Synthesis, Structure, and Spectroscopy of [PPh4]2[(NC)Cu(μ-Se)2M(μ-Se)2Cu(CN)]·CH3CN and [PPh4]2[(NC)Cu(μ-Se)2MSe2] (M = Mo, W)

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[PPh4]2[MoSe4] and [PPh4]2[WSe4] react with 2 equiv of CuCN in CH3CN to afford [PPh4]2[(NC)Cu(μ-Se)2Mo-(μ-Se)2Cu(CN)]·CH3CN (1) and [PPh4]2[(NC)Cu(μ-Se)2W(μ-Se)2Cu(CN)]·CH3CN (2), respectively. Compounds 1 and 2 are isostructural. Compound 1 crystallizes in the triclinic space group C_i^1-$P\overline{1}$ with two formula units in a cell of dimensions $a = 13.208(3)$ Å, $b = 14.254(3)$ Å, $c = 14.573(3)$ Å, $\alpha = 72.47(3)°$, $\beta = 74.09(3)°$, and $\gamma = 79.12(3)°$ at 113 K. Full anisotropic refinement of the structure on F_o^2 led to a value of $R(F) = 0.028$ for those 7546 data having $F_o^2 > 2\sigma(F_o^2)$. The [(NC)Cu(μ-Se)2Mo(μ-Se)2Cu(CN)]²⁻ anion of 1 comprises two CuCN fragments ligating the opposite edges of a tetrahedral [MoSe4]²⁻ moiety; the Cu−Mo−Cu angle is 179.13(2)°. Compounds 1 and 2 display an IR band at 2250 cm⁻¹, which may be assigned to a CN stretching mode of the CH3CN solvate. Such a solvate molecule was found in the crystal structure of 1. The ⁷⁷Se NMR spectra show a resonance at 1195 ppm for 1 and 920 ppm for 2. Addition of excess PMe2Ph to solutions of 1 and 2 results in the formation of [PPh4]2[(NC)Cu(μ-Se)2MoSe2] (3) and [PPh4]2[(NC)Cu(μ-Se)2WSe2] (4), respectively. Compounds 3 and 4 are isostructural. Compound 3 crystallizes in the monoclinic space group C_{2h}^6-$C2/c$ with four formula units in a cell of dimensions $a = 11.254(2)$ Å, $b = 20.153(4)$ Å, $c = 20.191(4)$ Å, and $\beta = 91.74(3)°$ at 113 K. Full anisotropic refinement of the structure on F_o^2 led to a value of $R(F) = 0.055$ for those 3588 reflections having $F_o^2 > 2\sigma(F_o^2)$. The [(NC)Cu(μ-Se)2MoSe2]²⁻ anion of 3, which has a crystallographically imposed 2-fold axis, comprises a CuCN fragment ligated across an edge of the tetrahedral [MoSe4]²⁻ moiety. The ⁷⁷Se NMR spectra show resonances at 1030 and 1820 ppm for compound 3 and at 782 and 1383 ppm for compound 4. The remaining NMR, IR, and electronic spectroscopic data of the four title compounds are also consistent with their solid-state structures.

Introduction

Although the reactivities of the [MoS4]²⁻ and [WS4]²⁻ anions have been extensively investigated,[1,2] the reactivities of the [MoSe4]²⁻ and [WSe4]²⁻ anions have not. Figure 1 presents sketches of relevant structures with M′:MQ4²⁻ ratios of 1:1 to 4:1 (M′ = Cu, Ag, or Au; M = Mo or W). In the sulfides, stoichiometric reactions of Cu(I) compounds with [MS4]²⁻ anions in ratios of 1:1 to 6:1 have afforded a rich structural chemistry.[3,4] In the selenides, structures with M′:[MSe4]²⁻ ratios of 2:1[5−9] (Figure 1b), 3:1[6,7] (Figure 1c), and 4:1[9] (Figure 1d) are known. The present study details the syntheses and characterization of four new selenides. While two have Cu:[MSe4]²⁻ ratios of 2:1, the other two have the previously unknown Cu:[MSe4]²⁻ ratio of 1:1 and thus expand the known structure types in the selenide system.

Experimental Section

Syntheses. All manipulations were carried out under a dry N2 atmosphere with the use of standard Schlenk-line techniques. [PPh4]2-

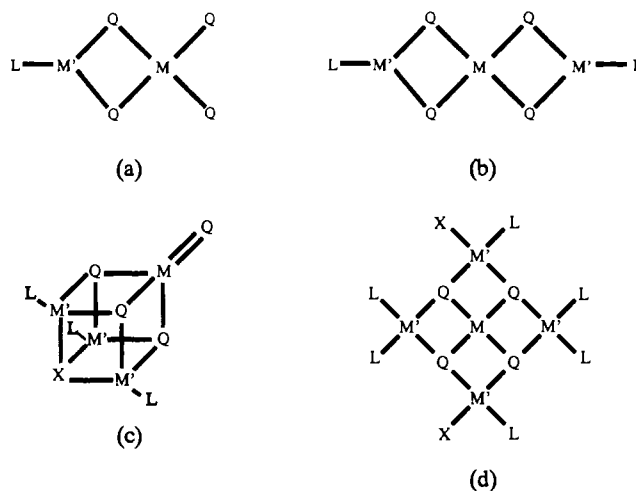**Figure 1.** Sketches of relevant structures in the [MQ4]²⁻ system (M = Mo, W; Q = S, Se; M′ = Cu, Ag, Au; L = ligand; X = Cl, Br). M′:[MQ4]²⁻ ratios are (a) 1:1, (b) 2:1, (c) 3:1, and (d) 4:1. Heterometallic sulfides are known for structure types a−d but heterometallic selenides have not been reported previously for structure type a.

