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Chemistry of the Tetraselenomolybdate Anion: Syntheses, Spectroscopic Results, and Structural Characterizations of Polynuclear Mo−Cu−Se Compounds Containing Thiolate Ligands

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In the study on the reactivity of tetraselenomolybdate, a DMF solution of $[Et_4N]_2[MoSe_4]$ was found to react with 3 equiv of CuCl in the presence of NaS_2CNR_2 [$R_2 = Et_2$, C_5H_{10}, $(PhCH_2)_2$, Me_2] to give a series of Mo−Cu−Se compounds, $[Et_4N]_2[MoCu_3Se_4(R_2NCS_2)_3]$ ($R_2 = Et_2$ (**1a**), C_5H_{10} (**1b**), $(PhCH_2)_2$ (**1c**)) and $[Et_4N]_2[MoCu_4Se_4(Me_2NCS_2)_4]$ (**2**). Furthermore, the reaction of **2** or $[Et_4N]_2[MoSe_4(CuCN)_2]$ with $[Et_4N]_2[Cu(SPh)_3]$ in DMF/MeCN afforded a polynuclear Mo−Cu−Se cluster compound, $[Et_4N]_4[MoCu_{10}Se_4(PhS)_{12}]$ (**3**). $[Et_4N]_2[MoCu_3Se_4(Et_2NCS_2)_3]$ (**1a**) crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 12.949(3)$ Å, $b = 13.339(3)$ Å, $c = 29.744(6)$ Å, $V = 5137.6$ Å^3, and $Z = 4$. Full anisotropic refinements of the structure led to convergence with a value of $R = 0.052$ ($R_w = 0.055$) for 453 variables and 6854 reflections ($F > 4.0\sigma(F)$). The $[MoCu_3Se_4(Et_2NCS_2)_3]^{2-}$ anion in **1a** comprises three Et_2NCS_2Cu fragments linked by a slightly distorted tetrahedral $MoSe_4$ moiety. Compound **2** crystallizes in the orthorhombic space group *Pbca* with cell constants $a = 14.600(3)$ Å, $b = 18.765(4)$ Å, $c = 37.781(8)$ Å, $V = 10351$ Å^3, and $Z = 8$. Anisotropic refinements with 5328 reflections ($F > 4.0\sigma(F)$) and 460 parameters for all non-hydrogen atoms yielded the values of $R = 0.075$ and $R_w = 0.080$. The $[MoCu_4Se_4(Me_2NCS_2)_4]^{2-}$ anion structure of **2**, which possesses a pseudo D_{2d} symmetry of the $MoSe_4Cu_4$ core and a nearly planar $MoCu_4$ array, consists of four Me_2NCS_2Cu fragments coordinated across four edges of the tetrahedral $[MoSe_4]^{2-}$ moiety. The compound $[Et_4N]_4[MoCu_{10}Se_4(PhS)_{12}]$ (**3**) crystallizes in the tetragonal space group $I\bar{4}$ with cell dimensions $a = 18.344(3)$ Å, $c = 18.368(4)$ Å, $V = 6180.9$ Å^3, and $Z = 2$. A value of $R = 0.079$ ($R_w = 0.084$) for 218 parameters and 3314 observations ($F > 4.0\sigma(F)$) was obtained from anisotropic refinements of the non-hydrogen atoms. The $[MoCu_{10}Se_4(PhS)_{12}]^{4-}$ anion structure of **3** can be described as six Cu atoms bonded across the six edges of a central $MoSe_4$ tetrahedron, forming an octahedral $MoSe_4Cu_6$ array, to which the other four Cu atoms are added in a tetrahedral array bridged by 12 μ-SPh ligands. The ^{95}Mo NMR spectra of the all compounds in DMF show a single resonance peak. Their chemical shifts are dependent on the deshielding effect from the number of the Cu atoms around Mo atom and the structures of the compounds. The ^{1}H NMR, IR, and electronic spectroscopic data of these compounds are also consistent with their solid-state structures.

Introduction

The chemistry of $[MS_4]^{2-}$ (M = Mo, W) anions and their related compounds has been extensively investigated owing to their relevance to biological systems, rich structural chemistry, and special reactive properties as well as potential application in nonlinear optical materials,[1−3] whereas that of $[MSe_4]^{2-}$ (M = Mo, W) anions and their related compounds have received attention only in recent years.[4] Up to the present, only a few examples of compounds containing $[MSe_4]^{2-}$ unit have been known.[5−8] Ibers has studied interactions of $[WSe_4]^{2-}$ or $[MoSe_4]^{2-}$ with the coinage-metal cations Cu^+, Ag^+, Au^+, and Ni^{2+} and reported successively a number of coinage-metal/MSe_4^{2-} (M = Mo, W) complexes with linear, cuboidal, and planar skeletons,[6] in which the tetraselenometalate $[MSe_4]^{2-}$ (M = Mo, W) acts as a versatility ligand coordinating to one to four coinage-metal M′ (M′ = Cu, Ag, Au) atoms.

Our studies on the reaction system consisting of MS_4^{2-} (M = Mo, W), CuX (X = Cl and Br), and/or $R_2NCS_2^-$ ligands

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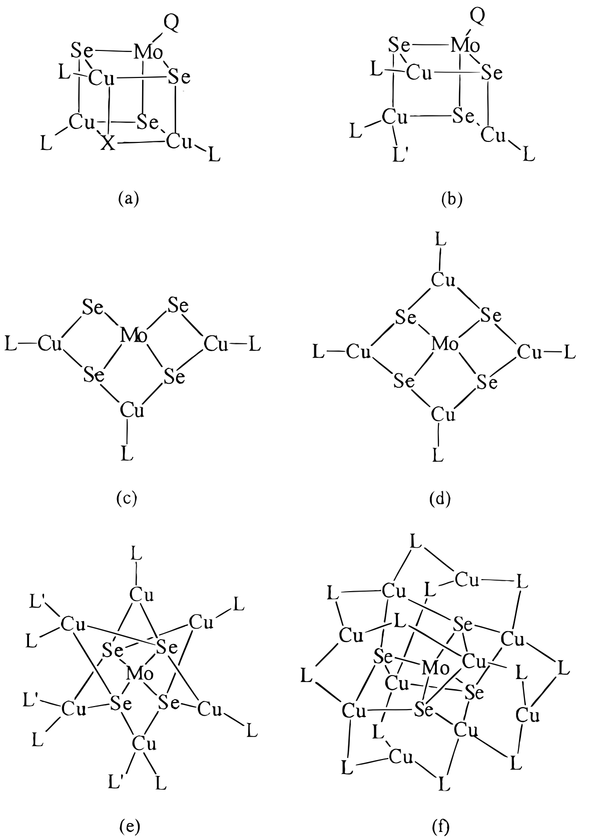

Figure 1. Sketches of some possible configurations of polynuclear Mo−Cu−Se molecular clusters. Configurations (a) and (b) are known, (c), (d), and (f) will be described in this work, but (e) has not been reported.

have allowed us to isolate a series of heterometallic sulfide complexes, such as $[MCu_3S_4(R_2NCS_2)_3]^{2-}$ (planar complexes),[9] $[S_2M_2Cu_4S_6(R_2NCS_2)_3]^{2-}$ (bibutterfly complexes),[10] $[S_2M_2Cu_5S_6(R_2NCS_2)_3]^{2-}$ (double defective cubane clusters),[11] and polynuclear $[MCu_{10}S_4X_{12}]^{4-}$.[12] For the extension of our studies, we have recently turned our attention to the exploration of the chemistry of selenide system including $MoSe_4^{2-}$/CuCl/L (L = Py, $R_2NCS_2^-$, PhS^-). In this system, some possible configurations of polynuclear Mo−Cu−Se molecular clusters are sketched in Figure 1. The configuration (a) is a so-called cubanelike structure, which has already been prepared and structurally characterized.[6a,8] We have recently isolated and characterized a compound of defective cubanelike $OMoSe_3Cu_3$ cluster core with mixed pyridine and chloride ligands,[13] which belongs to configuration (b). In this paper, we wish to describe the syntheses and spectroscopic properties of a series of Mo−Cu−Se compounds containing thiolate ligands and structrues with $MoCu_3$ planar (Figure 1c), $MoCu_4$ planar (Figure 1d), and polynuclear $MoCu_{10}$ clusters (Figure 1f), which will expand the known structure types in the selenide system.

Experimental Section

Syntheses. All syntheses and manipulations were performed in oven-dried glassware under a purified dinitrogen atmosphere using standard Schlenk techniques. The solvents were purified by conventional methods and degassed prior to use. All elemental analyses were carried out by the Elemental Analysis Laboratory in this Institute. $[Et_4N]_2[MoSe_4]$ was prepared by an improvement on the literature method[14] and our previous report.[8b] $[Et_4N]_2[Cu(SPh)_3]$[15] and $[Et_4N]_2$-$[MoSe_4(CuCN)_2]$[6c] were prepared as reported. Reagents R_2NCS_2Na (R_2 = Me_2, Et_2, C_5H_{10}, $(PhCH_2)_2$) were synthesized from the reaction of R_2NH, NaOH, and CS_2 in water. CuCl was purchased from Beijing Hongxin Huagong Chang and used without further purification.

