Three New Structural Types of Mo/Ag/S Polymeric Complexes**

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Transition metal sulfur complexes are of important biological and industrial significance.[1] The pioneering work of Müller and co-workers[2] has largely promoted research on Mo(W)/Cu(Ag)/S systems. Since the first characterization of $[PPh_4]_n\{[MoAgS_4]\}_n$ by resonance Raman spectroscopy,[3] a series of one-dimensional W/Ag/S polymeric compounds have been synthesized. It was found that their configurations are controlled by the valence states and the dimensions of the cations; a variety of structures exist, for example, single linear chains,[4a] double chains,[5] zigzag chains,[6] one-dimensional chains in which the square units were linked by Ag atoms,[7] and helical chains.[8] Only few polymeric Mo/Ag/S complexes have been characterized by X-ray crystallography.[4] We have reported on the self-assembly of $[NH_4]_2[WS_4]$ and $AgNO_3$ to form a variety of polymeric chains.[5–8] After the failure to achieve the analogous self-assembly of $[MoS_4]^{2-}$ and $AgNO_3$, we recently developed a new procedure: When $AgNO_3$ was substituted by Ag_2S as the starting material, reactions of $[MoS_4]^{2-}$ and Ag_2S provided three new types of polymeric complexes with unprecedented configurations. Compounds **1**–**3** (DMF = dimethylformamide, DMSO = dimethyl sulfoxide) have wavelike, zigzag, and helical polymeric anions, respectively.

$\{[N(C_6H_5CH_2)(C_2H_5)_3MoAgS_4]\}_n$ **1**

$\{[Ca(dmf)_6Mo_2Ag_2S_8]\}_n$ **2**

$\{[Nd(dmso)_8Mo_3Ag_3S_{12}]\}_n$ **3**

Compound **1** was synthesized by the reaction of $[NH_4]_2[MoS_4]$, Ag_2S, and $[N(C_6H_5CH_2)(C_2H_5)_3]Cl$ in DMF, and its crystal structure was determined[9] (Figure 1). The polymeric anion has a wavelike chain structure with a Ag-Mo-Ag bond angle of 157.14(5)° and a Mo-Ag-Mo bond angle of 156.47(5)°. This is in contrast to the nearly linear anion chains of $\{[AgMoS_4(\gamma\text{-MePyH})]\}_n$ and $\{[AgMoS_4(\alpha\text{-MePyH})]\}_n$[4a] (Py = pyridine), in which the Ag-Mo-Ag and Mo-Ag-Mo angles are 179.3(2)–180.0(1)°, and the linear $[WAgS_4]_n^-$ chain with Ag-W-Ag and W-Ag-W angles of 176.4(5) and 176.4(3)°, respectively;[5] in the case of the latter the large cation $H_3NC(CH_2CH_2OH)_3^+$ induces the linear structure. Therefore, the wavelike chain of **1** that deviates highly from linearity is unexpected. Within the cluster, all Ag atoms are bonded to four μ_2-S atoms, which also form bonds to Mo atoms; in this way each Ag atom interacts with two Mo atoms. All the Mo and Ag atoms are almost in the same plane. The chains have two orientations: one type runs parallel to the crystallographic *b* axis, whereas the other parallel to the *a* axis.

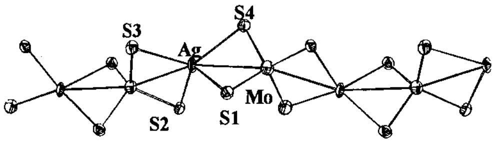

Figure 1. The structure of the polymeric anion of **1**. Selected bond lengths [Å] and angles [°]: Mo–Ag 2.893(1), 2.916(1); Mo–S 2.918(3), 2.216(4), 2.200(3), 2.193(3); Ag–S 2.601(3), 2.560(3), 2.460(4), 2.559(3); Mo-Ag-Mo 156.47(5), Ag-Mo-Ag 157.14(5).

When Ca^{2+} was used as the complementary cation in place of $[N(C_6H_5CH_2)(C_2H_5)_3]^+$, the reaction of $[NH_4]_2[MoS_4]$ and Ag_2S yields **2**, which displays zigzag polymeric anions (Figure 2).[10] As in the case of **1**, all the Mo and Ag atoms are almost in the same plane. Every Mo atom is linked to two Ag atoms through three μ_2-S atoms, and a highly distorted tetrahedral AgS_4 moiety (tetrahedral angle 93.6–118.8°) is formed. The whole chain looks like a string of "butterflies", and all the Mo and Ag atoms of one chain form an equilateral zigzag arrangement. Although a W/Ag/S polymeric compound with the same cation is not available for comparison, $\{[(Ca(dmso)_6)_2(W_4Ag_4S_{16})]\}_n$,[6] which has the similar cation $[Ca(dmso)_6]^{2+}$, has an uneven zigzag chain structure in which W-Ag-W units are perpendicular to W-Ag-W-Ag-W-Ag units. Compared with the linear M/Ag/S (M = W, Mo) chains induced by the univalent cations, this anionic structure indicates that use of cations with a higher valence state will result in more compact structures of the anionic chains.

