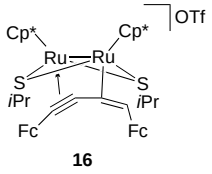
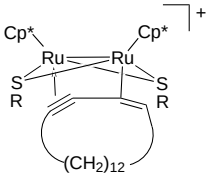
terized by spectroscopic methods, MS, and elemental analysis. Their configuration was determined from the vinyl coupling constants in the $^1$H NMR spectra, which are diagnostic of *cis* couplings. The molecular structure of one of the typical *endo*-macrocyclic (*Z*)-1-en-3-ynes, **15a**, was unambiguously determined by X-ray analysis, and an ORTEP drawing is shown in the Supporting Information.[10]

We previously reported the reaction of complex **5** with ferrocenylacetylene at ambient temperature to form the butenynyl complex [Cp*Ru{$\mu_2$-C(=CHFc)C≡CFc}($\mu_2$-S*i*Pr)$_2$-RuCp*]OTf (**16**; Fc = ferrocenyl), which catalyzes the stereoselective di- and trimerization of ferrocenylacetylene at 60 °C.[11] The $^1$H NMR analysis of the reaction mixture of **1** and **6a** at room temperature or 60 °C did not show the formation of such intermediate complexes. However, the present cyclization of $\alpha,\omega$-diynes is also considered to involve a butenynyl intermediate **17** similar to **16**. Noteworthy is that **7a** was not obtained from the cyclization of **6a** by using [Ir(biph)(PMe$_3$)$_3$Cl] (biph = biphenyl-2,2′-diyl), which is known to be effective for the selective head-to-head *Z* dimerization of aliphatic terminal alkynes.[12]




**16**




**17**

In summary, we have a novel cyclization of $\alpha,\omega$-diynes, which is catalyzed by the thiolate-bridged diruthenium complexes **1**, **2**, and **3** to produce the corresponding *endo*-cyclic (*Z*)-1-en-3-ynes in moderate to high yields with complete stereoselectivities.

### *Experimental Section*

Typical procedure for the cyclization: $NH_4BF_4$ (5.5 mg, 0.05 mmol), and **6a** (55 mg, 0.25 mmol) were added to a solution of complex **1** (16 mg, 0.025 mmol) in dry MeOH (125 mL). The reaction mixture was stirred at 60 °C for 1 h. The GLC analysis using naphthalene (10 mg) as an internal standard showed the formation of **7a** in 94 % yield. For the isolation of **7a**, the solvent was removed under reduced pressure and the residue was purified by HPLC ($CHCl_3$ eluent) to give pure **7a** (43 mg, 0.20 mmol, 78 %); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.34-1.50$ (br m, 20H, -$CH_2$-), 2.29–2.40 (m, 4H, C$H_2$C≡C, -CH=CHC$H_2$-), 5.44 (d, 1H, $J = 10.7$ Hz, -C*H*=CHCH$_2$-), 5.80 (dt, 1H, $J = 10.7$, 7.7 Hz, -CH=C*H*-CH$_2$-); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 19.2$ (t), 25.8 (t), 25.8 (t), 26.5 (t), 26.5 (t), 26.6 (t), 26.9 (t), 27.1 (t), 27.2 (t), 27.6 (t), 28.1 (t), 29.8 (t), 77.8 (s), 94.1 (s), 109.5 (d), 142.5 (d); GC-MS: *m*/*z* (%) 218 (17) [$M^+$], 189 (1), 161 (5), 147 (9), 133 (17), 105 (26), 91 (67), 79 (100), 67 (61), 41 (91); IR (neat): $\tilde{\nu}$ (cm$^{-1}$) = 1617 (C=C), 2211 (C≡C); elemental analysis calcd for $C_{16}H_{26}$: C 88.00, H 12.00; found: C 87.63, H 11.89.

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## A Semiconducting Lamella Polymer [{Ag($C_5H_4NS$)}$_n$] with a Graphite-Like Array of Silver(I) Ions and Its Analogue with a Layered Structure**

Weiping Su, Maochun Hong,* Jiabao Weng, Rong Cao,* and Shaofang Lu

A great deal of work has recently been devoted to inorganic–organic hybrid-framework assemblies such as multilayer perovskites,[1] metal phosphonates[2] and metal–ligand networks[3] because of their potential as functional solid materials. The diversity of organic components used has resulted in numerous inorganic–organic hybrid frameworks with fascinating structural topologies.[1–4] By carefully selecting the organic components one hopes to tune the physical properties of this type of compound by tailoring their structures and thus realize various applications, including electrical conductivity,[4a,b] magnetism,[4c] catalysis,[4d,e] shape specificity,[4f] and ion exchange.[4g,h] Structural isomers of coordination polymers can be prepared by controlling the synthetic conditions such as temperature and medium.[5] By using different thiolate ligands containing N-donor groups we

