

Cyanide-bridged bimetallic multidimensional structures derived from organotin(IV) and dicyanoaurate building blocks: ion exchange, luminescence, and gas sorption properties

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Published online: 24 January 2012

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Abstract The recent success of using methyltin(IV) cations in constructing multidimensional structures containing the Au–CN–Sn link with interesting physical properties will be surveyed. The methyltin(IV)-dicyanoaurates, $\text{Me}_3\text{Sn}[\text{Au}(\text{CN})_2]$ (**1**) and $\text{Me}_2\text{Sn}[\text{Au}(\text{CN})_2]_2$ (**2**) containing the Au–CN–Sn link can be easily prepared by aqueous reaction of Me_3SnCl or Me_2SnCl_2 with stoichiometric amounts of an aqueous solution of $\text{K}[\text{Au}(\text{CN})_2]$. The room temperature solid-state emission spectrum of **1** excited at 254 nm shows two intense emission bands at 442 and 670 nm, and a shoulder at 390 nm. When excited at 320 nm, the crystalline sample shows two intense emission bands at 442 and 720 nm, and a shoulder at 380 nm. After 2 min of grinding, only the blue emission band at 442 nm is observed. In contrast, the emission spectrum of **2** shows only one emission maximum at 422 nm. The porosity of **1** and **2** was

probed by gas sorption measurements performed at 77 K. **1** exhibited no detectable microporosity as revealed by the inspection of the N_2 , H_2 , as well as, O_2 isotherms. The gas adsorption studies reveal that only a small amount of N_2 and H_2 (3.82 and $4.66 \text{ cm}^3 \text{ g}^{-1}$, respectively) is adsorbed by the framework of **2** at 77 K. However, a CO uptake of $11.20 \text{ cm}^3 \text{ g}^{-1}$ can be reached at 1 atm. The framework of **2** can take up significant amounts of O_2 ($23.27 \text{ cm}^3 \text{ g}^{-1}$). In addition to intriguing photoluminescence and gas sorption behavior, these complexes also exhibit ion exchange properties in the presence of bivalent transition metal cations, such as cobalt(II), nickel(II), copper(II), and zinc(II).

Keywords Dicyanoaurate · Organotin(IV)-dicyanoaurates · Ion exchange · Photoluminescence · Gas sorption

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Introduction

The rational design and synthesis of cyanide-bridged bimetallic supramolecules containing cyanometallate building blocks are the focus of widespread research interest because of their interesting topological structures and diverse properties [1–3]. Among many metal cyanide anions, the dicyanoaurate $[\text{Au}(\text{CN})_2]^-$ building block, due to its affinity to bridge transition metal centers has been used in the construction of 2D and 3D cyano-bridged bimetallic Au–CN–M coordination polymers [4–7]. The unique ability of linear $[\text{Au}(\text{CN})_2]^-$ anion to form Au–Au aurophilic interaction plays a key role in controlling the dimensionality and topology of these dicyanoaurate-based heterometallic polymers [4–7]. The cyanoaurate-based heterometallic polymers may exhibit unusual structural motifs and physical properties, such as luminescence [8–11], vapo-chromism [12, 13], birefringence [14–18], colossal thermal expansion [19, 20],

magnetism [21–25] or ion exchange [26]. This dicyanoaurate anion also has significant importance in industrial and medical applications. It is used in gold electroplating [27], and it is considered as a pharmacologically active human metabolite of several antirheumatic gold(I) complexes of sulfur-containing ligands [28, 29]. In this light, it seems surprising that literature describing cyanoaurate-based coordination polymers of main-group metals is unusually sparse. A series of lead(II) coordination polymers containing the dicyanoaurate(I) bridging ligands were prepared and structurally characterized [14–18]. Some of them are highly birefringent materials [14–18]. We have previously reported the construction and structural characterization of multidimensional structures containing the Au–CN–Sn link generated by the reaction of the hard Lewis acidic organotin $R_nSn^{(4-n)+}$ cation and the soft Lewis basic dicyanoaurate $[Au(CN)_2]^-$ anion [26]. Single crystals of both compounds can be obtained by slow interdiffusion of aqueous solutions of Me_3SnCl or Me_2SnCl_2 and $K[Au(CN)_2]$. As observed under polarized light microscopy, the crystals of both **1** and **2** display striking pleochroism (Fig. 1). Pleochroism is the optical property of a crystal, whereby certain wavelengths of polarized light are absorbed in different amounts in different crystallographic directions. This may produce different colors when the crystal is viewed in polarized light [30].

