0.1929 (3)	0.1523 (3)	0.038 (2)
Se(4)	0.8054 (6)	0.0148 (4)	−0.0356 (3)	0.127 (4)
P(1)	0.5352 (10)	0.3869 (8)	−0.2342 (7)	0.042 (5)
P(2)	0.9670 (9)	−0.0545 (11)	0.2342 (9)	0.064 (6)
C(1)	0.6033 (26)	0.4678 (27)	−0.2756 (24)	0.039 (11)
C(2)	0.4540 (27)	0.3254 (28)	−0.3323 (26)	0.031 (10)
C(3)	0.4360 (38)	0.2352 (40)	−0.3421 (40)	0.089 (19)
C(4)	0.3912 (37)	0.1865 (40)	−0.4196 (37)	0.086 (18)
C(5)	0.3292 (39)	0.2370 (36)	−0.4801 (34)	0.067 (16)
C(6)	0.3520 (42)	0.3270 (44)	−0.4796 (44)	0.103 (21)
C(7)	0.4170 (52)	0.3718 (61)	−0.4094 (53)	0.160 (32)
C(8)	0.4566 (25)	0.4566 (28)	−0.1886 (32)	0.064 (19)
C(9)	0.4132	0.5379	−0.2330	0.065 (20)
C(10)	0.3513	0.5898	−0.1973	0.096 (22)
C(11)	0.3328	0.5603	−0.1172	0.110 (35)
C(12)	0.3761	0.4789	−0.0728	0.496 (97)
C(13)	0.4381	0.4270	−0.1085	0.330 (40)
C(14)	0.9088 (37)	−0.1597 (35)	0.2585 (33)	0.060 (15)
C(15)	0.9471 (39)	−0.2264 (35)	0.3295 (34)	0.063 (16)
C(16)	0.9021 (42)	−0.2988 (41)	0.3417 (39)	0.092 (19)
C(17)	0.8108 (50)	−0.3226 (54)	0.2916 (45)	0.132 (27)
C(18)	0.7580 (78)	−0.2336 (64)	0.2606 (61)	0.210 (44)
C(19)	0.8131 (66)	−0.1578 (70)	0.2273 (61)	0.204 (42)
C(20)	1.0261 (39)	−0.0003 (40)	0.3435 (35)	0.076 (16)
C(21)	1.0121 (40)	0.0852 (44)	0.3560 (39)	0.086 (18)
C(22)	1.0396 (57)	0.1452 (55)	0.4396 (55)	0.156 (30)
C(23)	1.1278 (40)	0.1040 (42)	0.5032 (36)	0.076 (17)
C(24)	1.1358 (39)	0.0187 (43)	0.4900 (41)	0.097 (19)
C(25)	1.1209 (54)	−0.0272 (59)	0.3950 (53)	0.175 (36)
C(26)	1.0659 (33)	−0.1031 (34)	0.1980 (32)	0.077 (16)

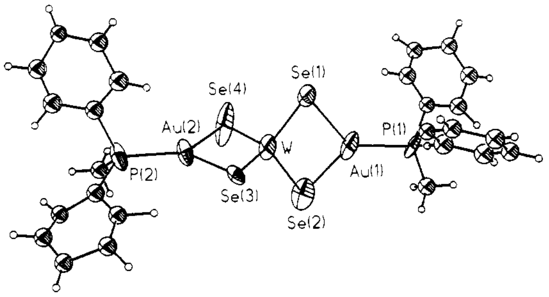

Figure 3. Structure of (μ-WSe_4)[($PMePh_2$)Au]$_2$ (**4**). The carbon atoms have been drawn on an arbitrary scale.

(2.317 (3)–2.356 (10) Å)[3,19] and complexed species (2.356 (1)–2.357 Å).[19] The W–Cu interactions of 2.868 (1) and 2.877 (2) Å are long compared with those in **5** and are, in fact, slightly longer than the W–Au interactions in **4**.

Figure 3 shows the structure of (μ-WSe_4)[($PMePh_2$)Au]$_2$ (**4**). The W center is slightly distorted from tetrahedral, more so than in the sulfur analogue.[20] The Au centers are distorted trigonal planar with small Se–Au–Se angles (102.8 (2) and 102.6 (2)°). The M–Se bonds are, of course, longer than the corresponding M–S bonds in the sulfide, but the formal W^{VI}–Au^{I} interactions are remarkably close (2.854 (3) and 2.858 (3) Å for the selenide, 2.836 (1) and 2.843 (1) Å for the sulfide).[20]

The structure of (μ_3-Cl)(μ_3-WSe_4)[(PPh_3)Cu]$_3$ (**5**) is shown in Figure 4. The compound has a cubane-like core, as detailed in Figure 5. Examples of related cubanes containing different MQ_4^{2-} moieties are known.[1,3,10,11] In the core, both the Cu and W atoms are tetrahedrally coordinated. The cube itself is distorted, as is evident from Figure 5. In general, the trends in bond distances and angles of Table V parallel those observed earlier in analogous structures.[1,3,10,11] The W–Cu interactions of 2.733 (3), 2.755 (3), and 2.771 (3) Å are significantly shorter than those in **1**, even though the formally W^{VI} and Cu^{I} centers in both **1** and **5** are tetrahedrally coordinated.

