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The unconventional semiconductors represent two novel structure types of polythiometalates: syntheses, structures and electrical properties of $\{[W_3Ag_3S_{12}]\cdot[La(DMAC)_5(H_2O)_3\cdot(DMAC)_4]\}_n$ and $\{[W_8Ag_{10}S_{32}]\cdot[M(DEF)_8]_2\}_n$ (M = La, Nd)†

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Polymeric transition metal chalcogenides have attracted much attention because of their possible properties directly derived from their peculiar structures. Compared with polyoxometalates, polythiometalate chemistry is still very young. We report here the syntheses, structural characterizations and electrical properties of the novel polythiometalates, $\{[W_3Ag_3S_{12}]\cdot[La(DMAC)_5(H_2O)_3\cdot(DMAC)_4]\}_n$ **1** and $\{[W_8Ag_{10}S_{32}]\cdot[M(DEF)_8]_2\}_n$ (M = La **2** and M = Nd **3**). The complexes were obtained by self-assembly of $(NH_4)WS_4$ and $AgNO_3$ with $Ln(NO_3)_3$ (Ln = La, Nd) in different solvents: DMAC (DMAC = *N*,*N′*-dimethylacetamide), DEF (DEF = *N*,*N′*-diethylformamide). The title compounds represent two novel structure types of W/Ag/S polythiometalates, **1**: a single-stranded helix chain; **2** and **3** are isomorphous: equal step zigzag chains with a double square unit. The unusual **1** has two helices: an anion chain and a cation chain simultaneously exist in the unit cell and the anion helix is defined by a pitch (length per turn) of 17.65 Å, and a radius of circumscribed cylinder of 8.88 Å. Room temperature conductivities of **1**, **2**/**3** are 1.16×10^{-4}, 2.58×10^{-4} S cm^{-1}.

Introduction

Polymeric complexes have gradually aroused great interest among synthetic and material chemists.[1–3] Polymeric transition metal chalcogenides have attracted much attention because of their possible properties directly derived from their peculiar solid-state structures.[4,5] Compared with polyoxometalates,[6–8] polythiometalate chemistry is still very young.[9] W/Ag/S polymeric cluster complexes are still scarce, there are only five structure types of this kind of compound: linear chain,[10,11] double chain,[12] zigzag chain with unequal steps,[13] loose helical chain[14] and one-dimensional chain.[15] During the active research on conducting and semiconducting solids in chemistry and physics,[16] unconventional semiconductors have become a fascinating area since these materials exhibit properties similar to artificial systems of conventional semiconductors. There are three-dimensional (3-D), two-dimensional (2-D), one-dimensional (1-D) and zero-dimensional (0-D) systems such as $MeNH_3PbI_3$ (1-D),[17] $(C_9H_{19}NH_3)_2PbI_4$ (2-D),[18] $[NH_2C(I){=}NH_2]_3PbI_5$ (3-D)[17,19] and $(MeNH_3I)_3SnI_5$ (1-D).[17] Non-linear optical properties have been studied, for example, for $\{MAg_3S_3[S_2P(OCH_2CH_3)_2\}(S)(Ph_3P)_3$[20] and $(Bu_4N)_4Mo_8Cu_{12}O_xS_{32-x}$.[21] Up to now, there have been no reports about the semiconducting properties of the Mo(W)/Cu(Ag)/S polymer system. Here we report two new structure types of W/Ag/S polythiometalates: a single-stranded helical chain and a double square unit zigzag chain with an equal step; the experiments carried out show that these three complexes have semiconductor character.

