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A Versatile Solvent-Free Mechanochemical Route to the Synthesis of Heterometallic Dicyanoaurate-Based Coordination Polymers

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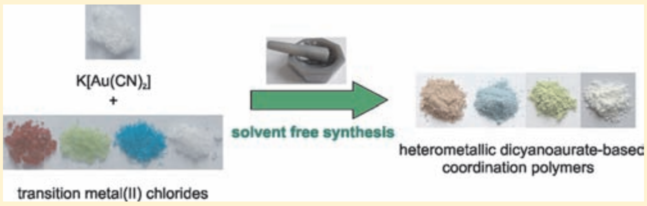
Supporting Information



ABSTRACT: The solid-state mechanochemical method was proved to be a fast, simple, and efficient route to the synthesis of heterometallic $[Au(CN)_2]$-based coordination polymers. Thus, a series of mixed-metal complexes, such as $KCo[Au(CN)_2]_3$, $KNi[Au(CN)_2]_3$, $Cu(H_2O)_2[Au(CN)_2]_2$, and $Zn[Au(CN)_2]_2$, was obtained by grinding stoichiometric amounts of $K[Au(CN)_2]$ and transition metal(II) chlorides. This solid-state method rapidly yields pure dicyanoaurate-based compounds, also in cases when the aqueous solution synthesis leads to an unseparable mixture of products. In addition, in some cases, the solid state reaction was faster than the corresponding solvent-based reaction. This mechanochemical method can be applied also to main group metals to obtain various cyanoaurate-based heterometallic coordination polymers, such as $Me_2Sn[Au(CN)_2]_2$ and $Ph_3Sn[Au(CN)_2]$. For the 2:1 mixture of $K[Au(CN)_2]$ and Me_2SnCl_2, the dramatic enhancement of the reaction rate by the presence of a minor amount of water was noticed. In $Ph_3Sn[Au(CN)_2]$, as was revealed by single-crystal X-ray diffraction, each Ph_3Sn unit is linked to two others by two $Au(CN)_2$ bridges via Sn−N bonds to form an infinite cyanide-bridged chain. There are no Au···Au contacts between the chains due to the sterical hindrance of the phenyl groups. A dehydrated blue $Co[Au(CN)_2]_2$ complex was obtained during grinding or heating of the moderate-pink $Co(H_2O)_2[Au(CN)_2]_2$ complex. This complex displays a vapochromic response when exposed to a variety of organic solvents, as well as water and ammonia vapors.

INTRODUCTION

The dicyanoaurate anion, $[Au(CN)_2]^-$, has significant importance in practical and medical applications. In industry, dicyanoaurate is used in electroplating processes,[1] while in medicine, it is considered as a pharmacologically active metabolite of gold(I) drugs, such as auranofin, aurothioglucose, and myochrysine.[2] Nowadays, this anion is also used in the design and synthesis of *cyano-bridged heterometallic coordination polymers (systems)*, which are the focus of widespread research interest.[3] This is due not only to their intriguing structural diversity but also to their magnetism,[4] luminescence,[5] vapochromism,[6] birefringence,[7] and colossal thermal expansion[8] as well as ion-exchange properties.[9] A popular approach to the synthesis of these materials is to use the $[Au(CN)_2]^-$ building block as a bridging ligand in conjunction with a transition metal cation for the construction of 2D and 3D polymers. In these cyanoaurate-based mixed-metal complexes, the dicyanoaurate moieties frequently undergo self-association through aurophilic Au···Au interaction.[10] These aurophilic interactions have been used to increase the structural dimensionality of these dicyanoaurate-based heterometallic polymers.[3]

Only a few examples of dicyanoaurate-based coordination polymers containing a main-group metal have been reported so far.[7a−e,9] In addition to these lead(II) and organotin(IV) dicyanoaurate-based coordination polymers,[7a−e,9] there are the $M[Au(CN)_2]$ (M = K, Cs, Tl) complexes, which consist of layers of linear $[Au(CN)_2]^-$ ions alternating with layers of M^+ ions.[7f−k] These salts show interesting photoluminescence properties that have been correlated with Au···Au interactions.[7f−k]

The majority of heterometallic dicyanoaurate-based coordination polymers are usually synthesized by simple mixing of the aqueous solutions of $K[Au(CN)_2]$ with stoichiometric amounts of transition metal salts.[4−9] However, as it was highlighted in the case of some transition metal(II) cations,[3−5] special care must be taken during the synthesis, since several different dicyanoaurate-based heterometallic complexes can coexist in solution, so that a mixture of products of different compositions might be obtained.[11−13]

Removing organic solvents in chemical synthesis is an important issue in the rapidly emerging field of green chemistry.[14] *Solvent-free mechanochemical methods* (grinding in a mortar with a pestle or ball milling) represent viable green routes for the preparation of novel molecular and supramolecular solids.[15] Mononuclear coordination compounds,[16] metallamacrocycles,[17] and coordination polymers and networks[18] as well as metal−organic frameworks (MOFs)[19] have been prepared by *solvent-free mechanochemical methods*. The grinding can have several effects on crystalline solids, including heating, local melting, particle size reduction with a concomitant increase in surface area, amorphization, phase changes to different polymorphic forms, etc.[15e] *Liquid-assisted grinding reactions* have also been utilized to

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construct mononuclear coordination compounds,[20] coordination networks,[21] and metal–organic frameworks.[22] Bowmaker and co-workers demonstrated that the enhancement of reaction by frictional heating is not necessary in some of the previously reported mechanochemical reactions, as the presence of small amounts of fortuitous solvent may accelerate the rate of these reactions.[20c] Nevertheless, such mechanochemical methods have been rarely used in the preparation of cyanometallates.[23−25] Kaupp reported that, depending on the molar ratio of CuCN and NaCN, different complex salts such as $Na[Cu(CN)_2]$, $Na_2[Cu(CN)_3]$, and $Na_3[Cu(CN)_4]$ have been obtained in ball milling experiments.[23] In an early study, the formation of Prussian Blue ($KFe[Fe(CN)_6]\cdot H_2O$) by grinding $FeCl_3\cdot 6H_2O$ and $K_4[Fe(CN)_6]\cdot 3H_2O$ powders has also been reported.[24] A deep-blue ferrocenium intercalate $(Cp_2Fe)(Me_3Sn)_3[Fe(CN)_6]$ has also been synthesized by grinding of the orange-yellow $(Me_3Sn)_3[Fe(CN)_6]$ with ferrocene (Cp_2Fe).[25] To our knowledge, *solvent-free solid-state reactions* have never been used to produce $[Au(CN)_2]$-based heterometallic compounds. We have applied, for the first time, solid-state reaction methods to synthesize various dicyanoaurate-based heterometallic polymers. We prepared under solvent-free or solvent-assisted mechanochemical conditions a series of mixed-metal complexes by reacting $K[Au(CN)_2]$ with transition metal(II) chlorides as well as organotin(IV) chlorides.