$[Et_4N]_2[MoCu_3Se_4(Et_2NCS_2)_3]$ (1a). A solution of $[Et_4N]_2[MoSe_4]$ (0.17 g, 0.25 mmol) and CuCl (0.076 g, 0.75 mmol) in DMF (10 mL) was stirred for 10 min at room temperature. The color of the solution turned quickly from blue to red-brown, and some brown precipitate appeared gradually. Upon addition of a solution of Et_2NCS_2Na (0.095 g, 0.55 mmol) in DMF (5 mL), the red-brown solution immediately turned dark-green and all precipitate was dissolved; the solution appeared dark red when light was shined through it. The resultant solution was stirred for about 1 h and then filtered. The filtrate was covered with a layer of Et_2O (20 mL). After 1 week, dark-red crystals of **1a** suitable for X-ray crystallographic analysis were collected and washed with MeOH and Et_2O, yield 0.11 g (33.3%). Anal. Calcd for $C_{31}H_{70}N_5MoCu_3Se_4S_6$: C, 28.5; H, 5.40; N, 5.36; S, 14.7; Cu, 14.6. Found: C, 29.8; H, 6.15; N, 5.42; S, 13.9; Cu, 13.3.

$[Et_4N]_2[MoCu_3Se_4(C_5H_{10}NCS_2)_3]$ (1b). To a slurry of CuCl (0.076 g, 0.75 mmol) and $C_5H_{10}NCS_2Na$ (0.11 g, 0.60 mmol) in DMF (10 mL) was added a solution of $[Et_4N]_2[MoSe_4]$ (0.17 g, 0.25 mmol) in DMF (10 mL). The mixture was stirred for 1 h at room temperature, resulting in a dark-green solution with a small amount of precipitate. After the mixture was filtered, the filtrate was added to 20 mL of Et_2O to allow the precipitation of the product. This crude product was recrystallized from mixed DMF/THF (1:3) solvent to give black-red microcrystals of **1b**, which were collected and washed with MeOH and Et_2O, yield 0.10 g (29.4%). Anal. Calcd for $C_{34}H_{70}N_5MoCu_3$-Se_4S_6: C, 30.4; H, 5.25; N, 5.21; S, 14.3; Cu, 14.2. Found: C, 31.1; H, 5.15; N, 5.62; S, 13.8; Cu, 13.9.

$[Et_4N]_2[MoCu_3Se_4\{(PhCH_2)_2NCS_2\}_3]$ (1c). A mixture of CuCl (0.076 g, 0.75 mmol), $(PhCH_2)_2NCS_2Na$ (0.18 g, 0.60 mmol) and $[Et_4N]_2[MoSe_4]$ (0.17 g, 0.25 mmol) in DMF (20 mL) was stirred for 2 h at room temperature. After filtration, the filtrate was covered with a layer of THF (30 mL) and left at 4 °C. After several days, black needle crystals of **1c** were collected and washed with MeOH and Et_2O, yield 0.14 g (32.9%). Anal. Calcd for $C_{61}H_{82}N_5MoCu_3Se_4S_6$: C, 43.6; H, 4.92; N, 4.17; S, 11.5; Cu, 11.4. Found: C, 44.3; H, 5.35; N, 5.15; S, 12.7; Cu, 10.8.

$[Et_4N]_2[MoCu_4Se_4(Me_2NCS_2)_4]$ (2). To a suspension of CuCl (0.081 g, 0.80 mmol) in DMF (5 mL) was added a solution of $[Et_4N]_2$-$[MoSe_4]$ (0.17 g, 0.25 mmol) in DMF (10 mL). After being stirred for 10 min, the reaction solution turned red-brown. A solution of Me_2NCS_2Na (0.093 g, 0.65 mmol) in DMF (5 mL) was then added to the reaction solution. The red-brown solution turned dark-green gradually. After the solution was stirred for 30 min, 40 mL of Et_2O was added. The resulting solution was allowed to stay for 1 day at room temperature to cause the deposition of inorganic salt which were removed by filtration. Black cubic crystals of **2** were collected and washed with MeOH and Et_2O after the filtrate was left in a refrigerator for several days, yield 0.14 g (39.2%). Anal. Calcd for $C_{28}H_{64}N_6MoCu_4Se_4S_8$: C, 23.9; H, 4.58; N, 5.97; S, 18.2; Cu, 18.1. Found: C, 24.4; H, 5.34; N, 5.61; S, 17.4; Cu, 18.8.

$[Et_4N]_4[MoCu_{10}Se_4(PhS)_{12}]$ (3). Method A. To a freshly prepared slurry of $[Et_4N]_2[MoSe_4(CuCN)_2]$ (0.085 g, 0.1 mmol) in CH_3CN (20 mL) was slowly added a solution of $[Et_4N]_2[Cu(SPh)_3]$ (0.98 g, 1.5

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Table 1. Crystallographic Data for $[Et_4N]_2[MoCu_3Se_4(Et_2NCS_2)_3]$ (**1a**), $[Et_4N]_2[MoCu_4Se_4(Me_2NCS_2)_4]$ (**2**), and $[Et_4N]_4[MoCu_{10}Se_4(PhS)_{12}]$ (**3**)

	1a	**2**	**3**
formula	$C_{31}H_{70}Cu_3N_5S_6$-Se_4Mo	$C_{28}H_{64}Cu_4N_6S_8$-Se_4Mo	$C_{104}H_{140}Cu_{10}N_4S_{12}$-$Se_4Mo$
fw	1307.7	1407.3	2878.2
space group	$P2_12_12_1$ (No. 19)	*Pbca* (No. 61)	$I\bar{4}$ (No. 82)
a, Å	12.949(3)	14.600(3)	18.344(3)
b, Å	13.339(3)	18.765(4)	
c, Å	29.744(6)	37.781(8)	18.368(4)
V, Å^3	5138	10351	6181
Z	4	8	2
ρ_{calcd}, g·cm^{-3}	1.69	1.81	1.55
μ, mm^{-1}	4.57	5.02	3.20
T, K	296	296	296
λ, Å	0.710 73	0.710 73	0.710 73
R^a	0.052	0.075	0.079
$R_w{}^b$	0.055	0.080	0.084

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2]/\sum w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **1a**

atom	*x*	*y*	*z*	*U*(eq)^a
Mo(1)	7111(1)	157(1)	1309(1)	36(1)
Se(1)	6499(1)	940(1)	644(1)	54(1)
Se(2)	6463(1)	−1460(1)	1352(1)	62(1)
Se(3)	6588(1)	1106(1)	1944(1)	56(1)
Se(4)	8899(1)	98(1)	1278(1)	48(1)
Cu(1)	5662(1)	−619(1)	743(1)	59(1)
Cu(2)	8405(1)	1075(1)	1903(1)	57(1)
Cu(3)	5967(1)	1883(1)	1280(1)	66(1)
S(1)	5007(3)	−1455(3)	116(1)	67(2)
S(2)	3757(3)	−649(5)	839(2)	113(2)
S(3)	9234(3)	768(3)	2631(1)	66(2)
S(4)	9435(3)	2506(3)	2040(1)	59(1)
S(5)	4255(3)	2572(3)	1291(2)	85(2)
S(6)	6187(3)	3678(3)	1211(2)	85(2)
C(1)	3819(12)	−1373(14)	359(5)	77(7)
C(2)	9780(10)	1901(10)	2532(5)	52(5)
C(3)	4861(12)	3685(14)	1259(7)	91(8)
N(1)	3000(11)	−1804(12)	190(5)	92(6)
N(2)	10448(9)	2328(10)	2812(4)	67(5)
N(3)	4362(13)	4575(13)	1263(9)	143(10)
N(4)	6788(9)	4539(11)	2753(4)	81(6)
N(5)	9471(9)	2999(11)	476(4)	68(5)
C(11)	3004(16)	−2347(16)	−221(6)	93(8)
C(12)	3205(20)	−3406(22)	−160(9)	180(17)
C(13)	2003(14)	−1836(20)	434(9)	141(13)
C(14)	1328(18)	−1051(23)	364(10)	192(20)
C(21)	10753(15)	1834(15)	3241(6)	99(9)
C(22)	10076(19)	2154(17)	3625(6)	131(11)
C(23)	10898(13)	3342(12)	2725(6)	77(7)
C(24)	11868(13)	3301(13)	2482(7)	97(8)
C(31)	4898(22)	5597(23)	1214(14)	222(25)
C(32)	5206(51)	5913(54)	785(21)	154(23)
C(32′)	4555(63)	6331(64)	956(26)	204(32)
C(33)	3187(20)	4552(23)	1478(16)	203(25)
C(34)	2808(73)	5081(78)	1029(34)	203(38)
C(34′)	2659(78)	4785(98)	1093(71)	194(63)
C(41)	5678(13)	4386(17)	2859(7)	110(9)
C(42)	5081(15)	3818(17)	2497(7)	108(9)
C(43)	6790(18)	5309(21)	2320(6)	139(13)
C(44)	6123(19)	6229(17)	2389(9)	156(15)
C(45)	7347(21)	3686(23)	2630(8)	181(16)
C(46)	7325(22)	2889(18)	3009(9)	174(16)
C(47)	7238(16)	5146(16)	3123(6)	107(9)
C(48)	8381(15)	5365(20)	3117(7)	139(12)
C(51)	10556(13)	3156(20)	513(6)	126(11)
C(52)	11097(15)	2464(18)	888(6)	130(11)
C(53)	8862(16)	3296(21)	885(7)	123(11)
C(54)	9046(26)	4294(26)	1016(10)	247(25)
C(55)	9228(20)	1909(21)	367(9)	150(14)
C(56)	9678(23)	1479(23)	−40(9)	189(19)
C(57)	9161(16)	3670(18)	83(7)	127(11)
C(58)	7943(15)	3619(21)	−17(8)	160(14)

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

mmol) in DMF (15 mL). The reaction mixture was stirred for 2 h and then filtered to give a bright green filtrate, which was diffused by Et_2O vapor. After 3 days black polyhedral crystals of **3** suitable for X-ray quality were collected and washed with CH_3CN and Et_2O, yield (0.15 g, 52.1%). Anal. Calcd for $C_{104}H_{140}N_4MoCu_{10}Se_4S_{12}$: C, 43.4; H, 4.90; N, 1.95; S, 13.4; Cu, 22.1. Found: C, 44.9; H, 5.17; N, 1.81; S, 14.8; Cu, 21.3.