Results and discussion

Crystal structures

Crystal structure of $\{[W_3Ag_3S_{12}]_n\cdot[La(DMAC)_5(H_2O)_3\cdot(DMAC)_4]_n\}$ 1, a single-stranded helix. The structure of the needle-like red compound **1** (Fig. 1) represents a novel structure type of the Mo(W)/Cu(Ag)/S system formed by a self-assembly process. The anion of compound **1** obtained from the mixed ammonium tetrathiotungstate and silver nitrate solution (see below) is a single-stranded helix. This polymeric anion chain has a cyclic unit $(W_3Ag_3S_{12})^{3-}$ (Fig. 1a), with an average W–Ag distance 2.973(7) Å, which is longer than those found in the linear chain complex $\{[WS_4Ag][H_3N(CH_2OH)_3](DMF)\}_n$[11] (2.931 Å), but comparable to those in $\{[W_3S_{12}Ag_3]\cdot[Nd(DMSO)_8]\}_n$[14] (2.970 Å). The average W–Ag–W and Ag–W–Ag angles of **1** are 173(1) and 169(2)°, respectively. All metal atoms are coordinated by four μ-S atoms with an approximately tetrahedral geometry (107.2(2)–113.1(3)° for W atoms and 91.13(14)–123.6(2)° for Ag atoms). The average W–μ-S and Ag–μ-S bond lengths of **1** are 2.197(7) and 2.55(2) Å. The helical polymeric anion chain of **1** is defined by a pitch (length per turn) of 17.65 Å, and a radius of circumscribed cylinder of 8.88 Å. By comparison, the pitch and radius of the hetero-duplex helicate $[Cu_3(bpy)_3(tpy)_3](CF_3SO_3)_6$[22] are 12 Å and 9 Å, respectively.

Interestingly, complex **1** simultaneously contains two helical polymeric chains, one is the anion helical chain described above, the other is a cation helix chain formed by strong hydrogen bond interactions (Fig. 2a,b). A view of the cationic chain $[La(DMAC)_5(H_2O)_3\cdot(DMAC)_4]^{3+}$ is shown in Fig. 2a, for clarity only lanthanum and oxygen atoms are displayed. Each La^{3+} atom is coordinated by five DMAC molecules and three H_2O molecules. The average La–O (DMAC) bond length is 2.44(2) Å, La–O (H_2O) is 2.60(5) Å. Hydrogen-bonding interactions exist between the oxygen atoms of H_2O (O10, O11, O12) and the oxygen atoms of DMAC (O6, O7, O8, O9). Through hydrogen-bond interaction O6 bonds to O11 and O12 of neighboring La^{3+} cations, thus bridging two neighboring La^{3+} cations together. O8 is bonded to O10 and O12 in the same La^{3+} cation, and O7, O9 are bonded to O10 O11 through one hydrogen bond, respectively.