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

have synthesized several silver thiolate polymers with different architectures.[6] Herein, we demonstrate that the formation of silver(I) thiolate polymers, $[\{Ag(C_5H_4NS)\}_n]$ (**1**) ($C_5H_4NS$ = pyridine-2-thiolate ($PyS^-$)) with a graphite-like array of silver(I) ions and $[\{Ag_5(C_5H_4NS)_4(C_5H_5NS)BF_4\}_n]$ (**2**) ($C_5H_5NS$ = 1H-pyridine-2-thione (HPyS)) with a layered structure, depends on the reaction temperature and the solvents used. In contrast to **2** and $[\{Ag_6(PyS)_6\}_n]$ (**3**) which has a one-dimensional chain structure, and other silver(I)-thiolate polymers synthesized in our laboratory,[6] all of which are insulators, **1** is a semiconductor.

The reaction of $AgBF_4$ with pyridine-2-thiol in DMF/$H_2O$ (20/1) at 0 °C followed by crystallization by the slow diffusion of $Et_2O$ into the solution resulted in the growth of a large amount of colorless, thin sheetlike hexagonal crystals of **1**. Elemental analysis showed the formula of the product to be $[Ag(C_5H_4NS)]$.An X-ray diffraction study confirmed the structure to be a layered polymer $[\{Ag(C_5H_4NS)\}_n]$ with a graphite-like array of silver(I) ions.[7] Polymer **1** has a two-dimensional lamella structure wherein the silver atoms are linked by $PyS^-$ ligands to form inorganic layers and the pyridyl groups of $PyS^-$ ligands protrude into the interlayer region (Figure 1). The interlayer distance is 17.17 Å. Each

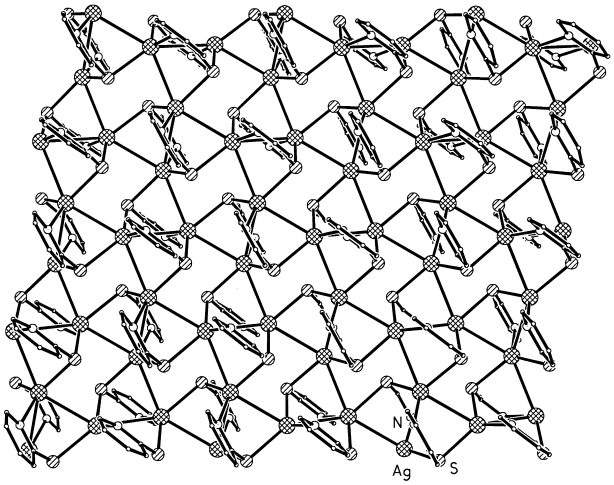
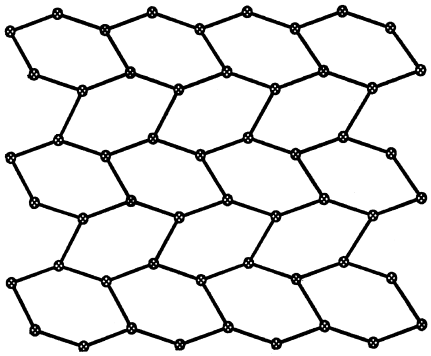



Figure 1. A view of the lamella structure in **1**.

$PyS^-$ ligand in **1** acts as a $\mu_3$ bridge to link two silver atoms through an S atom, and ligates another silver atom through an N atom with Ag–S bond distances of 2.424 and 2.647 Å and an Ag–N bond distance of 2.428 Å. Each silver atom is tricoordinated by two S atoms and one N atom from three different $PyS^-$ ligands in a distorted planar trigonal fashion (S-Ag-N angles are 103.4 and 125(1)°, and S-Ag-S is 127.0(2)°). The silver atoms of each layer are nearly coplanar (the deviation being within 0.13 Å), and they arrange to form a graphite-like hexagonal motif (Figure 2). The $Ag_6$ hexagon is somewhat distorted because of the different Ag-Ag-Ag angles (73.81, 140.40, and 142.20°). The three adjacent Ag–Ag bond lengths (3.215, 3.215, and 3.250 Å) are significantly shorter than the van der Waals contact distance (3.40 Å).[8]

The crystalline product of **1** is very stable in air at room temperature. However, when the thin hexagonal crystals of **1** were soaked in DMF at room temperature (about 30 °C), they transformed over four weeks into colorless needlelike crystals.



