Volume 34
Number 20
September 27, 1995

Inorganic Chemistry

Communications

Syntheses and Crystal Structures of Two Heterobimetallic Polymeric Cluster Complexes $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}2DMF]_n$ (Single Chain) and $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}H_2O]_n$ (Double Chain)

Qun Huang, Xintao Wu,* Tianlu Sheng, and Quanming Wang

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China

Received April 20, 1995

Polymeric complexes have gradually attracted much attention of synthetic and materials chemists because of their novel structural features and possibly the possibility of their having novel solid state properties.[1-3] As versatile adducts, tetrathiotungstate and tetrathiomolybdate have been extensively used in syntheses of cluster compounds. Although a lot of compounds of thiotungstate and thiomolybdate have been reported,[4-7] only a few of such species with polymeric structures have been identified,[8-11] which are mostly copper-containing, and very few silver-containing polymeric complexes have been characterized by single-crystal X-ray crystallography.[12,13] Herein, syntheses and structures of two tungsten−silver containing heterobimetallic polymeric cluster complexes $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}2DMF]_n$ (single chain) (**1**) and $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}H_2O]_n$ (double chain) (**2**) are described, of which complex **2** not only has a novel anion polymeric cluster structure but also simultaneously has a cation biochemical superstructure.

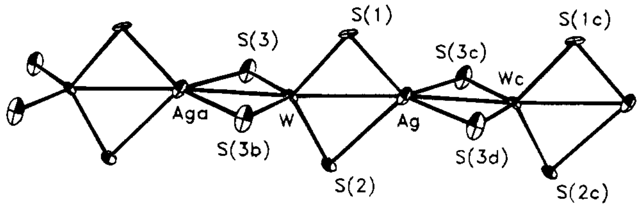

Figure 1. ORTEP drawing of a portion of the polymeric single-chain complex **1** with atomic labeling. For clarity, only the anion is shown. Selected distances (Å) and angles (deg): W−Ag 2.947(6), W−Ag(a) 2.915(6), W−S(1) 2.21(3), W−S(2) 2.25(2), W−S(3) 2.21(1), Ag−S(1) 2.75(2), Ag−S(2) 2.29(2), Ag−S(3c) 2.53(1), Ag−S(3d) 2.51(1); Ag−W−Ag(a) 176.4(3), W−Ag−W(c) 176.4(5), S(1)−W−S(2) 112.8(8), S(1)−W−S(3) 106.7(9), S(2)−W−S(3) 109.1(9), S(3)−W−S(3b) 114.5(4), S(1)−Ag−S(2) 94.3(7), S(1)−Ag−S(3c) 116.1(9), S(2)−Ag−S(3c) 119.1(9), S(3c)−Ag−S(3d) 94.1(4), W−S(1)−Ag 72.0(6), W−S(2)−Ag 81.0(6), W−S(3)−Ag(a) 75.8(4).

The single-chain polymeric complex **1** was prepared from reaction of ammonium tetrathiotungstate, silver nitrate and tris(hydroxymethyl)aminomethane in 1:2:1 molar ratio in DMF solution.[14] Orange crystals of **1** were obtained in 57% yield by slowly diffusing Et_2O into the reaction filtrate. However, dark-red crystals of the double-chain polymeric complex **2** were the only product of the recrystallization of complex **1** (yield: 83%) in ethanol and a little amount of water which plays a crucial role in the transformation of polymeric complex **1** into polymeric complex **2**;[14] in the presence of water, complex **1** in ethanol solution is probably decomposed into $[S_2WS_2Ag]$ fragments, which self-assemble the double-chain polymeric complex **2**. The isomorphous molybdenum complexes were not obtained.

The structure determination[15] show that complex **1** is composed of polymeric single chains of $[S_2WS_2Ag]^-$ anions. An ORTEP drawing of a portion of the single-chain structures is shown in Figure 1. Each metal atom displays an approximate

