

The novel heterometallic polymeric helical chain cluster

$\{[\text{W}_3\text{Ag}_3\text{S}_{12}]\}_n[\text{Nd}(\text{Me}_2\text{SO})_8]_n$

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$\{[\text{W}_3\text{Ag}_3\text{S}_{12}]\}_n[\text{Nd}(\text{Me}_2\text{SO})_8]_n$ showing a novel helical chain configuration and derived from the influence of the dimension of the cation on the self-assembly of $[\text{WS}_4]^{2-}$ and Ag^+ , is described.

Polymeric transition-metal chalcogenides have attracted much attention because of their possible properties directly derived from their peculiar solid-state structures.^{1,2} For example, low-dimensional chalcogenides with the general formula $\text{MCu}_2\text{S}_{n+1}$ (where M is a monovalent metal) were found to have relatively high conductivity, and furthermore an interesting structural relationship also found.^{3,4} The general polymeric configuration of $\text{W}(\text{Mo})\text{-Ag-S}$ complexes is linear, such as in $(\text{PPh}_4)\text{AgMoS}_4$,⁵ $\{[\text{AgMS}_4]\}_n[4\text{-Hmpy}]_n$ ⁶ and $\{[\text{AgWS}_4]\}_n[\text{H}_3\text{NC}(\text{CH}_2\text{OH})_3]_n[\text{dmf}]_{2n}$.⁷ Recently, we have found that the self-assembly of ammonium tetrathiotungstate and silver nitrate is subject to the appropriate small molecules and the valence state of the cation, which is very rare for polymeric transition-metal chalcogenides; for example, water molecules are conducive to the transformation of the single linear chain $\{[\text{WS}_4\text{Ag}]\}_n[\text{H}_3\text{NC}(\text{CH}_2\text{OH})_3]_n[\text{dmf}]_{2n}$ ⁷ to the double chain $\{[\text{WS}_4\text{Ag}]\}_n[\text{H}_3\text{NC}(\text{CH}_2\text{OH})_3]_n[\text{H}_2\text{O}]_n$,⁷ and the divalent cation $[\text{Ca}(\text{Me}_2\text{SO})_6]^{2+}$ and the trivalent cation $[\text{Nd}(\text{dmf})_8]^{3+}$ are conducive to the zigzag chain $\{[\text{W}_4\text{S}_{16}\text{Ag}_4]\}_n[\text{Ca}(\text{Me}_2\text{SO})_6]_n$ ⁸ and the one-dimensional chain $\{[\text{W}_4\text{S}_{16}\text{Ag}_5]\}_n[\text{Nd}(\text{dmf})_8]_n$,⁹ respectively. Herein, the synthesis and crystal structure of the polymeric cluster complex $\{[\text{W}_3\text{Ag}_3\text{S}_{12}]\}_n[\text{Nd}(\text{Me}_2\text{SO})_8]_n$ **1** with a novel helical chain configuration are reported, which is derived from the influence of the dimension of the cation on the self-assembly of ammonium tetrathiotungstate and silver nitrate.

The reaction of $(\text{NH}_4)_2[\text{WS}_4]$ and AgNO_3 in the presence of Nd^{3+} in $\text{Me}_2\text{SO-MeCN}$ solution (molar ratio of 2 : 4 : 1) leads to orange crystals of complex **1** in 45% yield after allowing the orange-red filtrate to stand in air for one day.† As in the synthesis of $\{[\text{W}_4\text{S}_{16}\text{Ag}_5]\}_n[\text{Nd}(\text{dmf})_8]_n$,⁹ the trivalent lanthanide cations Nd^{3+} , which are oxygenphilic, were also employed as complementary cations. The resulting larger complex cations $[\text{Nd}(\text{Me}_2\text{SO})_8]^{3+}$ are smaller than the cations $[\text{Nd}(\text{dmf})_8]^{3+}$ of the one-dimensional polymeric cluster $\{[\text{W}_4\text{S}_{16}\text{Ag}_5]\}_n[\text{Nd}(\text{dmf})_8]_n$. As a consequence of their smaller size, the cations $[\text{Nd}(\text{Me}_2\text{SO})_8]^{3+}$ induce WS_4^{2-} and Ag^+ to self-assemble into $[\text{W}_3\text{Ag}_3\text{S}_{12}]^{3-}$ helical chains rather than $[\text{W}_4\text{S}_{16}\text{Ag}_5]^{3-}$ one-dimensional chains. The synthesis of

complex **1** clearly shows that the self-assembly of WS_4^{2-} and Ag^+ is very flexible and subject to the size of the complex anion.