⊗=Ag

Figure 2. The graphite-like hexagonal motif of the array of silver(I) ions in **1**.

Single-crystal X-ray diffraction analysis showed this new product to be an isomer of **1**, $[\{Ag_6(PyS)_6\}_n]$ (**3**), which has been prepared in our laboratory by a different method,[6] this transformation of **1** into **3** indicates that **1** is metastable.

The results described above suggest that the reaction of $Ag^I$ with PySH might be temperature and solvent dependent. Thus the reaction conditions were changed; at room temperature the reaction of $AgBF_4$ and pyridine-2-thiol (1:1) in $CH_3CN$ followed by addition of 0.5 mL of $H_2O$ gave a clear solution. This solution was kept at room temperature for three days and gave pale yellow crystals of **2**. The structure of **2** (Figure 3),[7] also has an extended two-dimensional motif but

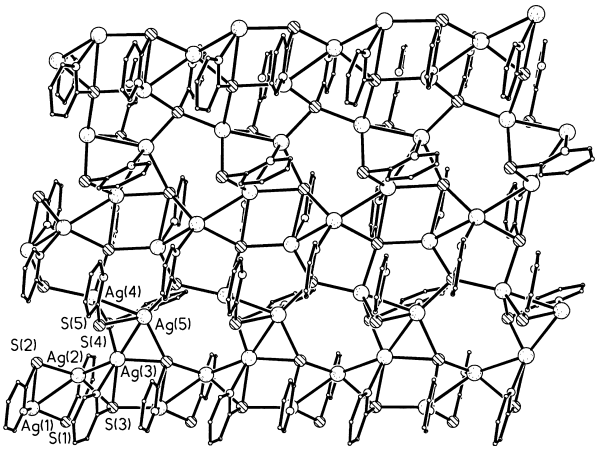
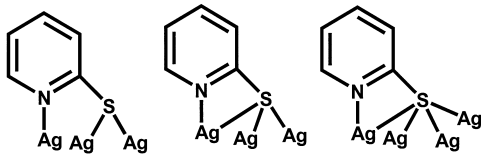



Figure 3. A view of the layered structure in **2**.

quite different from that of **1**. The $BF_4^-$ ions are embedded in the interlayer region. Pyridine-2-thiol exists in the forms pyridine-2-thiolate and 1*H*-pyridine-2-thione, where pyridine-2-thiolate can take the three different coordination modes shown in Scheme 1 while 1*H*-pyridine-2-thione acts only as a $\mu_2$ bridge to link two silver atoms through its sulfur atom.




Scheme 1. Coordination modes of pyridine-2-thiolate in **2**.

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In the infinite solid-state structure of **2**, the silver centers are found in three coordination environments, that is, $AgNS_2$ in a distorted planar trigonal geometry, and $AgNS_3$, and $AgS_4$ in a distorted tetrahedral geometry. The Ag–N and Ag–S bond lengths range from 2.28 to 2.44 Å, and from 2.45 to 2.90 Å, respectively. Unlike the array of silver ions in **1**, that in **2** is irregular and the adjacent Ag–Ag bond lengths range from 2.995 to 3.810 Å. As discussed below, the difference in structure between **1** and **2** results in their different conductivities.

An infinite hexagonal array of silver ions has recently been discovered by Shimizu et al. in the structure of silver benzenesulfonate.[9] The formation of a silver(I) layer with a uniform motif in different coordination polymers is likely to be because of Ag – Ag interactions, that is, argentophilicity.[10] This rational is supported by the specific orientation of the Ag – Ag interaction and by the observed inter-metallic distances that are close to those of ligand-unsupported Ag – Ag interactions.[11] According to Jansen,[10d] the evidence for interaction or bonding between the formally closed-shell $d^{10}$ cations in extended solid structures is provided not only by characteristic uniform structural features but also by their physical properties such as a large red-shift of the absorption in their UV/Vis spectra and by electrical conductivity. Therefore, the conductivity of **1**, **2**, and other related polymers synthesized in our laboratory[6] was studied. Determination of the conductivity of **1** (powder sample from ground crystals) demonstrated that its electrical conductivity is $2.04 \times 10^{-5}\,S\,cm^{-1}$ at 298 K and increases as the temperature rises (Figure 4), which indicates that **1** is a semiconductor. However, the conductivity studies of **2**, **3**, and other silver(I) thiolate polymers showed that their electrical conductivities

