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Synthesis and Structure of a Cyanoaurate-Based Organotin Polymer Exhibiting Unusual Ion-Exchange Properties

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Cyanide-bridged bimetallic supramolecules exhibiting fascinating structures and various magnetic, electrochemical, optical, gas-sorption, and colossal thermal expansion properties are the focus of widespread research interest.[1] Among many metal cyanide anions, the dicyanoaurate $[Au(CN)_2]^-$ has been successfully used in the construction of 2D and 3D cyano-bridged bimetallic coordination polymers.[2] Some of these cyanoaurate-based heterometallic polymers exhibit a particular targeted property, such as luminescence, magnetism, vapochromism, or birefringence.[2] In these bimetallic complexes, the Au···Au aurophilic interaction[3] has been widely used to control the polymeric structure and dimensionality. A recent review by Leznoff and co-workers[4] summarized the relevant gold(I)-containing polymers and materials, highlighting the use of aurophilic interactions as crystal-engineering design elements to increase structural dimensionality. Moreover, most studies have focused on transition-metal cations, and to a lesser extent on main-group metal ions, to construct heterometallic cyanoaurate-based coordination polymers. Only two examples of cyanoaurate-based coordination polymers containing a main-group metal have been reported; both contain lead and are highly birefringent materials.[2f,g] To the best of our knowledge, there have been no reports on structural characterization of tin cyanoaurates. Nevertheless, a series of organotin(IV) metal cyanates has been synthesized using various metal cyanide anions $[M(CN)_{2n}]^{n-}$ ($n = 2-4$) and triorganotin cations R_3Sn^+ (R = Me, Ph, ^{n}Bu).[5−7] In these examples, the metal cyanide contains the reactive CN^- sites in square-planar ($[Ni(CN)_4]^{2-}$),[5] octahedral ($[M(CN)_6]^{3-}$, M = Fe, Co),[6] or square-antiprismatic ($[M(CN)_8]^{4-}$, M = Mo, W)[7] orientations. The combination of R_3Sn^+ and linear $[Au(CN)_2]^-$ building units can lead to the formation of structures that differ considerably from those obtained with metal cyanide ions having square-planar, octahedral, or square-antiprismatic coordination. Therefore, the construction of multidimensional structures containing the Au−CN−Sn link generated by the reaction of the hard Lewis acidic organotin cation and the soft Lewis basic dicyanoaurate anion remains a great challenge. Moreover, it is still a challenge to obtain single crystals of these cyanoaurate-based heterometallic coordination polymers.[2d] As a continuance of our research on gold(I)[8] and organotin(IV)[9] supramolecules, we focused our interest on the design and synthesis of bimetallic complexes containing both gold and tin. To this end, we sought to prepare cyanoaurate-based organotin polymers using organotin(IV) cations and dicyanoaurate anions. Herein, we report the first organotin(IV)-containing cyanoaurate-based coordination polymer, which shows unusual solid-state structure and properties.

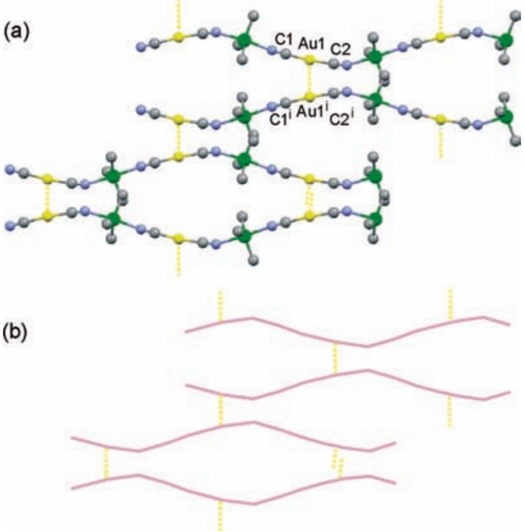

Figure 1. (a) Extended cyanide-bridged zigzag chains of **1** connected by weak [3.42(1) Å] Au···Au interactions. Color scheme: Au, yellow; Sn; green; N, blue; C, gray. The weak Au···Au interactions are shown as yellow dotted lines. Hydrogen atoms have been omitted. (b) Schematic drawing of violet-colored chains joined by interchain aurophilic interactions.