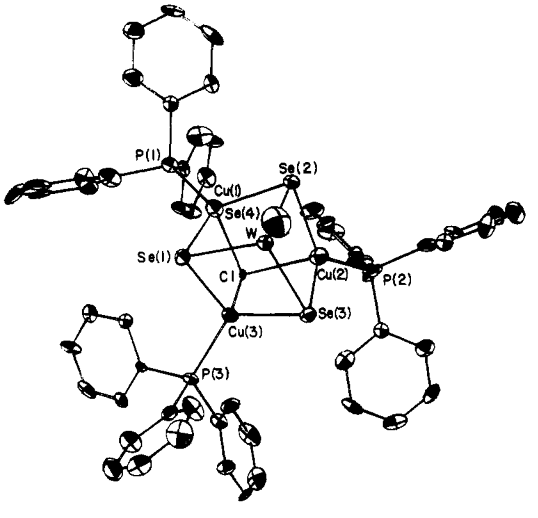

Figure 4. Structure of (μ_3Cl)(μ_3-WSe_4)[(PPh_3Cu]$_3$ (**5**). Hydrogen atoms have been omitted for clarity.

NMR Spectroscopy. In the related soluble sulfide systems, electronic and infrared spectroscopies are valuable tools for characterization. However, for WSe_4^{2-} derivatives these techniques are of limited use. W–Se vibrations are observed in the IR spectra of **1**–**5** in the region 280–325 cm^{-1}. All four species have intense bands in their absorption spectra, typically a broad peak in the 460–490-nm range and a less intense band between 320 and 340 nm. In related compounds, bands in this region have been assigned as charge-transfer bands[1,19] of the type (π(Se) $\rightarrow$ d(W)) arising from the WSe_4 moiety. A relatively weak ligand (WSe_4^{2-}) to metal (Cu^+, Ag^+, or Au^+) interaction may be inferred from a comparison of the band positions for compounds **1**–**5** to those for free WSe_4^{2-}.[19] Bands observed for complexes **1**–**4** are at higher energies than the bands from the WSe_4^{2-} anion.

As opposed to electronic and infrared spectroscopies, both ^{31}P and ^{77}Se NMR spectroscopies provide useful characterization of the present compounds. While numerous examples of mixed-metal chalcogen complexes with phosphine ligation are known,[1,21] NMR investigations have been rare.[22] Several ^{31}P NMR studies have been conducted on Cu, Ag, and Au phosphines in systems without chalcogens, however.[23] Preparation of the present (μ-WSe_4)[(PMe_2Ph)$_2$M]$_2$ series (M = Cu (**1**), Ag (**2**), and Au (**3**)) enables comparative data on NMR chemical shifts to be obtained (Table VI). Only one ^{31}P NMR resonance is observed; thus each coinage metal has only one coordination geometry. The sulfur analogues to compounds **2** and **3** contain metal atoms with differing coordination geometries.[9,10] No ^{31}P–^{107}Ag coupling is observed in **2**, probably because of phosphine exchange.[21,22] An interesting trend is observed in the ^{31}P NMR spectra: as the size of the coinage metal increases, the resonance shifts to lower field. This trend is the reverse of that reported in some systems that contain no metal–selenium bonding.[22,23] Since Cu^+, Ag^+, and Au^+ are all d^{10} systems, the deshielding effect from Cu^+ to Au^+ may result from increased orbital overlap. Interpretation of the downfield shift observed in (μ-WSe_4)[($PMePh_2$)Au]$_2$ (**4**) vs (μ-

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Table V. Selected Bond Lengths (Å) and Bond Angles (deg)