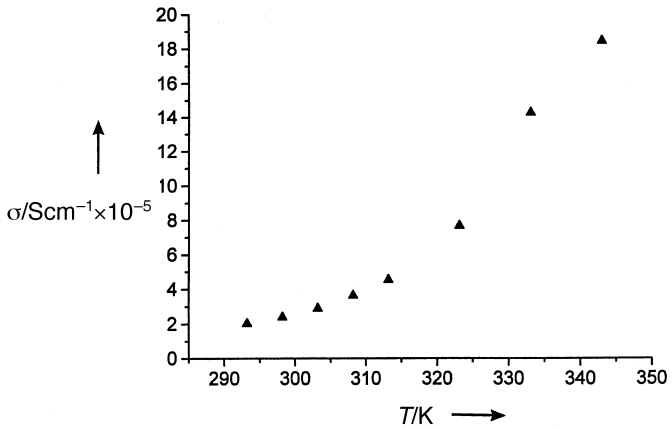


Figure 4. Temperature dependence of the electrical conductivity of **1**.

are in the range of $10^{-12}$ to $10^{-15}\,S\,cm^{-1}$ at room temperature and independent of the temperature, which indicates that they are insulators. By comparison of the polymer structures the semiconductivity of **1** can be attributed to its characteristic structural feature, the graphite-like array of silver(I) ions. In turn, this semiconductivity provides evidence for Ag – Ag interactions in **1**.

In summary, two layered silver(I) thiolate polymers were obtained from the reaction of silver salts with pyridine-2-thiol under different conditions, which suggests that the reaction conditions can influence the formation of silver thiolate polymers. The semiconductivity of **1** that distinguishes it from other silver(I) thiolate polymers results from its lamella structure with a graphite-like array of silver(I) ions. The semiconductivity provides evidence for Ag – -Ag interactions that have been considered as a factor directing the formation of the hexagonal array of silver ions. Since hexagonal structural units of $MoS_2$ can be used to construct nested inorganic fullerenes and nanotubes[12] a goal of our research is to assemble analogous aggregates by using $Ag_6$ hexagons as building blocks.

## *Experimental Section*

**1**: $AgBF_4$ (0.195 g, 1 mmol) was dissolved in DMF (10 mL) and added to a solution of pyridine-2-thiol (0.11 g, 1 mmol) in DMF (10 mL) in an ice bath. The mixture was stirred for 30 min at 0 °C, then $H_2O$ (0.5 mL) was added. Colorless, thin sheetlike hexagonal crystals of **1** were obtained after allowing $Et_2O$ vapor to diffuse into the resulting solution at 0 °C for 2 weeks. IR (KBr): $\tilde{\nu} = 3021$, 1559, 1443, 1414, 1126, 766, 721 $cm^{-1}$. Elemental analysis calcd (%) for $C_5H_4AgNS$: C 27.52, H 1.83, N 6.42; found: C 27.69, H 1.90, N 6.38. By using the experimental procedure above **1** could also be formed from the reaction of $AgNO_3$ with pyridine-2-thiol.

**2**: $AgBF_4$ (0.19 g, 1 mmol) was added to a solution of pyridine-2-thiol (0.11 g, 1 mmol) in $CH_3CN$ (20 mL). The mixture was stirred for 0.5 h, then $H_2O$ (0.5 mL) was added. The resulting solution was kept at room temperature for 3 d and gave pale yellow crystals of **2**. IR (KBr): $\tilde{\nu} = 3213$ – 2991, 1579, 1416, 1130, 1084, 1070, 1003, 777, 746, 721 $cm^{-1}$. Elemental analysis calcd (%) for $C_{25}H_{21}Ag_5BF_4N_5S_5$: C 25.47, H 1.78, N 5.94; found: C 25.37, H 1.82, N 6.02.

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[7] Crystal data for **1**: Crystal dimensions $0.06 \times 0.45 \times 0.45$ mm, formula $C_5H_4NAgS$, $M_r = 233.60$, monoclinic, space group $C2/c$, $a = 34.335(7)$, $b = 7.0167(14)$, $c = 6.0833(12)$ Å, $\beta = 97.98°$, $V = 1451.4$ Å$^3$, $Z = 8$, $R(wR) = 0.079(0.180)$ for 837 reflections with $F \geq 2.0\sigma(F_o)$. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation at room temperature. Crystal data for **2**: Crystal dimensions $0.35 \times 0.30 \times 0.06$ mm, formula $C_{25}H_{21}Ag_5BF_4N_5S_5$, $M_r = 1177.93$, monoclinic, space group $Pc$, $a = 7.0206(7)$, $b = 13.7308(13)$, $c = 16.9225(16)$ Å, $\beta = 93.133°$, $V = 1628.9(3)$ Å$^3$, $Z = 2$, $R(wR) = 0.0498(0.1336)$ for 5566 reflections with

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$F \geq 2.0\sigma(F_o)$. The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation at room temperature. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141837 for **1** and -141836 for **2**. 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).

