

Assembly of Ag(I) Polymers with Thioether-S Binding and Homochiral Helices

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Abstract: A novel coordination polymer $[\text{Ag}(\text{pyta})]_n$ ($\text{pyta}^- = 4\text{-pyridylthioacetate}$) containing bound thioether sulfurs and single-stranded helical chains has been synthesized and structurally characterized.

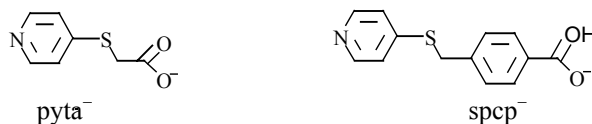
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Recently, self-assembly of coordination polymers with helical chains¹ or chiral cavities² has attracted attention because of their remarkable applications to various fields such as enantioselective catalysis^{2b,3}, nonlinear optical materials^{1b,4} and molecular recognition⁵. Thus, an important goal is to obtain resolved helices or homochiral cavities in noncentrosymmetric crystals. As a rule of thumb, infinite helices have been made through the use of “twisted” ligands that bridge metal ions. When prepared with achiral starting materials, the helical coordination polymers were found frequently to form a mixture of both enantiomers which crystallize in some centrosymmetric space groups, although several isolated examples of conglomerates are known and certain helical metal complexes tend to crystallize in chiral space groups⁶. On the other hand, single enantiomers of helical chains can be realized with resolved chiral “bridging” ligands⁷.

Among the achiral “twisted” bridging ligands, flexible thioethers are well-known in coordination and supramolecular chemistry. Up to now, much attention has been paid to dithioether-pyridine ligands because they contain rich structural information in which both the pyridine nitrogens and thioether sulfurs can act as donor atoms, and the flexible nature of spacers allows them to bend and rotate when coordinating to metal centers to conform to the coordination geometries of metal ions⁸. As the derivatives of dithioetherpyridines and the potentially tetradentate ligands, Hpyta and Hspcp (**Scheme 1** spcp⁻ = 4-sulfanylmethyl-4'-phenylcarboxylate pyridine), were chosen as bridging ligands to design novel coordination polymers $[\text{Zn}(\text{pyta})(\text{OH})]^{1b}$ and $[\text{Zn}(\text{spcp})(\text{OH})]^{1c}$ with two distinct homo-chiral helices. But thioether-sulfur coordination is not observed with these zinc centres. Switching to the softer silver(I) ion coordinated to the pyta^- ligand might allow access to the dithioether-S binding mode and keep the metal centre

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Scheme 1



tetrahedral geometry to design new helical chains different from the above ones. But the coordination modes may vary depended on the synthesis condition. For example, a three-connected silver framework with terdentate pyta^- ligand was reported recently^{1d}. Here we report the synthesis and crystal structure of a novel coordination polymer $[\text{Ag}(\text{pyta})]_n$, in which the Ag center is four-coordinated by N, O, O, and S atoms from three different tetradentate pyta^- ligands, together with its thermal stability.

Experimental

Silver acetate (166.9 mg, 1 mmol) and (4-pyridylthio)acetic acid (169.2 mg, 1 mmol) were dissolved in 10 mL of water. The aqueous ammonia was added dropwise to the above stirred solution until it turned transparent. The final pH of solution was about 11. The solution was left undisturbed in a dark place and become brown gradually. Several hours later, the black deposit appeared on the bottom of the beaker. After one day, the colourless rod-like crystals were obtained in 30 % yield. Elemental analysis, Found for $\text{C}_7\text{H}_6\text{NO}_2\text{SAg}$ (calculated): C, 30.28 (30.46); H, 2.12 (2.19); N, 4.92 (5.07) %. IR (KBr, cm^{-1}): 2909 (w), 1599 (s), 1401 (s), 1208 (m), 912 (w), 799 (m), 711 (w), 494 (m).

Diffraction data were collected on an Bruker Smart Spex CCD diffractometer with graphite monochromated Mo-K α radiation at 298K. The structures were solved by SHELXS97 and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all the non-hydrogen atoms⁹. H atoms were located from difference Fourier map. The chemical formula of the complex is $\text{C}_7\text{H}_6\text{NO}_2\text{SAg}$, $M = 276.06$, Monoclinic, $P2_1/c$, $a = 8.1250(5)$, $b = 10.0389(6)$, $c = 10.0172(6)$ Å, $\beta = 104.9570(10)^\circ$, $V = 789.38(8)$ Å³, $Z = 4$, 1814 unique data ($\theta_{\text{max}} = 28.24$), 1688 observed with $I > 2\sigma(I)$ which were used in all refinements. The final $R(I) = 0.0302$, $wR2 = 0.0825$. $\rho_{\text{max}} = 0.70$ eÅ⁻³. All calculations were performed on a microcomputer using SHELXL97 program.