Vapochromic or *vapoluminescent* compounds display dramatic color (optical) or luminescence changes upon exposure to vapors of volatile organic compounds (VOCs).[26] As a response to solvents or VOCs, these compounds show significant changes in their optical properties, which generally originate from molecular conformation changes in the solid state, the appearance of new bonding interactions such as hydrogen-bonding, metal–solvent bonds, and aurophillic interactions.[26] Several vapochromic Au(I) complexes have also been recently reported,[27] where the vapochromic behavior changes the visible absorption or emission spectra. Among gold(I) dicyanoaurates, the green and blue $Cu[Au(CN)_2]_2(DMSO)_2$ polymorphs display vapochromic behavior with reversible changes of color when they are exposed to a variety of organic vapors.[6a] In this context, we have prepared by mechanical grinding a new $[Au(CN)_2]$-based vapochromic complex, which in response to solvent vapors displays visible color changes.

■ EXPERIMENTAL SECTION

Materials and General Methods. All chemicals and solvents used for the syntheses were of reagent grade. The solvents for synthesis were used without further purification. All reactions were carried out at room temperature.

General Procedure for the Solvent Free Synthesis of $[Au(CN)_2]$-Based Heterometallic Compounds. A stoichiometric mixture of $K[Au(CN)_2]$ and the corresponding metal chloride ($CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$, $ZnCl_2$, Me_2SnCl_2, and Ph_3SnCl) was ground in a mortar with a pestle at room temperature until the reaction was completed (monitored by FT-IR spectroscopy). Then, the reaction mixture was washed with water to afford the pure products.[28]

*Preparation of $KCo[Au(CN)_2]_3$ (**1**).* The color of the mixed $K[Au(CN)_2]$ (0.45 g, 1.563 mmol) and $CoCl_2\cdot 6H_2O$ (0.124 g, 0.521 mmol) powder changed during the grinding from light-pink to light-purple. After thoroughly washing with distilled water, a light-purple product was obtained. Yield: 0.334 g (75.9%). IR data: 3410 (b, w), 2165 (s), 468 (m). Anal. Calcd for **1**·$2H_2O$: C, 8.18; H, 0.46; N, 9.54. Found: C, 8.21; H, 0.77; N, 9.26.

*Preparation of $KNi[Au(CN)_2]_3$ (**2**).* The color of the mixed $K[Au(CN)_2]$ (0.45 g, 1.563 mmol) and $NiCl_2\cdot 6H_2O$ (0.124 g, 0.521 mmol) powder changed during the grinding from light-green to light-turquoise. After thoroughly washing with distilled water, a turquoise product was obtained. Yield: 0.336 g (76.4%). IR data: 3358 (b, w), 2171 (s), 1615 (vw), 472 (w). Anal. Calcd for **2**·$4H_2O$: C, 7.86; H, 0.88; N, 9.17. Found: C, 7.94; H, 0.78; N, 9.06.

*Preparation of $Cu(H_2O)_2[Au(CN)_2]_2$ (**3**).* The color of the mixed $K[Au(CN)_2]$ (0.300 g, 1.042 mmol) and $CuCl_2\cdot 2H_2O$ (0.089 g, 0.521 mmol) powder changed during the grinding from turquoise to greenish-brown. After thoroughly washing with distilled water, a light-green product was obtained. Yield: 0.244 g (78.4%). IR data: 3179 (b, m), 2217 (m), 2172 (s), 706 (w), 568 (w), 470 (w). Anal. Calcd for **3**: C, 8.04; H, 0.67; N, 9.38. Found: C, 8.10; H, 0.73; N, 9.26.

*Preparation of $Zn[Au(CN)_2]_2$ (**4**).* The mixed powder of $K[Au(CN)_2]$ (0.300 g, 1.042 mmol) and $ZnCl_2$ (0.071 g, 0.521 mmol) formed a white paste, which after 15 min of grinding started to solidify to yield a white solid. After thoroughly washing with distilled water, a white product was obtained. Yield: 0.212 g (72.3%). IR data: 2198 (s), 518 (m). Anal. Calcd for **4**: C, 8.53; N, 9.94. Found: C, 8.46; N, 9.70.

*Preparation of $Me_2Sn[Au(CN)_2]_2$ (**5**).* The color of the mixed $K[Au(CN)_2]$ (0.300 g, 1.042 mmol) and Me_2SnCl_2 (0.115 g, 0.521 mmol) changed during the grinding from white to yellowish-green. After thoroughly washing with distilled water, a white product was obtained. Yield: 0.253 g (74.8%); IR data: 2169 (s), 814 (w), 596 (w), 458 (m). Anal. Calcd for **5**: C 11.14; H 0.94; N 8.66; Found: C 11.32; H 0.65; N 8.59.

*Preparation of $Ph_3Sn[Au(CN)_2]$ (**6**).* The liquid-assisted grinding of $K[Au(CN)_2]$ (0.150 g, 0.521 mmol) and Ph_3SnCl (0.201 g, 0.521 mmol) was performed with the addition of 2 drops of water during grinding. After 10 min of grinding, the white powder was thoroughly washed with water, and a white product was obtained. Yield: 0.263 g (84.3%). IR data: 2168 (s), 1483 (w), 1430 (m), 1079 (w), 999 (w), 735 (m, sh), 727 (m), 695 (m), 451 (m). Anal. Calcd for **6**: C, 40.1; H, 2.52; N, 4.68. Found: C, 39.73; H, 2.44; N, 4.63. This compound was then recrystallized from methanol. The powder pattern simulated from single crystal data agrees well with the experimental powder pattern of this white product, **6**; thus the recrystallized product is the same as the initial compound.

*Preparation of $Co(H_2O)_2[Au(CN)_2]_2$ (**7**).* As-synthesized crystals of $Me_3Sn[Au(CN)_2]$[9] (0.2 g, 0.484 mmol) were immersed in a concentrated aqueous solution of $CoCl_2\cdot 6H_2O$. After 2 days, the crystals were turned into a microcrystalline light-pink powder. The powder was thoroughly washed with distilled water. Yield: 0.104 g (cca 73%). IR data: 3015 (b, m), 2206 (m, sh), 2195 (s), 2173 (s, sh), 2161 (s), 1533 (m), 891 (m), 754 (b, w), 508 (w). Anal. Calcd for **7**: C, 8.10; H, 0.68; N, 9.45. Found: C, 8.25; H, 0.68; N, 9.38.

*Preparation of $Co[Au(CN)_2]_2$ (**8**).* Complex **8** was prepared by grinding complex **7** (0.1 g, 0.168 mmol) for 75 min. The color of the powder changed during the grinding from light-pink to blue. It can also be prepared by heating **7** at 180 °C for 10 min. Yield: 0.089 g (94.7%). IR data: 2183 (s), 538 (m), 517 (sh), 420 (w). Anal. Calcd for **8**: C, 8.63; N, 10.06. Found: C, 9.17; N, 9.96.