The X-ray structural analysis of **1** showed that each Me_3Sn unit is linked to two others by two $Au(CN)_2$ units and form infinite cyanide-bridged chains [26], as illustrated in Fig. 2. These cyanide-bridged chains are further crosslinked by Au–Au interactions of 3.12(1) Å into a 2D grid. The void space of these 2D grids is filled by the arrays of zigzag chains joined by weak Au–Au interactions of 3.42(1) Å.

The X-ray structural analysis of **2** showed that each Me_2Sn unit is connected to four others by four $Au(CN)_2$ bridges [26], so that an infinite set of self-penetrating layers are formed (Fig. 3). These cyanide-bridged networks are also joined by aurophilic interactions of 3.29(1) and 3.45(2) Å. By treating the Me_2Sn units as nodes and connecting them according to the connectivity defined by the $Au(CN)_2$ linkers, there are a set of cyanide-bridged uninodal four-connected 3D networks with $6^5\cdot 8$ topology. This topology corresponds to the $CdSO_4$ prototype [26].

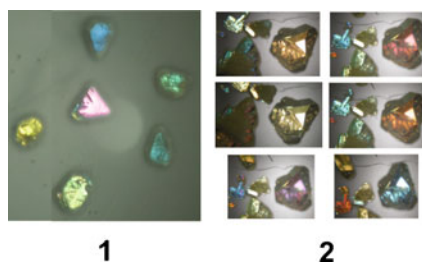


Fig. 1 The crystals of both **1** and **2** display pleochroism as observed under polarized light microscopy

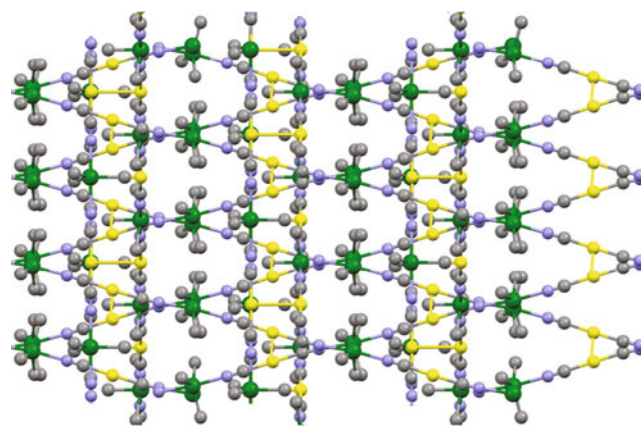


Fig. 2 Structure of complex **1** showing the arrays of interpenetrating cyanide-bridged $\{Me_3Sn-NC-Au-CN\}_n$ chains. Hydrogen atoms have been omitted. Color scheme: Au, yellow; Sn, green; N, blue; C, gray

Recently, we have shown that the solvent-free mechanochemical method (grinding stoichiometric amounts of $K[Au(CN)_2]$ and metal chlorides in a mortar with a pestle) is a fast, simple, and efficient route to the synthesis of cyanoaurate-based heterometallic coordination polymers [31]. This mechanochemical method was successfully applied also to main group metals to obtain $Ph_3Sn[Au(CN)_2]$ and **2** [31].

In this paper, we report the infrared characterization, as well as the luminescence and gas sorption properties of these multidimensional structures **1** and **2**, as well as, the ion exchange properties of **2**.

Results and discussion

The IR spectra of both organotin(IV)-dicyanoaurates **1** and **2** are consistent with their solid-state structures. Thus, the presence of a sharp ν_{CN} band at $2,169\text{ cm}^{-1}$ shows that all of the bridging cyanide groups are in an identical coordination

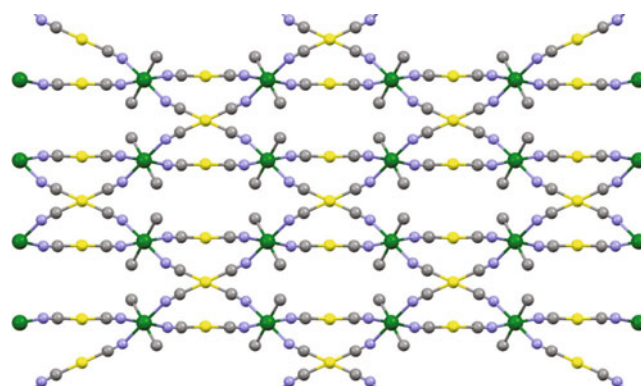


Fig. 3 Structure of complex **2** showing the arrays of fourfold-interpenetrated cyanide-bridged networks. Hydrogen atoms have been omitted. Color scheme: Au, yellow; Sn, green; N, blue; C, gray