Complex **1** crystallizes in the monoclinic system with space group $P2_1/n$.‡ An ORTEP drawing of a portion of the anion is shown in Fig. 1. The configuration of the polymeric anion can be viewed as a helical chain which is propagated along the crystallographic *b* axis. For clarity, the simplified diagram is shown (Fig. 2) with S atoms omitted. It is seen that the chain turns at each W atom.

All the W atoms are coordinated by one terminal S, two $\mu\text{-S}$ and one $\mu_3\text{-S}$ atoms with an approximately tetrahedral geometry $[106.7(2)\text{-}113.2(2)^\circ]$. However, the coordination tetrahedron around the Ag atoms, formed by two $\mu\text{-S}$ and two $\mu_3\text{-S}$ atoms, is much more distorted, the coordination angles ranging from $88.4(2)$ to $143.8(2)^\circ$. The average W-Ag-W and Ag-W-Ag angles are $167.63(7)$ and $93.26(5)^\circ$, respectively. The bond lengths W-S , $\text{W-}\mu\text{-S}$ and $\text{W-}\mu_3\text{-S}$ differ with average values being 2.136, 2.201 and 2.235 Å, respectively. By comparison, the W-S , $\text{W-}\mu\text{-S}$ and $\text{W-}\mu_3\text{-S}$ bond lengths are 2.128, 2.190 and 2.248 Å in $\{[\text{W}_4\text{S}_{16}\text{Ag}_5]\}_n[\text{Nd}(\text{dmf})_8]_n$,⁹ 2.146, 2.199 and 2.250 Å in $\{[\text{W}_4\text{S}_{16}\text{Ag}_4]\}_n[\text{Ca}(\text{Me}_2\text{SO})_6]_n$,⁸ and 2.144, 2.217

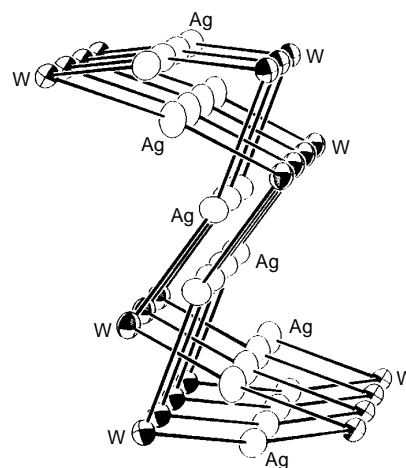


Fig. 2 Simplified diagram of the anionic helical chain. For clarity, the sulfur atoms are omitted.

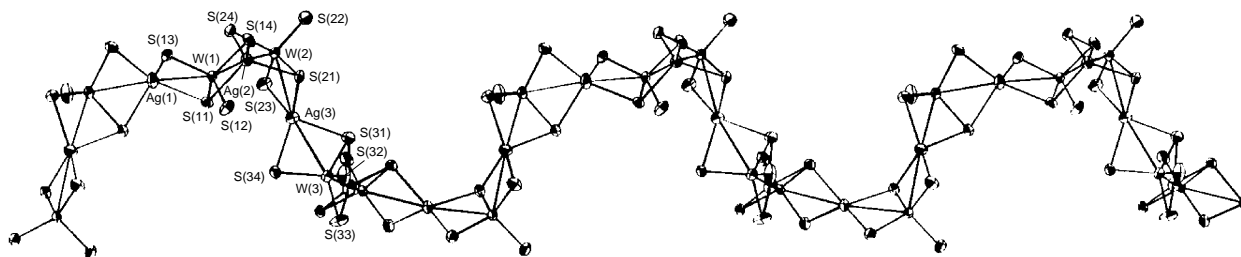


Fig. 1 ORTEP drawing of a portion of the anion of $\{[\text{W}_3\text{Ag}_3\text{S}_{12}]\}_n[\text{Nd}(\text{Me}_2\text{SO})_8]_n$ with atomic labelling (20% displacement ellipsoids)

and 2.242 Å in $\{[Ag(PPh_3)_3]_3WS_4\{S_2P(OEt)_2\}\}_n$,¹⁰ respectively. The average Ag–S length of 2.564 Å is comparable to the values observed in other polymeric complexes, such as 2.548 Å in $\{[W_4S_{16}Ag_4]_n[Ca(Me_2SO)_6]_n\}_n$,⁸ 2.565 Å in $\{[WS_4Ag]_n[H_3NC(CH_2OH)_3]_n[H_2O]_n\}_n$,⁷ and 2.543 Å in $\{[W_4S_{16}Ag_5]_n[Nd(dmf)_8]_n\}_n$.⁹ However, the average W–Ag length of 2.970 Å is longer than those found in the linear chain complexes $\{[WS_4Ag]_n[H_3NC(CH_2OH)_3]_n[dmf]_{2n}\}_n$ (2.931 Å) and $\{[WS_4Ag]_n[NH_4]_n\}_n$ (2.928 Å), but comparable to those in $\{[W_4S_{16}Ag_5]_n[Nd(dmf)_8]_n\}_n$ (2.964 Å) and in $\{[W_4S_{16}Ag_4]_n[Ca(Me_2SO)_6]_n\}_n$ (2.969 Å).