Results and Discussion

Reaction of (4-pyridylthio)acetic acid with silver acetate in the presence of excessive aqueous ammonia gave a clear solution from which colourless rod-like crystals of formula $[\text{Ag}(\text{pyta})]_n$ could be isolated and characterized by element analysis, IR and X-ray single crystal diffraction. The X-ray structure analysis reveals the title compound is a 3D network. As shown in **Figure 1**, in one structural unit each silver atom adopts a tetrahedral geometry with a thioether sulfur, a pyridine nitrogen and two carboxylate oxygen atoms from different pyta^- ligands coordinated in a distorted fashion, in which the bond angle ($74.25(5)^\circ$) between the pyridine nitrogen (N1A) and the carboxylate oxygen (O1) is significantly smaller than the other bond angles ($99.70(8)$ – $133.68(6)^\circ$).

Figure 1 Perspective view of the coordination environment of $[\text{Ag}(\text{pyta})]_n$ at 50 % probability level, with hydrogen atoms omitted for clarity

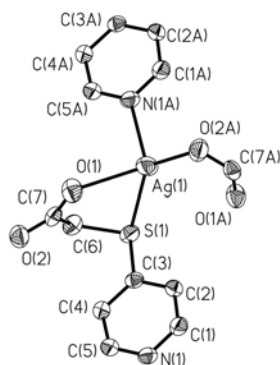
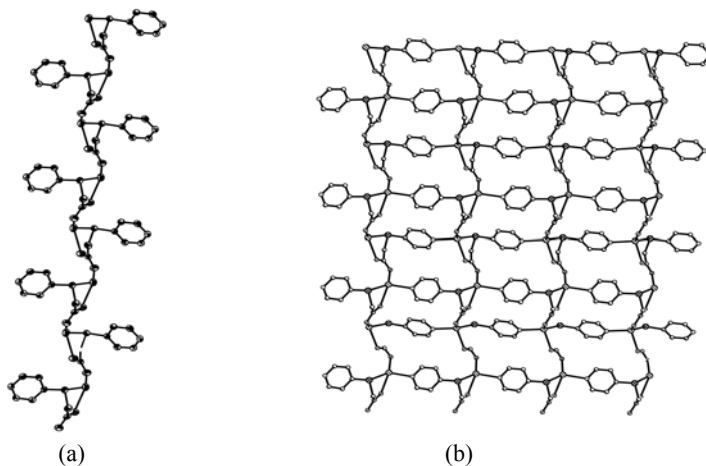


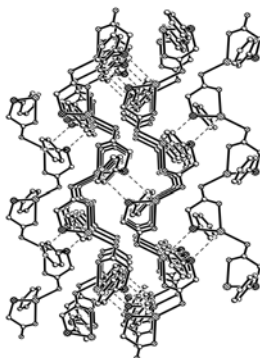
Figure 2 (a) View of a helical chain in $[\text{Ag}(\text{pyta})]_n$ with carboxylate oxygens as bridged atoms along the b axis; (b) View of $[\text{Ag}(\text{pyta})]_n$ along the c axis, with hydrogen atoms omitted, showing the layer-like arrangement of adjacent homochiral chains



An interesting structural feature of the polymeric $[\text{Ag}(\text{pyta})]_n$ is that two carboxylate oxygen atoms of the pyta ligand bridge two silver atoms to form a single-stranded helical chain (**Figure 2a**) with a 2_1 screw-axis, running along the b axis. The repeating distance of the helix is 10.039 Å. The adjacent homochiral chains are connected by strong coordination bonds between the pyridine nitrogen and the silver atom ($\text{Ag}(1)\text{-N}(1\text{A}) = 2.295(2)$ Å), leading to a chiral infinite grid structure (**Figure 2b**). These layers of the helices are stacked along the c axis (**Figure 3**) and the adjacent layers are self-assembled by weak Ag-S bond (3.525 Å), which is considerably longer than that of $\text{Ag}(1)\text{S}(1)$ (2.5346(8) Å). The chirality of neighbouring layers is opposite each other, resulting in the “meso-form” of the 3D network as documented by the centrosymmetric space group $P2_1/c$.

The TG/DTA results show the crystal was stable up to 187°C, but above 187°C it started to lose mass slowly.

Figure 3 Packing view of $[\text{Ag}(\text{pyta})]_n$ along the a axis, showing the opposite chirality of neighboring layers and weak Ag-S bonds with dotted lines



In conclusion, it was unusual to find a new coordination polymer in which the pyta^- ligand contribute all of its donor atoms to constructing helical structures with expected thioether-S binding and tetrahedral geometry. Such a flexible ligand can be considered to accommodate metal ions in a range of geometries and oxidation states to design the other novel coordination architectures.

Acknowledgments

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