environment in both compounds. This band is shifted toward higher energy with respect to the $2,141\text{ cm}^{-1}$ ν_{CN} stretching vibration of $\text{K}[\text{Au}(\text{CN})_2]$ [32]. As observed for other organotin(IV)-cyanometalates, the IR spectra of **1** and **2** exhibit ν_{SnC} stretching at 554 and 596 cm^{-1} [33, 34]. The ν_{AuC} stretching band is found at 455 cm^{-1} in **1** and at 459 cm^{-1} in **2**. This band is also shifted toward higher energy with respect to the corresponding 427 cm^{-1} ν_{AuC} stretching of $\text{K}[\text{Au}(\text{CN})_2]$ [32]. In the absence of low-frequency Raman spectra, we can tentatively assign bands at 62 (**1**) and 64 cm^{-1} (**2**) to the ν_{AuAu} stretching mode [35, 36].

The importance of the aurophilic interactions in influencing the luminescence properties of gold(I) compound is now well recognized [37]. The Au–Au bond distance in complexes showing aurophilic interactions ranges from 2.70 to 3.50 \AA [38–41], and owing to this interaction, the gold(I) complexes are potentially luminescent. In the crystal structure of **1**, there are aurophilic interactions with lengths of 3.12 and 3.45 \AA , and indeed, this complex is emissive when exposed to UV light at room temperature. Upon irradiation with 254 nm UV light, the crystals of **1** exhibit intense pink luminescence. The room temperature solid-state emission spectrum of **1** excited at 254 nm shows two intense emission bands at 442 and 670 nm , and a shoulder at 390 nm (Fig. 4). Thus, the visually observed pink-colored emission was generated by additive color mixing of the red and blue emissions. The excitation spectrum shows a maximum at 278 nm .

The emission spectra of $\text{K}[\text{Au}(\text{CN})_2]$ consists of two bands at about 390 and 630 nm , when excited with 337 nm [42]. The separation between the gold atoms in $\text{K}[\text{Au}(\text{CN})_2]$ is 3.64 \AA [37, 42], which is longer than those found in **1**. The emission peak at 390 nm in $\text{K}[\text{Au}(\text{CN})_2]$ has been attributed to this weak aurophilic interaction between the dicyanoaurate units [42]. An emission peak at 436 nm is observed for $[\text{C}_5\text{H}_{10}\text{NH}_2][\text{Au}(\text{CN})_2]$ and attributed to a short aurophilic interaction (3.10 \AA) between the dicyanoaurate units arranged into columns [43]. Thus, the peak at 442 nm observed for **1** could be tentatively attributed to aurophilic interaction. As in the case of $\text{K}[\text{Au}(\text{CN})_2]$ and

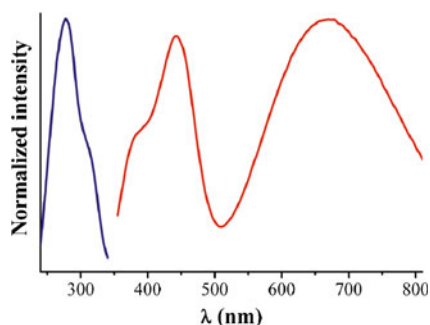


Fig. 4 Solid-state emission ($\lambda_{\text{ex}}=254\text{ nm}$) and excitation spectra of **1** at room temperature

$\text{Ti}[\text{Au}(\text{CN})_2]$, the low-energy band at 670 nm in **1** is probably due to luminescence traps caused by imperfections in the microcrystalline sample [10, 42]. The emission band at 670 nm (full width at half-maximum is 230 nm) is much broader than the peak at 442 nm (full width at half-maximum is 100 nm), which gives an indication of longer lifetime of the low-energy band.

The room temperature solid-state emission spectrum of crystalline sample of **1** excited at 320 nm shows two intense emission bands at 442 and 720 nm , and a shoulder at 380 nm (Fig. 5). Interestingly, after 2 min of grinding in a mortar with a pestle, this pink-emitting solid was converted into a solid exhibiting intense blue emission (maximum at 444 nm). As shown in Fig. 5, gently scrapping and pressing of **1** with a spatula progressively decreases the intensity of the 720 and 380 nm bands. After total conversion, only the blue emission band at 442 nm is observed.

