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Investigation into the Formation of Supramolecular Compounds from Mixed As/S-Ligand Complexes $[(Cp^*Mo)_2As_2S_3]$ ($Cp^* = C_5Me_5$) and Copper Halides

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The coordination behavior of $[(Cp^*Mo)_2As_2S_3]$ (**3**) ($Cp^* = C_5Me_5$) toward Cu(I) halides was investigated. One dimensional polymers of the general formula $[(Cp^*Mo)_2As_2S_3(CuHal)_2]_n$ (Hal = Cl, **4**; Br, **5**) and an oligomer of composition $[\{(Cp^*Mo)_2As_2S_3\}_3(CuI)_7]$ (**6**) formed upon the reaction of **3** with the corresponding copper halide. All of the compounds were characterized by ESI–MS, elemental analysis, and single-crystal X-ray crystallography. The solid-state structures of **4** and **5** are isostructural and contain 1D S-shaped chains. This peculiar folding is achieved by alternating planar and folded Cu_2Hal_2 rings linked together by the central monosulfide bridge of the middle deck of the organometallic unit. The structure of **6** is characterized by a novel $[CuI]_7$ aggregate, which forms a very flat $Cu_6I_3S_3$ bowl along with three integrated peripheral $[(Cp^*Mo)_2As_2S_3]$ building blocks. In contrast to earlier findings, the middle deck of the organometallic units consists in all structures of two trapezoidal AsS dumbbells and one monosulfide ligand.

Introduction

The self-organization of organoelement compounds into supramolecular networks has become a rapidly growing field of chemical research.[1] Most of the coordination polymers are organic−inorganic hybrid materials in which similar or different metal centers are connected by N-, O-, or S-containing donor ligands. Copper(I) halides are able to form a variety of coordination compounds ranging from low-dimensional complexes to three-dimensional networks. A novel concept employs the phosphorus donor functions of organometallic P-ligand complexes in the presence of Cu(I) or Ag(I) salts. That is, oligomers and polymers have been formed starting from $[\{(C_5H_5)Mo(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$[2] or spherical fullerene-like aggregates when using $[Cp^*Fe(\eta^5\text{-}P_5)]$.[3] Thus far, a comparable supramolecular chemistry of the heavier P homologues has been reported for $[Cp^*Mo(CO)_2(\eta^3\text{-}As_3)]$ (**1**) and $[\{CpMo(CO)_2\}_2(\mu,\eta^2\text{-}Sb_2)]$, respectively, in their reactions with copper halides.[4,5] The obtained results differ considerably from those described recently for coordination polymers of Cu(I) with PR_3 or AsR_3 ligands.[6,7] It is striking that the aggregation of S- or Se-organic compounds with copper halides has not been as frequently investigated.[9,10]

Ligands derived from group 15 (E15) and group 16 (E16) elements may be combined in organometallic complexes to give mixed E15/E16 ligands. The chemistry of this class of structurally diverse compounds lies between that of E15−

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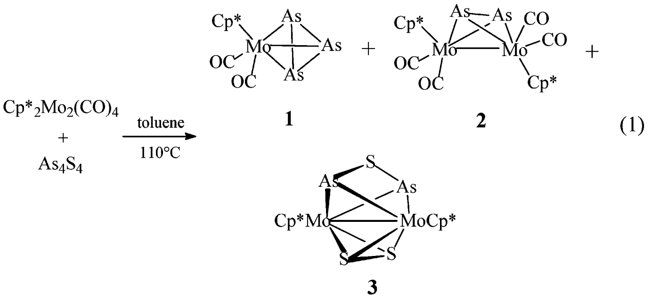
and E16−ligand complexes.[8] Thus, it may be of interest to know how the formation of coordination polymers using ligand complexes with mixed E15/E16 ligands is affected by the presence of chalcogenes. In this article, we report for the first time on the formation of supramolecular networks from a mixed As/S−ligand complex and various copper halides.