Platelike single crystals of the complex $Me_3Sn[Au(CN)_2]$ (**1**) were prepared by slow interdiffusion of aqueous solutions of Me_3SnCl and $K[Au(CN)_2]$ in a 1:1 molar ratio. Complex **1** is practically insoluble in water and in organic solvents. When the crystals are observed using polarized light microscopy, they display pleochroism by having a yellow, pink, green, or blue color depending on the orientation. Moreover, upon irradiation with 254 nm UV light, the crystals exhibit intense pink luminescence at room temperature. Single-crystal X-ray diffraction studies reveal that **1** crystallizes in the acentric orthorhombic space group *Fdd*2. The X-ray structural data for **1** indicate that it consists of three nonequivalent cyanide-bridged $(Me_3Sn)[Au(CN)_2]$ chains (colored violet, blue, and orange in the schematic drawings in this paper). Thus, each Me_3Sn unit is linked to two others by two $Au(CN)_2$ units via Sn−N bonds [average length 2.33(1) Å] to give infinite cyanide-bridged chains. As a result, the tin centers adopt a trigonal-bipyramidal C_3SnN_2 arrangement. Accordingly, one of the $(Me_3Sn)[Au(CN)_2]$ units is involved in the formation of infinite cyanide-bridged 1D zigzag chains (Au···Au···Au angle 160.9°), as illustrated in Figure 1. The Au(1) atoms in the backbone of each zigzag chain form weak interchain Au···Au interactions [3.42(1) Å] with Au(1)^i [$i = (1 - x, 1 - y, z)$] atoms on adjacent chains. This Au···Au distance between neighboring chains is less than 3.60 Å, the sum of the van der Waals radii of two Au atoms, and hence is a viable weak Au···Au interaction.[3] The C(1)−Au(1)−C(2) angle of 174.2° also supports this assignment, since compounds without Au···Au bonds have angles closer to 180°.[10] The C(1)−Au(1)···Au(1)^i−C(1)^i and C(2)−Au(1)···Au(1)^i−C(2)^i torsion angles between adjacent cyanoaurate units are 40.4 and 43.4°, respectively. It has been observed for dicyanoaurate-containing compounds that the C−Au−Au−C torsion angle between adjacent cyanoaurate units can vary from completely eclipsed (0°) to completely staggered (90°).[4,10]

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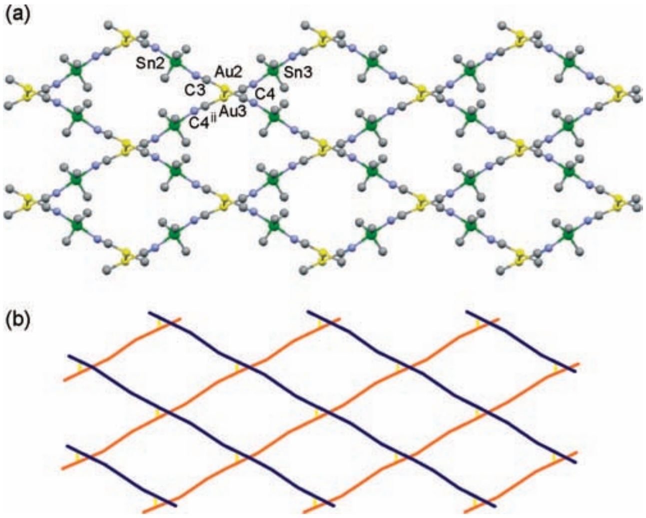


Figure 2. View showing the 2D grids of **1** formed via 3.12(1) Å Au···Au bonding. Color scheme: Au, yellow; Sn, green; N, blue; C, gray. The strong Au···Au interactions are shown as yellow lines. Hydrogen atoms have been omitted. (b) Schematic drawing of 2D grids formed by blue- and orange-colored chains joined by aurophilic interactions.

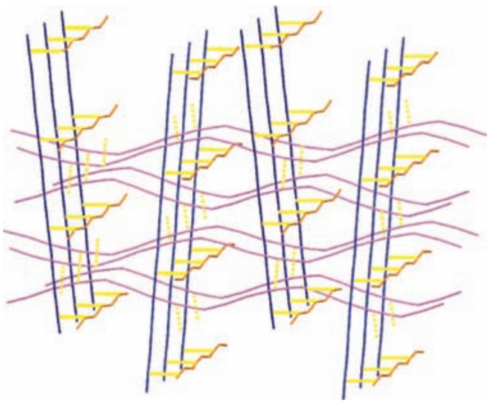
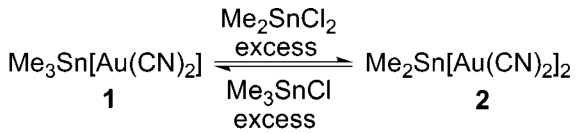


Figure 3. Complete 3D schematic picture of the structure of **1**, showing the arrays of zigzag chains (violet-colored) joined by weak Au···Au interactions interpenetrating the 2D grids (blue and orange-colored chains) linked via aurophilic interactions.