[MoSe4] and [PPh4]2[WSe4] were synthesized by a literature method.[10] All solvents were distilled from appropriate drying agents under dry N2 before use. CuCN (Aldrich Chemical Co., Milwaukee, WI) and PMe2Ph (Strem Chemical Co., Newburyport, MA) were used as received. Microanalyses were performed by Oneida Research Services, Whitesboro, NY.

[PPh4]2[(NC)Cu(μ-Se)2Mo(μ-Se)2Cu(CN)]·CH3CN (1). [PPh4]2-[MoSe4] (1091 mg, 1.0 mmol) dissolved in CH3CN (100 mL) was added with stirring to a suspension of CuCN (180 mg, 2.0 mmol) in CH3CN

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(25 mL). After 5 min the solution turned wine-red. After the reaction mixture was stirred for 30 min at 25 °C, it was filtered through a medium-porosity sintered-glass frit to afford a purple powder and a clear red filtrate. Et$_2$O (430 mL) was layered on top of the filtrate and after 9 days dark red crystals of **1** (990 mg, 75%) were harvested. Anal. Calcd for C$_{52}$H$_{43}$Cu$_2$MoN$_3$P$_2$Se$_4$: C, 47.65; H, 3.31; N, 3.21; Se, 24.10. Found: C, 47.14; H, 3.24; N, 3.23; Se, 24.14. ^{77}Se NMR (DMF-d_7, ppm): δ 1195. UV−vis (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 334 (15 000), 361 (sh), 425 (3650), 484 (2630), 565 (sh), 598 (4980). IR (KBr, cm^{-1}): 2121, 2123, 2250.

[PPh$_4$]$_2$[(NC)Cu(μ-Se)$_2$W(μ-Se)$_2$Cu(CN)]·CH$_3$CN (2). [PPh$_4$]$_2$-[WSe$_4$] (590 mg, 0.5 mmol) and CuCN (90 mg, 1.0 mmol) were dissolved in CH$_3$CN (50 mL) to afford a bright red solution. After the reaction mixture was stirred for 30 min at 25 °C, it was filtered through a medium-porosity sintered-glass frit to provide a dark red powder and an orange-red filtrate. Et$_2$O (55 mL) was layered on top of the filtrate, and after 5 days red crystals of **2** (493 mg, 70%) were collected. Anal. Calcd for C$_{52}$H$_{43}$Cu$_2$N$_3$P$_2$Se$_4$W: C, 44.65; H, 3.10; N, 3.01; Se, 22.58. Found: C, 44.18; H, 2.94; N, 2.86; Se, 22.20. ^{77}Se NMR (DMF-d_7, ppm): δ 920. UV−vis (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 316 (16 900), 380 (sh), 424 (3570), 467 (4440), 497 (4010). IR (KBr, cm^{-1}): 2119, 2123, 2250.

[PPh$_4$]$_2$[(NC)Cu(μ-Se)$_2$MoSe$_2$] (3). [PPh$_4$]$_2$[MoSe$_4$] (1091 mg, 1.0 mmol) dissolved in CH$_3$CN (100 mL) was added to a suspension of CuCN (180 mg, 2.0 mmol) in CH$_3$CN (25 mL). After 5 min the solution turned wine-red. An excess of neat PMe$_2$Ph (2.5 mL) was then added. After the solution was stirred for 30 min at 25 °C, the purple reaction mixture was filtered through a medium-porosity sintered-glass frit to separate a small amount of dark purple powder from a clear magenta filtrate. Et$_2$O (180 mL) was layered on top of the filtrate, and after 2 days purple crystals of **3** (655 mg, 55%) were obtained. Anal. Calcd for C$_{49}$H$_{40}$CuMoNP$_2$Se$_4$: C, 49.87; H, 3.42; N, 1.19; Se, 26.76. Found: C, 49.90; H, 3.40; N, 1.16; Se, 26.05. ^{31}P NMR (DMF, ppm): δ 23.8. ^{77}Se NMR (DMF-d_7, ppm): δ 1030, 1820. UV−vis (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 351 (19 500), 511 (5700), 576 (4700). IR (KBr, cm^{-1}): 2129.