As a suitable candidate, we chose $[(Cp^*Mo)_2As_2S_3]$ (**3**) belonging to the class of sandwich-like di(cyclopentadienyl-metal) complexes.[11,12] Complex **3** forms in the reaction of $[Cp^*Mo(CO)_2]_2$ with realgar in boiling toluene apart from side products $[Cp^*Mo(CO)_2As_3]$ (**1**) and $[\{Cp^*Mo(CO)_2\}_2As_2]$ (**2**) (eq 1).[11] A crystallographic determination of the positions of the main group elements in **3** was not possible because of crystal disorder. As an additional aspect of this work, the distribution of the atoms and their connectivity within the middle deck of $[(Cp^*Mo)_2As_2S_3]$ (**3**) are rediscussed.



Results

Interdiffusion of solutions of **3** in CH_2Cl_2 and the corresponding Cu(I) halide in CH_3CN (molar ratio 1:2) gave red-brown platelets of **4**−**6** (eq 2). The new compounds are sparingly soluble in acetonitrile and insoluble in dichloromethane or toluene. Their composition was determined by single-crystal X-ray diffraction analysis, elemental analyses, and electrospray (ESI) or field desorption (FD) mass spectrometry, respectively.

$$[(Cp^*Mo)_2As_2S_3] \begin{cases} \xrightarrow{CuCl} [(Cp^*Mo)_2As_2S_3(CuCl)_2]_n \quad \mathbf{4} \\ \xrightarrow{CuBr} [(Cp^*Mo)_2As_2S_3(CuBr)_2]_n \quad \mathbf{5} \\ \xrightarrow{CuI} [\{(Cp^*Mo)_2As_2S_3\}_3(CuI)_7] \quad \mathbf{6} \end{cases} \qquad (2)$$

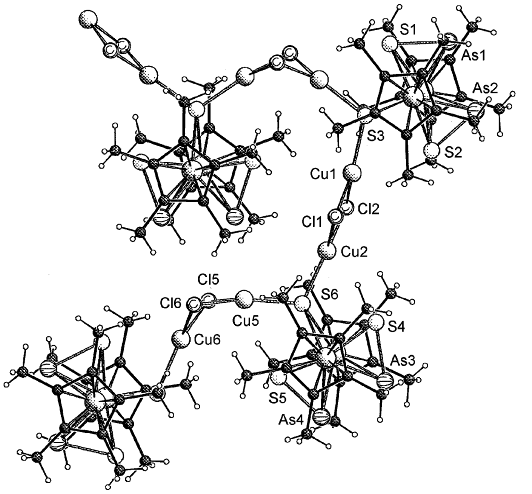


Figure 1. Structure of the asymmetric unit of $[(Cp^*Mo)_2As_2S_3(CuCl)_2]_n$ (**4**), which is also the repeat unit of the 1D polymer.

Table 1. Comparison of Important Distances (Å) of Compounds **4**−**6**

	4	**5**	**6**
Mo−Mo	2.598(2)−2.603(2)	2.596(2)−2.601(2)	2.591(2)−2.596(2)
Mo−As	2.610(2)−2.645(2)	2.611(2)−2.646(2)	2.606(2)−2.626(2)
Mo−S	2.484(2)−2.546(2)	2.482(3)−2.537(3)	2.482(3)−2.567(3)
As−S	2.191(3)−2.235(3)	2.182(3)−2.236(3)	2.206(3)−2.229(3)
Cu−S	2.189(3)−2.205(3)	2.207(3)−2.220(3)	2.230(3)−2.254(3)
Cu−Cl	2.307(3)−2.356(3)		
Cu−Br		2.424(2)−2.471(2)	
Cu−I			2.571(2)−2.774(2)
As···As	2.757(2)−2.762(2)	2.752((2)−2.762(3)	2.794(2)−2.811(2)
S···S	2.817(4)−2.872(4)	2.833(5)−2.875(5)	2.824(4)−2.840(3)
Cu···Cu	2.801(2)−3.086(2)	2.813(2)−3.257(2)	2.719(2)−2.938(2)

^{1}H NMR spectra of **4** and **5** in CD_3CN reveal for the Cp* protons singlets at $\delta = 2.15$ along with weaker singlets at 2.13 (**4**) and 2.14 (**5**). These signals may be explained by partial depolymerization under the influence of the coordinating solvent.[13] The spectrum of **6** contains singlets at $\delta =$ 2.14 and 2.18 ppm, the latter corresponding to uncoordinated $[(Cp^*Mo)_2As_2S_3]$.

