Chemistry of the WSe_4^{2-} Anion: Synthesis, NMR Spectroscopy, and Crystal Structure of the Selenium Insertion Product $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$

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Reaction of a CH_3CN solution of $[NEt_4]_2[WSe_4]$ with 1 equiv of lithium (2-thienyl)cyanocuprate, $Li[(CN)Cu(C_4H_3S)]$, affords $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ (**1**), in which a Se atom from the decomposition of the WSe_4^{2-} anion formally has been inserted into the 2-thienyl–copper bond of $Cu(C_4H_3S)$ to form the 2-selenothiophene ligand. $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ crystallizes with four formula units in the tetragonal space group $D_{2d}^7 - P\bar{4}b2$ in a cell of dimensions a = 15.732(2) Å and c = 14.992(3) Å (T = 113 K). Full anisotropic refinement (4934 unique data, 173 variables) of the structure on F_o^2 led to a value of $R(F)$ = 0.055 for those 4282 data having $F_o^2 \geq 2\sigma(F_o^2)$. The molecule has a crystallographically imposed 2-fold axis. Four Se atoms are arranged in an almost perfect tetrahedron about the W center; the Se atoms bridge to two Cu atoms, each of which in turn is bonded to a third Se atom in a distorted trigonal planar array. Each of these latter Se atoms is bonded to a thiophene group at the 2-position. The ^{77}Se NMR spectrum of a DMF solution of **1** exhibits two resonances at δ 905.8 and −18.1 ppm. The ^{13}C NMR spectrum displays six peaks at δ 15.5, 52.7, 65.9, 124.5, 127.9, and 131.6 ppm, consistent with the solid-state structure.

Introduction

The coinage-metal chemistry of the WS_4^{2-} and MoS_4^{2-} anions has been well-documented,[1] but until recently only two examples of compounds containing the WSe_4^{2-} core were known.[2,3] Our laboratory has uncovered a number of new coinage-metal/WSe_4^{2-} complexes,[4-6] some of which are sketched in Figure 1. Unknown among this chemistry are reactions involving chalcogen insertion. There are some reported examples of selenium insertion into metal–carbon bonds, where the carbon atom is part of an aromatic[7,8] or aliphatic[9] substituent. The present synthetic, NMR spectroscopic, and crystallographic study expands the known chemistry of coinage-metal/WSe_4^{2-} complexes and of selenium insertion reactions.

Experimental Section

Syntheses and Physical Measurements. All syntheses and manipulations were carried out in oven-dried glassware under purified N_2 with the use of standard inert-atmosphere techniques.[10] *N,N*-Dimethylformamide (DMF) was used as purchased from Baxter Healthcare Corp., Muskegon, MI. CH_3CN and Et_2O were distilled over appropriate drying agents[11] prior to use. Microanalyses were performed by Searle Analytical Services, Skokie, IL. $[NEt_4]_2[WSe_4]$ was prepared by a modification of the literature method.[12] $Li[(CN)Cu(C_4H_3S)]$ was used as received from Aldrich Chemical Co., Milwaukee, WI.

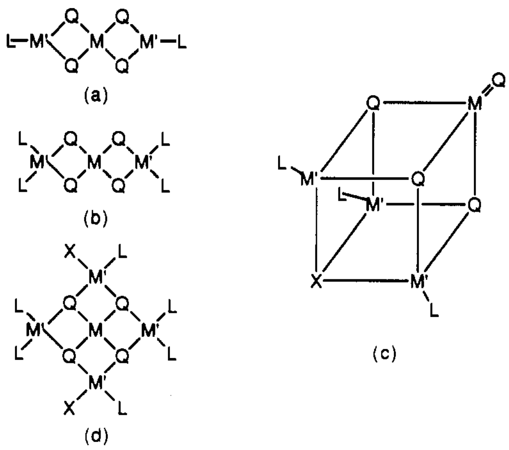

Figure 1. Sketches of relevant structures in the MQ_4^{2-} system (M = Mo, W; Q = S, Se; M' = Cu, Ag, Au; L = ligand; X = Cl, Br).