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4303/

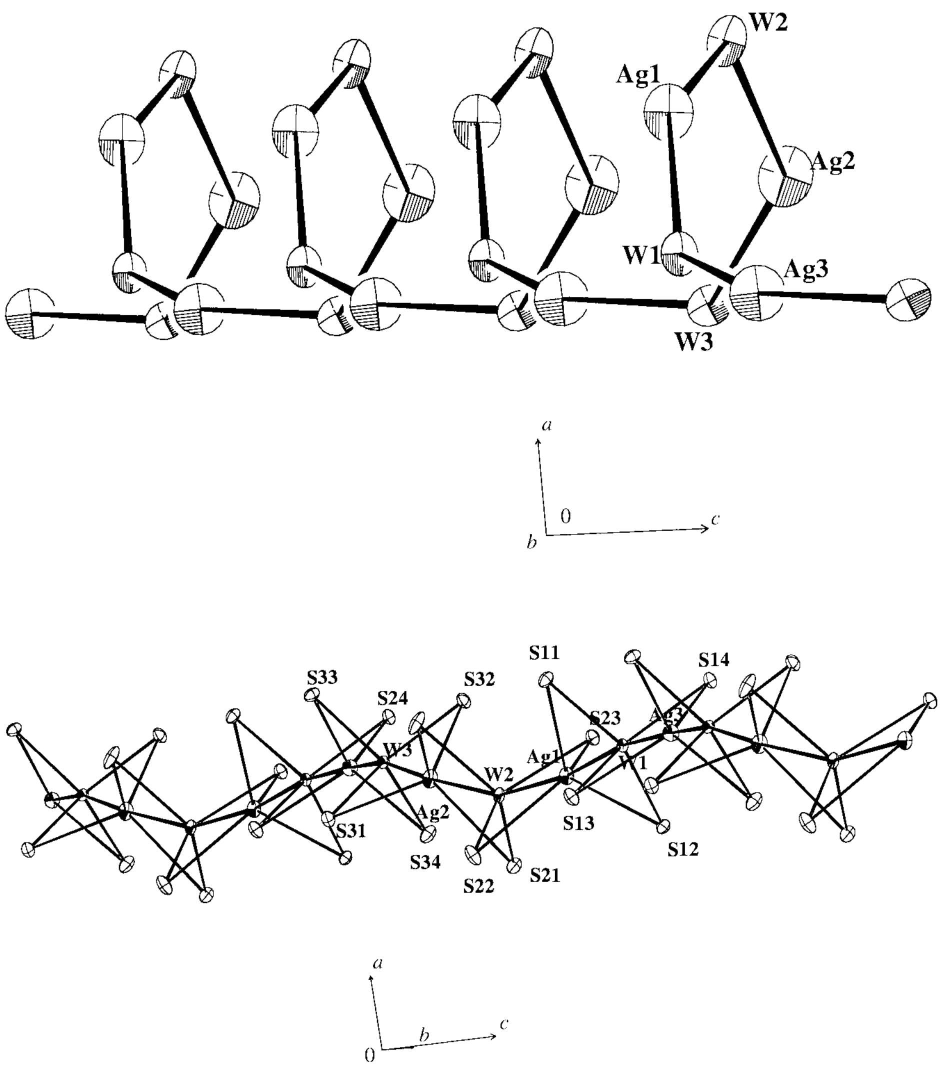

Fig. 1 (*a*) Simplified diagram of the anionic helical chain of complex **1**. For clarity, the sulfur atoms are omitted. (*b*) ORTEP[27] drawing of a proton of the anion of complex **1** with atomic labelling.

The hydrogen bond distances are listed in Table 1. As shown in Fig. 2b, the solvent molecule DMAC (O6) bridges two neighboring $[La(DMAC)_5(H_2O)_3]^{3+}$ cations to form a helical chain, the bond lengths of O6 ··· O12, O6 ··· O11 are around 2.8 Å, for clarity only La atoms and O6, O11, O12 atoms are displayed.

Like **1**, complex $\{[W_3S_{12}Ag_3]\cdot[Nd(DMSO)_8]\}_n$ **a**[14] also has the same anionic cyclic unit $(W_3Ag_3S_{12})^{3-}$ and the same valent state cation M^{3+}, but the size of their coordinated cations are different, and the method of linking their anions is very different. Maybe the hydrogen-bond helix structure in the cation chain of **1** induces the helical anion chain configuration, while the $Nd(DMSO)_8{}^{3+}$ in complex **a** is an isolated trivalent cation, and the anion of **a** is a loose helical chain.

Crystal structure of complex $\{[W_8Ag_{10}S_{32}]\cdot[La(DEF)_8]_2\}_n$ 2, an equal step zigzag chain with a double square unit. The anion of the red well-shaped crystal **2** (Fig. 3) represents a novel structure type of the Mo(W)/Cu(Ag)/S system which is an equal step zigzag chain with a double-square unit. The synthesis of complex **2** is analogous to complex $\{[W_4Ag_5S_{16}]\cdot[La(DMF)_8]\}_n$ **b**[15] except that DEF is used as the solvent instead of DMF (see below). But their structure types are very different (Fig. 4). One of the main differences is that the square unit $(W_4Ag_5S_{16})^{4-}$ has different linking modes. As shown in Fig. 4, the polymeric chain of complex **2** (Fig. 4a) is repeated by two square units, but in complex **b** (Fig. 4b), the anion chain is repeated by a single square unit. The anion polymeric chain of **2** can be viewed as a zigzag chain (Fig. 3) with an equal step. The edges formed by (W1#2, Ag5, W3, Ag2, W2, Agl, W1) and (W1, Ag5#1, W3#2, Ag2#1, W2#2, Agl#1, W1#2) are approximately perpendicular to each other alternately, the Agl–W1–Ag5#1 angle is 90.23(6)°. The average angle of Ag–W–Ag at the corners is 90(3)° in **2**, *cf.* 93.7° in $\{[W_4Ag_4S_{16}]\cdot 2Ca(DMSO)_8]\}_n$.[13] The average angles of W–Ag–W and Ag–W–Ag in **2** are 175(2) and 175(1)°, respectively. The W–Ag(average) distance is 2.97(3) Å. The S–W–S angles range from 106.2(3) to 113.0(3)°, and the mean W–S_t, W–(μ-S) and W–(μ_3-S) lengths in **2** are 2.129(2), 2.179(7) and 2.238(9) Å, respectively. Each La $^{3+}$ cation in **2** is coordinated by eight DEF molecules, the average La–O bond length is 2.47(3) Å.