The positive ion ESI mass spectra of **4** and **5** in CH_3CN also indicate that the compounds dissolve under depolymerization. Thus, similar fragments are observed. The highest peak at $m/z = 1481.0$ (intensities 64 and 40%, respectively) may be assigned to the fragment $[\{(Cp^*Mo)_2As_2S_3\}_2Cu]^+$ ($[2 \times \mathbf{3} + Cu]^+$). Interaction of this ion with CH_3CN and subsequent fragmentation leads to the ions $[\mathbf{3} + Cu + CH_3CN]^+$, $[\mathbf{3} + Cu]^+$, and $[\mathbf{3} + CH_3CN]^+$ and $[\mathbf{3}]^+$, respectively. The ESI−MS of **6** in CH_3CN contains the fragment $[2 \times \mathbf{3} + Cu_2I]^+$ ($m/z = 1670.8$, $I = 2.5\%$) as the highest peak. Apart from the peak for $[\mathbf{3}]^+$ (100%), the fragment $[2 \times \mathbf{3} + Cu]^+$ appears only in 2.5% intensity. The FD−MS of **6** contains peaks at $m/z = 707.9$ ($[\mathbf{3}]^+$, 100%) and 1479.7 ($[2 \times \mathbf{3} + Cu]^+$, 1%).

Crystal Structure of $[(Cp^*Mo)_2As_2S_3(CuCl)_2]_n$ (4). Suitable crystals for X-ray diffraction analysis were directly obtained from the reaction solution. The selected crystal was an inversion twin with a ratio of 91.7:8.3. Crystallographic data are listed in Tables 1 and 2. The asymmetric unit consists of four triple-decker-like $[(Cp^*Mo)_2(\mu,\eta^2\text{-}AsS)_2(\mu\text{-}S)]$ complexes and four four-membered Cu_2Cl_2 rings. These building blocks are assembled in an alternating manner forming a 1D S-shaped polymer (Figures 1 and 2). As a peculiarity, planar Cu_2Cl_2 rings alternate with folded ones. Accordingly, the Cu−Cu distances vary within the rings between 2.801(2) (bent) and 3.086(2) Å (planar). The mean Cu−Cl length of 2.332(3) Å is within the range observed in

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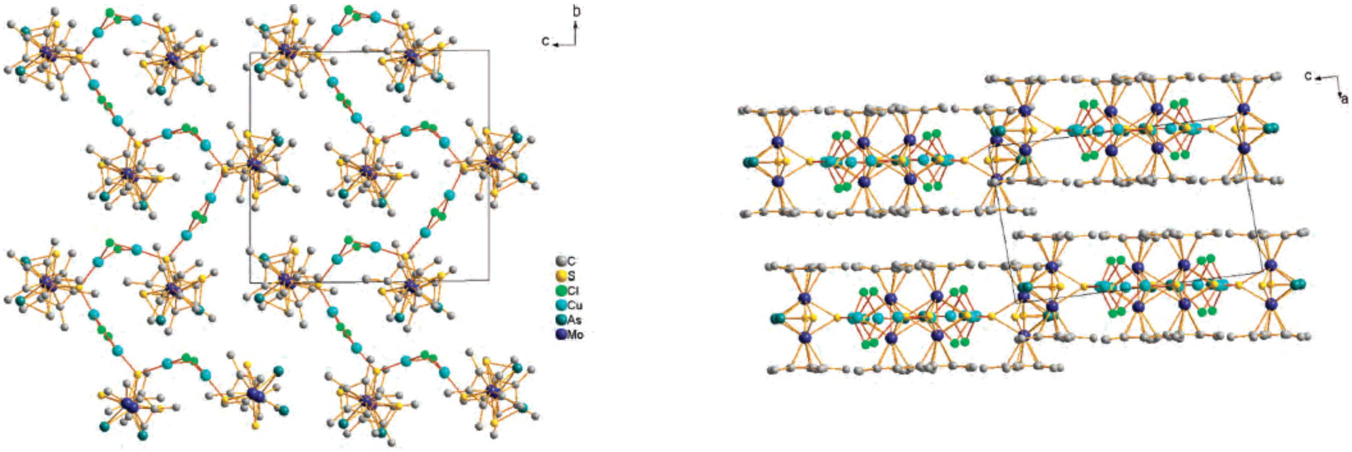