Vapochromic Studies. The sample of **8** was placed in a small, open container that, in turn, was placed in a larger vial containing the volatile oxygen- or nitrogen-donor solvent. Then, the larger container was tightly closed. The exposure of **8** to vapors of the volatile solvent vapors leads to a perceptible change in the color of the samples.

In a parallel test, the powdered sample of **8** was deposited on filter paper and was exposed to selected organic vapors. This also leads to quick and perceptible change in the color of the samples.

IR data for H_2O-treated **8**: 3015 (b, m), 2206 (m, sh), 2195 (m), 2172 (s), 2162 (s), 1534 (m), 890 (m), 794 (w).

IR data for MeOH-treated **8**: 3564 (w), 3455 (b, w), 2952 (w), 2180 (s), 1445 (w), 1388 (w), 1074 (w), 1016 (m), 975 (w).

Table 1. Crystal Data and Structure Refinement Parameters for Complex 6

empirical formula	$C_{20}H_{15}AuN_2Sn$
fw	599.0
cryst size [mm]	0.24 × 0.24 × 0.34
color	colorless
cryst syst	monoclinic
space group	$C2/c$
temp. (K)	11
θ range for data collection (deg)	$1.9 \leq \theta \leq 25.0$
λ (Å)	0.71073
a [Å]	14.6109(6)
b [Å]	18.7252(6)
c [Å]	7.4017(3)
β [deg]	113.806(2)
V [Å^3]	1852.75(13)
Z	4
d_{calc} [Mg/m^3]	2.148
μ [mm^{-1}]	9.259
F(000)	1112
index ranges	$-17 \leq h \leq 17$ $-22 \leq k \leq 22$ $-8 \leq l \leq 8$
no. of collected reflns	16687
no. of indep. reflns/R_{int}	1643/0.058
no. of obsd. reflns $I > 2\sigma(I)$	1639
no. of params	108
GOF	1.43
R1 (obsd. data)	0.0259
wR2 (all data)	0.1100
largest diff. peak/hole (e Å^{-3})	−1.43/1.00

IR data for EtOH-treated **8**: 3387 (b, m), 2980 (m), 2901 (w), 2185 (s), 1395 (w), 1269 (w), 1091 (w, sh), 1039 (m), 879 (w).

IR data for DMF-treated **8**: 2182 (m), 1657 (s), 1435 (w), 1380 (w), 1110 (m), 687 (m). The synthesis, crystal structure and spectral characterization of this complex, namely, $Co(DMF)_2[Au(CN)_2]_2$, has been previously reported.[29]

IR data for DMSO-treated **8**: 2177 (s), 1419 (w, sh), 1409 (w), 1031 (m), 997 (s), 957 (m).

IR data for THF-treated **8**: 2960 (b, w), 2887 (w), 2183 (s), 1039 (m), 888 (m).

IR data for py-treated **8**: 2172 (s), 2142 (m), 1601 (s), 1577 (w), 1489 (m), 1445 (s), 1217 (m), 1068 (m), 1042 (m), 1011 (m), 776 (w, sh), 768 (m), 756 (m), 707 (s), 630 (m).

IR data for NH_3-treated **8**: 3328 (b, s), 2168 (m, sh), 2143 (s), 1608 (b, m), 1290 (b, m), 1216 (m, sh), 1201 (m), 819 (b, w), 603 (b, w).

Single Crystal X-Ray Diffraction. Crystal data, data collection, and refinement details for **6** are listed in Table 1. A crystal of **6** was mounted in Paratone-N oil within a conventional cryo-loop, and intensity data were collected on a Rigaku R-AXIS RAPID image plate diffractometer, fitted with an X-stream low temperature attachment. Several scans in the φ and ω direction were made to increase the number of redundant reflections, which were averaged over the refinement cycles. The structures were solved by direct methods (SIR92)[30] and refined by full-matrix least-squares (SHELXL-97).[31] All calculations were carried out using the WinGX package of crystallographic programs.[32] The anisotropic displacement parameters for C(3B) and C(4B) atoms were constrained to be the same (EADP). All non-hydrogen atoms were refined anisotropically in F^2 mode. The riding model was applied for the hydrogen atoms.

Scheme 1

$$3\,K[Au(CN)_2] + MCl_2{\cdot}6H_2O \rightarrow KM[Au(CN)_2]_3 + 2\,KCl + 6\,H_2O$$

1: M = Co; and **2**: M =Ni

$$2\,K[Au(CN)_2] + MCl_2{\cdot}\,nH_2O \rightarrow M(H_2O)_n[Au(CN)_2]_2 + 2\,KCl$$

3: M = Cu, $n = 2$

4: M = Zn, $n = 0$

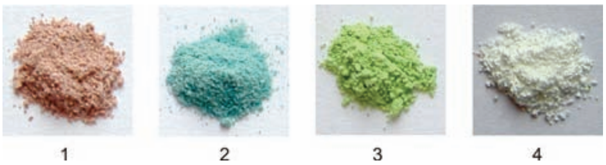

Figure 1. Photographs showing the colors of complexes **1**−**4** obtained in solvent-free solid-state reactions between $K[Au(CN)_2]$ and transition metal(II) chlorides.

Infrared spectra were recorded in the 450 or 550 to 4000 cm^{-1} spectral range on a Bio-Rad (Digilab Division) FTS-60A FT-IR spectrometer equipped with a UMA-500 infrared microscope with a Ge plate. Powder diffractograms were produced with Cu Kα radiation on a vertical high-angle Philips PW 1050 powder diffractometer. The elemental analysis was carried out with an Elementar Vario EL III apparatus at the Analytical Laboratory for Organic Chemistry, Chemical Research Center, Hungarian Academy of Sciences.

RESULTS AND DISCUSSION

Preparation of Transition Metal Dicyanoaurates. As part of our studies on cyanometallate coordination polymers,[9] now we report a solid-state mechanochemical route to the synthesis of heterometallic $[Au(CN)_2]$-based coordination polymers. These solvent-free solid-state reactions between $K[Au(CN)_2]$ and transition metal(II) chlorides occur within minutes of grinding (Scheme 1), and after thorough washing with water they give pure microcrystalline dicyanoaurate-based heterometallic polymers (Figure 1).

These solid-state reactions imply extensive solid-state rearrangement and the formation of new metal−cyanide M−NC−Au bonds. The presence of the cyanide group provides a useful probe to monitor these solid-state reactions via FTIR spectroscopy.