Method B. To a solution of compound **2** (0.14 g, 0.1 mmol) in DMF (10 mL) was added a solution of $[Et_4N]_2[Cu(SPh)_3]$ (0.52 g, 0.8 mmol) in DMF (10 mL) with stirring, resulting in a dark-green solution. The solution was stirred for 2 h, and then 20 mL of CH_3CN was added. After filtration, the dark green filtrate was diffused by Et_2O vapor. Black polyhedral crystals were collected, washed with EtOH, and dried under vacuum to yield 0.11 g (38.4%). Anal. Found: C, 44.1; H, 4.74; N, 2.13; S, 13.8; Cu, 20.9. IR, elemental analyses, and cell constant determination showed the compound was identical to **3** prepared by method A.

Physical Measurements. Infrared spectra were recorded on an FTS-40 spectrophotometer with the use of pressed KBr pellets. Electronic absorption spectra were obtained in DMF solution on a Shimazu UV-3000 spectrophotometer. The ^{95}Mo and ^1H NMR spectra for all compounds were measured on a Varian Unity-500 spectrometer at 20 °C in $(CD_3)SO$ with 2 mol·dm^{-3} Na_2MoO_4 and TMS as standard, respectively.

Crystallographic Studies. Single crystals for **1a**, **2**, and **3** were carefully chosen, coated with epoxy resin, and mounted on glass fibers. Cell dimension measurements and data collections were performed on a Siemens Smart CCD diffractometer with graphite-monochromitized Mo Kα radiation at 23 ± 1 °C. Intensity data for all crystals were obtained in the range $3.5 < 2\theta < 46.6°$ by using an ω scan technique. The data reductions were performed on a silicon graphics computer station with Smart CCD software. Crystallographic data are listed in Table 1.

For the structural analyses, all calculations were performed on an HP/586 computer with SHELXL-PC program.[16a] The structures were refined through the use of the SHELXL-93 program.[16b] The positions of the molybdenum, selenium, and copper atoms were determined by direct methods, and successive difference electron density maps located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C−H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement. For **1a**, two carbon atoms [C(32) and C(34)] in an ethyl group of $[S_2CNEt_2]^-$ were treated as disordered[17] and refined isotropically and the others were refined anisotropically. The final refinement based on F_o for 6854 observations ($F > 4.0\sigma(F)$) and 453 variables led to convergence. For **2**, the final anisotropic refinement of all non-hydrogen atoms on F_o for 5328 observations ($F > 4.0\sigma(F)$) and 460 variables led to convergence. For **3**, one phenyl ring exhibiting disorder was fixed as an idealized rigid group. The final anisotropic refinement of all non-hydrogen atoms on F_o for 3314 observations ($F > 4.0\sigma(F)$) and 218 variables led to convergence. Final positional parameters for **1a**, **2**, and **3** are given in Tables 2−4, respectively.

Results and Discussion

Syntheses. Generally, Mo(W)−Cu−S cluster compounds can be prepared by ligand substitution or stepwise addition

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(16) (a) Sheldrick, G. M. *SHELXTL/PC Users Manual*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990. (b) Sheldrick, G. M. SHELXTL93. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.

(17) The C(32) and C(34) atoms in **1a** were treated as disordered. The final refined values of the multiplicities are 0.523 for C(32), 0.471 for C(32′), 0.590 for C(34), and 0.421 for C(34′).

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for **2**

atom	*x*	*y*	*z*	*U*(eq)[a]
Mo	9912(1)	2054(1)	3783(1)	32(1)
Se(1)	11020(1)	1877(1)	4230(1)	51(1)
Se(2)	9421(1)	945(1)	3554(1)	53(1)
Se(3)	8606(1)	2627(1)	4017(1)	54(1)
Se(4)	10560(1)	2748(1)	3323(1)	46(1)
Cu(1)	9786(2)	1749(1)	3082(1)	53(1)
Cu(2)	9762(2)	2541(1)	4462(1)	58(1)
Cu(3)	9262(2)	3338(1)	3562(1)	56(1)
Cu(4)	10665(1)	765(1)	3945(1)	54(1)
S(11)	8327(3)	2087(2)	2740(1)	53(2)
S(12)	9973(3)	1287(3)	2530(1)	65(2)
C(10)	8864(12)	1554(8)	2444(4)	56(7)
N(10)	8461(10)	1352(7)	2139(3)	58(6)
C(11)	7511(12)	1558(10)	2052(4)	80(8)
C(12)	8927(12)	916(11)	1874(4)	85(9)
S(21)	10313(3)	3653(2)	4779(1)	64(2)
S(22)	9292(3)	2420(2)	5048(1)	61(2)
C(20)	9816(11)	3219(9)	5127(4)	52(6)
N(20)	9814(10)	3501(8)	5465(3)	71(6)
C(21)	10263(14)	4180(10)	5531(5)	96(10)
C(22)	9419(16)	3111(12)	5771(4)	120(12)
S(31)	8231(3)	3864(2)	3149(1)	56(2)
S(32)	9350(3)	4604(2)	3677(1)	65(2)
C(30)	8535(11)	4663(9)	3349(4)	50(6)
N(30)	8156(9)	5270(7)	3250(3)	53(5)
C(31)	7492(14)	5298(9)	2959(4)	85(9)
C(32)	8381(13)	5926(9)	3426(5)	93(10)
S(41)	12149(3)	297(2)	3742(1)	61(2)
S(42)	10800(3)	−349(2)	4216(1)	54(2)
C(40)	11885(10)	−382(7)	4027(4)	42(6)
N(40)	12458(9)	−895(7)	4103(3)	50(5)
C(41)	12264(12)	−1473(9)	4350(5)	73(8)
C(42)	13382(11)	−906(9)	3952(5)	73(8)
N(1)	9854(10)	3652(7)	2025(3)	56(6)
C(111)	10116(14)	3509(10)	2396(4)	81(8)
C(112)	10889(16)	3977(13)	2529(6)	133(13)
C(121)	9556(15)	4396(10)	1983(6)	98(10)
C(122)	8711(15)	4633(11)	2191(5)	108(11)
C(131)	9091(14)	3151(10)	1942(5)	85(9)
C(132)	8665(16)	3178(12)	1584(5)	122(12)
C(141)	10632(15)	3536(11)	1772(5)	94(10)
C(142)	11033(16)	2782(12)	1771(6)	138(14)
N(2)	7951(9)	−593(7)	4667(3)	54(5)
C(211)	8541(12)	83(10)	4699(5)	73(8)
C(212)	8084(14)	753(11)	4595(6)	106(11)
C(221)	8574(12)	−1194(10)	4785(4)	65(8)
C(222)	8159(13)	−1923(11)	4766(5)	89(9)
C(231)	7627(11)	−697(9)	4295(4)	64(7)
C(232)	8342(15)	−784(13)	4020(5)	122(12)
C(241)	7080(12)	−565(10)	4887(5)	73(8)
C(242)	7227(15)	−482(12)	5280(5)	122(12)

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

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for **3**

atom	*x*	*y*	*z*	*U*(eq)[a]
Mo	5000	5000	0	45(1)
Se(1)	4043(1)	4537(1)	741(1)	53(1)
Cu(1)	5000	5000	1548(1)	62(1)
Cu(2)	4448(1)	3527(1)	−41(1)	63(1)
Cu(3)	4294(1)	6605(1)	1281(1)	68(1)
S(1)	4861(2)	2659(2)	788(3)	71(2)
S(2)	3474(2)	3170(2)	−799(3)	68(2)
S(3)	4590(3)	5967(3)	2271(2)	69(2)
C(11)	5308(8)	1916(7)	327(8)	69(5)
C(12)	5779	1475	729	211(17)
C(13)	6057	837	424	542(73)
C(14)	5864	639	−283	142(10)
C(15)	5393	1080	−686	127(8)
C(16)	5116	1718	−381	107(7)
C(21)	3850(10)	2568(9)	−1469(11)	78(8)
C(22)	3534(13)	1861(13)	−1552(17)	125(12)
C(23)	3838(21)	1409(16)	−2080(26)	172(20)
C(24)	4424(19)	1515(18)	−2388(25)	163(18)
C(25)	4735(13)	2270(16)	−2403(13)	121(11)
C(26)	4430(11)	2750(10)	−1931(12)	85(8)
C(31)	5394(13)	6372(15)	2727(11)	102(10)
C(32)	5395(14)	7110(19)	2744(16)	149(15)
C(33)	5956(21)	7418(18)	3151(21)	159(16)
C(34)	6529(19)	6953(21)	3540(14)	140(15)
C(35)	6429(23)	6228(23)	3434(27)	216(23)
C(36)	5905(18)	5877(16)	3007(17)	156(15)
N(1)	2400(13)	1953(12)	1185(14)	116(7)
C(1)	2546(31)	2744(31)	978(32)	252(23)
C(2)	2655(28)	1556(32)	606(30)	234(19)
C(3)	1851(42)	1896(39)	1384(43)	370(35)
C(4)	2829(38)	1563(36)	1923(34)	285(25)
C(5)	2678(27)	3263(26)	1544(30)	243(21)
C(6)	2818(81)	1130(78)	392(103)	468(118)
C(7)	1452(47)	2285(51)	753(58)	421(45)
C(8)	3542(46)	1211(38)	1966(43)	324(35)

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

reactions.[9,12b,18] Similarly, tetranuclear Mo−Cu−Se compound **1a** was obtained by a two-step reaction, the reaction of $[Et_4N]_2[MoSe_4]$ and CuCl in a 1:3 Mo:Cu ratio and the substitution of Cl^- by $R_2NCS_2^-$:

$$[Et_4N]_2[MoSe_4] + 3CuCl \rightarrow [Et_4N]_2[MoSe_4(CuCl)_3] \quad (1)$$

$$[Et_4N]_2[MoSe_4(CuCl)_3] + 3R_2NCS_2Na \rightarrow [Et_4N]_2[MoSe_4(CuR_2NCS_2)_3] + 3NaCl \quad (2)$$

1a

When $[Et_4N]_2[MoSe_4]$ reacted with CuCl in DMF solution, the characteristic blue-purple color of $[MoSe_4]^{2-}$ disappeared rapidly and a red-brown slightly soluble Mo−Cu−Se−Cl compound was formed. Addition of Et_2NCS_2Na allowed the substitution of three Cl^- by $Et_2NCNS_2^-$ and the formation of the bright green soluble compound **1a**.