Crystal structure of $\{[W_8Ag_{10}S_{32}]\cdot[Nd(DEF)_8]_2\}_n$ 3, an equal step zigzag chain with a double square unit. Complexes **3** and **2** are isomorphous, so only a simple description concerning **3** is reported here. The mean W–S_t, W–(μ-S) and W–(μ_3-S) lengths are 2.138(8), 2.189(9) and 2.23(1) Å respectively, the W–Ag-(mean) bond length is 2.96(2) Å. The average Nd–O bond length is 2.42(3) Å. The complexes **2**, **3** and **b**, have the same cation and the same anion cyclic unit but have different structure types. The main factor is that the ligand DEF has a larger substituent (ethyl) than that of DMF (methyl). It can be concluded from the above that in the self-assembly processes of ammonium tetrathiotungstate and silver nitrate, the size of the cation plays an important role in inducing different configurations.

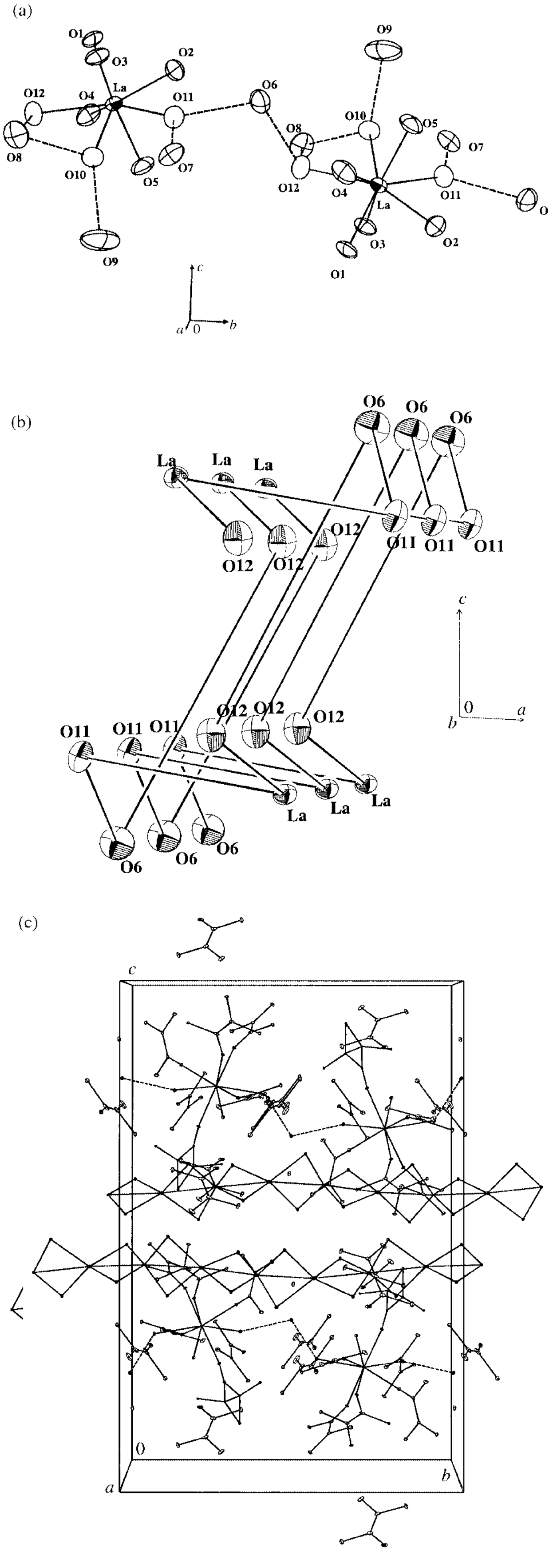

Fig. 2 (*a*) Diagram of cationic helical chain of complex **1**, for clarity, only lanthanum and oxygen atoms are displayed. O1–O5 are oxygen atoms of DMAC coordinated to La, O10–O12 are oxygen atoms of H_2O coordinated to La, O6–O9 are oxygen atoms of the solvent molecule DMAC. (*b*) Simplified diagram of the cationic helical chain of complex **1**. For clarity only lanthanum and oxygen atoms which form a helical chain are displayed. (*c*) Packing drawing of the unit cell of complex **1**.