	$(\mu\text{-}WSe_4)[(PMe_2Ph)_2Cu]_2$ (**1**)		
W–Se(1)	2.327 (1)	Se(1)–Cu(1)	2.430 (1)
W–Se(2)	2.317 (1)	Se(2)–Cu(2)	2.427 (1)
W–Cu(1)	2.868 (1)	Cu(1)–P(1)	2.243 (2)
W–Cu(2)	2.877 (2)	Cu(2)–P(2)	2.242 (2)
Se(1)–W–Se(2)	109.39 (4)	Se(1′)–Cu(1)–P(11)	108.04 (6)
Se(1)–W–Se(1′)	109.17 (5)	Se(1)–Cu(1)–Se(1′)	102.60 (7)
Se(2)–W–Se(2′)	108.85 (5)	P(11)–Cu(1)–P(11′)	131.2 (1)
Se(2)–W–Se(1′)	110.01 (3)	Se(2)–Cu(2)–P(21)	110.62 (6)
W–Se(1)–Cu(1)	74.10 (5)	Se(2′)–Cu(2)–P(21)	101.41 (6)
W–Se(2)–Cu(2)	74.62 (7)	Se(2)–Cu(2)–Se(2′)	101.93 (7)
Se(1)–Cu(1)–P(11)	101.94 (6)	P(21)–Cu(2)–P(21′)	128.1 (1)
	$(\mu\text{-}WSe_4)[(PMePh_2)Au]_2$ (**4**)		
W–Se(1)	2.350 (6)	Au(1)–Se(1)	2.503 (6)
W–Se(2)	2.346 (7)	Au(1)–Se(2)	2.502 (7)
W–Se(3)	2.340 (4)	Au(2)–Se(3)	2.498 (5)
W–Se(4)	2.332 (8)	Au(2)–Se(4)	2.472 (5)
W–Au(1)	2.858 (3)	Au(1)–P(1)	2.252 (10)
W–Au(2)	2.854 (3)	Au(2)–P(2)	2.265 (13)
Se(1)–W–Se(2)	112.8 (2)	W–Se(3)–Au(2)	72.2 (2)
Se(1)–W–Se(3)	105.7 (2)	W–Se(4)–Au(2)	72.8 (2)
Se(1)–W–Se(4)	109.9 (3)	Se(1)–Au(1)–Se(2)	102.8 (2)
Se(2)–W–Se(3)	109.2 (2)	Se(1)–Au(1)–P(1)	130.6 (4)
Se(2)–W–Se(4)	107.1 (3)	Se(2)–Au(1)–P(1)	126.6 (4)
Se(3)–W–Se(4)	112.3 (2)	Se(3)–Au(2)–Se(4)	102.6 (2)
W–Se(1)–Au(1)	72.1 (2)	Se(3)–Au(2)–P(2)	129.9 (4)
W–Se(2)–Au(1)	72.2 (2)	Se(4)–Au(2)–P(2)	127.4 (4)
	$(\mu_3\text{-}Cl)(\mu_3\text{-}WSe_4)[(PPh_3)Cu]_3$ (**5**)		
W–Se(1)	2.390 (3)	Cu(2)–Cl	2.520 (6)
W–Se(2)	2.377 (2)	Cu(3)–Cl	2.702 (6)
W–Se(3)	2.360 (3)	Se(1)–Cu(1)	2.385 (4)
W–Se(4)	2.201 (4)	Se(1)–Cu(3)	2.406 (3)
W–Cu(1)	2.733 (3)	Se(2)–Cu(1)	2.390 (4)
W–Cu(2)	2.771 (3)	Se(2)–Cu(2)	2.430 (3)
W–Cu(3)	2.755 (3)	Se(3)–Cu(2)	2.431 (4)
Cu(1)–Cu(2)	3.085 (4)	Se(3)–Cu(3)	2.405 (4)
Cu(1)–Cu(3)	3.280 (4)	Cu(1)–P(1)	2.191 (6)
Cu(2)–Cu(3)	3.133 (4)	Cu(2)–P(2)	2.216 (6)
Cu(1)–Cl	2.769 (5)	Cu(3)–P(3)	2.222 (7)
Se(1)–W–Se(2)	108.84 (9)	Cu(1)–Se(1)–Cu(3)	86.4 (1)
Se(1)–W–Se(3)	109.57 (8)	Cu(3)–Se(3)–Cu(2)	80.8 (1)
Se(1)–W–Se(4)	111.4 (1)	Se(1)–Cu(1)–Cl	96.2 (1)
Se(2)–W–Se(3)	108.13 (8)	Se(2)–Cu(1)–Cl	99.7 (1)
Se(2)–W–Se(4)	109.8 (1)	Se(2)–Cu(2)–Cl	105.8 (1)
Se(3)–W–Se(4)	109.0 (1)	Se(3)–Cu(2)–Cl	102.5 (2)
Se(1)–Cu(1)–Se(2)	108.6 (1)	Se(3)–Cu(3)–Cl	98.1 (1)
Se(1)–Cu(3)–Se(3)	107.5 (1)	Se(1)–Cu(3)–Cl	97.5 (1)
Se(3)–Cu(2)–P(2)	112.1 (1)	Cu(1)–Cl–Cu(2)	71.2 (1)
Se(3)–Cu(3)–P(3)	120.2 (1)	Cu(1)–Cl–Cu(3)	73.7 (1)
Se(2)–Cu(2)–Se(3)	104.2 (1)	Cu(2)–Cl–Cu(3)	73.6 (2)
W–Se(1)–Cu(1)	69.8 (1)	Cl–Cu(1)–P(1)	99.9 (1)
W–Se(1)–Cu(3)	70.11 (9)	Cl–Cu(2)–P(2)	105.6 (1)
W–Se(3)–Cu(3)	70.64 (9)	Cl–Cu(3)–P(3)	106.0 (1)
W–Se(3)–Cu(2)	70.66 (9)	Se(1)–Cu(1)–P(1)	129.3 (1)
W–Se(2)–Cu(1)	70.0 (1)	Se(2)–Cu(1)–P(1)	116.1 (1)
W–Se(2)–Cu(2)	70.38 (8)	Se(2)–Cu(2)–P(2)	124.5 (1)
Cu(1)–Se(2)–Cu(2)	79.6 (1)	Se(1)–Cu(3)–P(3)	122.0 (1)