Compound **1b** was prepared by the direct combination reaction of the $[MoSe_4]^{2-}$ anion and a dithiocarbamate-substituted Cu^+ species in DMF:

$$CuCl + R_2NCS_2Na \rightarrow (R_2NCS_2)Cu + NaCl \quad (3)$$

$$[Et_4N]_2[MoSe_4] + 3(R_2NCS_2)Cu \rightarrow [Et_4N]_2[MoSe_4(CuR_2NCS_2)_3] \quad (4)$$

1b

The self-assembly reaction or so called one-pot reaction was applied for the preparation of **1c**:

$$[Et_4N]_2[MoSe_4] + 3CuCl + 3R_2NCS_2Na \rightarrow [Et_4N]_2[MoSe_4(CuR_2NCS_2)_3] + 3NaCl \quad (5)$$

1c

In these reactions, all reactants were dissolved in DMF and stirred for a suitable period of time to give the final products. The elemetal analyses and spectroscopic results of **1a**−**c** confirm that the three compounds have similar structures.

When similar methods were used for the reaction of $[Et_4N]_2[MoSe_4]$, CuCl, and Me_2NCS_2Na in DMF, instead of $[MoSe_4(CuS_2CNMe_2)_3]^{2-}$, a pentanuclear cluster compound **2** was isolated. As we know, the chemical properties of dithio-

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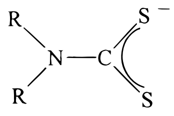
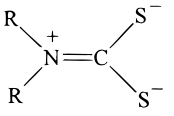
carbamate complexes are susceptible to the nature of the substituents on the dithiocarbamate ligands because of the existence of resonance forms described as follows:[19]


(I)


(II)

The increase in the electron-donating ability of the R groups favors resonance form (II) and hence induces an increase in the electron on the sulfur atoms bound to the copper atom. Moreover, when the substitutent is a methyl group, there exits a strong super-conjugation effect from the methyl H atoms to the N═C double bond[20] that may result in the formation of the novel structural cluster compound. Therefore, the compound obtained from the methyl group substitutent system is different from those from the other substitutent systems.

In comparison with the synthetic system using tetrathiometalate synthon $[MS_4]^{2-}$ ($M = Mo, W$),[9,11] the synthetic methods for **1a**−**c** of the $MoCu_3$ planar structure are similar to that of $[MoCu_3S_4(R_2NCS_2)_3]^{2-}$ ($R_2 = Et_2, C_5H_{10}$).[9] We attempted to use $[Et_4N]_2[MoSe_4]$, CuCl, and Me_2NCS_2Na in different ratios to prepare the cluster compounds with higher nuclearity, such as the $MoCu_6Se_4$ compound, but failed. It was mentioned that the formation of double defective cubane compounds with $[S_2Mo_2Cu_5S_6]$[11] cores can be prepared by using two cubanelike units $[SMoS_3Cu_2]$ and $[SMoS_3Cu_3]$ as building blocks linked by two bridging $Me_2NCS_2^-$ ligands. In the Mo−Cu−Se system, an effort has been made to use $[MoCu_3Se_4(R_2NCS_2)_3]^{2-}$ as building blocks to prepared similar double defective cubane compounds with the $[Se_2Mo_2Cu_5Se_6]$ core; no matter what reaction condition was used, the products obtained were always those with $MoCu_3$ or $MoCu_4$ cores. This suggests that not all reaction chemistry of the $[MoSe_4]^{2-}$ anion parallels that of the sulfide analogues $[MoS_4]^{2-}$.

Besides, thiolate ligands may play an important role in the synthetic reaction. All Cl^- ligands in the slightly soluble intermediates $[MoSe_4(CuCl)_3]^{2-}$ were replaced by $R_2NCS_2^-$ ligands in DMF and a series of cluster compounds with $MoCu_3$ and $MoCu_4$ cores and $R_2NCS_2^-$ ligands can be isolated. Moreover, the usage of a relatively small amount of R_2NCS_2Na is necessary, because the excess $R_2NCS_2^-$ ligands will result in the formation of $Cu(R_2NCS_2)_2$ complexes as the separable product. Therefore, inadequate $R_2NCS_2^-$ ligand can avoid the formation of $Cu(R_2NCS_2)_2$.

In an attempt to prepare Mo−Cu−Se cluster compounds with mixed ligands of $Me_2NCS_2^-$ or CN^- and PhS^- by the reaction of $[Et_4N]_2[Cu(PhS)_3]$ and $[Et_4N]_2[(NC)CuSe_2MoSe_2Cu(CN)]$ or **2**, suprisingly, instead of simple ligand substitution, the polynuclear compound **3** with $MoCu_{10}$ core was obtained. It has been documented that, in the corresponding tetrathiometalate system, the cyano ligands in $[MoS_4(CuCN)_2]^{2-}$ can only be displaced by PhS^- ligands.[21] In the present system, the reaction may undergo two steps: First, the active fragment of CuSPh is released from $[Et_4N]_2[Cu(PhS)_3]$,[15]

$$[Et_4N]_2[Cu(PhS)_3] \rightleftharpoons CuSPh + 2Et_4N^+ + 2PhS^- \quad (6)$$

Second, the presence of excess PhS^- induces the substitution of CN^- in $[MoSe_4(CuCN)_2]^{2-}$ or $Me_2NCS_2^-$ in **2** by PhS^- and the aggregations of $[MoSe_4(CuSPh)_n]^{2-}$ ($n = 2$ or 4) and PhSCu to form the polynuclear $MoSe_4Cu_{10}$ compound. All attempts to isolate the $MoSe_4Cu_2$, $MoSe_4Cu_4$, or $MoSe_4Cu_{10}$ core cluster compounds containing PhS^- ligands by the direct reactions of $[Et_4N]_2[MSe_4]$, CuX, and NaSPh in different molar ratios have failed. The polynuclear cluster compounds $[Et_4N]_4[MCu_{10}S_4L_{12}]$ ($M = Mo, W$; $L = Cl, Br$)[12] were synthesized from the reactions of $[NH_4]_2[MS_4]$, CuX, and Et_4NX in an equilibrium molar ratio in acac/DMSO mixed solvent, while trying to prepare $MoSe_4Cu_{10}$ core cluster compounds with halide ligands by running a similar reaction was not successful.

Table 5. Bond Lengths (Å) and Angles (deg) for **1a**

Mo(1)−Se(1)	2.373(2)	Cu(1)−S(2)	2.484(4)
Mo(1)−Se(2)	2.317(2)	Cu(2)−S(3)	2.452(4)
Mo(1)−Se(3)	2.373(2)	Cu(2)−S(4)	2.364(4)
Mo(1)−Se(4)	2.319(2)	Cu(3)−S(5)	2.400(4)
Mo(1)−Cu(1)	2.724(2)	Cu(3)−S(6)	2.420(5)
Mo(1)−Cu(2)	2.726(2)	S(1)−C(1)	1.704(16)
Mo(1)−Cu(3)	2.739(2)	S(2)−C(1)	1.725(18)
Se(1)−Cu(1)	2.363(2)	S(3)−C(2)	1.694(14)
Se(1)−Cu(3)	2.375(3)	S(4)−C(2)	1.730(14)
Se(2)−Cu(1)	2.368(2)	S(5)−C(3)	1.682(18)
Se(3)−Cu(2)	2.357(2)	S(6)−C(3)	1.722(16)
Se(3)−Cu(3)	2.373(3)		
Se(4)−Cu(2)	2.357(2)		
Cu(1)−S(1)	2.332(5)		