Cobalt(II) dicyanoaurates are usually prepared in solutions; however, for example, the aqueous reactions of $K[Au(CN)_2]$ with $Co(ClO_4)_2{\cdot}6H_2O$ yield a mixture of products of different compositions that cannot be separated.[1,11] The potassium cobalt(II) dicyanoaurate(I) is a component in the electrodeposition processes for cobalt-hardened gold and precipitates as a side-product from concentrated solutions of $K[Au(CN)_2]$ and cobalt(II) salt.[33] Although the crystallization and structure of $KCo[Au(CN)_2]_3$ was reported previously, no further structural characterization was performed.[33b] Furthermore, to our knowledge, the solvent-based synthesis of $KCo[Au(CN)_2]_3$ has also never been reported. Mechanochemical methods could represent an alternative route to preparing pure cobalt(II) dicyanoaurate complexes in high yields. Grinding of 2:1 or 3:1 powdered mixtures of $K[Au(CN)_2]$ and $CoCl_2{\cdot}6H_2O$ at room temperature for 35 min produces a pink microcrystalline product. Inspection of the

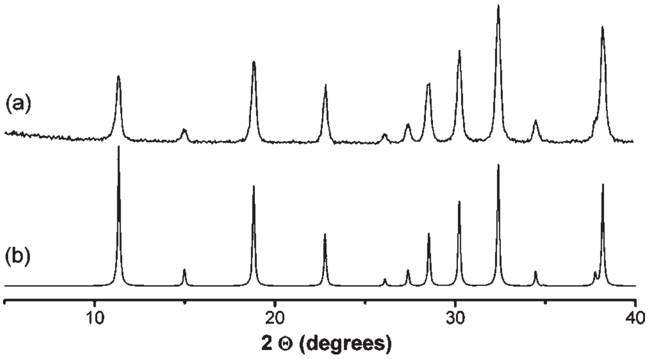

Figure 2. Powder X-ray diffraction patterns of **1** (a) prepared by solvent-free grinding and (b) its simulated diffraction pattern based on the single crystal structure (ICSD 201056).[33b]

bands in the ν_{CN} region shows that after ca. 5 min of grinding the reaction is practically completed. The IR spectrum of the pure product **1** shows a single cyanide vibration at 2165 cm^{-1}, suggesting that all of the cyanide groups are in an identical coordination environment. The powder diffractogram of **1** (Figure 2) was observed to be similar to that of KCo[Au(CN)$_2$]$_3$ calculated from single crystal data.[33b] Elemental analysis of this pink powder **1** is also consistent with KCo[Au(CN)$_2$]$_3$.

The aqueous solution synthesis of KNi[Au(CN)$_2$]$_3$ (**2**) took more than 4 days, as long as the pale-green Ni(H$_2$O)$_2$[Au(CN)$_2$]$_2$ complex converted into a pale-blue powder.[13] Complex **2** has also been synthesized hydrothermally over more than 8 h.[13] In striking contrast, we found that on simply grinding together stoichiometric amounts of K[Au(CN)$_2$] and NiCl$_2$·6H$_2$O for 30 min, compound **2** was obtained. After washing the reaction mixture with water, **2** is isolated in its pure form. This was confirmed by the ν_{CN} value of 2172 cm^{-1} and powder diffraction patterns as well as elemental analysis. These mixed-metal potassium cobalt(II) and nickel(II) dicyanoaurates obtained in these solid-state reactions (Scheme 1) may also be found as side products in the aqueous solution synthesis of aqua-bridged Co(H$_2$O)$_2$[Au(CN)$_2$]$_2$ or Ni(H$_2$O)$_2$[Au(CN)$_2$]$_2$ complexes, if a slight excess of K[Au(CN)$_2$] is used or if the reaction mixture is very concentrated.[11−13]

Complexes **3** and **4** were also prepared under solvent-free conditions (Scheme 1). The IR spectra of the green product resulting from the 2:1 reaction of K[Au(CN)$_2$] and CuCl$_2$·2 H$_2$O showed that after 35 min of grinding only a small portion of the K[Au(CN)$_2$] remained unreacted. This mixture was thorough washed with water, and the ν_{CN} values (2217 and 2172 cm^{-1}) of the as-obtained green compound **3**, its powder diffraction pattern, and elemental analysis are consistent with those of Cu(H$_2$O)$_2$[Au(CN)$_2$]$_2$.[6a,9,11] As we already mentioned, the DMSO analogues of this complex, namely, the blue and green polymorphs of Cu(DMSO)$_2$[Au(CN)$_2$]$_2$, display vapochromic properties when exposed to a variety of solvents as well as ammonia vapors.[6a]

The formation of the α polymorph of **4**[9,34] was confirmed by IR spectrum (ν_{CN} = 2201 cm^{-1}) and powder X-ray diffraction patterns. The previously reported four polymorphs of Zn[Au(CN)$_2$]$_2$ can reversibly bind NH$_3$ vapor with very high sensitivities and act as vapoluminescent sensors for ammonia.[6b]

Preparation of Organotin(IV) Dicyanoaurates. We probed the mechanochemical method to synthesize organotin(IV) dicyanoaurates (Scheme 2), such as **5** and **6**.

Scheme 2

$$2\ \mathrm{K[Au(CN)_2]} + \mathrm{Me_2SnCl_2} \rightarrow \underset{\mathbf{5}}{\mathrm{Me_2Sn[Au(CN)_2]_2}} + 2\ \mathrm{KCl}$$

$$\mathrm{K[Au(CN)_2]} + \mathrm{Ph_3SnCl} \rightarrow \underset{\mathbf{6}}{\mathrm{Ph_3Sn[Au(CN)_2]}} + \mathrm{KCl}$$

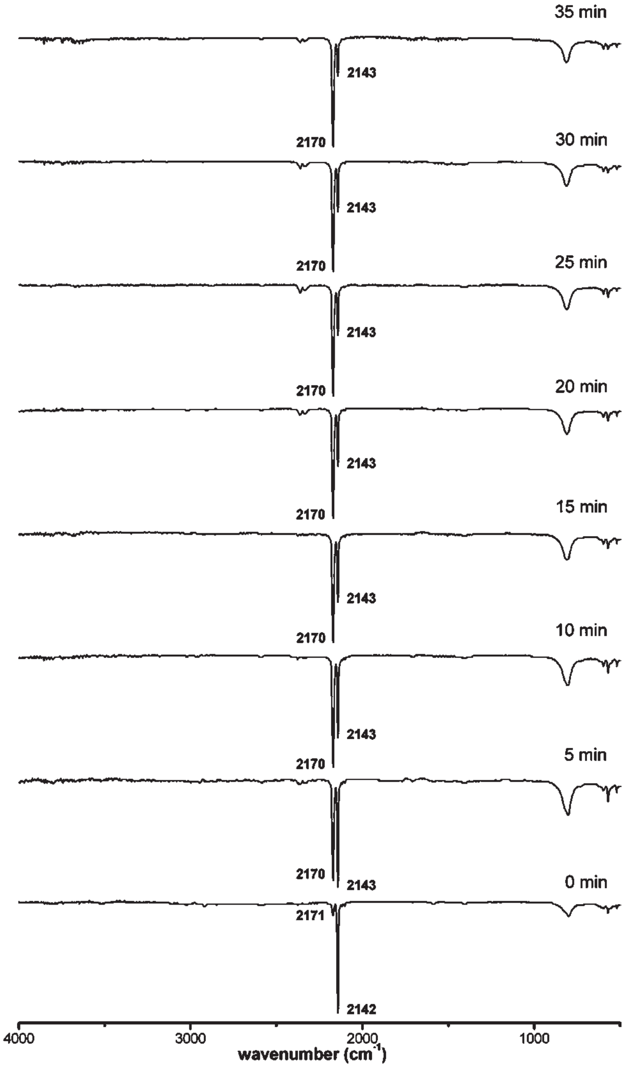

Figure 3. FT-IR spectra of a 2:1 powdered mixture of K[Au(CN)$_2$] with Me$_2$SnCl$_2$ measured at different times of grinding.