[PPh$_4$]$_2$[(NC)Cu(μ-Se)$_2$WSe$_2$] (4). [PPh$_4$]$_2$[WSe$_4$] (590 mg, 0.5 mmol) and CuCN (90 mg, 1.0 mmol) were dissolved in CH$_3$CN (50 mL). After it was stirred for 30 min at 25 °C the solution turned orange-red. An excess of neat PMe$_2$Ph (0.8 mL) was then added and the solution was stirred for an additional 5 min. The clear dark red solution was then filtered through a medium-porosity sintered-glass frit to yield a small amount of dark red powder and a clear red filtrate. Et$_2$O (200 mL) was layered on top of the filtrate and after 2 days red crystals of **4** (350 mg, 55%) were isolated. Anal. Calcd for C$_{49}$H$_{40}$CuNP$_2$Se$_4$W: C, 46.41; H, 3.18; N, 1.10; Se, 24.91. Found: C, 46.81; H, 3.18; N, 0.87; Se, 24.39. ^{31}P NMR (DMF, ppm): δ 23.8. ^{77}Se NMR (DMF-d_7, ppm): δ 782, 1383. UV−vis (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 312 (22 100), 438 (7270), 462 (6250). IR (KBr, cm^{-1}): 2129.

Physical Measurements. Electronic absorption spectra were obtained in the 280−900 nm region on a Cary-1E UV-visible spectrophotometer at 1 nm resolution. Infrared spectra were recorded over the expected cyanide region on a Mattson Galaxy FT-IR spectrometer at 0.5 cm^{-1} resolution through the use of pressed KBr pellets. The ^{77}Se NMR spectra for compounds **1** and **3** were obtained at 20 °C in 5 mm round-bottom tubes on a Varian VXR-300 spectrometer equipped with a tunable probe and deuterium lock, with a scanning frequency of 57 MHz, a delay time of 0.5 s, a pulse width of 16.5 μs, and an acquisition time of 0.300 s. The ^{77}Se NMR spectra for compounds **2** and **4** were obtained at 20 °C in 10-mm round-bottom tubes on a Varian Unity Plus 400 MHz spectrometer equipped with a tunable probe and deuterium lock, with a scanning frequency of 76 MHz, a delay time of 0.5 s, a pulse width of 14.5 μs, and an acquisition time of 0.640 s. All ^{77}Se NMR chemical shifts are referenced to the external secondary standard PhSeSePh at δ = 460 ppm. The chemical shift scale is based on (CH$_3$)$_2$Se at δ = 0.0 ppm. ^{31}P NMR spectra were obtained at 20 °C in 5-mm round-bottom tubes on a Gemini 300 spectrometer with automatic tuning capabilities and a deuterium lock. Chemical shifts are referenced to the external standard 85% H$_3$PO$_4$ at δ = 0 ppm.

Crystallographic Studies. Unit cells of the four title compounds were determined by least-squares refinement of centered setting angles of 25 reflections obtained at 113 K on an Enraf-Nonius CAD4

Table 1. Crystallographic Details for [PPh$_4$]$_2$[(NC)Cu(μ-Se)$_2$Mo(μ-Se)$_2$Cu(CN)]·CH$_3$CN (**1**) and [PPh$_4$]$_2$[(NC)Cu(μ-Se)$_2$Mo(μ-Se)$_2$] (**3**)^a

	1	3
formula	C$_{52}$H$_{43}$Cu$_2$MoN$_3$P$_2$Se$_4$	C$_{49}$H$_{40}$CuMoNP$_2$Se$_4$
fw	1310.69	1180.08
a, Å	13.208(3)	11.254(2)
b, Å	14.254(3)	20.153(4)
c, Å	14.573(3)	20.191(4)
α, deg	72.47(3)	90.00
β, deg	74.09(3)	91.74(3)
γ, deg	79.12(3)	90.00
V, Å^3	2499.1(9)	4577.2(15)
space group	C_i^1-$P\bar{1}$	C_{2h}^6-$C2/c$
Z	2	4
ϱ_{calcd}, g cm^{-3}	1.742	1.712
μ, cm^{-1}	41.06	40.24
T, K	113	113
$R(F_o)$,^{b} $F_o^2 > 2\sigma(F_o^2)$	0.028	0.055
$R_w(F_o^2)$,^{c} all data	0.073	0.131

^{a} Compounds **1** and **2** are isostructural. Compound **2** crystallizes in the space group $P\bar{1}$ in a cell of dimensions a = 13.204(4) Å, b = 14.241(5) Å, c = 14.580(2) Å, α = 72.42(2)°, β = 74.06(2)°, and γ = 79.19(3)° at 113 K. Compounds **3** and **4** are isostructural. Compound **4** crystallizes in space group $C2/c$ in a cell of dimensions a = 11.279(3) Å, b = 20.161(3) Å, c = 20.188(3) Å, and β = 91.67(2)° at 113 K. ^{b} $R(F_o)$ = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_w(F_o^2)$ = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$; w^{-1} = $\sigma^2(F_o^2) + (0.04F_o^2)^2$; w^{-1} = $\sigma^2(F_o^2)$, $F_o^2 < 0$.

diffractometer. Data sets were collected for compounds **1** and **3**. The intensities of six standard reflections, which were measured every 3 h, remained constant in both data collections. Crystallographic data for compounds **1** and **3** are listed in Table 1, and additional data are given in Table SI.[11]