Figure 2. Projections of sections of the S-shaped 1D polymer of $[(Cp^*Mo)_2As_2S_3(CuCl)_2]_n$ (**4**); hydrogen atoms are omitted for clarity: (left) view down *a*; (right) view down *b*.

Table 2. Crystallographic Data for Compounds **4**−**6**

	4	5	6
formula	$C_{80}H_{120}As_8Cl_8Cu_8Mo_8S_{12}$	$C_{80}H_{120}As_8Br_8Cu_8Mo_8S_{12}$	$C_{60}H_{90}As_6Cu_7I_7Mo_6S_9$
M_w	3625.5	3981.1	3458.3
crystal size (mm^{-1})	0.11 × 0.05 × 0.05	0.12 × 0.07 × 0.04	0.32 × 0.24 × 0.02
crystal system	triclinic	triclinic	triclinic
space group	$P1$	$P1$	$P\bar{1}$
a (Å)	10.609(1)	10.594(1)	15.608(1)
b (Å)	16.035(2)	16.371(2)	16.051(1)
c (Å)	16.561(2)	16.638(2)	21.119(2)
α (deg)	90.4(0)	91.1(1)	100.4(1)
β (deg)	92.5(1)	92.3(1)	93.6(1)
γ (deg)	96.2(1)	97.4(1)	118.9(1)
V (Å^3)	2797.9(5)	2858.0(6)	4484.1(9)
Z	1	1	2
σ_{calcd} (g cm^{-3})	2.152	2.313	2.561
μ (Mo$_{K\alpha}$,mm^{-1})	5.147	7.648	7.280
instrument	STOE-IPDS	STOE-IPDS	STOE-IPDS
T (K)	123	123	123
scan range	$2.20 < \Theta < 25.88$	$2.17 < \Theta < 25.84$	$1.74 < \Theta < 25.26$
reflns collected	28 818	27 587	38 938
unique			
observed [$I > 2\sigma(I)$]	14 347	14 898	11 936
parameters refined	1108	1113	418
absorption correction	numerical	numerical	analytical
transmission	0.5962/0.4382	0.7080/0.5004	0.7773/0.1371
max/min residual density (e/Å^{-3})	1.164/−0.689	1.435/−0.804	2.722/−1.855
R_1, wR_2 ($I > 2\sigma$)	0.036, 0.076	0.037, 0.082	0.070, 0.192
R_1, wR_2 (all data)	0.057, 0.079	0.054, 0.085	0.083, 0.201

CuCl-derived oligomers and polymers (Table 1).[7,14] Although each of the copper chloride structural motifs is known, the simultaneous existence of such motifs in polymeric structures has not yet been reported to our knowledge.

Two trigonal-planar copper centers of different Cu_2Cl_2 rings are tightly fixed at the central sulfur ligand of each dimolybdenum building block, forming Cu−S−Cu angles of 112.2(2)° on average. The Cu−S distances correspond to those of Cu−S bonds within cubane-like homo- or heterometallic sulfide clusters incorporating CuHal (Hal = Cl, Br, I) moieties.[15] All of the copper and sulfur atoms and the midpoints of the Mo−Mo vectors of one strand lie within the *bc* plane. Because all Mo−Mo vectors are parallel to each other, the Cp* ligands within each chain are coplanar, forming narrow ribbons that are stacked along the *a* axis but displaced slightly stepwise with respect to the *bc* plane (Figure 2).