The IR spectrum of the product resulting from the 2:1 reaction of K[Au(CN)$_2$] and Me$_2$SnCl$_2$ showed that after 35 min of grinding only a portion of the K[Au(CN)$_2$] remains unreacted (Figure 3). This mixture was thoroughly washed with water to yield the pure compound **5** (ν_{CN} = 2170 cm^{-1}). The experimental powder pattern agrees well with those simulated from single crystal data and obtained on a sample prepared by aqueous (solution-based) synthesis.[9] In striking contrast, there is an immediate and complete reaction if a trace of water is added to form a paste during the 2:1 mechanochemical reaction of K[Au(CN)$_2$] and Me$_2$SnCl$_2$. Thus, the addition of a few drops of water resulted in the complete conversion of the mixture into

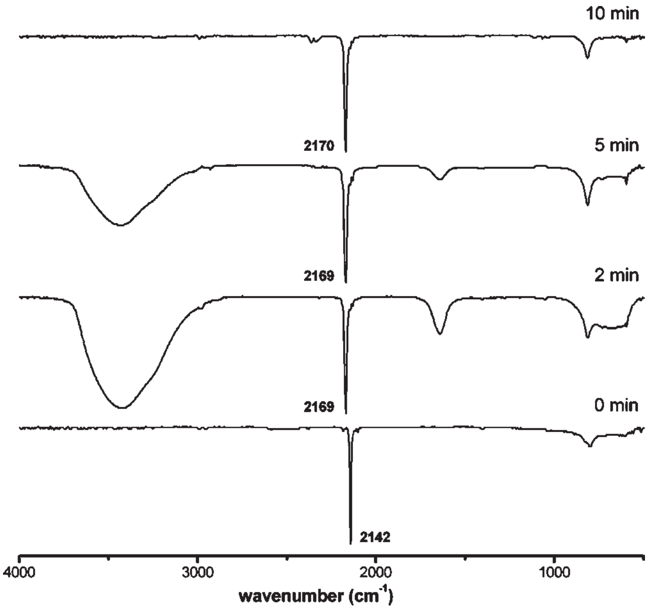

Figure 4. FT-IR spectra of a 2:1 powdered mixture of $K[Au(CN)_2]$ and Me_2SnCl_2 (after the addition of a few drops of water) measured at different times of grinding.

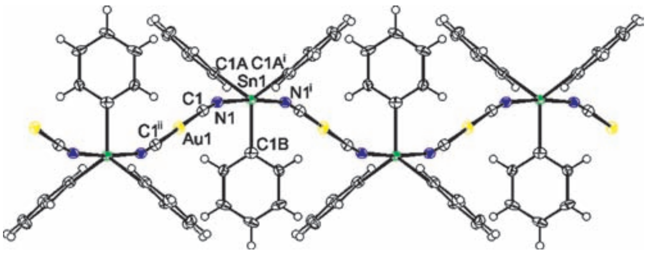

Figure 5. Ortep view of the cyanide-bridged zigzag chains of **6**. Ellipsoids are shown at the 50% probability level. Equivalent atoms generated by $i = (-x, y, 1/2 - z)$ and $ii = (-1/2 - x, 1/2 - y, -1 - z)$. Selected distances (Å) and angles (deg): Sn(1)−N(1) 2.333(6); Sn(1)−C(1A) 2.137(8); Sn(1)−C(1B) 2.138(9); Au(1)−C(1) 1.987(8); N(1)−Sn(1)−N(1)^i 174.8(2); C(1A)−Sn(1)−C(1A)^i 117.4(3); C(1A)−Sn(1)−C(1B)^i 121.3(2); C(1B)−Sn(1)−C(1A)^i 121.3(2); C(1)−Au(1)−C(1)^{ii} 180.0.

complex **5** after only 2 min of grinding (Figure 4). The water content of the paste was evaporated after 10 min of grinding. Recently, it was shown that grinding the reactants (metal compounds and ligands) in the presence of a catalytic amount of solvent dramatically increased the rate of formation of metal coordination compounds.[20]

Since the powdered mixture of $K[Au(CN)_2]$ and Ph_3SnCl (1:1 molar ratio) is highly electrostatically charged and tended to stick to gloves, we performed the grinding only after the addition of a few drops of water (Scheme 2). The IR spectrum of the mixture shows complete consumption of the starting materials after only 10 min of grinding. The IR spectrum of the pure product **6** shows a single cyanide vibration at 2168 cm^{-1}.

As was revealed by single-crystal X-ray diffraction, each Ph_3Sn unit is linked to two others by two $Au(CN)_2$ bridges via Sn−N bonds [2.33(2) Å] to form an infinite cyanide-bridged chain (Figure 5). Therefore, the tin center adopts a trigonal-bipyramidal C_3SnN_2 arrangement. In contrast to the crystal structure of $Me_3Sn[Au(CN)_2]$, where the infinite cyanide-bridged chains are joined through aurophilic interactions,[9] there are no Au···Au contacts between the chains due to the sterical hindrance of the phenyl groups. The observed PXRD pattern of compound **6** obtained in the water-assisted mechanochemical reaction closely matched the pattern simulated from the crystal structure; thus the same compound was obtained by recrystallization.

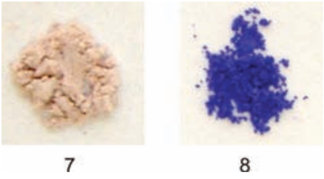

Figure 6. Photographs showing the color of complexes **7** and **8**. Complex **8** was obtained by grinding **7** in a mortar.