Intensity profile data for compounds **1** and **3** were processed[12] and then corrected for absorption effects.[13] The positions of the heavy atoms were determined by direct methods,[14] and the positions of the remaining non-hydrogen atoms were found from successive difference electron density maps. In this and ensuing analyses the SHELXTL-PC graphics programs[14] were employed. The structures were refined on F^2 with use of the SHELXL-93 least-squares program.[15] All non-hydrogen atoms were refined anisotropically. For both structures the positions of the hydrogen atoms were calculated and were included in the final refinements. For those reflections having $F_o^2 > 2\sigma(F_o^2)$ the final cycle of least-squares refinement converged to values of $R(F_o)$ of 0.028 (compound **1**, 577 variables, 7546 observations) and 0.055 (compound **3**, 264 variables, 3588 observations). Final non-hydrogen atom positions and equivalent isotropic displacement parameters are given in Tables 2 and 3, anisotropic displacement parameters are provided in Tables SIV and SV,[11] and hydrogen atom positions are provided in Tables SVI and SVII.[11]

Results and Discussion

Synthesis. Compounds **1** and **2** have been synthesized by two different methods. The first, as described above in the protocol of **1**, involves the addition of a CH$_3$CN solution of 1 equiv of [PPh$_4$]$_2$[MSe$_4$] (M = Mo or W) to a suspension of 2 equiv of CuCN in CH$_3$CN. For **1**, the characteristic blue-purple color of [MoSe$_4$]$^{2-}$ is rapidly lost and a wine-red reaction mixture is formed, but for **2** the color change from [WSe$_4$]$^{2-}$ is less apparent. Despite these immediate color changes, a relatively long reaction time is used to ensure complete conversion of starting materials and to improve yield. No

(11) Supplementary material.
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Table 2. Atomic Positions ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[PPh_4]_2[(NC)Cu(\mu\text{-Se})_2Mo(\mu\text{-Se})_2Cu(CN)]\cdot CH_3CN$ (1)

	x	y	z	U (eq)
Mo(1)	8452(1)	2271(1)	10577(1)	17(1)
Cu(1)	8359(1)	1202(1)	12456(1)	21(1)
Cu(2)	8558(1)	3315(1)	8688(1)	23(1)
Se(1)	8517(1)	2886(1)	11880(1)	22(1)
Se(2)	8291(1)	581(1)	11178(1)	26(1)
Se(3)	10013(1)	2528(1)	9345(1)	26(1)
Se(4)	7001(1)	3081(1)	9909(1)	26(1)
C(1)	8226(3)	471(3)	13801(3)	20(1)
N(1)	8117(3)	71(2)	14627(3)	27(1)
C(2)	8651(3)	3990(3)	7336(3)	25(1)
N(2)	8706(3)	4404(3)	6513(3)	31(1)
P(1)	7844(1)	8192(1)	7362(1)	20(1)
C(111)	8897(3)	7860(3)	6411(3)	22(1)
C(112)	8942(3)	6959(3)	6189(3)	29(1)
C(113)	9741(3)	6711(3)	5454(3)	32(1)
C(114)	10509(3)	7333(3)	4923(3)	34(1)
C(115)	10476(3)	8215(3)	5139(3)	28(1)
C(116)	9672(3)	8486(3)	5890(3)	24(1)
C(121)	7747(3)	7124(3)	8422(3)	26(1)
C(122)	8671(4)	6526(3)	8607(4)	41(1)
C(123)	8616(4)	5709(4)	9410(4)	47(1)
C(124)	7650(4)	5476(3)	10035(3)	41(1)
C(125)	6737(4)	6073(3)	9859(3)	36(1)
C(126)	6784(3)	6898(3)	9062(3)	26(1)
C(131)	6626(3)	8534(3)	6959(3)	19(1)
C(132)	5733(3)	8948(3)	7543(3)	26(1)
C(133)	4787(3)	9221(3)	7250(3)	31(1)
C(134)	4724(3)	9090(4)	6367(3)	35(1)
C(135)	5610(3)	8695(3)	5771(3)	33(1)
C(136)	6557(3)	8416(3)	6068(3)	25(1)
C(141)	8097(3)	9238(3)	7674(3)	20(1)
C(142)	7739(3)	10189(3)	7184(3)	28(1)
C(143)	7906(4)	10996(3)	7437(4)	36(1)
C(144)	8431(3)	10855(3)	8183(3)	32(1)
C(145)	8808(3)	9914(3)	8657(3)	31(1)
C(146)	8646(3)	9097(3)	8407(3)	24(1)
P(2)	5548(1)	6493(1)	12829(1)	16(1)
C(211)	6746(3)	6154(3)	13260(3)	18(1)
C(212)	7703(3)	5919(3)	12632(3)	25(1)
C(213)	8622(3)	5641(3)	12983(3)	30(1)
C(214)	8574(3)	5593(3)	13956(3)	30(1)
C(215)	7631(3)	5827(3)	14579(3)	27(1)
C(216)	6709(3)	6116(3)	14232(3)	21(1)
C(221)	5183(3)	5431(3)	12625(3)	18(1)
C(222)	5896(3)	4583(3)	12624(3)	22(1)
C(223)	5615(3)	3772(3)	12455(3)	31(1)
C(224)	4628(3)	3802(3)	12304(3)	31(1)
C(225)	3907(3)	4643(3)	12300(3)	28(1)
C(226)	4171(3)	5459(3)	12474(3)	24(1)
C(231)	4523(3)	6932(3)	13740(3)	17(1)
C(232)	4473(3)	7902(3)	13800(3)	21(1)
C(233)	3743(3)	8209(3)	14564(3)	22(1)
C(234)	3071(3)	7569(3)	15257(3)	25(1)
C(235)	3112(3)	6615(3)	15197(3)	26(1)
C(236)	3836(3)	6287(3)	14437(3)	24(1)
C(241)	5749(3)	7478(3)	11711(3)	17(1)
C(242)	4997(3)	7739(3)	11135(3)	23(1)
C(243)	5122(3)	8534(3)	10304(3)	28(1)
C(244)	5982(4)	9063(3)	10039(3)	30(1)
C(245)	6706(4)	8813(3)	10614(3)	30(1)
C(246)	6594(3)	8027(3)	11454(3)	27(1)
N(21)	6949(3)	8516(3)	13452(3)	39(1)
C(21)	7840(4)	8418(3)	13321(3)	27(1)
C(20)	8994(3)	8291(3)	13139(4)	34(1)