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 spectrum was 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 δ = 460 ppm. The chemical shift scale was based on $(CH_3)_2Se$ at δ = 0 ppm. Detailed experimental procedures have been described elsewhere.[13] The ^{13}C NMR spectrum was obtained on a Gemini 300 spectrometer with automatic tuning capabilities and a deuterium lock. Chemical shifts were referenced to CD_3CN at δ = 118 ppm. The ^{13}C NMR data were collected from a sample in a 5-mm round-bottom NMR tube, while a 10-mm NMR tube was employed for ^{77}Se NMR spectroscopy. A scanning frequency of 10 400 Hz, a delay time of 4 s, a pulse width of 11.8 μs, and an acquisition time of 0.603 s were employed for the collection of ^{13}C NMR data.

$[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ (1). A $Li[(CN)Cu(C_4H_3S)]$ solution in THF (5.1 mL, 0.25 M) was added dropwise with stirring to a solution of $[NEt_4]_2[WSe_4]$ (1.0 g, 1.3 mmol) in CH_3CN (20 mL). The clear red solution obtained was stirred for 15 min before filtration. Slow addition of Et_2O produced within 1 day X-ray-quality crystals of $[NEt_4]_2[\mu$-

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(1) Müller, A.; Bögge, H.; Schimanski, U.; Penk, M.; Nieradzik, K.; Dartmann, M.; Krickemeyer, E.; Schimanski, J.; Römer, C.; Römer, M.; Dornfeld, H.; Wienböker, U.; Hellmann, W.; Zimmermann, M. *Monatsh. Chem.* **1989**, *120*, 367–391.

(2) Müller, A.; Wienböker, U.; Penk, M. *Chimia* **1989**, *43*, 50–52.

(3) Müller, A.; Scbimanski, U.; Schimanski, J. *Inorg. Chim. Acta* **1983**, *76*, L245–L246.

(4) Ansari, M. A.; Chau, C.-N.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 650–654.

(5) Christuk, C. C.; Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* **1992**, *31*, 4365–4369.

(6) Christuk, C. C.; Ansari, M. A.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1477–1478.

(7) Fischer, H.; Zeuner, S.; Gerbing, U.; Riede, J.; Kreiter, C. G. *J. Organomet. Chem.* **1989**, *377*, 105–122.

(8) Gautheron, B.; Tainturier, G.; Pouly, S.; Théobald, F.; Vivier, H.; Laarif, A. *Organometallics* **1984**, *3*, 1495–1499.

(9) Gautheron, B.; Tainturier, G.; Meunier, P. *J. Organomet. Chem.* **1981**, *209*, C49–C51.

(10) Shriver, D. F.; Drezdon, M. A. *Manipulation of Air Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

(11) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley and Sons: New York, 1972.

(12) O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971–1973.

(13) Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747–1755.

0020-1669/93/1332-5105$04.00/0

Table I. Crystal Details for $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$

empirical formula	$C_{24}H_{46}Cu_2N_2S_2Se_6W$
fw	1211.44
T	113 K
space group	$D_{2d}^7 - P\bar{4}b2$
a, Å	15.732(2) Å
c, Å	14.992(3) Å
V, Å^3	3710.5(10)
Z	4
d(calcd)	2.169 g/cm^3
abs coeff	10.24 mm^{-1}
no. of reflns collected	5107
no. of indep refns	4934 [R(int) = 0.0230]
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.055, wR2 = 0.111
R indices (all data)^a	R1 = 0.068, wR2 = 0.114

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/wF_o^4]^{1/2}$.

$WSe_4][(SC_4H_3)SeCu]_2$ (**1**) (0.143 g, 18.5% yield) as red scalenohedra. Anal. Calcd: C, 23.79; H, 3.83; N, 2.31. Found: C, 23.81; H, 3.58; N, 2.37. UV–vis (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 276 (1710), 314 (2400), 336 (2400), 484 (580). IR (KBr): 330, 290, 280 cm^{-1}. ^{13}C NMR (DMF): δ 15.5 (CH_3), 52.7 (CH_2), 65.9 ($C(1)$), 124.5, 127.9 ($C(3)$, $C(4)$), 131.6 ($C2$). ^{77}Se NMR (DMF): δ −18.1 (*Se*–*C*), 905.8 (*Se*–*W*).