Scheme 3

$$\underset{\mathbf{7}}{Co(H_2O)_2[Au(CN)_2]_2} \rightarrow \underset{\mathbf{8}}{Co[Au(CN)_2]_2} + 2\,H_2O$$

We successfully applied this liquid-assisted grinding or solvent-assisted mechanochemical method in the synthesis of compounds **5** and **6**, and as pointed out by a reviewer, other reactions use a hydrated reagent (synthesis of compounds **1**−**3**) or a deliquescent reagent (synthesis of compound **4**). In most of these reactions, the products contain no water, or less water than the reactants, so that water is produced as a byproduct of the reaction, and this water could function in the same way as added water to accelerate the reaction as it progresses.[20c]

Vapochromic Behavior. As we already mentioned, in the aqueous solution syntheses of cobalt(II)- or nickel(II)-dicyanoaurates, a mixture of products of different compositions, such as hydrated, dehydrated, and other mixed metal(II) dicyanoaurates, are obtained.[11−13] Thus, the aqueous reaction of $K[Au(CN)_2]$ with cobalt(II) salts yields a red-colored mixture of **1**,[33] $Co(H_2O)_2[Au(CN)_2]_2$ (**7**),[11] and $Co[Au(CN)_2]_2$ (**8**)[35] complexes that cannot be separated.[1,11] Although, the change in solvent from water to acetonitrile leads to the exclusive formation of a hydrated **7** compound.[11] Previously, we performed metal-exchange experiments in which the $Me_3Sn[Au(CN)_2]$ complex was soaked in aqueous solutions of bivalent transition-metal M^{2+} (M = Co, Ni, Cu, Zn) cations.[9] After 2 days, the crystals of $Me_3Sn[Au(CN)_2]$ in the presence of cobalt(II) chloride were completely converted into the moderate-red **7** complex (Figure 6). Thus, the change in the starting material from $K[Au(CN)_2]$ to $Me_3Sn[Au(CN)_2]$ also leads to the exclusive formation of hydrated complex **7**.[9]

As analogues of the vapochromic $Cu(DMSO)_2[Au(CN)_2]_2$[6a] and $Zn[Au(CN)_2]_2$[6b] complexes, we targeted these cobalt(II) dicyanoaurates, as the coordination geometry of the Co(II) cation in these complexes shows flexibility when converting between octahedral and tetrahedral forms.[11,33,35] To probe the vapochromic behavior of **7**, the sample was ground in a mortar with a pestle at room temperature until its color changed from pale-pink to blue (Scheme 3).

The progress of the solid-state reaction was monitored by measuring the IR spectra; as the grinding time proceeded, the splitting of the ν_{CN} cyanide vibrations faded with concomitant water loss. The IR spectrum of the resulting blue compound **8**

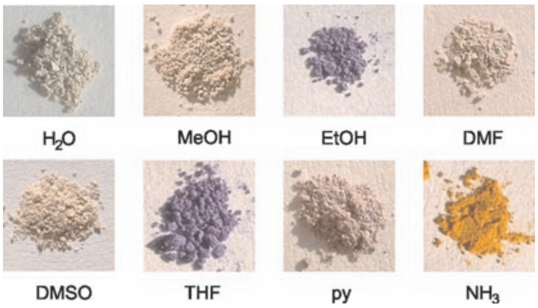

Figure 7. Colored **8·v** samples changed by adding various solvent vapors to the powdered blue sample of **8**.

Table 2. Characteristic ν_{CN} Frequencies (cm^{-1}) of Vapor-Treated 8·v Complexes

vapor	color after exposure	ν_{CN}
water	pale-pink	2206 (m), 2195 (s), 2173 (s), 2161 (s)
MeOH	pale-pink	2179 (s)
EtOH	light-violet	2185 (s)
DMF	pale-pink	2182 (s)
DMSO	pale-pink	2177 (s)
THF	light-violet	2183 (s)
pyridine	pale-pink	2172 (s), 2142 (m)
NH_3	ochre	2168 (m), 2143 (s)

shows only a single cyanide vibration at 2181 cm^{-1}, suggesting that all of the cyanide groups are in an identical coordination environment. Moreover, there are no traces of water in the spectrum (for details, see the Supporting Information). The PXRD pattern of this mechanochemically obtained **8** showed the formation of a partially crystalline material. The heating of **7** at 180 °C in a vacuum for 10 min also yields this dehydrated complex **8**. The PXRD pattern of this material differs from that of hydrated **7**. This, taken together with the large changes in the ν_{CN} frequencies, indicates that structural changes also occur in response to the removal of water molecules. Thus, as a consequence of mechanical grinding or heating, the cobalt-aqua bonds were broken and the water molecules were lost, and this was accompanied by a dramatic and rapid color change from light-pink to blue (Figure 6). Nevertheless, the peaks in the powder diffractogram of **8** do not match those of $Co[Au(CN)_2]_2$ calculated from single crystal data.[35] Therefore, this phase formed upon dehydration might correspond to a possible polymorph of cobalt(II) dicyanoaurate. This dehydrated blue complex **8** is stable over 10 days in the presence of ambient water vapor and temperature. However, upon exposure to water vapors for 20 h, the PXRD pattern of the as-obtained sample is identical to that of the hydrated pink powder of **7**.

Upon exposure of blue **8** to the vapors of MeOH, EtOH, DMF, DMSO, THF, pyridine, and NH_3, under ambient temperature, vapochromic responses were observed in which the solid changes to the pale-pink, light-violet, or ochre color of **8·v** samples (Figure 7).

The IR spectrum of all of these **8·v** samples contains characteristic bands associated with corresponding oxygen- and nitrogen-donor ligands. As previously reported for metal-cyanide-based vapochromic materials, the ν_{CN} region in the IR spectrum is sensitive to the presence of volatile vapors of oxygen and nitrogen donors.[6a,36] Despite the presence of different oxygen donors, such as MeOH, EtOH, DMF, DMSO, and THF, the ν_{CN} vibration of these **8·v** complexes is shifted by only ±1 to 4 cm^{-1} wavenumbers as compared with **8** (Table 2). Thus, owing to these narrow changes in the ν_{CN} frequencies, the ν_{CN} region in the IR spectrum of these oxygen-donor complexes is not a sensitive and characteristic signature for the corresponding solvent. The only exceptions occur with very strong nitrogen donors, such as pyridine and ammonia, when the spectrum of these samples contains two ν_{CN} bands. The pyridine complex shows a strong peak at 2172 and a medium one at 2142 cm^{-1}, while the NH_3 complex exhibits a medium and a strong peak at 2168 and 2143 cm^{-1}, respectively. The bands at higher frequencies may be attributed to the coordinated cyanide and those at 2142 or 2143 cm^{-1} to terminal or uncoordinated cyanide ligands of the $[Au(CN)_2]^-$ anion. For comparison, the $K[Au(CN)_2]$ and $Na[Au(CN)_2]$ complexes display ν_{CN} stretching frequencies at 2140 and 2153 cm^{-1}, respectively.[37] In contrast, exposure of **8** to vapors of acetonitrile did not induce any changes in the IR spectrum of **8**; thus the vapochromic response is negative for this nitrogen-donor ligand.

All of these vapochromic responses are fully reproducible with conversion from **8·v** samples back to **8**, accomplished by heating the sample under vacuum conditions.