Se(1)−Mo(1)−Se(2)	109.5(1)	Se(1)−Cu(1)−Se(2)	108.2(1)
Se(1)−Mo(1)−Se(3)	109.5(1)	Se(1)−Cu(1)−S(1)	119.2(1)
Se(2)−Mo(1)−Se(3)	110.4(1)	Se(2)−Cu(1)−S(1)	122.9(1)
Se(1)−Mo(1)−Se(4)	108.4(1)	Se(1)−Cu(1)−S(2)	119.0(2)
Se(2)−Mo(1)−Se(4)	109.4(1)	Se(2)−Cu(1)−S(2)	109.8(1)
Se(3)−Mo(1)−Se(4)	109.5(1)	S(1)−Cu(1)−S(2)	73.9(2)
Cu(1)−Mo(1)−Cu(2)	173.9(1)	Se(3)−Cu(2)−Se(4)	108.8(1)
Se(4)−Mo(1)−Cu(3)	124.6(1)	Se(3)−Cu(2)−S(3)	113.2(1)
Cu(1)−Mo(1)−Cu(3)	85.8(1)	Se(4)−Cu(2)−S(3)	119.0(1)
Cu(2)−Mo(1)−Cu(3)	88.6(1)	Se(3)−Cu(2)−S(4)	122.7(1)
Mo(1)−Se(1)−Cu(1)	70.2(1)	Se(4)−Cu(2)−S(4)	115.4(1)
Mo(1)−Se(1)−Cu(3)	70.5(1)	S(3)−Cu(2)−S(4)	74.7(1)
Cu(1)−Se(1)−Cu(3)	103.5(1)	Se(1)−Cu(3)−Se(3)	109.5(1)
Mo(1)−Se(2)−Cu(1)	71.1(1)	Se(1)−Cu(3)−S(5)	118.8(2)
Mo(1)−Se(3)−Cu(2)	70.4(1)	Se(3)−Cu(3)−S(5)	118.0(2)
Mo(1)−Se(3)−Cu(3)	70.5(1)	Se(1)−Cu(3)−S(6)	115.0(2)
Cu(2)−Se(3)−Cu(3)	107.6(1)	Se(3)−Cu(3)−S(6)	117.5(2)
Mo(1)−Se(4)−Cu(2)	71.3(1)	S(5)−Cu(3)−S(6)	74.4(2)

The use of $[MoSe_4]^{2-}$ as starting material has allowed access to several novel polynuclear Mo−Cu−Se cluster compounds. Although not many heterobimetallic complexes of copper(I) with tetraselenomolybdate have been prepared until now, the reactivity of $[MoSe_4]^{2-}$ represents a feasible proof for the belief that such a synthetic method may provide a rich source of new transition-metal clusters containing the selenium ligand.

Structures. Crystal structures of **1a**, **2**, and **3** have been determined. All crystal structures consist of discrete $[Et_4N]^+$ cations and Mo−Cu−Se cluster anions. In all three structures, the $[Et_4N]^+$ cations have their expected structure as well as normal distances and angles, which will not be discussed further. Selected bond distances and angles for **1a**, **2**, and **3** are collected in Tables 5−7, respectively.

The structure of the anion, $[MoCu_3Se_4(Et_2NCS_2)_3]^{2-}$, in **1a** is shown in Figure 2. Although the similar structures have been seen previously in the $[MS_4Cu_3L_3]^{2-}$ compound ($M = Mo, W$; $L = Cl, SCN, Et_2NCS_2$),[9,22] the current arrangement appears to

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Table 6. Bond Lengths (Å) and Bond Angles (deg) for **2**

Mo−Se(1)	2.363 (2)	Mo−Se(2)	2.365 (2)
Mo−Se(3)	2.362(2)	Mo−Se(4)	2.371(2)
Mo−Cu(1)	2.717(2)	Mo−Cu(2)	2.731(2)
Mo−Cu(3)	2.723(2)	Mo−Cu(4)	2.726(2)
Se(1)−Cu(2)	2.385(3)	Se(1)−Cu(4)	2.407(3)
Se(2)−Cu(1)	2.395(2)	Se(2)−Cu(4)	2.365(3)
Se(3)−Cu(2)	2.386(3)	Se(3)−Cu(3)	2.379(3)
Se(4)−Cu(1)	2.371(3)	Se(4)−Cu(3)	2.374(3)
Cu(1)−S(11)	2.572(5)	Cu(1)−S(12)	2.276(5)
Cu(2)−S(21)	2.538(5)	Cu(2)−S(22)	2.330(4)
Cu(3)−S(31)	2.381(5)	Cu(3)−S(32)	2.418(5)
Cu(4)−S(41)	2.461(5)	Cu(4)−S(42)	2.337(5)

Se(1)−Mo−Se(2)	110.3(1)	Se(1)−Mo−Se(3)	110.4(1)
Se(2)−Mo−Se(3)	107.1(1)	Se(1)−Mo−Se(4)	109.2(1)
Se(2)−Mo−Se(4)	109.6(1)	Se(3)−Mo−Se(4)	110.3(1)
Cu(1)−Mo−Cu(3)	82.2(1)	Cu(2)−Mo−Cu(3)	87.9(1)
Cu(1)−Mo−Cu(4)	93.3(1)	Cu(2)−Mo−Cu(4)	96.9(1)
Cu(3)−Mo−Cu(4)	174.3(1)	Mo−Se(1)−Cu(2)	70.2(1)
Mo−Se(1)−Cu(4)	69.7(1)	Cu(2)−Se(1)−Cu(4)	116.8(1)
Mo−Se(2)−Cu(1)	69.6(1)	Mo−Se(2)−Cu(4)	70.4(1)
Cu(1)−Se(2)−Cu(4)	112.6(1)	Mo−Se(3)−Cu(2)	70.2(1)
Mo−Se(3)−Cu(3)	70.1(1)	Cu(2)−Se(3)−Cu(3)	105.2(1)
Mo−Se(4)−Cu(1)	69.9(1)	Mo−Se(4)−Cu(3)	70.0(1)
Cu(1)−Se(4)−Cu(3)	97.7(1)	Se(2)−Cu(1)−Se(4)	108.6(1)
Se(2)−Cu(1)−S(11)	110.2(1)	Se(4)−Cu(1)−S(11)	113.1(1)
Se(2)−Cu(1)−S(12)	118.0(1)	Se(4)−Cu(1)−S(12)	126.6(2)
S(11)−Cu(1)−S(12)	74.5(2)	Se(1)−Cu(2)−Se(3)	108.8(1)
Se(1)−Cu(2)−S(21)	111.0(1)	Se(3)−Cu(2)−S(21)	120.1(1)
Se(1)−Cu(2)−S(22)	121.6(1)	Se(3)−Cu(2)−S(22)	117.8(2)
S(21)−Cu(2)−S(22)	74.0(2)	Se(3)−Cu(3)−Se(4)	109.6(1)
Se(3)−Cu(3)−S(31)	116.9(1)	Se(4)−Cu(3)−S(31)	116.6(1)
Se(3)−Cu(3)−S(32)	116.2(1)	Se(4)−Cu(3)−S(32)	119.0(1)
S(31)−Cu(3)−S(32)	75.2(2)	Se(1)−Cu(4)−Se(2)	108.8(1)
Se(1)−Cu(4)−S(41)	105.0(1)	Se(2)−Cu(4)−S(41)	122.2(1)
Se(1)−Cu(4)−S(42)	124.1(1)	Se(2)−Cu(4)−S(42)	117.8(1)
S(41)−Cu(4)−S(42)	75.1(2)		

Table 7. Bond Lengths (Å) and Angles (deg) for **3**

Mo−Se(1)	2.378(2)	Mo−Cu(1)	2.844(3)
Mo−Cu(2)	2.886(2)	Se(1)−Cu(1)	2.449(2)
Se(1)−Cu(2)	2.458(3)	Cu(1)−S(3)	2.340(5)
Cu(1)−Cu(3)	3.251(3)	Cu(2)−Cu(3)	3.301(3)
Cu(2)−S(1)	2.330(5)	Cu(2)−S(2)	2.358(5)
Cu(3)−S(3)	2.230(5)	Cu(3)−S(1A)	2.246(5)
Cu(3)−S(2A)	2.248(5)	S(1)−C(11)	1.802(15)
S(2)−C(21)	1.792(20)		

Cu(1)−Mo−Cu(2)	91.5(1)	Se(1)−Mo−Se(1A)	110.2(1)
Se(1)−Mo−Se(1B)	109.1(1)	Se(1A)−Mo−Se(1B)	109.1(1)
Se(1)−Mo−Se(1C)	109.1(1)	Se(1A)−Mo−Se(1C)	109.1(1)
Se(1B)−Mo−Se(1C)	110.2(1)	Cu(1)−Mo−Cu(1A)	180.0(1)
Cu(2)−Mo−Cu(1A)	88.5(1)	Cu(1)−Mo−Cu(2A)	91.5(1)
Cu(2)−Mo−Cu(2A)	177.0(1)	Cu(1A)−Mo−Cu(2A)	88.5(1)
Cu(1)−Mo−Cu(2B)	88.5(1)	Cu(2)−Mo−Cu(2B)	90.0(1)
Cu(1A)−Mo−Cu(2B)	91.5(1)	Cu(2A)−Mo−Cu(2B)	90.0(1)
Cu(1)−Mo−Cu(2C)	88.5(1)	Cu(2)−Mo−Cu(2C)	90.0(1)
Cu(1A)−Mo−Cu(2C)	91.5(1)	Cu(2A)−Mo−Cu(2C)	90.0(1)
Cu(2B)−Mo−Cu(2C)	177.0(1)	Mo−Se(1)−Cu(1)	72.2(1)
Mo−Se(1)−Cu(2)	73.3(1)	Cu(1)−Se(1)−Cu(2)	113.5(1)
Mo−Se(1)−Cu(2B)	73.4(1)	Cu(1)−Se(1)−Cu(2B)	109.3(1)
Cu(2)−Se(1)−Cu(2B)	112.5(1)	Se(1)−Cu(1)−S(3)	112.1(1)
Se(1)−Cu(1)−Se(1A)	105.5(1)	S(3)−Cu(1)−Se(1A)	108.1(1)
Se(1)−Cu(1)−S(3A)	108.1(1)	S(3)−Cu(1)−S(3A)	110.8(2)
Se(1A)−Cu(1)−S(3A)	112.1(1)	Se(1)−Cu(2)−S(1)	103.4(2)
Se(1)−Cu(2)−S(2)	109.0(1)	S(1)−Cu(2)−S(2)	116.3(2)
Se(1)−Cu(2)−Se(1C)	104.2(1)	S(1)−Cu(2)−Se(1C)	111.0(1)
S(2)−Cu(2)−Se(1C)	111.9(2)	S(3)−Cu(3)−S(1A)	118.5(2)
S(3)−Cu(3)−S(2A)	120.7(2)	S(1A)−Cu(3)−S(2A)	120.8(2)
Cu(2)−S(1)−Cu(3A)	94.4(2)	Cu(2)−S(2)−Cu(3B)	91.5(2)
Cu(1)−S(3)−Cu(3)	90.8(2)		