Table 3. Atomic Positions ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[PPh_4]_2[(NC)Cu(\mu\text{-Se})_2MoSe_2]$ (3)

	x	y	z	U (eq)
Mo(1)	0	303(1)	2500	15(1)
Se(1)	1074(1)	990(1)	3257(1)	19(1)
Se(2)	1299(1)	−337(1)	1928(1)	23(1)
Cu(1)	0	1630(1)	2500	21(1)
P(1)	−4135(2)	−1329(1)	−740(1)	18(1)
C(11)	−2796(6)	−1103(4)	−292(3)	21(1)
C(12)	−1685(6)	−1205(4)	−553(3)	25(2)
C(13)	−675(7)	−970(5)	−216(3)	33(2)
C(14)	−778(7)	−655(4)	382(3)	31(2)
C(15)	−1877(7)	−552(4)	648(3)	30(2)
C(16)	−2888(7)	−780(4)	311(3)	28(2)
C(21)	−5192(6)	−1605(4)	−155(3)	21(1)
C(22)	−4838(8)	−2078(4)	328(3)	32(2)
C(23)	−5654(9)	−2310(4)	770(3)	40(2)
C(24)	−6807(8)	−2068(5)	760(3)	37(2)
C(25)	−7167(7)	−1607(5)	294(4)	42(2)
C(26)	−6353(7)	−1372(4)	−162(3)	28(2)
C(31)	−4689(6)	−622(3)	−1179(3)	18(1)
C(32)	−4194(6)	3(4)	−1091(3)	22(1)
C(33)	−4699(7)	543(3)	−1432(3)	24(2)
C(34)	−5683(6)	456(4)	−1848(3)	25(2)
C(35)	−6150(6)	−175(4)	−1947(3)	24(2)
C(36)	−5668(6)	−713(4)	−1614(3)	22(1)
C(41)	−3876(6)	−1970(3)	−1333(3)	19(1)
C(42)	−3280(6)	−1790(4)	−1904(3)	24(2)
C(43)	−3035(7)	−2273(4)	−2369(3)	31(2)
C(44)	−3360(7)	−2924(4)	−2271(3)	34(2)
C(45)	−3989(7)	−3103(4)	−1707(3)	32(2)
C(46)	−4215(7)	−2624(4)	−1235(3)	28(2)
C(100)	0	2569(6)	2500	30(2)
N(100)	0	3128(5)	2500	46(3)

as shown in (1). The *in situ* ^{31}P NMR spectrum for each

$[PPh_4]_2[(NC)Cu(\mu\text{-Se})_2M(\mu\text{-Se})_2Cu(CN)]$ +

$3PMe_2Ph \rightarrow [PPh_4]_2[(NC)Cu(\mu\text{-Se})_2MSe_2]$ +

$(PMe_2Ph)_3Cu(CN)$ (M = Mo or W) (1)
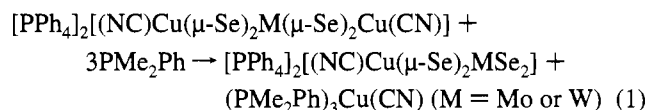
reaction shows a singlet at 18.1 ppm, consistent with the presence of $(PMe_2Ph)_3Cu(CN)$.[16]

Copper(I) thiometallate complexes with $Cu:[MS_4]^{2-}$ ratios of 1:1 to 6:1 and a variety of ligands have been recently reviewed.[4] The anions of compounds **1-4** have sulfur analogues: those of **1** and **2** have been crystallized as the monohydrated $AsPh_4^+$ salts,[17] whereas those of **3** and **4** have been isolated as the PPh_4^+,[18] NMe_4^+,[18] and $N(n\text{-Pr})_4^+$ salts.[17] The corresponding selenide chemistry is not as well developed. The only related selenides are $[(PMe_2Ph)M(\mu\text{-Se})_2W(\mu\text{-Se})_2M(PMe_2Ph)]$ (M = Cu, Ag, and Au),[7] $[(PMePh_2)Au(\mu\text{-Se})_2W(\mu\text{-Se})_2Au(PMePh_2)]$,[7] $[(PPh_3)_2Au(\mu\text{-Se})_2W(\mu\text{-Se})_2Au(PPh_3)]\cdot DMF$,[6] and $[(PPh_3)_2Ag(\mu\text{-Se})_2W(\mu\text{-Se})_2Ag(PPh_3)]\cdot 0.8CH_2Cl_2$.[5]