---

(1) Houlding, V. H.; Miskowski, V. M. *Coord. Chem. Rev.* **1991**, *111*, 145.
(2) McAuley, A.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1321.
(3) Christio, D. D.; Subramnian, S.; Thampson, L. K.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2563.
(4) Holloway, C. E.; Melnik, M. *Rev. Inorg. Chem.* **1993**, *13*, 233.
(5) Zhu, N.-Y.; Zheng, Y.-F.; Wu, X-T. *Inorg. Chem.* **1990**, *29*, 2705.
(6) Du, S.-W.; Zhu, N.-Y.; Chen, P.-C.; Wu, X.-T.; Lu, J.-X. *J. Chem. Soc., Dalton Trans.* **1992**, 339.
(7) Du, S.-W.; Zhu, N.-Y.; Chen, P.-C.; Wu, X-T. *Angew. Chem., Int. Ed. Engl.* **1992**, *8*, 31.
(8) Müller, A.; Dartmann, D.; Romer, C.; Clegg, W.; Sheldrich, G. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1060.
(9) Potvin, C.; Manoli, J. M.; Secheresse, F.; Marzak, S. *Inorg. Chem.* **1987**, *26*, 4370.
(10) Nicholson, J. R.; Flood, A. C.; Garner, C. D.; Clegg, W. *J. Chem. Soc. Chem. Commun.* **1983**, 1179.
(11) Müller, A.; Krickemeyer, E.; Hildebrand A.; Bögge, H.; Schncider, K.; Lemke, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1685.
(12) In 1985, the anion polymeric chain of $(PPh_4)AgMoS_4$ was first identified by resonance Raman spectroscopy (Müller, A.; Hellmann, W.; Schncider, J.; Schimanski, U.; Demmer, U.; Trautwein, A.; Bender, U. *Inorg. Chim. Acta* **1982**, *65*, L41. Müller, A.; Hellmann, W. *Spectrochim. Acta* **1985**, Vol. *41A*, 359).
(13) Lang, J.-P.; Li, J.-G. Bao, S.; Xin, X.-Q. *Polyhedron* **1993**, *12*, 801.
(14) Complex **1** is soluble in C_2H_5OH, CH_3CN, and DMF and slightly soluble in *i*-PrOH; in contrast, complex **2** is only soluble in DMF. Anal. for **1**: C, 17.45; H, 3.81; N, 6.10; S, 18.63; W, 26.71. Found: C, 17.87; H, 3.90; N, 6.29; S, 18.35; W, 26.40. Anal. Calcd for **2**: Calcd: C, 8.58; H, 2.52; N, 2.50; S, 22.89; W, 32.82. Found: C, 8.70; H, 2.55; N, 2.41; S, 22.45; W, 32.47. IR (KBr pellet, cm^{-1}): W−μ_2-S 439.7 for **1**, 445.5 and 476.4 for **2**.

0020-1669/95/1334-4931$09.00/0

tetrahedron coordination; comparatively, the coordination geometry [94.1(4)−119.1(9)°] of silver atoms is more largely distorted. The AgS_2W units are planar, and neighboring ones are perpendicular to each other. Compared with the average W−Ag distances in $[(PPh_3)_3Ag_2WS_4{\cdot}0.8CH_2Cl_2]$ (2.971 Å)[16] and in $[Ag_4W_2S_8(PPh_3)_4]$ (2.997 Å),[17] the average W−Ag distance of 2.931 Å in complex **1** suggests that there is stronger continuous metal−metal interaction in the chain.

Like the case in complex **1**, the $[S_2WS_2Ag]^-$ anions also act as cyclic units of the double-chain complex **2**, but their linking way is different from that in complex **1**. The anion structure of **2** can be viewed as two zigzag −SWSAg− chains linked by μ_2-S atoms.[15] The ORTEP diagram of a portion of the polymeric complex **2** is shown in Figure 2. Through hydrogen bonds, H_2O groups bridge two neighboring $NH_3C(CH_2OH)_3$ cations—the distances of O(1b)···O(11b) and O(1b)···O(13a) are 2.733 and 2.700 Å, respectively, and the angle of O(11b)···O(1b)···O(13a) is 108.0°; so two cation chains are formed on both sides of the anion chain and run parallel to this chain. This kind of hydrogen bond structure is conducive to the stability of the complex **2**, and may be one of the main factors of transformation of complex **1** into complex **2**. The average W−S and Ag−S distances are 2.204 and 2.565 Å, respectively, similar to those reported; the W−Ag distance of 2.980(2) Å can be compared with those of 2.971 Å in $[(PPh_3)_3Ag_2WS_4{\cdot}0.8CH_2Cl_2]$[16] and 2.997 Å in $[Ag_4W_2S_8(PPh_3)_4]$.[17] Each metal atom is coordinated by four μ_2-S atoms with an approximate tetrahedron geometry, but the coordination geometry of Ag atoms is more largely distorted with bond angles varying from 92.1(2) to 126.7(2)°. Obtained from the comparison between the W−S−Ag angles, μ_2-S atoms in complex **2** are in two different environments, this is reflected in the split of the $\nu(W{-}\mu_2{-}S)$ IR stretching vibration peak (IR spectrum: $\nu(W{-}\mu_2{-}S)$ 476.4 and 445.5 cm^{-1}).