■ CONCLUSIONS

In summary, the solid-state mechanochemical method using $K[Au(CN)_2]$ and transition metal(II) chlorides was proved to be a fast, simple, and efficient route to the synthesis of heterometallic dicyanoaurate-based coordination polymers. A surprising aspect of our studies is that, in some cases, the solid state reaction is faster than the corresponding solvent-based reaction. In addition, this solid-state method rapidly yields pure cyanoaurate-based complexes also in cases when the aqueous solution synthesis leads to an unseparable mixture of products. This mechanochemical method can be applied not only to transition metals but also to main group metals to obtain various dicyanoaurate-based heterometallic polymers. For the 2:1 mixture of $K[Au(CN)_2]$ and Me_2SnCl_2, the dramatic enhancement of the reaction rate by the presence of a minor amount of solvent was noticed. Complex **8**, obtained as an additional result of the present study, displays a vapochromic response when exposed to a variety of organic solvents, as well as water and ammonia vapors. Now, we focus on understanding the factors that influence the vapochromic response and on experiments aimed at tuning the sensitivity and specificity of optical response for possible sensor application.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic file in CIF format for compound **6**, FT-IR monitoring spectra of all solid-state reactions, as well as PXRD spectra of all pure compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Eisenmann, E. T. *J. Electrochem. Soc.* **1977**, *124*, 1957–1958.

(2) (a) Eisler, R. *Inflamm. Res.* **2003**, *52*, 487–501. (b) Graham, G. G.; Whitehouse, M. W.; Bushell, G. R. *Inflammopharmacology* **2008**, *16*, 126–132.

(3) (a) Pham, D. M.; Rios, D.; Olmstead, M. M.; Balch, A. L. *Inorg. Chim. Acta* **2005**, *358*, 4261–4269. (b) Stork, J. R.; Rios, D.; Pham, D.; Bicocca, V.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2005**, *44*, 3466–3472. (c) Katz, M. J.; Sakai, K.; Leznoff, D. B. *Chem. Soc. Rev.* **2008**, *37*, 1884–1895. (d) Leznoff, D. B.; Lefebvre, J. *Gold Bull.* **2005**, *38*, 47–54.

(4) (a) Niel, V.; Thompson, A. L.; Muñoz, M. C.; Galet, A.; Goerta, A. E.; Real, J. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3760–3763. (b) Galet, A.; Muñoz, M. C.; Martínez, V.; Real, J. A. *Chem. Commun.* **2004**, 2268–2269. (c) Galet, A.; Muñoz, M. C.; Real, J. A. *Chem. Commun.* **2006**, 4321–4323. (d) Agusti, G.; Gaspar, A. B.; Muñoz, M. C.; Real, J. A. *Inorg. Chem.* **2007**, *46*, 9646–9654. (e) Agusti, G.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A. *Inorg. Chem.* **2008**, *47*, 2552–2561.

(5) (a) Assefa, Z.; DeStefano, F.; Garepapaghi, M.; LaCasce, J. H.; Ouellete, S.; Corson, M. R.; Nagle, J. K.; Patterson, H. H. *Inorg. Chem.* **1991**, *30*, 2868–2876. (b) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H.; Fackler, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 11237–11247. (c) Dong, W.; Zhu, L.-N.; Sun, Y.-Q.; Liang, M.; Liu, Z.-Q.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Cheng, P. *Chem. Commun.* **2003**, 2544–2545. (d) Stender, M.; White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2003**, *42*, 4504–4506. (e) Katz, M. J.; Michaelis, V. K.; Aguiar, P. M.; Yson, R.; Lu, H.; Kaluarachchi, H.; Batchelor, R. J.; Schreckenbach, G.; Kroeker, S.; Patterson, H. H.; Leznoff, D. B. *Inorg. Chem.* **2008**, *47*, 6353–6363.

(6) (a) Lefebvre, J.; Batchelor, R. J.; Leznoff, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 16117–16125. (b) Katz, M. J.; Ramnial, T.; Yu, H.-Z.; Leznoff, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 10662–10673.

(7) (a) Katz, M. J.; Aguiar, P. M.; Batchelor, R. J.; Bokov, A. A.; Ye, Z.-G.; Kroeker, S.; Leznoff, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 3669–3676. (b) Katz, M. J.; Kaluarachchi, H.; Batchelor, R. J.; Bokov, A. A.; Ye, Z.-G.; Leznoff, D. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8804–8807. (c) Katz, M. J.; Michaelis, V. K.; Aguiar, P. M.; Yson, R.; Lu, H.; Kaluarachchi, H.; Batchelor, R. J.; Schreckenbach, G.; Kroeker, S.; Patterson, H. H.; Leznoff, D. B. *Inorg. Chem.* **2008**, *47*, 6353–6363. (d) Katz, M. J.; Leznoff, D. B. *J. Am. Chem. Soc.* **2009**, *131*, 18435–18444. (e) Greer, B. J.; Michaelis, V. K.; Katz, M. J.; Leznoff, D. B.; Schreckenbach, G.; Kroeker, S. *Chem.—Eur. J.* **2011**, *17*, 3609–3618. (f) Nagasundaram, N.; Roper, G.; Biscoe, J.; Chai, J. W.; Patterson, H. H.; Blom, N.; Ludi, A. *Inorg. Chem.* **1986**, *25*, 2947–2951. (g) Blom, N.; Ludi, A.; Bürgi, H.-B.; Tichy, K. *Acta Crystallogr.* **1984**, *C40*, 1767–1769. (h) Assefa, Z.; DeStefano, F.; Garepapaghi, M. A.; LaCasce, J. H.; Ouellete, S.; Corson, M. R.; Nagle, J. K.; Patterson, H. H. *Inorg. Chem.* **1991**, *30*, 2868–2876. (i) Hettiarachchi, S. R.; Rawashdeh-Omary, M. A.; Kanan, S. M.; Omary, M. A.; Patterson, H. H.; Tripp, C. P. *J. Phys. Chem. B* **2002**, *106*, 10058–10064. (j) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H.; Fackler, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 11237–11247. (k) Assefa, Z.; Omary, M. A.; McBurnett, B. G.; Mohamed, A. A.; Patterson, H. H.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* **2002**, *41*, 6274–6280.

(8) (a) Korčok, J. L.; Katz, M. J.; Leznoff, D. B. *J. Am. Chem. Soc.* **2009**, *131*, 4866–4871. (b) Goodwin, A. L.; Kennedy, B. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 6334–6335.

(9) Deák, A.; Tunyogi, T.; Pálinkás, G. *J. Am. Chem. Soc.* **2009**, *131*, 2815–2817.

(10) (a) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417–419. (b) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3–10. (c) Schmidbaur, H. *Nature* **2001**, *413*, 31–33. (d) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2008**, *37*, 1931–1951.

(11) Lefebvre, J.; Tyagi, P.; Trudel, S.; Pacradouni, V.; Kaiser, C.; Sonier, J. E.; Leznoff, D. B. *Inorg. Chem.* **2009**, *48*, 55–67.

(12) Lefebvre, J.; Callaghan, F.; Katz, M. J.; Sonier, J. E.; Leznoff, D. B. *Chem.—Eur. J.* **2006**, *12*, 6748–6761.

(13) Lefebvre, J.; Trudel, S.; Hill, R. H.; Leznoff, D. B. *Chem.—Eur. J.* **2008**, *14*, 7156–7167.

(14) Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun.* **2001**, 2159–2169.