The successful crystal structure determination of **4** (and **5**, below) allows a re-evaluation of the element distribution in the middle deck of the $[(Cp^*Mo)_2As_2S_3]$ building block (Figure 3). Originally, a ligand distribution **A** was assumed (Scheme 1).[11] A similar arrangement of P/S ligands in $[(Cp^*Mo)_2P_2S_3]$ was assumed on the basis of ^{31}P NMR spectroscopy.[16] Now it is evident that two μ,η^2-AsS dumbbells [$d(\text{As}-\text{S})_{mean} = 2.234(3)$ Å] and a monosulfide bridge (Scheme 1, structure **C**) form the trapezoid middle deck. No hint has been found thus far for structural arrangements like type **B** or **D**. The As−As distance of 2.752(2) Å indicates only weak bonding interactions, which seem to be too weak

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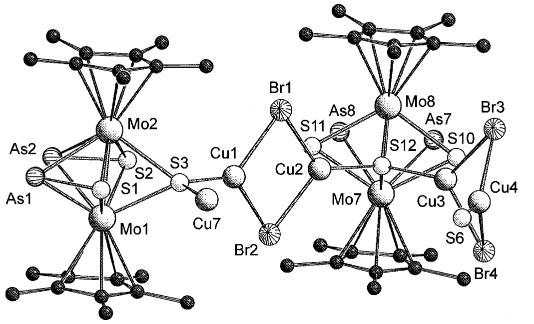
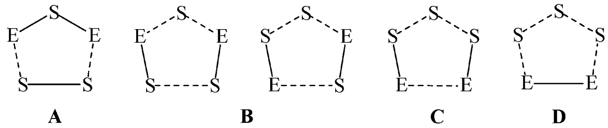


Figure 3. Section of the 1D structure of $[(Cp^*Mo)_2As_2S_3(CuBr)_2]_n$ (**5**) viewed down the *b* axis. Hydrogen atoms are omitted.

Scheme 1. Distribution and Connectivity of E (P, As) and Sulfur Atoms within the Middle Deck of $[(Cp^*Mo)_2E_2S_3]$ Complexes



for the postulation of a $\mu,\eta^{2:2}$-As_2S_2 ligand. Triple-decker-like complexes with such an As_2X_2 (X = S, Se) ligand have been described in the redox system $[(Cp^*Fe)_2As_2X_2]$ $[(Cp^*Fe)_2(AsX)_2]^+ + e^-$ as the result of the reductive dimerization of two $\mu,\eta^{2:2}$-AsX bridges.[17,18] The As−As separation in this example (X = Se) is 2.587(3) Å compared to 2.89(1) Å in the corresponding cation.

Central sulfur ligands S(3), S(6), S(9), and S(12), which serve as linkers for the different Cu_2Cl_2 units, are clearly monosulfide bridges without any bonding contacts [d(S···S) > 2.8 Å] with the neighboring sulfur atoms.

Crystal Structure of $[(Cp^*Mo)_2As_2S_3(CuBr)_2]_n$ (5). Analogous to the structure of **4**, the structure of **5** is composed of 1D S-shaped polymers (Figure 3). The Cp* rings of all $[(Cp^*Mo)_2As_2S_3]$ building blocks in both compounds are oriented in an eclipsed conformation. Whereas the Cu−Cu distances in the planar four-membered Cu_2Hal_2 rings increase by 0.16 Å when going from **4** to **5**, they do not change in the bent rings [$d(Cu-Cu)_{mean}$ = 2.822(2) Å]. Accordingly, the Cu−Hal−Cu angles in the bent rings decrease from 74.0(1)° (Cu−Cl−Cu) to 70.5(2)° (Cu−Br−Cu) in order to compensate for the larger covalent radius of Br.