Table 1 Selected bond lengths (Å) and bond angles (°) for **1**

W(1)–S(13)	2.184(4)	W(2)–S(22)	2.190(5)
W(1)–S(11)	2.204(4)	W(2)–S(23)	2.191(4)
W(1)–S(12)	2.208(4)	W(2)–S(21)	2.196(4)
W(1)–S(14)	2.210(4)	W(2)–S(24)	2.194(4)
W(3)–S(31)	2.192(4)	W(3)–S(34)	2.199(4)
W(3)–S(33)	2.195(4)	W(3)–S(32)	2.202(4)
La–O(1)	2.469(10)	La–O(3)	2.432(10)
La–O(2)	2.421(10)	La–O(4)	2.445(12)
La–O(5)	2.424(11)		
La–O(10)	2.538(9)	La–O(11)	2.619(10)
La–O(12)	2.650(10)		
Hydrogen bond distances			
O6···O11	2.826	O8···O10	2.753
O6···O12	2.802	O8···O12	2.854
O7···O11	2.784	O9···O10	2.675
S(13)–W(1)–S(11)	107.7(2)	S(22)–W(2)–S(23)	112.0(2)
S(13)–W(1)–S(12)	107.2(2)	S(22)–W(2)–S(21)	108.2(2)
S(11)–W(1)–S(12)	113.1(2)	S(23)–W(2)–S(21)	108.0(2)
S(13)–W(1)–S(14)	113.0(2)	S(22)–W(2)–S(24)	108.2(2)
S(11)–W(1)–S(14)	108.1(2)	S(23)–W(2)–S(24)	108.0(2)
S(12)–W(1)–S(14)	107.8(2)	S(21)–W(2)–S(24)	112.5(2)
S(31)–W(3)–S(33)	107.2(2)	S(31)–W(3)–S(32)	112.2(2)
S(31)–W(3)–S(34)	108.2(2)	S(33)–W(3)–S(32)	107.9(2)
S(33)–W(3)–S(34)	113.0(2)	S(34)–W(3)–S(32)	108.4(2)
Ag(1)–W(1)–Ag(3)	171.98(4)	Ag(1)–W(2)–Ag(2)	166.38(5)
Ag(3)#1–W(3)–Ag(2)	169.87(4)	W(3)#2–Ag(3)–W(1)	174.77(5)
W(2)–Ag(2)–W(3)	171.13(6)		

Symmetry transformations used to generate equivalent atoms: #1 $x, y - 1, z$; #2 $x, y + 1, z$.

Electrical properties

The electrical conductivities of complexes **1**–**3** were measured with pressed pellets (two-probe electrode). The conductivity is a function of temperature (Fig. 5). Acording to the definition of Kittel,[23] the conductivity of semiconductors is 10^{-9} to 10^2 S cm^{-1}, complexes **1**–**3** are therefore all semiconductors.

Experimental

Chemicals were used as purchased. Elemental analyses were performed by the elemental analysis laboratory in our institute. Infrared spectra (KBr pellets) were recorded on a Nicolet Magna 750 FT-IR spectrometer, and Raman spectra were collected on a Nicolet 910 FT-Raman laser spectrometer. Electrical conductivity measurements were made with pressed pellets (two probe) on a ZL5-LCR conductometer.

Synthesis of $\{[W_3Ag_3S_{12}]\cdot[La(DMAC)_5(H_2O)_3\cdot(DMAC)_4]\}_n$ 1

To a solution of 0.088 g (0.25 mmol) of $(NH_4)WS_4$ in 2 ml DAMC was added a solution of $AgNO_3$ (0.085 g, 0.5 mmol), and $La(NO_3)_3$ (0.041 g, 0.125 mmol) in 2 ml CH_3CN and a solution of $NaHCO_3$ (0.0105 g, 0.125 mmol) in 0.5 ml H_2O. After allowing the red filtrate to stand in air for two weeks red needle-like crystals of **1** were obtained. Anal. Calc. (Found): W, 24.66 (25.04); N, 5.64 (5.85); C, 19.33 (19.68); H, 3.92 (3.65)%. IR(cm^{-1}): ν_{CO} (DMAC):[24] 1606vs; $\nu_{C-C,C-N}$: 1255–1020m; ν_{C-H}: 2926–2816w, δ_{C-H}: 1420–1360m; W–(μ_n-S) ($n = 2,3$): 500w, 488(sh), 446(sh), 438vs, 421(sh). Raman(cm^{-1}): W–(μ_n-S) ($n = 2,3$): 492m, 460, 445s; ν_s(Ag–S): 246m; δ(WS): 169m.