Structures. The crystal structure of $[PPh_4]_2[(NC)Cu(\mu\text{-Se})_2Mo(\mu\text{-Se})_2Cu(CN)]\cdot CH_3CN$ (1) consists of well-separated cations, anions, and solvent molecules. The PPh_4^+ cations have distances and angles in the expected ranges (P—C = 1.784(3)−1.802(3) Å; C—C = 1.370(5)−1.404(5) Å; C—P—C angles = 107.1(2)−111.1(1)°) (Table SII).[11] The anion of **1** comprises two CuCN fragments ligating opposite edges of a tetrahedral $[MoSe_4]^{2-}$ moiety. Distances from the Mo atom to the four bridging Se atoms (Se_b) range from 2.331(1) to 2.346(1) Å, while the Se_b—Mo—Se_b angles range from

starting materials have been detected as contaminants in the harvested crystals by either UV−vis spectrophotometry or ^{77}Se NMR spectroscopy. The second synthetic method, as described above in the protocol of **2**, is the direct combination of the solid reagents followed by dissolution and reaction in CH_3CN. In either case, compounds **3** and **4** may be synthesized by the reaction of **1** and **2**, respectively, with excess PMe_2Ph,

(16) Addition of excess PMe_2Ph to $(PPh_3)_3CuCl$ in CH_3CN results in a new ^{31}P NMR resonance at 19.6 ppm.

(17) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519−2528.

(18) Müller, A.; Dartmann, M.; Römer, C.; Clegg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1060−1061.
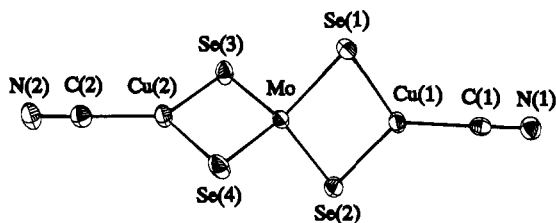
Figure 2. Structure of the [(NC)Cu(μ-Se)₂Mo(μ-Se)₂Cu(CN)]²⁻ anion in [PPh₄]₂[(NC)Cu(μ-Se)₂Mo(μ-Se)₂Cu(CN)]·CH₃CN (1). For all atoms the 50% probability ellipsoids are depicted.
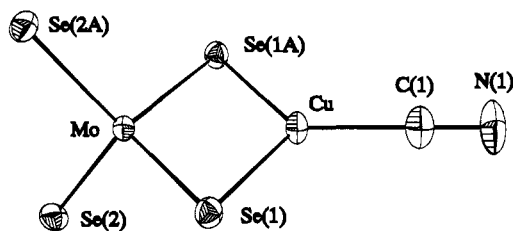
Figure 3. Structure of the [(NC)Cu(μ-Se)₂Mo(Se)₂]²⁻ anion in [PPh₄]₂[(NC)Cu(μ-Se)₂Mo(Se)₂] (3). For all atoms the 50% probability ellipsoids are depicted.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [PPh₄]₂[(NC)Cu(μ-Se)₂Mo(μ-Se)₂Cu(CN)]·CH₃CN (1)

Mo—Se(1)	2.346(1)	Cu(2)—C(2)	1.897(3)
Mo—Se(2)	2.331(1)	Cu(1)—Se(1)	2.321(1)
Mo—Se(3)	2.338(1)	Cu(1)—Se(2)	2.317(1)
Mo—Se(4)	2.338(1)	Cu(2)—Se(3)	2.327(1)
Mo—Cu(1)	2.684(1)	Cu(2)—Se(4)	2.325(1)
Mo—Cu(2)	2.685(1)	C(1)—N(1)	1.144(4)
Cu(1)—C(1)	1.903(3)	C(2)—N(2)	1.151(4)
Se(2)—Mo—Se(4)	109.23(3)	Se(2)—Cu(1)—Se(1)	110.29(3)
Se(2)—Mo—Se(3)	109.83(4)	C(1)—Cu(1)—Mo	177.44(9)
Se(4)—Mo—Se(3)	109.28(3)	Se(2)—Cu(1)—Mo	54.96(2)
Se(2)—Mo—Se(1)	108.93(3)	Se(1)—Cu(1)—Mo	55.33(3)
Se(4)—Mo—Se(1)	110.44(3)	C(2)—Cu(2)—Se(4)	125.73(10)
Se(3)—Mo—Se(1)	109.12(3)	C(2)—Cu(2)—Se(3)	124.09(10)
Se(2)—Mo—Cu(1)	54.48(3)	Se(4)—Cu(2)—Se(3)	110.11(3)
Se(4)—Mo—Cu(1)	125.77(3)	C(2)—Cu(2)—Mo	177.07(10)
Se(3)—Mo—Cu(1)	124.95(3)	Se(4)—Cu(2)—Mo	55.08(3)
Se(1)—Mo—Cu(1)	54.45(2)	Se(3)—Cu(2)—Mo	55.04(3)
Se(2)—Mo—Cu(2)	124.74(3)	Cu(1)—Se(1)—Mo	70.22(3)
Se(4)—Mo—Cu(2)	54.60(3)	Cu(1)—Se(2)—Mo	70.56(3)
Se(3)—Mo—Cu(2)	54.68(3)	Cu(2)—Se(3)—Mo	70.28(3)
Se(1)—Mo—Cu(2)	126.33(2)	Cu(2)—Se(4)—Mo	70.32(3)
Cu(1)—Mo—Cu(2)	179.13(2)	N(1)—C(1)—Cu(1)	176.8(3)
C(1)—Cu(1)—Se(2)	125.75(9)	N(2)—C(2)—Cu(2)	179.5(3)
C(1)—Cu(1)—Se(1)	123.88(9)	N(21)—C(21)—C(20)	179.1(4)