Crystal Structure of $[\{(Cp^*Mo)_2As_2S_3\}_3(CuI)_7]$ (6). The structure of **6** is characterized by a novel $[CuI]_7$ aggregate. Three folded Cu_2I_2 rings are linked together by the lone pairs of the central monosulfide ligands of the peripheral $[(Cp^*Mo)_2As_2S_3]$ units and by a central CuI unit (Figure 4). Central copper atom Cu(7) is tetrahedrally surrounded by four iodine atoms [$d(Cu-I)_{mean}$ = 2.642(2) Å] (Figure 5). The diameter of the $Cu_7I_7S_3$ core is 8.2 Å, whereas the edges of the triangle defined by the As atoms are about 17 Å long. Terminal iodine atom I(7) is directed more toward Cu(3) and Cu(4) than toward Cu(2) and Cu(6), by about 0.5 Å. Concomitantly, this slight asymmetry is reflected by inequivalent Cu−Cu distances in the Cu_2I_2 rings, which range from 2.719(2) Å [Cu(2)−Cu(3)] to 2.938(2) Å [Cu(1)−Cu(6)]. This means that they are shorter than comparable Cu−Cu distances in the structures of **4** and **5**. Whereas the Cu−S distances [$d(Cu-S)_{mean}$ = 2.240(3) Å] are close to those of **4** and **5**, the Cu−S−Cu angles are smaller by more than 10°, probably as a consequence of steric constraints within the $Cu_6I_3S_3$ macrocycle of **6**.

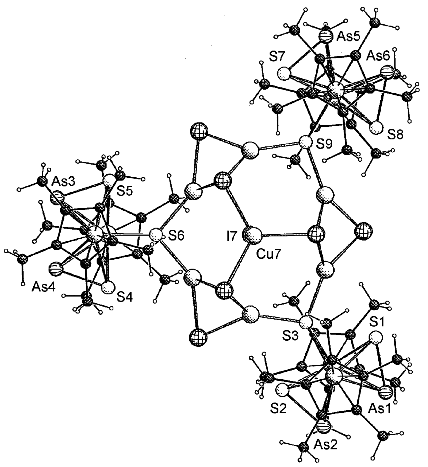


Figure 4. Molecular structure of $[\{(Cp^*Mo)_2As_2S_3\}_3(CuI)_7]$ (**6**).

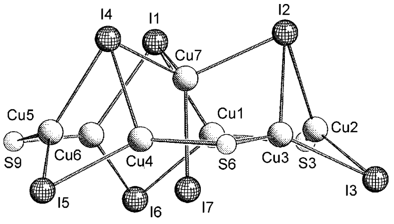


Figure 5. Structure of the $Cu_7I_7S_3$ core of $[\{(Cp^*Mo)_2As_2S_3\}_3(CuI)_7]$ (**6**) (side view).

As in the structures of **4** and **5**, the arrangement of As/S ligands within the $[(Cp^*Mo)_2As_2S_3]$ units corresponds to type **C** (Scheme 1), giving rise to comparable structural parameters of the organometallic moiety. The only difference is the staggered conformation of two of the $(Cp^*Mo)_2$ sandwich units, whereas the Cp* ligands bound to Mo(1) and Mo(2) come close to an eclipsed conformation.

Conclusions

This work reports for the first time on the potential of mixed As/S−ligand complexes in the formation of supramolecular networks. In all of the products, the assembly of the building blocks is promoted by the lone pairs of the central monosulfide bridge of the organometallic complex. The nature of the products depends on the employed copper halide, and unprecedented structural motifs are found.[19] Thus, products **4** and **5** obtained from CuCl and CuBr are 1D polymers, whereas **6** still has molecular architecture. Because the formation of coordination polymers from As containing donor ligands and CuHal is known,[5,20] the participation of arsenic in our case will be a goal for future investigations.

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A further result of this investigation is that the originally proposed arrangement (**A**, Scheme 1) within the sandwichlike structure of **3** has to be revised. The connectivity of As/S ligands is unexpected as well. Taking into account previous work,[11,16] one may consider isomerization within the main group element ligand sphere to be affected by the coordination of Lewis acid complex fragments or metal cations. This point is currently under investigation employing the homologous P/S−ligand complex [(Cp*Mo)$_2$P$_2$S$_3$].

Experimental Section

General Methods. All manipulations were carried out under nitrogen using glovebox or Schlenk techniques. [(Cp*Mo)$_2$As$_2$S$_3$] (**3**) was prepared from [Cp*Mo(CO)$_2$]$_2$ and As$_4$S$_4$ in boiling toluene.[11] ESI−MS spectra were measured on a Finnigan Thermoquest TSQ 7000 mass spectrometer, and FD−MS spectra were measured on a Finnigan MAT95 spectrometer.