Synthesis of $\{[W_8Ag_{10}S_{32}]\cdot[La(DEF)_8]_2\}_n$ 2

To a solution of 0.088 g(0.25 mmol) of $(NH_4)WS_4$ in 1 ml DEF was added a solution of $AgNO_3$ (0.085 g, 0.5 mmol) and $La(NO_3)_3$ (0.041 g, 0.125 mmol) in 2 ml CH_3CN. The dark precipitate was filtered off, and red crystals of **2** were obtained after allowing the red filtrate to stand in air for one week. Anal. calc. (Found): W, 26.88 (26.24); S, 18.75 (18.71); N, 4.10 (4.62); C, 17.56 (17.71); H, 3.24 (3.04)%. IR(cm^{-1}): this polymeric

Table 2 Crystal data and structure refinement for complexes **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{36}H_{87}Ag_3LaN_9O_{12}S_{12}W_3$	$C_{80}H_{176}Ag_{10}La_2N_{16}O_{16}S_{32}W_8$	$C_{80}H_{176}Ag_{10}N_{16}Nd_2O_{16}S_{32}W_8$
M_w	2236.94	5471.61	5482.27
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal size/mm	0.70 × 0.08 × 0.08	1.2 × 0.40 × 0.40	0.82 × 0.70 × 0.55
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
μ/mm^{-1}	6.555	7.664	7.880
R^a, $R_w{}^b$	0.0606, 0.1336	0.0840, 0.1668	0.0779, 0.1740
a/Å	15.5919(5)	21.6534(3)	21.6360(9)
b/Å	17.6515(6)	18.11250(10)	17.9851(8)
c/Å	26.1720(9)	22.1818(3)	22.0251(9)
β/°	92.7390(10)	108.5310(10)	108.2570(10)
V/Å^3	7194.8(4)	8248.6(2)	8139.1(6)
T/K	293(2)	293(2)	293(2)
Z	4	2	2
Reflections collected	21960	22388	26838
Independent reflections	11974 [R(int) = 0.0627]	12480 [R(int) = 0.0524]	11501 [R(int) = 0.0668]
Data/restraints/ parameters	11974/0/664	12470/37/560	11493/36/561

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = \{\Sigma w([(F_o{}^2 - F_c{}^2)^2/\Sigma w[(F_o{}^2)^2]\}^{1/2}$ for complex **1**: $w = [\sigma^2(F_o{}^2) + (0.0674P)^2]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ for complex **2**: $w = [\sigma^2(F_o{}^2) + (0.0690P)^2 + 49.1613P]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ for complex **3**: $w = [\sigma^2(F_o{}^2) + (0.0521P)^2 + 110.2108P]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