The single-crystal diffraction analysis shows that one trivalent cation $[Nd(Me_2SO)_8]^{3+}$ is related with the cyclic anionic unit $[W_3Ag_3S_{12}]^{3-}$. The trivalent cations $[Nd(Me_2SO)_8]^{3+}$ are arrayed among the anionic helical chains; these cations are well separated from each other and from the anionic chains. The packing diagram of the unit cell is shown in Fig. 3. Each Nd^{III} atom is coordinated by eight Me_2SO molecules. The average Nd–O bond length is 2.41 Å, and the O–Nd–O angles vary between 64.8(7) and 146.1(6)°; these are comparable to those of another trivalent complex cation $[Nd(dmf)_8]^{3+}$ (average Nd–O lengths of 2.43 Å and O–Nd–O angles between 70.4 and 144.8°) in $\{[W_4S_{16}Ag_5]_n[Nd(dmf)_8]_n\}_n$.⁹ The shortest distance between two Nd atoms is 11.01 Å.

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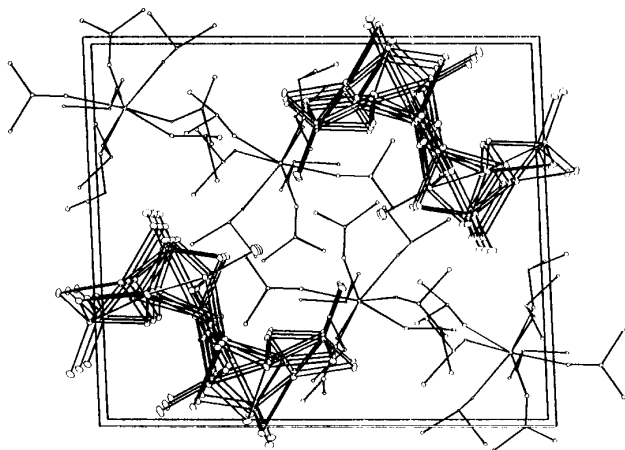


Fig. 3 Packing drawing of the unit cell viewed down the *b* axis

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Footnotes

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† Complex **1** is only slightly soluble in Me_2SO . Elemental analysis. Found: C, 9.52; H, 2.34; S, 31.51; W, 27.24. Calc.: C, 9.47; H, 2.38; S, 31.60; W, 27.18%. IR (KBr pellet, cm^{-1}): S=O 1004.9, 954.7 and 935.4; 489.9 (W–S), 439.7 (W– μ -S), 422.4 and 407.2 (W– μ_3 -S).

‡ *Crystal data* for **1**. $Ag_3S_{12}W_3 \cdot C_{16}H_{48}NdO_8S_8$, $M = 2029.24$, monoclinic, space group $P2_1/n$; $0.30 \times 0.20 \times 0.10$ mm; $a = 15.3985(1)$, $b = 20.0716(2)$, $c = 17.7791(3)$ Å, $\beta = 92.54(1)^\circ$, $U = 5489.65(11)$ Å³, $Z = 4$, $D_c = 2.453$ g cm^{-3} , $\lambda(Mo-K\alpha) = 0.71069$ Å, $\mu(Mo-K\alpha) = 91.26$ cm^{-1} . The intensity data were collected at room temperature on a Siemens Smart CCD diffractometer. 6070 Absorption-corrected reflections with $I > 2.0\sigma(I)$ of the unique 7875 reflections were used to solve the structure using the SHELXTL-93 program. Except for the sulfur atoms of the Me_2SO groups, metal and other sulfur atoms were refined anisotropically. No attempt was made to locate hydrogen atoms. The final cycle of full-matrix least-squares refinement was converged with $R = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.056$ and $wR = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w[F_o^2]^2\}^{1/2} = 0.13$ [$w = [\sigma^2(F_o^2) + (0.0584 P)^2 + 108.1857 P]^{-1}$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/401.

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