Crystallographic Study. Crystals of **1** are remarkably stable with respect to oxidation and hydrolysis. A unit cell of a suitable crystal of **1** was obtained at 113 K from the setting angles of 25 reflections that had been centered on an Enraf-Nonius CAD4 diffractometer. During 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.[14]

Intensity data for **1** were processed by methods standard to this laboratory.[15] The structure was solved with the direct methods program SHELXTL.PC[16] and refined by full-matrix least-squares methods on F_o^2.[17] The positions of the hydrogen atoms were determined from geometrical considerations and were idealized. All non-hydrogen atoms were refined anisotropically. The final refinement of F_o^2 for 4934 data and 173 variables led to a value of $R_w(F_o^2)$ (wR2) of 0.114 for all data and to a value of $R(F)$ (R1) of 0.055 for those 4282 data having $F_o^2 \geq 2\sigma(F_o^2)$. No unusual features were observed in the final difference electron density map. Final positional parameters are given in Table II; anisotropic displacement parameters of all non-hydrogen atoms may be found in Table SII; positional and isotropic displacement parameters for the hydrogen atoms are given in Table SIII.[14]

Results

Synthesis and Spectroscopy. M/WSe$_4$ complexes (M = Cu, Ag, Au) have been found to be stable in M:W ratios of 2:1 and 3:1 when M is ligated by phosphine.[5] Compounds with M:W ratios of 4:1 are also known for WS$_4$[18,19] and WSe$_4$ systems.[20] Our attempts to obtain a compound with a Cu:W ratio of 1:1 have failed. However, examples possessing cyano ligands are known in the corresponding sulfide systems.[1] Although the reagent lithium (2-thienyl)cyanocuprate, $Li[(CN)Cu(C_4H_3S)]$, is used principally to effect a number of carbon–carbon and carbon–heteroatom bond-forming reactions,[22] we thought it offered an interesting alternative to the usual Cu(I) sources. Reaction of 1 equiv of $Li[(CN)Cu(C_4H_3S)]$ with 1 equiv of $[NEt_4]_2[WSe_4]$ did not afford a 1:1 species but rather the 1:2 species $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ (**1**) in 18.5% crystalline yield. The nature of the other products was not investigated, nor was there an attempt made to maximize the yield. The only source of Se for this reaction is decomposition of the WSe_4^{2-} anion, for which there is precedent.[4] Formally, Se is released from WSe_4^{2-} and is inserted into the Cu–C bond[23] of the Cu-(C_4H_3S) moiety to afford the 2-selenothiophene ligand.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$

	x	y	z	U(eq)^a
W	7316(1)	7684(1)	10000	16(1)
Se(1)	8408(1)	7557(1)	11050(1)	22(1)
Se(2)	7411(1)	9000(1)	9273(1)	19(1)
Se(3)	7661(1)	7990(1)	6717(1)	42(1)
Cu	7525(1)	7906(1)	8231(1)	24(1)
S	7809(2)	9950(2)	7129(3)	46(2)
C(1)	7540(7)	9160(7)	6436(7)	28(6)
C(2)	7579(9)	10726(8)	6411(9)	46(9)
C(3)	7283(9)	10389(10)	5597(9)	53(10)
C(4)	7219(5)	9500(5)	5536(6)	13(4)
N(1)	0	10000	10000	14(4)
C(11)	524(6)	9393(6)	9424(7)	21(5)
C(12)	13(7)	8867(7)	8767(8)	34(6)
N(2)	10000	10000	5000	34(6)
C(21)	10077(10)	8893(9)	6247(9)	49(10)
C(22)	9528(8)	9346(8)	5576(8)	39(8)
N(3)	5000	10000	7787(8)	25(7)
C(31)	5561(7)	9434(9)	7237(8)	43(6)
C(32)	4415(7)	9464(7)	8364(7)	26(5)
C(33)	4838(8)	8808(8)	8948(9)	39(7)
C(34)	5091(11)	8821(11)	6647(11)	75(12)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Infrared and electronic spectra for **1** are well within the range observed for other WSe$_4$ derivatives.[5] W–Se vibrations in the IR spectrum are observed in the region 280–330 cm^{-1} while intense bands in the region 310–340 nm are found in the absorption spectrum. Further interpretations have been detailed previously.[5]

The ^{77}Se NMR spectrum contains two resonances; the peak at 905.8 ppm is within the range established for metal-bridging Se atoms, particularly for Cu/W compounds.[5,25] This resonance is upfield of the resonance observed for $(\mu\text{-}WSe_4)[(PMe_2Ph)_2Cu]_2$, but the environments around the Cu atoms in these two compounds are significantly different. The resonance at −18.1 ppm in the ^{77}Se NMR spectrum of **1** is also within the limits established for Se atoms bearing organic substituents.[25] Consistent with the solid-state structure, the ^{13}C NMR spectrum of $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ displays six resonances. The two peaks assigned to the cations are within expected ranges (15.5 and 52.7 ppm).[26] Free thiophene displays two chemical shifts at 124.4 and 126.2 ppm.[26] The spectrum of **1** contains four additional resonances attributed to the anion: 65.9, 124.5, 127.9, and 131.6 ppm. The C atom attached to Se should experience the most marked shift

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(14) Supplementary material.