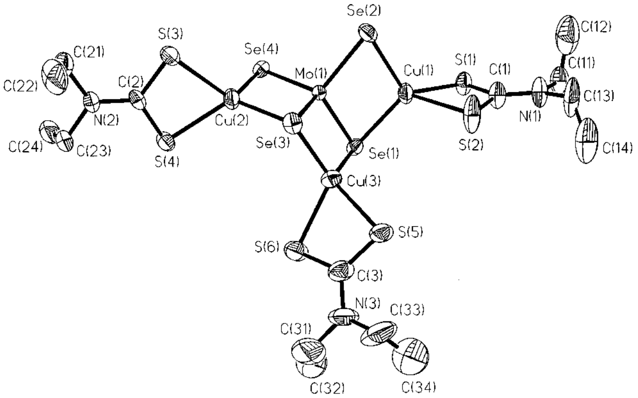

Figure 2. ORTEP plot of the anion $[\mathrm{MoCu_3Se_4(Et_2NCS_2)_3}]^{2-}$ in **1a** with the ellipsoids drawn at 30% probability level.

be the first example of a planar $\mathrm{MoCu_3}$ with $[\mathrm{MoSe_4}]^{2-}$ unit and different from those with incomplete cubane $\mathrm{QMoSe_3Cu_3}$ (Q = O, Se)[13] and with cubane $\mathrm{QMoSe_3Cu_3X}$ (Q = O, Se; X = Cl, Br)[8] complexes in which the O or one of Se atom acts as terminal. The anion structure possesses a 2-fold axis through Mo(1) and Cu(3) atoms. The $[\mathrm{MoSe_4}]^{2-}$ tetrahedral unit coordinates to three $\mathrm{Et_2NCS_2Cu}$ groups from three of the six tetrahedral Se−Se edges in a nearly plane fashion and leaves the other three Se−Se edges opened. Therefore, $[\mathrm{MoSe_4}]^{2-}$ is a slightly distorted tetrahedron. The four metal atoms Mo(1), Cu(1), Cu(2), and Cu(3) lie approximately in a plane within 0.06 Å of deviations from the idealized $\mathrm{MoCu_3}$ plane. Two types of Se atoms are present: μ_2-Se and μ_3-Se. The Mo−μ_3-Se bonds (an average value of 2.373(2) Å) are longer than those in Mo−μ_2-Se (an average value of 2.318(2) Å). The coordination sphere of Cu atoms is a highly distorted tetrahedron consisting of two Se atoms from $[\mathrm{MoSe_4}]^{2-}$ and two S atoms from one $\mathrm{Et_2NCS_2}^-$ ligand with average bite angle of 74.3° in the four-membered chelate ring. The Cu−Se distances are not clearly influenced by the different Se coordination modes and are comparable with those found in $[\mathrm{SeMoSe_3Cl(CuPPh_3)_3}]$[8b] [Cu−$\mu_3$-Se = 2.376(5)−2.426(5) Å] and $[\mathrm{OMoSe_3Cu_3Cl_3(Py)}]^{2-}$ [13] [Cu−μ_3-Se = 2.332(2)−2.396(2) Å] (see Table 8).

The structure of the anion, $[\mathrm{MoCu_4Se_4(Me_2NCS_2)_4}]^{2-}$, of **2** is shown in Figure 3. The core structure is different from that of the anion in **1a** and has no sulfur analogues found in the compounds containing the $[\mathrm{MoS_4}]^{2-}$ unit and dialkydithiocarbamate ligands, but similar structures have been found previously in $[\mathrm{MoCu_4S_4L_4}]^{2-}$ (L = Cl, Br, SCN).[23] The anion structure comprises four $\mathrm{Me_2NCS_2Cu}$ fragments ligating through four of six edges of the tetrahedral $[\mathrm{MoSe_4}]^{2-}$ moiety. In the $\mathrm{MoCu_4}$ core, both the Mo and Cu atoms are tetrahedrally coordinated, and five metal atoms are nearly coplanar with deviations of not more than 0.1 Å from the least-squares plane. Distances from the Mo atom to the four Se atoms range from 2.362(2) to 2.371(2) Å, while the Se−Mo−Se angles range from 107.1(1) to 110.4(1)°. The Cu(1)−Mo−Cu(2) and Cu(3)−Mo−Cu(4) angles are 168.8(1) and 174.3(1)°, respectively; thus, the anion structure is of pseudo D_{2d} symmetry. The Cu−Se bond lengths [2.365(3)−2.407(3) Å] in **2** agree well with those in **1a** [2.356(2)−2.374(2) Å], which suggests that Cu−Se distances are not affected by the coordination geometries of the Cu atoms and different dialkyldithiocarbamate ligands. The average Mo−Cu distance of 2.724(2) Å in **2** with tetrahedral coordinated Cu atoms is compatible to that (2.730(2) Å) in **1a** and longer than those with trigonal coordinated Cu atoms found in $[\mathrm{Se_2MoSe_2(CuCN)}]^{2-}$ [2.674(1) Å],[6b] $[\mathrm{MoSe_4(CuCN)_2}]^{2-}$ [2.685(1) Å],[6b] and $[\mathrm{OMoSe_3Cu_3Cl_3(Py)}]^{2-}$ [2.667(2) and

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[23] (a) Clegg, W.; Scattergood, C. D.; Garner, C. D. *Acta Crystallogr.* **1987**, *C43*, 78. (b) Nicholson, J. R.; Flood, A. C.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1983**, 119. (c) Manoli, J. M.; Potvin, C.; Sécheresse, F.; Marzak, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1557.

Table 8. Comparative Structural Parameters[a] for Related Mo−Cu−Se Compounds

compd	type	Mo−Se(O)$_t$[b]	Mo−Se$_b$[c]	Cu−Se	Mo−Cu	Se−Mo−Se	Se−Cu−Se	ref
$[MoSe_4]^{2-}$		2.293(1)						14
$[MoSe_4Cu(CN)]^{2-}$		2.288(1)	2.368(1)	2.313(1)	2.674(1)	108.39(5)−111.39(5)	112.28(3)	6c
$[MoSe_4Cu(Me_2PhP)_2]^{-}$	range	2.294(1)	2.345(1)−2.355(1)	2.421(1)−2.428(1)	2.857(1)	108.25(3)−110.19(3)	103.51(3)	6d
	mean		2.350(1)	2.425(1)				
$[MoSe_4Cu_2(CN)_2]^{2-}$	range		2.331(1)−2.346(1)	2.317(1)−2.327(1)	2.684(1)−2.685(1)	108.93(3)−110.44(3)	110.11(3)−110.29(3)	6c
	mean		2.338(1)	2.323(1)	2.685(1)			
$[MoSe_4Cu_3Cl(PPh_3)_3]$	range	2.184(6)	2.359(4)−2.388(4)	2.376(5)−2.426(6)	2.736(5)−2.768(5)	108.2(1)−112.0(3)	104.6(2)−108.8(2)	8b
	mean		2.376(4)	2.395(6)	2.749(5)			
$[MoSe_3OCu_3Cl_3(Py)]^{2-}$	range	1.689(5)[d]	2.391(1)−2.400(1)	2.332(2)−2.393(2)	2.667(2)−2.757(2)	109.18(5)−109.67(6)[e]	109.73(6)−112.48(6)	13
	mean		2.395(1)	2.359(2)	2.704(2)			
1a	range		2.317(2)−2.373(2)	2.356(2)−2.374(2)	2.724(2)−2.739(2)	108.4(1)−110.4(1)	108.2(1)−109.5(1)	this work
	mean		2.345(2)	2.365(3)	2.730(2)			
2	range		2.362(2)−2.371(2)	2.365(3)−2.407(3)	2.717(2)−2.731(2)	107.1(1)−110.4(1)	108.6(1)−109.6(1)	this work
	mean		2.365(2)	2.383(3)	2.724(2)			
3	range		2.378(2)	2.449(2)−2.458(3)	2.844(3)−2.886(2)	109.1(1)−110.2(1)	104.2(1)−105.5(1)	this work
	mean			2.453(2)	2.865(3)			

[a] Bond distances in Å, bond angles in deg. [b] t = terminal. [c] b = bridging. [d] Mo−O bond length. [e] O−Mo−Se angles are not included.