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## Controlled Assembly of Polyoxometalate Chains from Lacunary Building Blocks and Lanthanide-Cation Linkers**

Masahiro Sadakane, Michael H. Dickman, and Michael T. Pope*

Polyoxometalates, in addition to their considerable potential as catalysts and catalytic precursors, and their applications in biochemistry and medicine,[1] are attracting increased attention as components of supramolecular complexes and materials.[2]

In recent years, a number of very large polyoxometalate anions have been synthesized and structurally characterized. Beginning with the "big wheel" $Mo_{154}$ anion, Müller's group have reported several giant mixed-valence polyoxomolybdates with cyclic ($Mo_{176}$),[3] icosahedral ($Mo_{132}$),[4] capped cyclic ($Mo_{248}$),[5] and "basket" ($Mo_{116}$)[6] architectures. In polytungstate chemistry we have described quite different structures (for example $W_{148}$),[7] and Zubieta and co-workers have reported one- and two-dimensional polymeric oxometalates in several organic-inorganic hybrid materials.[8] Although these substances and materials can be synthesized in modest to good yield from monometallic components in one-pot reactions, it is of course generally true that the composition and structure of the products could not have been predicted. However, once structural principles are recognized, syntheses of targeted species can be designed, as has been demonstrated by the work of Müller and co-workers with the large polymolybdates.

In the course of our investigations into the construction of large inorganic clusters from lacunary polyoxotungstate anions with lanthanide (Ln) or actinide cations as assembling groups,[9] we report a new simple strategy to yield infinite one-dimensional polyxoxometalates that are recrystallizable from aqueous solution. Two types of polymer chain are exemplified in the structures of the ammonium salts of **1** and **2**. These are 1:1 complexesof the type first reported by Peacock and Weakley,[10] and they can be isolated by mixing solutions of the lacunary polytungstates with approximately 3.8 equivalents of $Ln(NO_3)_3$, and recrystallization from aqueous ammonium chloride. The excess $Ln(NO_3)_3$ ensures high yields of the desired product. Decreasing the amount of $Ln(NO_3)_3$ results in the formation of the 1:2 complex ($[Ln(\alpha\text{-}SiW_{11}O_{39})_2]^{13-}$) as a side product. If present, this 1:2 complex can be removed by recrystallization.

$[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ **1**

$[La(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ **2**

As shown in Figures 1 and 2, the anions are polymeric in the solid state. The $\alpha\text{-}SiW_{11}O_{39}$ units are connected by the

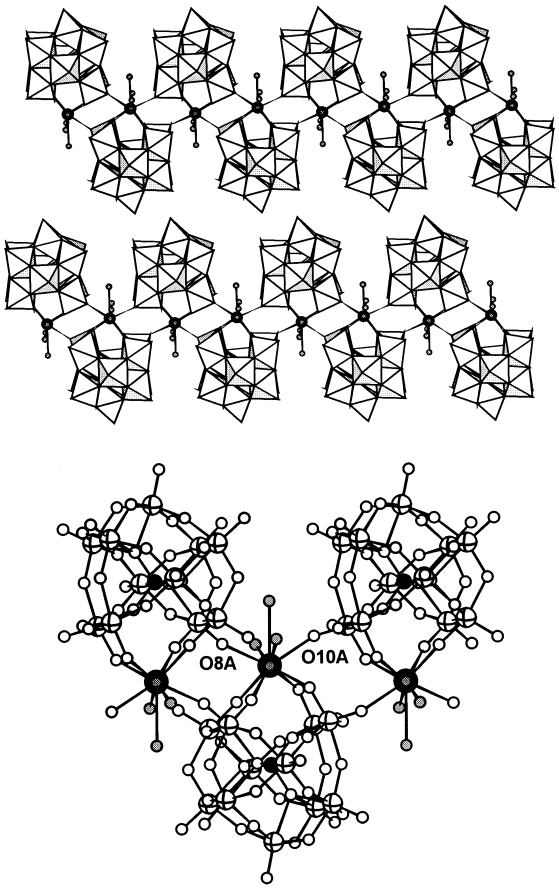


Figure 1. Structure of **1** Top: Polyhedral representation (black circle: cerium and gray circle: water oxygen). Bottom: Ball-and-stick representation (large black circle: cerium, small black circle: silicon, open circle: oxygen, gray circle: water oxygen, and crossed circle: tungsten). The chain is parallel to the crystallographic *a* axis.

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