In contrast, the emission spectrum of **2** shows only one emission maximum at 422 nm (Fig. 6). The excitation spectrum of **2** shows two strong bands at 298 and 367 nm . The room temperature luminescence behavior of **2** is very similar to that of β - and γ -polymorphs of $\text{Zn}[\text{Au}(\text{CN})_2]_2$, which have only one emission maximum at 450 and 440 nm , respectively. In crystal structures of these polymorphs, the network interpenetration is supported by Au–Au interactions with lengths of 3.15 – 3.29 \AA [12].

Recently, Long and others published a series of paper using Prussian blue analogues for hydrogen storage at 77 K [44, 45]. In addition to the promising H_2 storage materials, the cyano-bridged frameworks may be useful for CO_2 storage and separation applications [46, 47]. Accordingly, we studied the gas sorption properties of these organotin(IV)-dicyanoaurates. To our knowledge, these are the first gas sorption measurements reported for organotin(IV)-dicyanoaurates. Thus, the porosity of **1** and **2** was probed by gas sorption measurements performed at 77 K . **1** exhibited no detectable microporosity as revealed by the inspection of the N_2 , H_2 , as well as, O_2 isotherms. The gas adsorption studies reveal that only a small amount of N_2 and H_2 (3.82

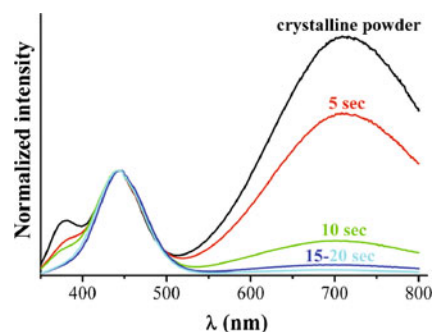


Fig. 5 Solid-state emission ($\lambda_{\text{ex}}=320\text{ nm}$) spectra of **1** in various states (crystalline and solid samples scrapped and pressed with spatula for 5 to 20 s)

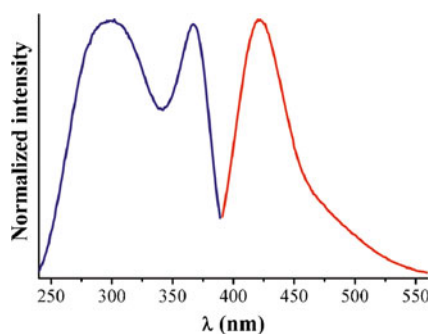


Fig. 6 Solid-state emission ($\lambda_{\text{ex}}=300$ nm) and excitation spectra of **2** at room temperature

and $4.66 \text{ cm}^3 \text{ g}^{-1}$, respectively) is adsorbed by the framework of **2** at 77 K (Fig. 7). However, a CO uptake of $11.20 \text{ cm}^3 \text{ g}^{-1}$ can be reached at 1 atm. In contrast, as seen in Fig. 7, the framework of **2** can take up significant amounts of O_2 ($23.27 \text{ cm}^3 \text{ g}^{-1}$). This complex adsorbs higher amounts (more than six times) of O_2 than N_2 at 77 K.

Some cyanometallates also show high selectivity for oxygen over nitrogen [48]. This could be due to the fact that the unsaturated metal centers of the framework interact with O_2 more strongly than with N_2 [49]. Other cyano-bridged coordination solids containing coordinatively unsaturated metal centers have been shown to interact with H_2 at high loading [44, 45]. The maximum O_2 uptake is 3.39 wt.%, which corresponds to approximately 0.67 O_2 molecules per formula unit of **2**. To our knowledge, there are only few cyano-bridged frameworks that adsorb O_2 at 77 K [48, 50]. The oxygen plot represents a type I isotherm characteristic for microporous materials. The surface area, which was determined from the O_2 adsorption data by applying Langmuir equation, was $67.8 \text{ m}^2/\text{g}$. This result is comparable to the $49 \text{ m}^2/\text{g}$ estimated for dehydrated Prussian blue [51]. The pore volume of $0.029 \text{ cm}^3/\text{g}$ calculated from O_2 isotherm is