(15) Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(16) Sheldrick, G. M. SHELXTL PC Version 4.1: An integrated system for solving, refining, and displaying crystal structures from diffraction data, Siemens Analytical X-Ray Instruments, Inc., Madison, WI.

(17) Sheldrick, G. M. SHELXL-92 Unix Beta-test Version.

(18) Zhou, G.; Guo, Y.; Zhang, S.; Tang, Y. *Acta Chim. Sin.* **1985**, *43*, 107–112.

(19) Jin, G.; Xin, X.; Dai, A.; Wu, J.; Wang, B.; Zheng, P. *Ziran Zazhi* **1987**, *10*, 873.

(20) Reaction of $[NPr_4]_2[WSe_4]$ with 4 equiv of CuCl in pyridine (py) at 170 °C affords $(\mu_4\text{-}WSe_4)[(py_2Cu)_2(pyClCu)_2]$. This compound crystallizes with four molecules in the monoclinic space group $C_{2h}^6 - C2/c$ in a cell of dimensions a = 14.748(3) Å, b = 12.670(3) Å, c = 20.270(4) Å, and β = 98.51(3)° (T = 113 K). Values of $R(F)$ = 0.102 and $R_w(F)$ = 0.106 for 209 variables and 3703 unique reflections were obtained from anisotropic refinement of the heavy atoms.[21] There is considerable disorder in the structure. The compound has analogues in the MoS$_4$ and WS$_4$ systems[18,19] but is the first reported example of a tetradentate WSe$_4$ group.

(21) Christuk, C. C.; Ibers, J. A. Unpublished results.

(22) Lipshutz, B. H.; Koerner, M.; Parker, D. A. *Tetrahedron Lett.* **1987**, *28*, 945–948.

(23) Although the crystal structure of $Li[(CN)Cu(C_4H_3S)]$ has not been determined, the reaction chemistry of this reagent is fully consistent with its formulation as lithium (2-thienyl)cyanocuprate[22] and hence as possessing a Cu–C bond. There is NMR evidence that the closely related compound $Li[MeCu(C_4H_3S)]$ possesses a Cu–C bond.[24]

(24) Lindstedt, E.-L.; Nilsson, M.; Olsson, T. *J. Organomet. Chem.* **1987**, *334*, 255–261.

(25) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223–266.

(26) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981.

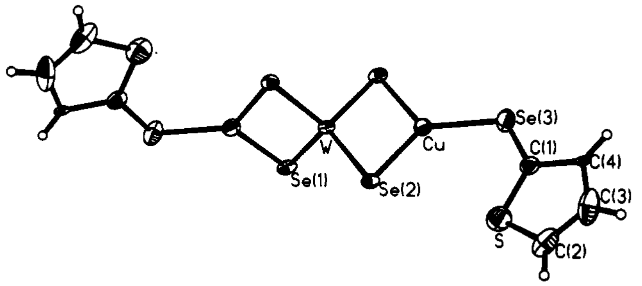

Figure 2. Structure of the $[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2^{2-}$ anion in $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ (**1**). For the non-hydrogen atoms the 50% probability ellipsoids are depicted.

Table III. Selected Bond Lengths [Å] and Angles [deg] for $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$[a]

W–Se(1)	2.338(1)	S–C(2)	1.667(14)
W–Se(2)	2.344(1)	S–C(1)	1.674(11)
W–Cu	2.696(2)	C(1)–C(4)	1.54(2)
Se(2)–Cu	2.331(2)	C(2)–C(3)	1.41(2)
Se(3)–C(1)	1.898(11)	C(3)–C(4)	1.40(2)
Se(1)–W–Se(1′)	109.14(6)	Cu–Se(2)–W	70.42(4)
Se(1)–W–Se(2)	109.97(4)	C(1)–Se(3)–Cu	105.5(3)
Se(1′)–W–Se(2)	109.31(4)	Se(3)–Cu–Se(2)	129.13(7)
Se(1)–W–Se(2′)	109.30(4)	Se(3)–Cu–Se(1′)	121.02(7)
Cu′–Se(1)–W	70.44(5)	Se(2)–Cu–Se(1′)	109.83(6)