Moreover, this angle has been found to become more staggered with decreasing Au···Au distance.[4,10] Accordingly, the array of interpenetrating zigzag chains is held together by the 3.42(1) Å interchain aurophilic interactions (Figure 1). The other two $(Me_3Sn)[Au(CN)_2]$ units are involved in the formation of infinite cyanide-bridged linear chains (in both chains, the Au···Au···Au angle is 180°). The Au(2) and Au(3) centers of different chains are linked via aurophilic Au···Au interactions having a length of 3.12(1) Å, and the C(3)−Au(2)−Au(3)−C(4)^{ii} [ii = ($^3/_2 - x$, $^1/_2 - y$, z)] torsion angle is 52.8°. Therefore, these cyanide-bridged chains are linked via aurophilic interactions into a 2D grid (Figure 2). Overall, the void space of the 2D grids formed via Au···Au bonding is filled by the arrays of zigzag chains joined by weak Au···Au interactions. The complete 3D schematic picture of the structure of **1** is shown in Figure 3.

Scheme 1



It has been reported that some ferrocyanide-based heterometallic coordination polymers are effective ion exchangers of Cs^+,[11] organic R_4N^+ (R = Et, Bu), and organometallic (Cp_2Co^+) ions.[12] Moreover, metal exchange is a powerful and efficient method for modifying the properties of crystalline materials by varying the metal ions under moderate conditions.[13] Thus, with the above in mind, we performed a series of experiments testing the metal-exchanging properties of **1**. As a preliminary test for metal exchange, some crystals of **1** were soaked in a saturated methanolic solution of Me_2SnCl_2. After 3 h, the metathesis reaction took place; the crystals dissolved completely, and a microcystalline powder was formed overnight. The IR spectrum of the ion-exchanged powder displays a 596 cm^{-1} band characteristic of the Me_2Sn group[14] and absorptions at 2166 and 458 cm^{-1} attributable to the C≡N and Au−C stretching vibrations. Thus, the complete replacement of the Me_3Sn^+ cations with divalent Me_2Sn^{2+} cations led to the isolation of the complex $Me_2Sn[Au(CN)_2]_2$ (**2**). We succeeded in preparing suitable single crystals of complex **2** by slow interdiffusion of aqueous solutions of Me_2SnCl_2 and $K[Au(CN)_2]$ (1:2 molar ratio). The crystals of **2** grew as large, colorless prisms and showed pleochroism under polarized light microscopy. Compound **2**, like its parent complex **1**, is practically insoluble in water and organic solvents. Interestingly, **2** can be converted back into **1** by metathesis with Me_3SnCl in methanol (Scheme 1).

As was revealed by single-crystal X-ray diffraction, complex **2** crystallizes in space group *C*2/*c*. Each Me_2Sn unit is connected to four others by four $Au(CN)_2$ bridges, and therefore, the tin center adopts an octahedral C_2SnN_4 arrangement with the C atoms in the axial positions. Every $Au(CN)_2$ unit displaying a linear geometry is coordinated to Me_2Sn units by Sn−N bonds [average length 2.32(1) Å]. As Figure 4a shows, the resulting set of edge-sharing rectangles defines the infinite set of self-penetrating layers. These rectangles [N(1)−Sn(1)−N(2) angle 87.2°] have Sn···Sn edges of

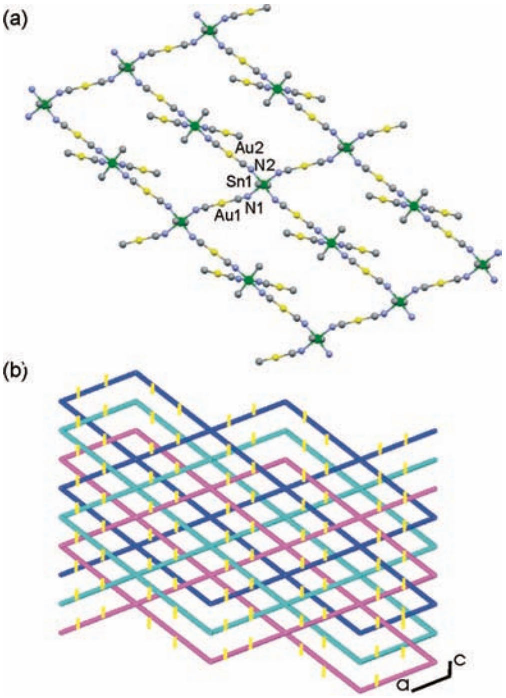
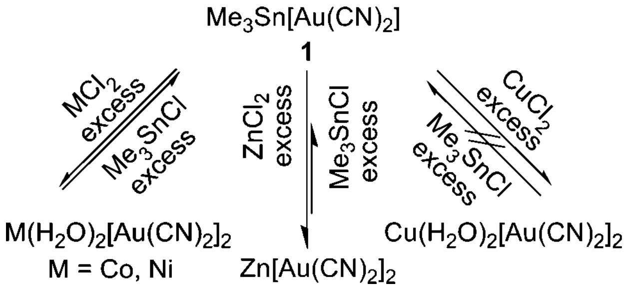