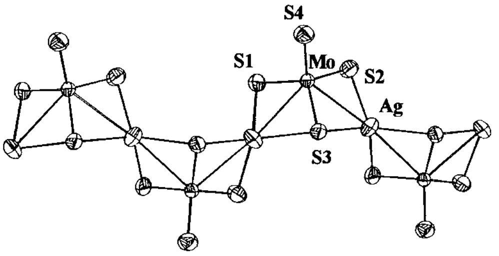

Figure 2. The structure of the polymeric anion of **2**. Selected bond lengths [Å] and angles [°]: Ag–Mo 2.9603(5), 2.9611(5); Ag–μ_2-S 2.5098(3), 2.5503(13); Ag–μ_3-S 2.5591(12), 2.5920(12); Mo-$S_{terminal}$ 2.1447(12); Mo–μ_2-S 2.150(5), 2.223(12); Mo–μ_3-S 2.2551(12); Mo-Ag-Mo 173.30(2), Ag-Mo-Ag 96.964(10).

Compound **3** was synthesized by the reaction of $[NH_4]_2[MoS_4]$ and Ag_2S with the complementary cation $[Nd(dmso)_8]^{3+}$ (Figure 3).[10] It has different structural features than the polymeric $\{[Nd(dmso)_8W_3Ag_3S_{12}]\}_n$ (**4**), which was self-assembled from $[NH_4]_2[WS_4]$ and $AgNO_3$.[8] Both **3** and **4** have helical chains consisting of SMS_3Ag_2 (M = Mo, W) butterfly-type units. Every chain in **3** is made up of two sets of helices which alternatively propagate along the chain (this

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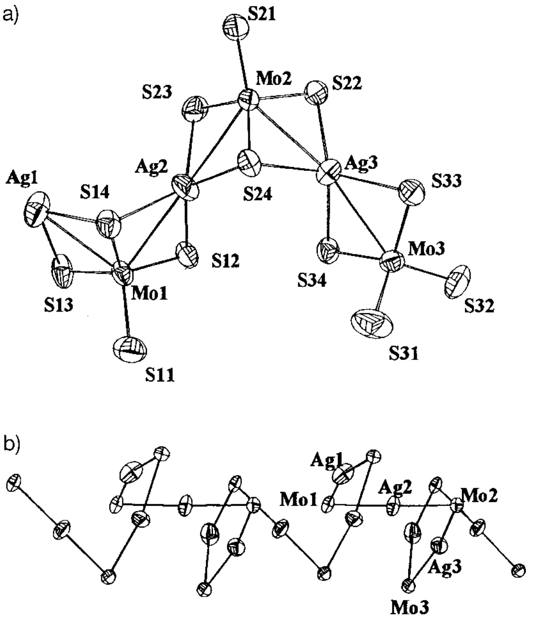

Figure 3. a) The framework of the polymeric anion of **3** (ORTEP representation, 50% displacement ellipsoids). b) The structure of the polymeric anion of **3**. Selected bond lengths [Å] and angles [°]: Ag–Mo 2.9220(13)–2.9625(12); Ag–μ_2-S 2.463(3)–2.617(4); Ag–μ_3-S 2.546(3)–2.592(3); Mo–$S_{terminal}$ 2.139(4), 2.154(3), 2.157(4); Mo–μ_2-S 2.193(3)–2.212(3); Mo–μ_3-S 2.237(3), 2.244(3), 2.249(3); Ag-Mo-Ag 82.53(4), 86.18(4), 88.08(4); Mo-Ag-Mo 177.43(5), 162.69(5), 166.04(5); dihedral angle Mo2-S24-Ag2/Mo2-S24-Ag3 60.12.

remarkable structure is shown Figure 3a), while **4** has a relatively unruly helical structure. These differences may arise from the different spreading of the "wings" of the butterfly. The smaller dihedral angle Ag2-Mo2-S24/Ag3-Mo2-S24 of 60.12° in **3** (69.45° in **4**) results in a much more compact anionic partial structure in **3** (Figure 3b). The topological structure of **3** is the same as that of **2**, which further reflects the steric constraints imposed by the cations on Mo/Ag/S polymeric compounds. Furthermore, the structures of **3** and **4** demonstrate the different ways in which their anionic parts are adopted to suit a certain kind of cation.