Reaction of [(Cp*Mo)$_2$As$_2$S$_3$] with CuHal (Hal = Cl, Br, I). A solution of 0.28 mmol of CuHal (Hal = Cl, 28 mg; Br, 40 mg; I, 54 mg) in acetonitrile (10 mL) was layered carefully over a solution of **3** (100 mg, 0.14 mmol) in CH$_2$Cl$_2$ (10 mL). After complete diffusion, an X-ray amorphous powder formed, which was removed by filtration. Then, the resulting dark solution was layered with diethylether (20 mL). Bright-red plates were obtained after storing at ambient temperature and then at −4 °C. All of the products were washed with ether and dried in vacuum.

[(Cp*Mo)$_2$As$_2$S$_3$(CuCl)$_2$]$_n$ (**4**): Yield: 20 mg (16%). ^{1}H NMR (300 MHz, CD$_3$CN, 21 °C): δ 2.15 (s; C$_5$Me$_5$). PI−ESI−MS (CH$_3$CN): *m*/*z* (%) 707.9 (78 [**3**]$^+$), 738.9 (100), 749.9 (62, [**3** + CH$_3$CN]$^+$, 774.9 (26, [**3** + Cu]$^+$), 815.9 (29, [**3** + Cu + CH$_3$CN]$^+$), 843.9 (26), 1438.0 (20), 1481.0 (64, [2 × **3** + Cu]$^+$). Elemental analysis calcd (%) for C$_{20}$H$_{30}$Mo$_2$As$_2$S$_3$Cu$_2$Cl$_2$ (906.38): C 26.50, H 3.34, S 10.61. Found: C 25.81, H 3.40, S 9.64.

[(Cp*Mo)$_2$As$_2$S$_3$(CuBr)$_2$]$_n$ (**5**): Yield: 25 mg (18%). ^{1}H NMR (300 MHz, CD$_3$CN, 21 °C): δ 2.15 (s; C$_5$Me$_5$). ESI−MS (CH$_3$CN): PI-ESI: *m*/*z* (%) 707.9 (100,$^{3+}$), 738.9 (57), 749.9 (45, [**3** + CH$_3$CN]$^+$), 815.8 (20, [**3** + Cu + CH$_3$CN]$^+$), 1403.9 (20), 1480.9 (40, [2 × **3** + Cu]$^+$). NI-ESI: *m*/*z* (%) 222.8 (100, [CuBr$_2$]$^-$). Elemental analysis calcd for C$_{20}$H$_{30}$Mo$_2$As$_2$S$_3$Cu$_2$Br$_2$ (995.28) C 24.14, H 3.04, S 9.67. Found: C 24.08, H 3.06, S 9.59.

[{(Cp*Mo)$_2$As$_2$S$_3$}$_3$(CuI)$_7$] (**6**): Yield: 19 mg (12%).^{1}H NMR (300 MHz, CD$_3$CN, 21 °C): δ 2.14 (s; C$_5$Me$_5$); FD−MS (CH$_2$Cl$_2$): *m*/*z* (%) 707.9 (100,$^{3+}$), 1479.7 (1, [2 × **3** + Cu]$^+$). PI−ESI−MS: *m*/*z* (%) 707.8 (100, [**3**]$^+$), 1480.0 (2.5, [2 × **3** + Cu]$^+$), 1670.8 (2.5, [2 × **3** + Cu$_2$I]$^+$). Elemental analysis calcd (%) for C$_{60}$H$_{90}$Mo$_6$As$_6$S$_9$Cu$_7$I$_7$ (3458.26): C 20.84, H 2.62, S: 8.35. Found: C 20.78, H 2.64, S 8.07.

X-ray Structure Determination of Compounds 4, 5, and 6. Inversion twins were measured for **4** (ratio 92:8) and **5** (86:14). Crystal data were collected on a Stoe-IPDS diffractometer (Mo Kα radiation, graphite monochromator). Crystallographic details are given in Table 2. The structures were solved by direct methods and refined by full-matrix least squares (SHELXL97 program) with all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, the H atoms were calculated geometrically, and a riding model was used during the refinement process.

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Supporting Information Available: Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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