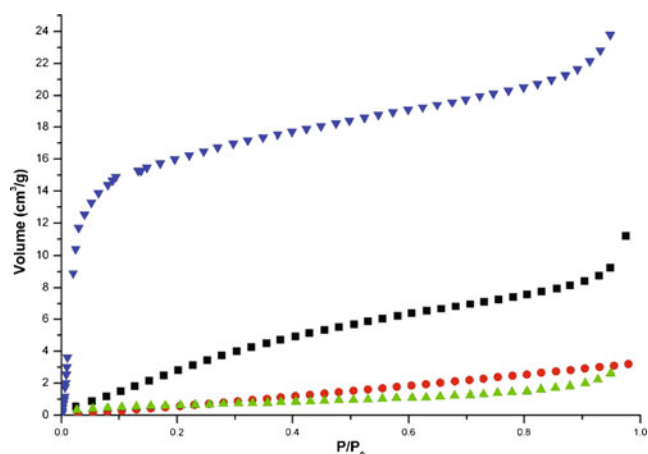


Fig. 7 Gas adsorption isotherms of **2** for N_2 (green), CO (black), H_2 (red), and O_2 (blue) at 77 K

in good agreement with the pore volume ($0.027 \text{ cm}^3/\text{g}$) estimated from the crystal structure of **2**.

In contrast to porous metal-organic frameworks and other zeolite-like materials, which upon standard ion exchange reactions preserve their original crystal structure, **1** shows *unusual* ion exchange behavior [26]. As we previously reported, the Me_3Sn^+ cations are removed completely from cyanide-bridged $\{\text{Me}_3\text{Sn}-\text{NC}-\text{Au}-\text{CN}\}_n$ chains and replaced by $\text{Me}_2\text{Sn}^{2+}$ or bivalent transition metal cations [26]. In a concentrated aqueous solution of Me_3SnCl , the dimethyltin (IV)-, cobalt(II)-, and nickel(II)-dicyanoaurates can be easily converted back into the starting compound **1**. However, the metathesis of zinc(II)-dicyanoaurate with Me_3SnCl afforded partial reaction, but for copper(II)-dicyanoaurate, no reaction occurs [26].

Now, we performed subsequent metal exchange experiments to study the ion exchange behavior of **2** containing $\text{Me}_2\text{Sn}^{2+}$ framework ions. In this regard, **2** was soaked in concentrated aqueous solutions of bivalent transition-metal Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} cations (ten times excess). After 2 days, the microcrystalline white powder displayed obvious color changes in the case of Co^{2+} , Ni^{2+} , and Cu^{2+} (Fig. 8). As was confirmed by IR spectroscopy, the $\text{Me}_2\text{Sn}^{2+}$ cations are exchanged with bivalent transition metal cations, and **2** converted into corresponding $\text{Co}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ [52, 53], $\text{Ni}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ [54], $\text{Zn}[\text{Au}(\text{CN})_2]_2$ [12], and $\text{Cu}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ [13, 54] transition-metal dicyanoaurates. Consequently, these transition-metal dicyanoaurates were soaked into the concentrated aqueous solution of Me_2SnCl_2 (ten times excess) for 40 days. In striking contrast to **1**, these transition-metal dicyanoaurates cannot be converted back into the starting compound **2**.

Experimental

General procedures and materials 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. The elemental analysis has been carried out with an Elementar Vario EL III apparatus at the Laboratory of Organic Analysis, Institute of Organic Chemistry, Research Centre for

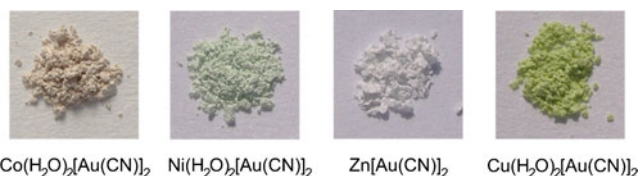


Fig. 8 Transition metal dicyanoaurates $\text{M}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ ($\text{M}=\text{Co}^{2+}$, Ni^{2+} and Cu^{2+}) and $\text{Zn}[\text{Au}(\text{CN})_2]_2$ obtained in metathesis reactions of **2** with corresponding MCl_2 salts

Natural Sciences, Hungarian Academy of Sciences. Infrared spectra were recorded in the 500 to 4,000 cm^{-1} spectral range on a Bio-Rad (Digilab Division) FTS-60A FTIR spectrometer equipped with UMA-500 infrared microscope with Ge plate and in the 50 to 500 cm^{-1} spectral range on a PIKE GladiATR spectrometer with diamond plate. Steady-state luminescence spectra were recorded on an Edinburgh Instrument FS920 spectrofluorometer. Spectral corrections were applied using excitation and emission correction functions of the instrument. Powder samples were placed on a Quartz Suprasil plate in a front-face sample holder. Long-pass filters were used to exclude the scattered excitation light. The adsorption isotherms were measured by static volumetric method using fully automated Autosorb 1C (Quantachrome) equipment. Prior to analysis, the sample was heated and kept at 25°C under vacuum for 24 h to remove all the previously adsorbed gases from the surface and the pores. All the measurements were carried out at the boiling temperature of liquid nitrogen (77.3 K).