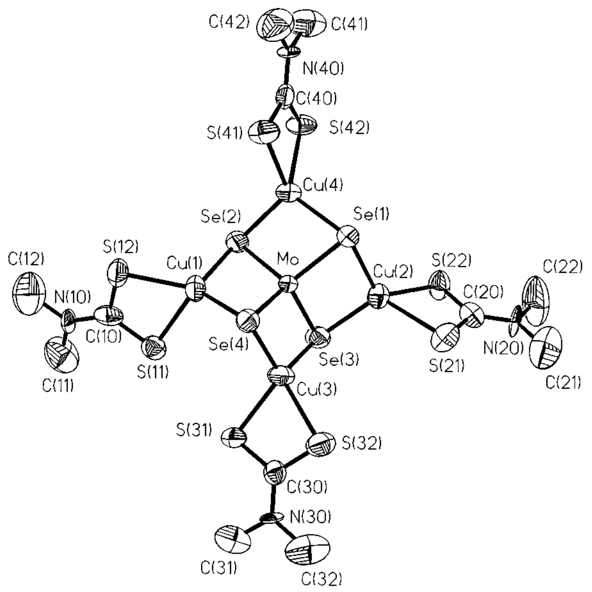

Figure 3. ORTEP plot of the anion $[MoCu_4Se_4(Me_2NCS_2)_4]^{2-}$ in **2** with the ellipsoids drawn at 30% probability level.

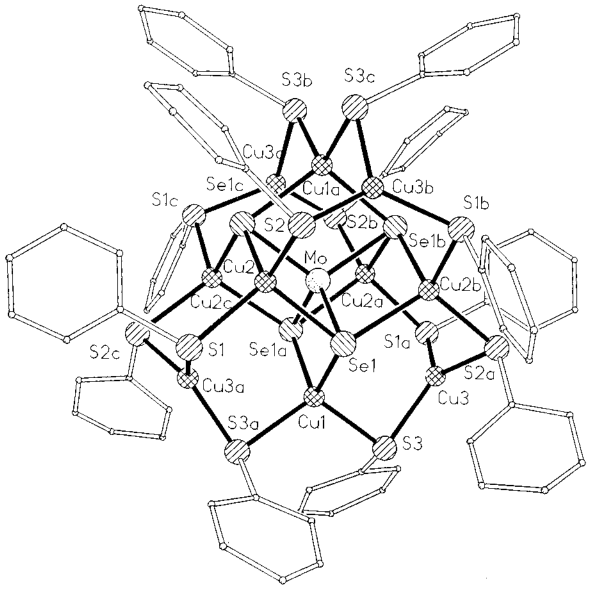

Figure 4. Structure of anion $[MoCu_{10}Se_4(PhS)_{12}]^{4-}$ in **3**.

2.689(1) Å].[13] These values, together with the very acute angles of Mo−Se−Cu are an indication of a possible Mo−Cu bonding interaction.

Figure 4 depicts the perspective view of the $[MoCu_{10}Se_4(PhS)_{12}]^{4-}$ anion structure in **3**. Examples of related structures, $[MCu_{10}S_4X_{12}]^{4-}$ (M = Mo, W; X = Cl, Br), containing different $[MS_4]^{2-}$ moieties and halide ligands are reported.[12] The structure possesses a crystallographic D_2 and pseudo T_d symmetry. The inner core is formed of a central $MoSe_4$ tetrahedron encapsulated by six copper atoms across the six edges of an Se_4 tetrahedron, quite similar to that of the $[MoS_4Cu_6Cl_9]^{5-}$ anion.[24] The central $MoSe_4$ retains the idealized geometry of free selenidomolybdate, and the six copper atoms form a regular octahedral array. Then further addition of the other four copper atoms to $[MoSe_4Cu_6]$ in tetrahedral array by Cu−S−Cu bonding from four of eight Cu_3 faces of the Cu_6 octahedron led to the compound **3**. The six copper atoms in the octahedral array are each in a slightly distorted

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Table 9. UV−Vis Electronic and IR Spectral Data[a]

	UV−vis in DMF	IR,[b] maxima, cm^{-1}			
compd	λ, nm ($10^{-3}\epsilon$, M^{-1}·cm^{-1})	ν(C═N)	ν(C−S)	ν(Mo−Se)	ν(Cu−S)
$[Et_4N]_2[MoSe_4]$	640, 566, 367[c]			341[d]	
1a	565 (5.14), 478 sh, 428 (11.7), 285 sh, 270 (26.1)	1480	992	327, 303	351, 338 sh
1b	548 (5.37), 480 sh, 425 (10.8), 280 sh, 262 (25.9)	1476	1000	322, 295	355, 340 sh
1c	550 (5.07), 485 sh, 430 (10.5), 295 sh, 260 (24.2)	1479	949	316, 305	333
2	558 (5.95), 440 (15.1), 288 sh, 275 (28.4)	1523	976	314	352
3	545 (6.52), 375 (21.4), 286 (36.2)			292	321

[a] sh, shoulder. [b] KBr pellets. [c] Reference 26. [d] Reference 1c.

tetrahedral environment formed by two Se atoms from $MoSe_4$ and two bridge S atoms from PhS^-, while four copper atoms of the tetrahedral array are each in triangular environment formed by three S atoms from SPh^-. It can also been described that the four copper atoms in Cu_4 array are added from the directions of four faces of the Se_4 tetrahedron, while the six copper atoms of the Cu_6 array are bound across the six edges of the Se_4 tetrahedron. The four Mo−Se distances are equal to 2.378(2) Å, which is slightly longer than average values of 2.345(2) Å in **1a** and 2.365(2) Å in **2**. The Se−Mo−Se angles, ranging from 109.1(1) to 110.2(1)°, are compatible to that expected in an idealized tetrahedron. It is interesting to note that the Mo−Cu average bond length of 2.865(3) Å in **3** is longer than those in the other Mo−Cu−Se compounds shown in Table 8, indicating that there are more or less metal−metal bonding interactions, which affect the ^{95}Mo NMR chemical shift being discussed later. In comparison with the Cu−S_{SPh} distances in $[S_2MoS_2(CuSPh)]^{2-}$ [2.188(2) Å] and $[MoS_4(CuSPh)_2]^{2-}$ [2.171(2) Å],[21] elongation of Cu−S_{SPh} bond lengths in **3** [2.246(5)−2.358(5) Å] is due to PhS^- as bridging ligands. The average distance of Cu−S_{SPh} [2.287(5) Å] in **3** is significantly shorter than those of Cu−S_{dtc} in **1a** [2.409(5) Å] and in **2** [2.414(5) Å].

UV and IR Spectra. Data for the electronic spectra of **1a**−**c**, **2**, and **3** are given in Table 9. The electronic absorption spectrum for each compound with R_2NCS_2 ligands shows one high-energy absorption at about 270 nm with a shoulder at about 285 nm, one strong broad peak in the 425−440 nm range, and another lower energy absorption in the 545−565 nm range. The first absorption may be attributed to an intraligand transition, and the shoulder is from the charge transfer of ligand to metal [LMCT (S → Cu)] in accordance with a similar assignment in $[VS_4Cu_4(R_2NCS_2)_n(PhS)_{4-n}]^{3-}$ (R_2 = Et, C_4H_8O; n = 0, 1, 2).[25] The strong broad peak in the range 425−445 nm can be assigned as a charge-transfer band of the type (π)Se → (d)Mo arising from the $MoSe_4$ moiety,[6a] which is red-shifted compared to the free $[MoSe_4]^{2-}$ anion (367 nm).[26] The lowest absorption band at about 555 nm is relatively weak and may be due to the electron transfer between $MoSe_4^{2-}$ and metal Cu. Interestingly, as the four edges of the $[MoSe_4]^{2-}$ anion are coordinated by a Cu^+ cation, the shoulder of the broad band disappears in the spectrum of **2**. The absorption peaks of **3** at 286, 375, and 545 nm are very similar to that of $[MoS_4(PhSCu)_2]^{2-}$.[21]

IR absorption data for all compounds are also given in Table 9. In the low-frequency region, the Cu−S_{dtc} vibrations show a broad band in the region of 333−355 cm^{-1}; however, the Cu−S_{SPh} vibrations are present at 321 cm^{-1} at a little lower frequency. In the 285−330 cm^{-1} region where ν(Mo−Se) frequencies are expected,[27] the Mo−Se stretching vibrations for all compounds are red-shifted compared to that of $[MoSe_4]^{2-}$ (341 cm^{-1})[1c] owing to the coordination of Cu atoms. For the three tetranuclear compounds **1a**−**c**, two types of Mo−Se absorptions in the ranges of 295−305 and 316−327 cm^{-1} are observed, of which those in the range of 314−327 cm^{-1} are assigned to Mo−μ_2-Se bond vibrations and those in the range of 295−305 cm^{-1} are due to Mo−μ_3-Se bond vibrations. The Mo−μ_3-Se bond vibration for **2** and the Mo−μ_4-Se bond vibration for **3** appear as single peaks at 314 and 292 cm^{-1}, respectively.