$WSe_4)[(PMe_2Ph)_2Au]_2$ (**3**) is not possible because the phosphines are different and the geometries about the Au centers are different. $(\mu_3\text{-}Cl)(\mu_3\text{-}WSe_4)[(PPh_3)Cu]_3$ (**5**) displays a single peak at 24.8 ppm in its ^{31}P NMR spectrum, consistent with the solid-state structure.

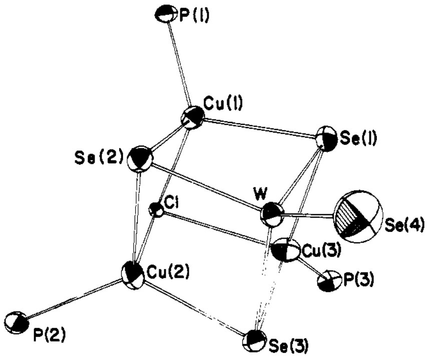

Figure 5. Structure of the $(\mu_3\text{-}Cl)(\mu_3\text{-}WSe_4)[(PPh_3)Cu]_3$ core.

Table VI. ^{77}Se and ^{31}P NMR Chemical Shifts

compound	δ, ppm	
	^{31}P	^{77}Se
$(\mu\text{-}WSe_4)[(PMe_2Ph)_2Cu]_2$ (**1**)	–40.1	1044
$(\mu\text{-}WSe_4)[(PMe_2Ph)_2Ag]_2$ (**2**)	–36.0	1092
$(\mu\text{-}WSe_4)[(PMe_2Ph)_2Au]_2$ (**3**)	–34.3	1234
$(\mu\text{-}WSe_4)[(PMePh_2)Au]_2$ (**4**)	–20.5	1244
$(\mu_3\text{-}Cl)(\mu_3\text{-}WSe_4)[(PPh_3)Cu]_3$ (**5**)	24.8	1232, 1651

Earlier work in this laboratory[19,24,25] mapped out a wide range of ^{77}Se chemical shifts in soluble transition-metal selenide anions. The ^{77}Se NMR resonances in Table VI for compounds **1**–**4** appear downfield of the region (δ_{max} = 1000 ppm) previously specified for Se atoms bridging two metal atoms. Earlier we inferred[19] from the ^{77}Se chemical shifts that second-row transition metals, such as Mo and Pd, have better orbital overlap with Se than do first- or third-row transition metals. However, in the present d^{10} series (**1**–**3**) the ^{77}Se resonances shift downfield on going from Cu^+ to Au^+, a trend that can again be ascribed to a smooth increase in orbital overlap. The chemical shift for **4** is 10 ppm downfield of the related gold species **3**. Thus the Se–Au interaction is relatively insensitive to the change of geometry about gold and to the change of phosphine, or else the effects of these two changes offset one another.

As expected, two peaks are found in the ^{77}Se NMR spectrum of $(\mu_3\text{-}Cl)(\mu_3\text{-}WSe_4)[(PPh_3)Cu]_3$ (**5**), one arising from the terminal Se and the other from the Se nuclei in the cubane core. From previous studies[26] and from the chemical shifts in compounds **1**–**4** (1044–1244 ppm), the resonance at 1232 ppm in **5** most likely arises from the Se centers in the core while the second resonance at δ = 1651 ppm arises from the terminal Se nucleus.

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Supplementary Material Available: Additional crystallographic details (Table SI), hydrogen atom positions and anisotropic thermal parameters for non-hydrogen atoms for **1** (Table SII) and **5** (Table SIII), anisotropic thermal parameters for **4** (Table SVI), and hydrogen atom positions for **4** (Table SVII) (6 pages). Ordering information is given on any current masthead page.

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