As is well known, Ag ions have a higher affinity for the $[MoS_4]^{2-}$ ion than for the $[WS_4]^{2-}$ ion. As a result, it is more difficult to control the self-assembly of $[MoS_4]^{2-}$ and $AgNO_3$ than that of $[WS_4]^{2-}$ and $AgNO_3$. The scarce Ag^+ ion in solution released by Ag_2S is very beneficial for the control of the reaction.

Experimental Section

1: A mixture of $[N(C_6H_5CH_2)(C_2H_5)_3]Cl$ (2 mmol), $[NH_4]_2[MoS_4]$ (2 mmol), and Ag_2S (2 mmol) in DMF (10 mL) was stirred for 30 h, and then filtered. The dark filtrate was allowed to stand for several days at ambient temperature in the air, and dark red crystals of **1** were produced (0.30 g, 50% yield). IR (KBr): $\tilde{\nu}$(Mo–S) [cm^{-1}] = 459.0 (vs), 439.7 (sh).

2: The synthesis of **2** was similar to that of **1**, except for the use of $Ca(NO_3)\cdot 4H_2O$ instead of $[N(C_6H_5CH_2)(C_2H_5)_3]Cl$ in DMF (10 mL). The procedure give dark red crystals of **2** (30% yield). IR (KBr): $\tilde{\nu}$(Mo–S) [cm^{-1}] = 501.4 (m), 455.1 (s), 416.6 (w).

3: The synthesis of **3** was similar to that of **1**, except for the use of $Nd(NO_3)_3\cdot nH_2O$ in DMSO. The yield was about 50%. IR (KBr): $\tilde{\nu}$(Mo–S) [cm^{-1}] = 495.6 (s), 453.29 (vs), 405.5 (s), $\tilde{\nu}$(S=O) = 1004.7, 954.6, 935.3.

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[9] a) Crystal structure analysis of **1**: Data were collected on an Enraf-Nonius CAD4 diffactometer with $\lambda(Mo_{K\alpha}) = 0.71073$ Å. A red crystal of dimensions $0.25 \times 0.12 \times 0.12$ mm was used; tetragonal, space group $P4_12_12$, $a = 11.15(9)$, $c = 29.84(3)$ Å, $V = 3711.1(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.5$ g cm^{-3}, $\mu = 9.4$ cm^{-1}, $2\theta_{max} = 50°$, $T = 296$ K; of 3719 reflections collected, 3719 were independent and 2887 observed ($I > 3\sigma(I)$). The structure was solved by direct methods with the MolEN/PC program. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were not included (181 parameters). Final $R = 0.055$ and $Rw = 0.067$. Largest difference peak and hole: 1.53 and -0.62 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102085 (**1**), -102086 (**2**), and -102087 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] Crystal structure analyses of **2** and **3**: Data were collected on a Siemens Smart CCD area diffractometer with $\lambda(Mo_{K\alpha}) = 0.71073$ Å. **2**: A red prism of dimensions $0.10 \times 0.12 \times 0.15$ mm was used, monoclinic, space group $P2_1/c$, $a = 9.4600(1)$, $b = 24.6284(4)$, $c = 8.8526(2)$ Å, $\beta = 95.1230(10)°$, $V = 2054.28(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.847$ g cm^{-3}, $\mu = 2.104$ cm^{-1}, $2\theta_{max} = 46.48°$, $T = 293$ K; of 7994 reflections collected, 2943 were independent and 2639 observed ($I > 2\sigma(I)$). The structure was solved by direct methods with the SHELXTL-93 program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were not included (196 parameters). The final cycle of full-matrix least-square refinement converged with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0287$ and $Rw = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{0.5} = 0.0750$, $w = [\sigma^2F_o^2 + (0.0346\,P)^2 + 3.7068\,P]^{-1}$, $P = F_o^2 + 2\,F_c^2)/3$. Largest difference peak and hole: 0.396 and -0.661 e Å^{-3}. **3**: A red crystal of dimensions $0.25 \times 0.15 \times 0.20$ mm was used, monoclinic, space group $P2_1/n$, $a = 12.4879(3)$, $b = 23.7262(4)$, $c = 19.2383(2)$ Å, $\beta = 103.7040(10)°$, $V = 5537.9(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.111$ g cm^{-1}, $\mu = 3.235$ cm^{-3}, $2\theta_{max} = 50.06°$, $T = 296$ K; of 19625 reflections collected, 9378 were independent and 6908 observed ($I > 2\sigma(I)$). The structure was solved by direct methods with the SHELXTL-93 program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were not included (460 parameters). The final cycle of full-matrix least-square refinement converged with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0589$ and $Rw = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{0.5} = 0.1561$, $w = [\sigma^2F_o^2 + (0.0947\,P)^2 + 17.2245\,P]^{-1}$, $P = F_o^2 + 2\,F_c^2)/3$. Largest difference