The IR spectra in the 400−4000 cm^{-1} region for all compounds show bands corresponding to the R_2NCS^{2-} and PhS^- ligand fingerprint regions. Except for the C−S and C═N absorptions, very few changes are observed for both kinds of ligands upon complexation with copper atoms. The C−S absorptions appear in the range 950−1000 cm^{-1} and are red-shifted by about 20−40 cm^{-1} from the free ligand of R_2NCS^{2-}.[28] It is interesting to note that the stretching vibration of the C═N bond at 1523 cm^{-1} in **2** shifts evidently to a higher frequency region than those in other compounds. This indicates an important contribution of the C═N double bond affected by the masses of the alkyl substitutes.[29]

NMR Spectra. ^{1}H and ^{95}Mo NMR data for **1a**−**c**, **2**, **3**, and some related compounds are listed in Table 10. The absorption peaks of the ^{1}H NMR spectra for all the compounds are very close to those of the free ligands $[R_2NCS_2]^-$ and PhS^-, indicating that all compounds are diamagnetic and the geometric structures of the cluster cores have little influence on the proton chemical shielding of coordinated ligands. A similar result is seen in the corresponding sulfide system.[9,30]

^{95}Mo NMR spectra for the $[MoS_4]^{2-}$ cluster system demonstrate that the chemical shifts decrease monotonically with the addition of the CuL (L = Cl, Br, I, CN, PhS, R_2NCS_2) fragment to $[MoS_4]^{2-}$, e.g. each successive addition of a CuL moiety to the $[MoS_4]^{2-}$ core resulting in a decrease of the chemical shift of the molybdenum nucleus by 210−420 ppm.[31] However, the situation in the Mo−Cu−Se complexes is quite different. Although the ^{95}Mo chemical shifts for the compounds containing the $[MoSe_4]^{2-}$ unit decrease as the additional CuL fragments are bound to the $[MoSe_4]^{2-}$ unit, no regularity of the chemical shift decrease was observed. For instance, trinuclear compound $[MoSe_4Cu_2(PPh_3)_2]$ has a resonance absorption at about 2400 ppm,[32] while the tetranuclear compounds $[MoSe_4Cu_3(R_2NCS_2)_3]^{2-}$

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Table 10. ^1H NMR and ^{95}Mo NMR Data[a] for Related Mo−Cu−Se Compounds

	^1H NMR, ppm[b]				^{95}Mo NMR[c]	
compd	$\delta_{\alpha-H}$	$\delta_{\beta-H}$	$\delta_{\gamma-H}$	δ_{Ph-H}	δ, ppm	$\Delta\nu_{1/2}$, Hz
$[MoSe_4]^{2-}$ [d]					3339	< 10
$[MoSe_4Cu_3(Et_2NCS_2)_3]^{2-}$ in **1a**	3.85	1.20			2086	358
$[MoSe_4Cu_3(C_5H_{10}NCS_2)_3]^{2-}$ in **1b**	4.04	1.56	1.10		2052	333
$[MoSe_4Cu_3\{(PhCH_2)_2NCS_2\}_3]^{2-}$ in **1c**	3.38			7.04−7.35	2028	324
$[MoSe_4Cu_4(Me_2NCS_2)_4]^{2-}$ in **2**	3.36				−1.50	28
$[MoSe_4Cu_{10}(PhS)_{12}]^{4-}$ in **3**				6.44−7.52	−1.31	25
$[SeMoSe_3ClCu_3(PPh_3)_3]$[e]					1301	115
$[MoSe_4\{Cu(PPh_3)_2\}]$[f]					2400	<100

[a] Recorded at ambient temperature. [b] In DMSO-d_6. [c] In DMF. [d] In CH_3CN. [e] Reference 8b. [f] Reference 32.

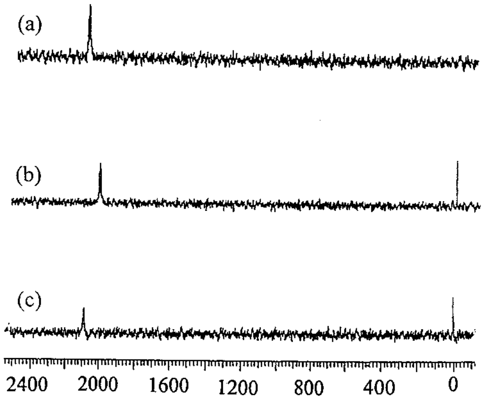

Figure 5. (a) ^{95}Mo NMR spectrum of **1a** in DMSO. (b) ^{95}Mo NMR spectrum of the sample drawn from the reaction mixture of $[Et_4N]_2[MoSe_4]$ with 3 equiv of CuCl in DMSO. (c) Addition of 3 equiv of NaS_2CNEt_2 to (b).

have a resonance absorption at about 2000 ppm, which have Mo nuclei less effectively deshielded than that in $[MoSe_4]^{2-}$ by ca. 1000 and 1400 ppm, respectively. Surprisingly, the ^{95}Mo NMR spectra of both the pentanuclear compound **2** and the polynuclear compound **3** show a sharp resonance peak ($\Delta\nu \approx$ 25 Hz) at about −2.0 ppm. ^{95}Mo NMR spectra of the cubanelike $[MoSe_4Cu_3X(PPh_3)_3]$ complexes show a resonance peak at about 1300 ppm,[8b] of which the molybdenum nucleus has been shielded by 2100 ppm after the $[MoSe_4]^{2-}$ moiety coordinates to three $(CuPPh_3)^+$ species, being much more deshielding than those in **1a**−**c** with $MoCu_3$ planar core. All of these results demonstrate that ^{95}Mo NMR chemical shifts are very sensitive to structural variations of the complexes in the selenide system. One possible reason can be explained as a better orbital overlap in the selenomolybdates due to the similar size of Mo and Se atoms;[26] thus, the Se atom would cause a greater withdrawal of electron density after the $[MoSe_4]^{2-}$ entity coordinates to Cu(I) atoms to give the unusual variations of the chemical shifts as compared to the corresponding thiomolybdate and oxomolybdate derivatives. Within the three $MoSe_4Cu_3$ complexes, the differences in the ^{95}Mo NMR data are small, ca. 58 ppm for chemical shifts and ca. 40 Hz for line widths, indicating very small electronic influences on the ^{95}Mo nucleus from the outermost ligands.

For the furtherance of understanding the reactivity of the $[MoSe_4]^{2-}$ anion and reaction mechanism in the present Mo−Cu−Se reaction system, the ^{95}Mo NMR spectrum has been used to monitor several reaction processes.

Figure 5a shows the ^{95}Mo NMR spectrum of the sample drawn from the synthetic reaction mixture for **1a**. Only one resonance peak at 1999 ppm ($\Delta\nu$ = 366 Hz), which may be assigned to $[MoSe_4(CuCl)_3]^{2-}$, was observed from the reaction mixture of $[Et_4N]_2[MoSe_4]$ and CuCl in a molar ratio of 1:3 in DMF. Nearly no change of the ^{95}Mo NMR signal was observed after the addition of the Et_2NCS_2Na salt to the above reaction solution, and the signal is independent of the reaction time. In the light of this result, it may be suggested that the $MoSe_4Cu_3$ complex is the only product in the reaction of the $[MoSe_4]^{2-}$ anion and CuCl in DMF, and the final product **1a** is formed through the substitution reaction of Cl^- by $Et_2NCS_2^-$.

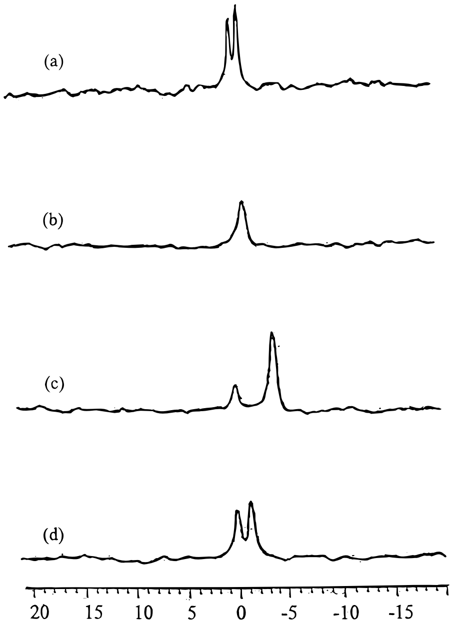

Figure 6. (a) ^{95}Mo NMR spectrum of **3** in DMSO. (b) ^{95}Mo NMR spectrum of **2** in DMSO. (c) ^{95}Mo NMR spectrum of the sample drawn from the reaction mixture of **2** and 2 equiv of $[Et_4N]_2[Cu(PhS)_3]$ in DMSO. (d) Addition of 4 equiv of $[Et_4N]_2[Cu(PhS)_3]$ to (c).

Figure 6c shows the ^{95}Mo NMR spectrum of the sample drawn from the reaction mixture of **2** and $[Et_4N]_2[Cu(PhS)_3]$. When **2** reacted with 2 equiv of $[Et_4N]_2[Cu(PhS)_3]$ in DMF−CH_3CN, only one resonance peak at −4.33 ppm ($\Delta\nu$ < 50 Hz) was found. Further addition of 4 equiv of $[Et_4N]_2[Cu(PhS)_3]$ to the above reaction mixture gave rise to a disappearance of the signal at −4.33 ppm and appearance of a new one at −1.14 ppm ($\Delta\nu$ < 50 Hz) (Figure 6d). With reference to the ^{95}Mo NMR data of the $MoCu_4$ and $MoCu_{10}$ core complexes, the resonance peak at −4.33 ppm may be assigned to the center Mo atom in the $MoSe_4Cu_6$ complex and it means that the $MoSe_4Cu_6$ complex may be an intermediate during the transformation from the $MoCu_4$ to $MoCu_{10}$ core complexes. The ^{95}Mo chemical shifts of these three complexes do not have obvious differences even if they are undergoing structural variations. The result may indicate that the Mo nucleus deshielding effect from four Cu atoms in the $MoSe_4Cu_4$ compound is much larger than those from three Cu atoms in the MSe_4Cu_3 compounds and has almost reached saturation. Thus, further addition of Cu atoms to the $MoSe_4Cu_4$ moiety led to little change of the ^{95}Mo NMR data. Thus, the sensitivity of the ^{95}Mo NMR data to subtle structural features and the saturation of the Mo nucleus shielding effect caused by the further coordination of the $MoSe_4$ moiety to the Cu atoms observed in the Mo−Cu−Se complexes in general are apparent from this work.

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Supporting Information Available: Listings of additional crystallographic details, complete bond distances and angles, anisotropic displacement parameters, and hydrogen atom positions for **1a**, **2**, and **3** (16 pages). Ordering information is given on any current masthead page.

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