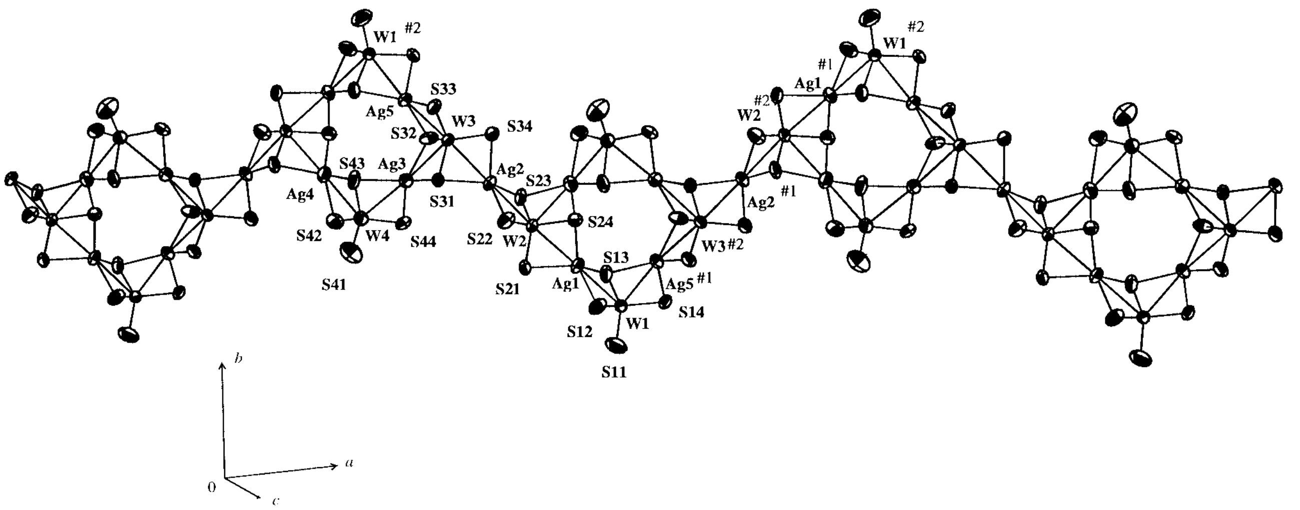

Fig. 3 ORTEP drawing of a portion of the anion of complex **2** with atomic labelling (25% displacement ellipsoids).

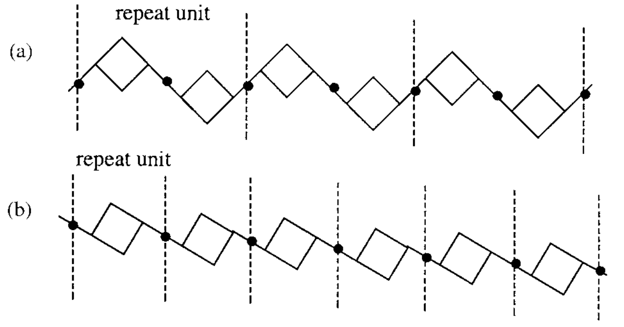

Fig. 4 Sketch diagram of complex **2** (a) a zigzag chain with two square units and complex **b** (b) a one-dimensional chain with a single square unit. The black circles represent the Ag$^+$ bridge atom.

complex displays DEF vibration in the range of 4000–550 cm^{-1};[24] W–S$_t$: 494m; W–(μ_n-S) (n = 2,3): 469w, 446(sh), 420m. Raman(cm^{-1}): W–S$_t$: 497m; W–(μ_n-S) (n = 2,3): 462s, 429m; ν_s(Ag–S): 254m, 231m; δ(WS): 186m.

Synthesis of $\{[W_8Ag_{10}S_{32}]\cdot[Nd(DEF)_8]_2\}_n$ 3

Complex **3** was synthesized similarly to complex **2** except that neodymium nitrate was used instead of lanthanum nitrate, and red crystals were obtained after allowing the red filtrate to stand in air for one week. Anal. Calc. (Found): W, 26.83 (26.04); S, 18.71 (18.60); N, 4.09 (4.65); C, 17.53 (17.68); H, 3.24 (3.04)%. IR(cm^{-1}): this polymeric complex displays DEF vibrations in the range 4000–550 cm^{-1};[24] W–S$_t$: 496m; W–(μ_n-S) (n = 2,3): 471w, 446(sh), 420m. Raman(cm^{-1}): W–S$_t$: 497m; W–(μ_n-S) (n = 2,3): 468s, 429m; ν_s(Ag–S): 256m, 231m; δ(WS): 186m.

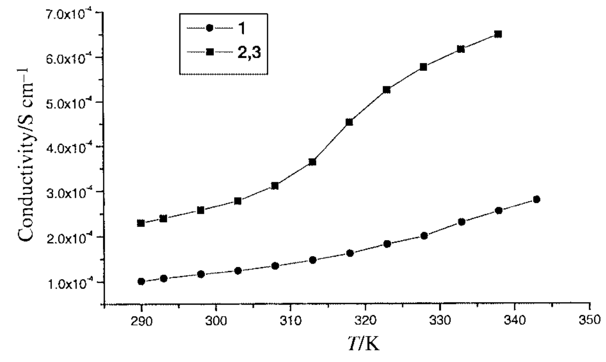

Fig. 5 The conductivity is a function of temperature. Complexes **2** and **3** have nearly the same conductivity.

Single crystal structure determinations

The intensity data were collected at room temperature on a Siemens Smart CCD area-detector diffractometer using graphite monochromatized Mo radiation. The exposure time per frame was 10 s. Cell data and specific parameters pertaining to the data collection are reported in Table 1. All calculations were performed on an INDY workstation using the SHELXL 93 program package.[25] Both structures were solved by the heavy-atom method. Successive least-square refinements and difference Fourier calculations revealed the positions of the remaining atoms. The structure was refined by full-matrix least-squares on F^2.