Figure 4. (a) View illustrating one of the cyanide-bridged 3D network of **2**, showing the set of edge-sharing rectangles with Sn···Sn edges. Hydrogen atoms have been omitted. (b) Schematic representation of **2** showing the fourfold-interpenetrated 3D networks with $6^5\cdot8$ topology that are supported by Au···Au interactions.

Scheme 2



10.67 Å. The crystal structure of **2** can be reduced to a schematic one by treating the Me_2Sn units as nodes and connecting them according to the connectivity defined by the $Au(CN)_2$ linkers. As determined by program package TOPOS,[15] **2** displays cyanide-bridged uninodal four-connected 3D networks with $6^5 \cdot 8$ topology corresponding to the $CdSO_4$ prototype (Figure 4b). Communication between these cyanide-bridged networks is realized through aurophilic Au(1)•••Au(1) interactions of length 3.29(1) Å (49.4° torsion angle) and longer Au(1)•••Au(2) contacts of length 3.45(2) Å (−52.5° torsion angle).

In contrast to porous metal−organic frameworks and other zeolite-like materials, which preserve their original crystal structure upon standard ion-exchange reactions,[13] the coordination polymer **1** undergoes an *unusual* ion-exchange process[16] in which the Me_3Sn^+ cations in the polymeric chains of **1** are removed completely and replaced by bivalent Me_2Sn^{2+} cations, which have entirely different charge and connectivity characteristics, as observed in **2**; the reverse process is similar. Obviously, replacement of the central metal ion is controlled by the ingoing metal ion's coordination ability toward the dicyanoaurate anions. In the case of **1** and **2**, the coordination ability of the ingoing ions is completely different from that of central metal ions, and thus, the resulting product cannot preserve the original structure.

We performed subsequent metal-exchange experiments in which **1** was soaked in aqueous solutions of bivalent transition-metal cations M^{2+} (M = Co, Ni, Cu, Zn). As a result, **1** was completely converted into transition-metal dicyanoaurates,[2a−d] as was well-confirmed by IR spectroscopy and powder X-ray diffraction (PXRD) patterns. In order to assess the reversibility of this process, the as-obtained transition-metal dicyanoaurates were immersed in a concentrated aqueous solution of Me_3SnCl (Scheme 2). It was interesting to observe that **1** can also be regenerated starting from cobalt(II) and nickel(II) dicyanoaurates. In the case of zinc(II) dicyanoaurate, IR spectroscopy indicated that the Zn^{2+} ions were partially replaced by the Me_3Sn^+ ions. More interestingly, the metathesis of copper(II) dicyanoaurate with Me_3SnCl afforded no reaction.

On the basis of a referee's suggestion, we also performed experiments in which **1** was treated with equal amounts of two different metal ions. Therefore, **1** was reacted with equal amounts of Me_2Sn^{2+} and Co^{2+}, Me_2Sn^{2+} and Cu^{2+}, Ni^{2+} and Co^{2+}, Ni^{2+} and Zn^{2+}, Co^{2+} and Cu^{2+}, Cu^{2+} and Ni^{2+}, and Cu^{2+} and Zn^{2+}. These preliminary studies showed that the coordination strength of divalent metal cations toward the $[Au(CN)_2]^-$ anions increases in the order $Me_2Sn^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+}$.

In conclusion, we have synthesized and structurally characterized the first cyanoaurate-based organotin polymer, which exhibits unusual ion-exchange properties. To our knowledge, this represents the first study revealing the metal-exchange properties of a cyanoaurate-based heterometallic polymer.

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Supporting Information Available: Synthetic details, X-ray crystallographic data for **1** and **2** in CIF format, IR data, and PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) As one referee pointed out, the term "ion exchange" can be misleading, as a standard ion-exchange substrate has a more-or-less rigid ionic skeleton containing voids where ion-exchange can proceed. Herein, we alternatively have applied the term "*unusual* ion exchange".

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