108.93(3) to 110.44(3)°. The Cu—Mo distances are 2.684(1) and 2.685(1) Å. There is a small distortion from ideal D_{2d} symmetry of the anion as a result of bending along the N—C—Cu—Mo—Cu—C—N axis that results in a Cu—Mo—Cu angle of 179.13(2)° and Cu—C—N angles of 176.8(3) and 179.5(3)°. The structure of the anion in **1** is shown in Figure 2 while important metrical data are presented in Table 4.

The crystal structure of [PPh₄]₂[(NC)Cu(μ-Se)₂MoSe₂] (3) also consists of well-separated cations and anions. The PPh₄⁺ cation has distances and angles in the normal ranges (P—C = 1.788(6)−1.794(6) Å, C—C = 1.374(9)−1.406(9) Å, C—P—C angles = 107.8(3)−111.8(3)°) (Table SIII).[11] The Mo, Cu, C, and N atoms of the anion in **3** all lie on a crystallographic 2-fold axis. As expected, within the anion the Mo—Se$_{terminal}$ distance of 2.288(1) Å is shorter than the Mo—Se$_b$ distance of 2.368(1) Å. The Cu—Mo distance is 2.675(1) Å. The Se—Mo—Se angles range from 108.39(5) to 111.39(5)°. The structure of the anion in **3** is shown in Figure 3 while important metrical data are presented in Table 5. The Mo—Se$_t$ distance in **3** is

Table 5. Selected Bond Distances (Å) and Angles (deg) for [PPh₄]₂[(NC)Cu(μ-Se)₂MoSe₂] (3)

Mo—Se(1)	2.368(1)	Cu—Se(1)	2.313(1)
Mo—Se(2)	2.288(1)	Cu—C(1)	1.887(10)
Mo—Cu	2.674(1)	C(1)—N(1)	1.133(14)
Se(2)—Mo—Se(2′)	111.39(5)	Cu—Se(1)—Mo	69.67(4)
Se(2)—Mo—Se(1)	109.50(3)	C(1)—Cu—Se(1)	123.86(3)
Se(2)—Mo—Se(1′)	109.00(3)	C(1)—Cu(1)—Mo	180
Se(1)—Mo—Se(1′)	108.39(5)	Se(1)—Cu—Mo	56.14(3)
Se(1)—Mo—Cu	54.19(2)	N(1)—C(1)—Cu	180
Se(2)—Mo—Cu	124.31(2)		

similar to that in the [PPh₃]₃[Cu₃Cl(MoSe₄)] cubane (2.226(5) Å)[6] and in the [MoSe₄]²⁻ dianion (2.293(1) Å).[10] There have been no previously reported compounds in which Se atoms bridge a Mo atom and a single Cu center, but there are two examples in which Se atoms bridge a Mo atom and two Cu atoms.[6] In these cases the Mo—Se$_b$ distances are similar to those found in the anions of **1** and **3**. The Cu—Mo distances in both structures are consistent with a Cu^I—Mo^{VI} interaction. All other distances in the anions are within the expected ranges. The Se—Mo—Se angles in both anions deviate less than 2° from ideal tetrahedral values.

Spectroscopy. Both compounds **1** and **2** show three bands in the CN⁻ region of their IR spectra. The band at 2250 cm⁻¹ in both is typical for the CN⁻ stretch of aliphatic nitriles and this absorbance we assign to the CH₃CN solvent molecules in the structures. The other two are from the anions. The IR spectra of compounds **3** and **4** each show a ligand band at 2129 cm⁻¹.

The electronic spectra for compounds **1-4** show intense bands in the UV region with weaker bands in the visible region. The patterns for both types of anions are dominated by the internal transitions of the [MSe₄]²⁻ moiety, as has been described in detail for the parallel sulfide chemistry.[17]

The ³¹P NMR spectra of compounds **3** and **4** each show only a singlet at 23.8 ppm, which is attributable to the PPh₄⁺ cation. Thus in neither compound is PMe₂Ph ligated to the metal center.

⁷⁷Se NMR chemical shifts of compounds that are relevant to the following discussion are presented in Table 6. Earlier studies in this laboratory mapped out a wide range of ⁷⁷Se NMR chemical shifts in soluble transition-metal selenide anions.[19] The present results are consistent with those results, in particular with resonances of Se atoms bonded to a third-row metal being shifted upfield from Se bonded to a second-row metal and with the resonances of δ(Se$_{terminal}$) being greater than δ(Se$_{bridging}$). Comparisons of the resonances of compounds **1** and **2** (1195 vs 920 ppm) and compounds **3** and **4** (1030 and 1820 vs 782 and 1383 ppm) illustrate the first trend, while assignment of the upfield resonances to the Se$_b$ atoms and the downfield resonances to the Se$_t$ atoms in the structures of **3** and **4** relies on the second trend.