(15) (a) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558–1564. (b) Braga, D.; Curzi, M.; Johansson, A.; Polito, M.; Rubini, K.; Grepioni, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4002–4011. (c) Braga, D.; Grepioni, F. *Chem. Commun.* **2005**, 3635–3645. (d) Braga, D.; Giaffreda, S. L.; Grepioni, F.; Pettersen, A.; Maini, L.; Curzi, M.; Polito, M. *Dalton Trans.* **2006**, 1249–1263. (e) Garay, A. L.; Pichon, A.; James, S. L. *Chem. Soc. Rev.* **2007**, *36*, 846–855. (f) Chandrasekhar, V.; Baskar, V.; Boomishankar, R.; Gopal, K.; Zacchini, S.; Bickley, J. F.; Steiner, A. *Organometallics* **2003**, *22*, 3710–3716.

(16) (a) Nichols, P. J.; Raston, C. L.; Steed, J. W. *Chem. Commun.* **2001**, 1062–1063. (b) Orita, A.; Jiang, L.; Nakano, T.; Ma, N.; Otera, J. *Chem. Commun.* **2002**, 1362–1363. (c) Nakamura, A.; Sato, T.; Kuroda, R. *Chem. Commun.* **2004**, 2858–2859.

(17) Balema, V. P.; Wiench, J. W.; Pruski, M.; Pecharsky, V. K. *Chem. Commun.* **2002**, 1606–1607.

(18) (a) Braga, D.; Curzi, M.; Grepioni, F.; Polito, M. *Chem. Commun.* **2005**, 2915–2917. (b) Yoshida, J.; Nishikiori, S.-i.; Kuroda, R. *Chem.—Eur. J.* **2008**, *14*, 10570–10578. (c) Kuroda, R.; Yoshida, J.; Nakamura, A.; Nishikiori, S.-i. *Cryst. Eng. Comm.* **2009**, *11*, 427–432.

(19) (a) Pichon, A.; Lazuen-Garay, A.; James, S. L. *Cryst. Eng. Comm.* **2006**, *8*, 211–214. (b) Fujii, K.; Lazuen Garay, A; Hill, J.; Sbircea, E.; Pan, Z.; Xu, M.; Apperley, D. C.; James, S. L.; Harris, K. D. M. *Chem. Commun.* **2010**, 7572–7574.

(20) (a) Bowmaker, G. A.; Chaichit, N.; Pakawatchai, C.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2008**, 2926–2928. (b) Bowmaker, G. A.; Hanna, J. V.; Skelton, B. W.; White, A. H. *Chem. Commun.* **2009**, 2168–2170. (c) Bowmaker, G. A.; Hanna, J. V.; Hart, R. D.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2008**, 5290–5292.

(21) Braga, D.; Curzi, M.; Johansson, A.; Polito, M.; Rubini, K.; Grepioni, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 142–146.

(22) (a) Friščić, T.; Reid, D. G.; Halasz, I.; Stein, R. S.; Dinnebier, R. E.; Dauer, M. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 712–715. (b) Yuan, W.; Friščić, T.; Apperley, D.; James, S. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 3916–3919.

(23) Kaupp, G. *Cryst. Eng. Comm.* **2006**, *8*, 794–804.

(24) Kulesza, P. J. *Inorg. Chem.* **1990**, *29*, 2395–2397.

(25) Brandt, P.; Brimah, A. K.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1521–1522.

(26) (a) Wadas, T. J.; Wang, Q.-M.; Kim, Y.-J.; Flaschenreim, C.; Blanton, T. N.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 16841–16849. (b) Du, P.; Schneider, J.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2008**, *47*, 69–77.

(27) (a) Osawa, M.; Kawata, I.; Igawa, S.; Hoshino, M.; Fukunaga, T.; Hashizume, D. *Chem.—Eur. J.* **2010**, *16*, 12114–12126. (b) Laguna, A.; Lasanta, T.; López-de-Lazuriaga, J. M.; Monge, M.; Naumov, P.; Olmos, M. E. *J. Am. Chem. Soc.* **2010**, *132*, 456–457. (c) Strasser, C. E.; Catalano, V. J. *J. Am. Chem. Soc.* **2010**, *132*, 10009–10011. (d) Fernández, E. J.; López-de-Lazuriaga, J. M.; Monge, M.; Olmos, M. E.; Puelles, R. C.; Laguna, A.; Mohamed, A. A.; Fackler, J. P. *Inorg. Chem.* **2008**, *47*, 8069–8076. (e) Luquin, A.; Elosúa, C.; Vergara, E.; Estella, J.; Cerrada, E.; Bariáin, C.; Matías, I. R.; Garrido, J.; Laguna, M. *Gold Bull.* **2007**, *40*, 225–233. (f) Fernández, E. J.; López-de-Lazuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 2022–2023. (g) Mansour,

M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329–1330.

(28) These mechanochemical reactions produce two products (metal dicyanoaurate + KCl), one of which can be easily removed by washing. Thus, in all cases, the pure products are water-washed compounds. Since the water molecules can act as ligands, and coordinate to the metal ion, the unwashed and washed compounds are not normally identical. From the υ_{CN} values of unwashed and washed compounds (see Supporting Information), it can be seen that the unwashed and washed products were the same, except in the case of copper(II), where the aqua-bridged light-green $Cu(H_2O)_2[Au(CN)_2]_2$ complex was obtained.

(29) Colacio, E.; Lloret, F.; Kivekäs, R.; Ruiz, J.; Suárez-Varela, J.; Sundberg, M. R. *Chem. Commun.* **2002**, 592–593.

(30) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(31) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(32) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(33) (a) Eisenmann, E. T. *J. Electrochem. Soc.* **1977**, *124*, 1957–1958. (b) Abrahams, S. C.; Bernstein, J. L.; Liminga, R. *J. Chem. Phys.* **1980**, *73*, 4585–4590.

(34) Hoskins, B. F.; Robson, R.; Scarlett, N. V. Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1203–1204.

(35) Abrahams, S. C.; Zyontz, L. E.; Bernstein, L. *J. Chem. Phys.* **1982**, *76*, 5458–5462.

(36) (a) Exstrom, C. L.; Sowa, J. R.; Daws, C. A.; Janzen, D.; Mann, K. R. *Chem. Mater.* **1995**, *7*, 15–17. (b) Daws, C. A.; Exstrom, C. L.; Sowa, J. R.; Mann, K. R. *Chem. Mater.* **1997**, *9*, 363–368. (c) Exstrom, C. L.; Pomije, M. K.; Mann, K. R. *Chem. Mater.* **1998**, *10*, 942–945. (d) Buss, C. E.; Anderson, C. E.; Pomije, M. K.; Lutz, C. M.; Britton, D.; Mann, K. R. *J. Am. Chem. Soc.* **1998**, *120*, 7783–7790.

(37) Gans, P.; Gill, J. B.; Johnson, L. H. *J. Chem. Soc., Dalton Trans.* **1987**, 673–675.