[a] Symmetry transformation used to generate equivalent atoms: $-y + {}^3/_2, -x + {}^3/2, -z + 2$.

and thus is assigned to the resonance at 65.9 ppm. The remaining resonances are close to the expected region, but they reflect the inequivalencies of the carbon atoms within the thiophene ligand.

Structure. The structure of $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ (**1**) consists of well-separated anions and cations. The structure of the anion is shown in Figure 2. Selected metrical data for the anion are given in Table III, while complete metrical data are given in Table SIV.[14] This anion is most closely related structurally to anions in the Cu/MoS_4[1] and Cu/WS_4[27–29] systems. The present anion possesses a crystallographically imposed 2-fold axis. The W center is nearly tetrahedral (Se–W–Se angles varying from 109.14(6) to 109.97(4)°); it shows the least amount of distortion of the known WSe_4 compounds.[5,6] The geometry about the Cu atom is roughly trigonal with the angle that includes the metal-bridging Se atoms being significantly less (Se(2)–Cu–Se(1′) = 109.83(6)°) than the angles that involve the inserted Se atom ((Se(3)–Cu–Se(1′) = 121.02(7) and Se(3)–Cu–Se(2) = 129.13(7)°). Steric restrictions imposed by the thiophene moiety are evident in this last angle. The Cu–Se–C bond angle (105.5(3)°) is in the range expected for atoms in a bent environment.

W–Se bond lengths (2.338(1) and 2.344(1) Å) are within the range reported for other mixed-metal[1,4–6] species. The W–Cu distance, 2.696(2) Å, is the shortest reported in such systems and may be a manifestation of a weak W^{VI}–Cu^{I} interaction.[30] Bond lengths for the Cu and metal-bridging Se atoms are similar to those reported for analogous compounds[5,6] (2.331(2) and 2.336(2) Å) but are clearly longer than the $Cu\text{–}Se_{insertion}$ distance (2.284(2) Å).

Discussion

There are a few examples of selenium insertion into a metal–carbon bond. Through the use of the selenocyanate anion Se has been inserted at −90 °C into the metal–benzylidene bond in several $M(CO)_5$ systems, M = Cr, W.[7] Elemental Se can also be employed, but the reaction is less facile. Elemental Se has been employed as a source of Se for insertion into M–C bonds in $(\eta^5\text{-}RC_5H_4)_2MMe_2$[9] and in $(\eta^5\text{-}RC_5H_4)_2M(C_6H_4R')_2$[8] compounds, where M = Zr, Hf; R = H, *t*-Bu; and R′ = H, *p*-Me. These reactions were carried out in boiling heptane. But the present use of WSe_4^{2-} as a source of Se for insertion into a metal–carbon bond is unique.

2-Selenothiophene is a potential ligand for a variety of other metal systems, as it should be highly nucleophilic. The tellurium analogue, 2-tellurothiophene, has been ligated to a metal system by direct reaction.[31]

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Supplementary Material Available: Additional crystallographic details (Table SI), anisotropic displacement parameters (Table SII), hydrogen atom positions (Table SIII), and bond lengths and angles (Table SIV) for $[NEt_4]_2[\mu\text{-}WSe_4][(SC_4H_3)SeCu]_2$ (5 pages). Ordering information is given on any current masthead page.

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(27) Manoli, J.-M.; Potvin, C.; Sécheresse, F.; Marzak, S. *Inorg. Chim. Acta* **1988**, *150*, 257–268.

(28) Annan, T. A.; Kumar, R.; Mabrouk, H. E.; Tuck, D. G.; Chadha, R. K. *Polyhedron* **1989**, *8*, 865–871.

(29) Sécheresse, F.; Salis, M.; Potvin, C.; Manoli, J.-M. *Inorg. Chim. Acta* **1986**, *114*, L19–L23.

(30) Huffman, J. C.; Roth, R. S.; Siedle, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 4340–4341.

(31) Zhao, J.; Adcock, D.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1990**, *29*, 4358–4360.