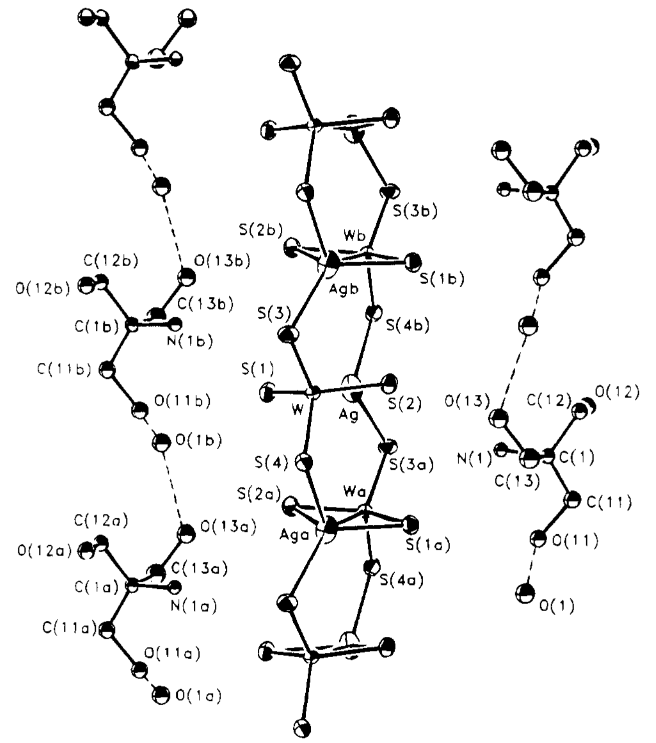

Figure 2. ORTEP diagram of a portion of the polymeric complex **2** with atomic labeling. Selected distances (Å) and angles (deg): W−Ag 2.980(2), W−S(1) 2.187(5), W−S(2) 2.217(5), W−S(3) 2.213(8), W−S(4) 2.197(7), Ag−S(1) 2.546(6), Ag−S(2) 2.563(6), Ag−S(3a) 2.613(8), Ag−S(4b) 2.538(8), S−W−S (average) 109.4(3), S(1)−Ag−S(2) 92.1(2), S(1)−Ag−S(3a) 107.9(2), S(1)−Ag−S(4b) 115.2(2), S(2)−Ag−S(3a) 116.0(2), S(2)−Ag−S(4b) 126.7(2), S(3a)−Ag−S(4b) 98.6(3), W−S(1)−Ag 77.6(2), W−S(2)−Ag 76.7(2), W−S(3)−Ag(b) 106.3(3), W−S(4)−Ag(a) 97.5(3).

Acknowledgment. This research was supported by grants from the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, and the National Science Foundations of China and Fujian Province.

Supporting Information Available: Listings of crystallographic data and experimental details, atomic coordinates, bond lengths and angles, thermal parameters, and least-squares planes (10 pages). Ordering information is given on any current masthead page.

IC9504809

---

(15) Crystal data for **1**, $WS_4Ag{\cdot}C_4H_{12}NO_3{\cdot}C_3H_7NO{\cdot}C_3H_7NO$: $M = 688.31$, orthorhombic, dimensions 0.60 × 0.10 × 0.10 mm; space group $Pmn2_1$, $a = 8.708(5)$ Å, $b = 5.859(2)$ Å, $c = 25.559(13)$ Å, $V = 1304(1)$ Å^3, $Z = 2$, $D_c = 1.75$ g cm^{-3}, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 55.7 cm^{-1}. The intensity data were collected at room temperature on a Rigaku AFC5R diffractometer. A total of 627 absorption-corrected reflections with $I > 3.0\sigma(I)$ of the unique 1392 reflections were ued to solve the structure using the MolEN program.[18] Oxygen atoms of two DMF groups are disordered, and these two DMF groups and the $NH_3C(CH_2OH)_3$ cation were rigidly refined. Metal and sulfur atoms were refined anisotropically. The direction of the polar axis (z) was determinted using the Rogers method.[19] No attempt was made to locate hydrogen atoms. The final cycle of full-matrix least-squares refinement converged with $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.078$ and $R' = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.086$ ($w = [\sigma^2(|F_o|^2) + (0.020|F_o|)^2 + 1.000]^{-1}$). Crystal data for **2**; $WS_4Ag{\cdot}C_4H_{12}NO_3{\cdot}H_2O$: $M = 560.14$, monoclinic dimensions 0.30 × 0.15 × 0.15 mm; space group $P2_1/n$ (alternate $P2_1/c$, No. 14), $a = 9.461(2)$ Å, $b = 7.381(1)$ Å, $c = 19.023(5)$ Å, $\beta = 101.96(2)°$, $V = 1299.5(5)$ Å^3, $Z = 4$, $D_c = 2.86$ g cm^{-3}, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 111.4 cm^{-1}. The intensity data were collected at room temperature on a Rigaku AFC5R diffractometer. A total of 1340 absorption-corrected reflections with $I > 3.0\sigma(I)$ of the unique 2490 reflections were used to solve the structure using the MolEN program. Metal and sulfur atoms were refined anisotropically. No attempt was made to locate hydrogen atoms. The final cycle of full-matrix least-squares refinement converged with $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.049$ and $R' = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.066$ ($w = [\sigma^2(|F_o|^2) + (0.020|F_o|)^2 + 1.000]^{-1}$).

(16) Müller, A.; Bögge, H.; Koniger-Ahlborn, E. *Z. Naturforsch* **1979**, *34B*, 1698.

(17) Müller, A.; Bögge, H.; Koniger-Ahlborn, E.; Hellmann, W. *Inorg. Chem.* **1979**, *18*, 2301.

(18) MolEN, An Interactive Structure Solution Procedure. Enraf-Nonius, Delft, The Netherlands, 1990.

(19) Rogers, D. *Acta Crystallogr., Sect. A* **1981**, *A37*, 734.