Synthesis of 1 and 2: The syntheses of both complexes have been previously reported [26]. **Complex 1:** Anal. Calcd for $\text{C}_5\text{H}_9\text{N}_2\text{AuSn}$: C 14.55; H 2.20; N 6.79. Found: C 14.83; H 1.92; N 6.71; m. p. >300°C; IR data: 2,169 (s), 791 (b, m), 554 (m), 453 (m), 200–80 (lattice vibration), 62 (s). **Complex 2:** Anal. Calcd for $\text{C}_6\text{H}_6\text{N}_4\text{Au}_2\text{Sn}$: C 11.14; H 0.94; N 8.66. Found: C 11.44; H 0.65; N 8.58; m. p. >300°C; IR data: 2,167 (s), 809 (b, m), 596 (w), 459 (m), 216 (w), 200–80 (lattice vibration), 142 (w), 64 (s).

Metathesis of 2 with transition metal halides

The microcrystalline powder of **2** was immersed in concentrated aqueous solution of transition-metal MCl_2 ($\text{M}=\text{Co}$, Ni , Zn , Cu) salts. After 2 days, the microcrystalline white powder displayed obvious color changes in the case of Co(II) , Ni(II) , and Cu(II) . Upon decanting the metal chloride solution, the products were washed with water. The ion exchanged products were characterized by IR spectroscopy.

$\text{Co(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$: starting from **2** (90 mg, 0.139 mmol), the metathesis yielded 39.5 mg (48%) product; IR (per centimeter): 2,999 (b, m), 2,206 (m), 2,194 (s), 2,172 (s), 2,161 (s), 1,535 (m), 889 (b, m), 748 (b, m). These characteristic vibrations in the IR spectrum indicate the formation of the $\text{Co(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$ complex [26, 52, 53]

$\text{Ni(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$: starting from **2** (90 mg, 0.139 mmol), the metathesis yielded 64.3 mg (78%) product; IR (per centimeter): 3,002 (b, m), 2,215 (m), 2,204 (sh), 2,172 (s), 2,165 (s), 1,540 (m), 907 (b, m), 757 (b, m). These characteristic vibrations in the IR spectrum indicate the formation of the $\text{Ni(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$ complex [26, 54].

$\text{Zn[Au(CN)}_2]_2$: starting from **2** (90 mg, 0.139 mmol), the metathesis yielded 68.8 mg (88%) product; IR (per centimeter): 2,198 (s), 2,160 (w). These characteristic vibrations in the IR spectrum indicate the formation of the $\text{Zn[Au(CN)}_2]_2$ complex [12, 26].

$\text{Cu(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$: starting from **2** (90 mg, 0.139 mmol), the metathesis yielded 77.6 mg (93%) product; IR (per centimeter): 3,144 (b, s), 2,218 (s), 2,173 (s), 1,483 (b, m), 710 (b, m). These characteristic vibrations in the IR spectrum indicate the formation of the $\text{Cu(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$ complex [13, 26, 54].

Metathesis of transition metal dicyanoaurates with Me_2SnCl_2

The microcrystalline powders of $\text{Co(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$, $\text{Ni(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$, $\text{Cu(H}_2\text{O)}_2[\text{Au(CN)}_2]_2$, and $\text{Zn[Au(CN)}_2]_2$, respectively, were immersed in concentrated aqueous solution of Me_2SnCl_2 and left undisturbed at room temperature. After 40 days, the powders retained their original colors, indicating the preservation of original transition metal dicyanoaurates. Upon decanting the solution, the powders were washed with successive aliquots of water (3×10 mL), and were characterized by IR spectroscopy. The IR spectroscopy data showed that the bivalent transition-metal Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} cations are not exchanged with $\text{Me}_2\text{Sn}^{2+}$ cations. Thus, these transition-metal dicyanoaurates cannot be converted back into the starting compound **2**.

Acknowledgments We gratefully acknowledge the financial support of this work by the Hungarian Scientific Research Funds (OTKA) K68498 project and National Development Agency (Project ID: KMOP-1.1.2-07/1-2008-0002). We are grateful to Dr. Csaba Németh for his assistance in recording the FTIR spectra. We also thank Mrs. Márta Rockov for the EA measurements.

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