Absorption corrections have been carried out for all complexes by using SADABS.[26] Selected bond distances and angles of **1** are shown in Table 2.

CCDC reference number 186/1712.

See http://www.rsc.org/suppdata/dt/1999/4303/ for crystallographic files in .cif format.

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References

1 V. H. Houlding and V. M. Miskowski, *Coord. Chem. Rev.*, 1991, **111**, 145.
2 A. McAuley, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1321.
3 S. D. Christie, S. Subramanian, L. K. Thompson and M. J. Zaworotko, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2563.
4 G. V. Vajenine and R. Hoffmann, *Inorg. Chem.*, 1996, **35**, 451.
5 R. Berger, R. Dronskowski and L. Norén, *J. Solid State Chem.*, 1994, **112**, 120.
6 (*a*) A. Müller, F. Peters, M. I. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239; (*b*) A. Müller, J. Meyer, E. Krickemeyer, C. Beugholt, H. Bögge, F. Peters, M. Schmidtmann, P. Kogerler and M. J. Koop, *Chem. Eur. J.*, 1998, **4**, 1000.
7 E. Coronado and C. J. Gomes-Carcia, *Chem. Rev.*, 1998, **98**, 273.
8 D. E. Katsoulis, *Chem. Rev.*, 1998, **98**, 359.
9 E. I. Stiefel and K. Matsumoto, *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, American Chemical Society, Washington, DC, 1996, ch. 1, pp. 2–39; ch. 17, pp. 282–296; ch. 20, pp. 324–335.
10 (*a*) A. Müller, W. Jaegermann and W. Hellmann, *J. Mol. Struct.*, 1983, **100**, 559; (*b*) A. Müller and W. Hellmann, *Spectrochim. Acta A*, 1985, **41**, 359; (*c*) J. P. Lang, J. G. Li, S. A. Bao and X. Q. Xin, *Polyhedron*, 1993, **12**, 801.
11 (*a*) Q. Huang, X. Wu, T. Sheng and Q. Wang, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 29; (*b*) Q. Huang, X. Wu, T. Sheng and Q. Wang, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 795.
12 Q. Huang, X. Wu, T. Sheng and Q. Wang, *Inorg. Chem.*, 1995, **34**, 4931.
13 Q. Huang, X. Wu and J. Lu, *Inorg. Chem.*, 1996, **35**, 7445.
14 Q. Huang, X. Wu and J. Lu, *Chem. Commun.*, 1997, 703.
15 Q. Huang, X. Wu, Q. Wang, T. Sheng and J. Lu, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 68.
16 G. C. Papavassiliou, *Prog. Solid State Chem.*, 1997, **25**, 125.
17 I. B. Koutselas, D. B. Mitzi, G. C. Papavassiliou, G. J. Papaioannou and H. Krautscheid, *Synth. Met.*, 1997, **86**, 2171.
18 S. S. Nagapetyan, Y. I. Dolzhenko, E. R. Avakelova, V. M. Koshkin, Yu. T. Struchkov and V. E. Shklower, *Russ. J. Inorg. Chem.*, 1988, **33**, 1614.
19 G. C. Papavassiliou, *Mol. Cryst. Liq. Cryst.*, 1996, **286**, 231.
20 X. Wu, Q. Wang and S. Shi, *Polyhedron*, 1997, **16**, 945.
21 (*a*) S. Shi, W. Ji and X. Q. Xin, *J. Phys. Chem.*, 1995, **99**, 894; (*b*) Q. Huang, X. Wu, T. Sheng and Q. Wang, *Polyhedron*, 1996, **15**, 3405.
22 B. Hasenknopf, J. M. Lehn, G. Baum and D. Fenske, *Proc. Natl. Acad. Sci. USA*, 1996, **93**, 1397.
23 C. Kittel, *Solid State Physics*, John Wiley and Sons, Inc., 5th edn., 1976.
24 (*a*) R. A. Nyquist and R. O. Kagel, *Infrared spectra of inorganic compounds*, Academic Press, New York and London, 1971; (*b*) Inorganics IR grating spectra, SADTLER Research Laboratories, Division of Bio-Rad Laboratories, Inc., 1980, DMAC 33010K; DEF 36781K.
25 Siemens(1994), SHELXTL™ Version 5 Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, USA.
26 G. M. Sheldrick, SADABS, Program for Siemens area detector absorption correction, Universität Göttingen, 1996.
27 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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