The recently reported compound [NEt₄]₂[(SC₄H₃)SeCu-(μ-Se)₂W(μ-Se)₂CuSe(SC₄H₃)],[9] which has δ(Se$_b$) of 906 ppm, is similar in structure and charge distribution to the anion of **2** because both involve the ligation of a [WSe₄]²⁻ moiety by two neutral CuL fragments. Hence the ⁷⁷Se chemical shifts are very similar. The compound [PPh₄]₂[(Se₂)Ni(μ-Se)₂WSe₂],[20] which has a value of δ(Se$_b$) of 855 ppm, is similar to the anion of **4** in that formally they both have one neutral fragment ligating a [WSe₄]²⁻ moiety. But since the heterometals are different, a larger difference in their chemical shifts is not surprising. In the comparison of compounds **1** and **2** with compounds **3** and

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Table 6. ^{77}Se Chemical Shifts (δ, ppm) for Heterometallic Selenides

species	chem shifts[a]	ref
[MoSe$_4$]$^{2-}$	t 1643	22
[WSe$_4$]$^{2-}$	t 1235	23
[(NC)Cu(μ-Se)$_2$Mo(μ-Se)$_2$Cu(CN)]$^{2-}$	b 1195	this work
[(NC)Cu(μ-Se)$_2$W(μ-Se)$_2$Cu(CN)]$^{2-}$	b 920	this work
[(NC)Cu(μ-Se)$_2$MoSe$_2$]$^{2-}$	t 1820, b 1030	this work
[(NC)Cu(μ-Se)$_2$WSe$_2$]$^{2-}$	t 1383, b 782	this work
[(C$_4$H$_3$S)SeCu(μ-Se)$_2$W(μ-Se)$_2$CuSe(C$_4$H$_3$S)]$^{2-}$	b 906, o −18.1	9
[(Se$_2$)Ni(μ-Se)$_2$WSe$_2$]$^{2-}$	t 1399, b 855, mbr 608	20
[Se$_2$W(μ-Se)$_2$Ni(μ-Se)$_2$WSe$_2$]$^{2-}$	t 1628, b 994	20
[Se$_2$W(μ-Se)$_2$Pd(μ-Se)$_2$WSe$_2$]$^{2-}$	t 1673, b 1135	20
[Se$_2$W(μ-Se)$_2$Pt(μ-Se)$_2$WSe$_2$]$^{2-}$	t 1627, b 949	21
(PMe$_2$Ph)Cu(μ-Se)$_2$W(μ-Se)$_2$Cu(PMe$_2$Ph)	b 1044	7
(PMe$_2$Ph)Ag(μ-Se)$_2$W(μ-Se)$_2$Ag(PMe$_2$Ph)	b 1092	7
(PMe$_2$Ph)Au(μ-Se)$_2$W(μ-Se)$_2$Au(PMe$_2$Ph)	b 1234	7
(PMePh$_2$)Au(μ-Se)$_2$W(μ-Se)$_2$Au(PMePh$_2$)	b 1244	7
{[(PPh$_3$)Cu]$_3$[μ^3-WSe$_4$]Cl}	t 1651, b 1232	7

[a] Key: t = terminally bonded Se atom; b = bridging Se atom; mbr = metal-bound ring Se atom; o = Se atom bound to organic fragment.

4, the singlet assigned to the four equivalent Se$_b$ atoms of the symmetric anions splits into two singlets assigned to the Se$_b$ and Se$_t$ resonances of the asymmetric anions; in both cases, the Se$_b$ resonance is shifted upfield while the Se$_t$ resonance is shifted downfield. This observation indicates a shift in electron density away from the Se$_t$ centers toward the CuCN fragment. Thus the Se$_b$ atoms are shielded and the Se$_t$ atoms are deshielded relative to the Se$_b$ nuclei in the symmetric anions.

The other heterometallic selenide anions for which there are ^{77}Se NMR data available are in the compounds [PPh$_4$]$_2$[Se$_2$W-(μ-Se)$_2$M(μ-Se)$_2$WSe$_2$] (M = Ni,[20] Pd,[20] Pt[21]). The central heterometal affects the chemical shifts of both bridging and terminal Se atoms. The chemical shifts for the Pd anion are shifted downfield from those of the Ni or Pt anions in accordance with the trend discussed above. In addition, the heterometal affects the chemical shift of the Se$_b$ atoms more than that of the Se$_t$ atoms, presumably because of its closer proximity to the Se$_b$ atoms. A different trend is found[7] for the chemical shifts of the Se$_b$ nuclei in the three neutral compounds [(Me$_2$PhP)M'(μ-Se)$_2$W(μ-Se)$_2$M'(PMe$_2$Ph)] (M' = Cu, Ag, Au).

Supplementary Material Available: Additional crystallographic details (Table SI), complete listings of bond distances and angles for 1 (Table SII) and 3 (Table SIII), anisotropic displacement parameters for 1 (Table SIV) and 3 (Table SV), and hydrogen atom positions for 1 (Table SVI) and 3 (Table SVII) (13 pages). Ordering information is given on any current masthead page.

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