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Structure and Properties of One-Dimensional Heterobimetallic Polymers Containing Dicyanoaurate and Dirhodium(II) Fragments

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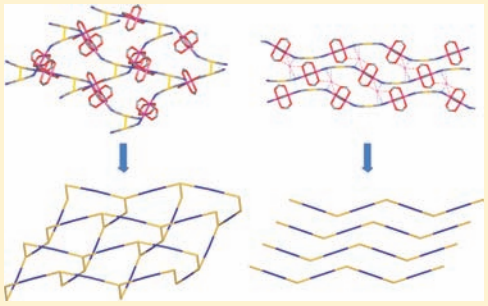
S *Supporting Information*

ABSTRACT: The synthesis and characterization of compound $[Rh_2(O_2CEt)_4(H_2O)_2]$ (**1**) and one-dimensional heterobimetallic polymers $K_n\{Rh_2(O_2CEt)_4[Au(CN)_2]\}_n$ (**2**) and $K_n\{Rh_2(O_2CMe)_4[Au(CN)_2]\}_n \cdot 4nH_2O$ (**3**), constructed from dirhodiumtetracarboxylato units, $[Rh_2(O_2CR)_4]^+$, and dicyanoaurate, $[Au(CN)_2]^-$, fragments are described. In both compounds **2** and **3** the resulting polymeric chains are nonlinear and have in common similar structural parameters, although the solid state supramolecular arrangement is very different. These structural differences explain the fact that complex **2** displays aurophilic interactions while this type of interactions are absent in complex **3**. As a result, compound **2** shows rich blue luminescent properties whereas compound **3** is not luminescent. The electrical conductivity in solid state of compounds **2** and **3** is also studied.



■ INTRODUCTION

Since the discovery of a direct metal−metal bond[1] by X-ray analysis, numerous complexes of different transition metals displaying metal−metal bonds have been reported, giving rise to a very rich and varied chemistry.[1] Focusing on the case of dimetallic units of dirhodium complexes where carboxylate ligands occupy the equatorial positions, several hundreds of compounds with a variety of architectures, properties, and obtained by different scientific approaches have been reported.[1,2]

Although many of these compounds are based on discrete units, rhodium dimetallic fragments can be successfully used to achieve an emerging number of coordination polymers, mainly one-dimensional, with interesting properties.[3] To form one-dimensional polymeric species the dirhodium carboxylate fragments are usually joined by bidentate axial ligands which are, in most cases, organic moieties.[4] The use of halide ligands as linkers leads to a new type of one-dimensional MMX polymer. However, very few examples of this type of complexes with Rh_2 units have been published.[5] In one of these studies, Kawamura et al.[5] have reported the electrical studies in solid state of the first examples of halide-bridged paddlewheel chains enclosing a Rh_2^{5+} core with wrapping acetamide (CH_3CONH_2 = *acam*) ligands. Also very recently, our research group has published[6] several Rh_2^{n+} (n = 4, 5 and 6) carboxylato complexes including some examples of MMX chains and the confirmation of their semiconductor behavior.

Another approach for the formation of linear chains involves the inclusion of metal-halide cores as linkers. In this regard, Ebihara et al.[7] reported the solid state electrical properties of compounds formed by reaction of K_2MCl_4 (M = Pd, Pt) with the cationic complex $Rh_2(acam)_4^+$. However, derivatives of dirhodium carboxylato complexes containing metallic spacing groups to form polymers are scarce.[8]

Another strategy to prepare one-dimensional compounds could be the use of metal-cyanide compounds as linkers to form heterobimetallic polymers.[9] This approximation involves some interesting aspects as the ability to form both σ and π interactions of μ-CN ligands that allow strong electronic coupling between the linked metal centers. Another important feature is the fact that MCN-M bonds are amenable to reversible cleavage.[10] In this sense, although several octahedral or square-planar cyanometallates have been used to build coordination polymers, the $[Au(CN)_2]^-$ unit has been little used, despite its capability to increase connectivity and complexity.[10,11]

In this work we have used the linear $[Au(CN)_2]^-$ fragment as a linker to bond dirhodium(II) moieties to obtain one-

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Table 1. Crystal and Refinement Data for 1, 2, and 3

crystal data	1	2	3
empirical formula	$C_{12}H_{24}O_{10}Rh_2$	$C_{14}H_{20}AuKN_2O_8Rh_2$	$C_{10}H_{20}AuKN_2O_{12}Rh_2$
crystal dimensions (mm)	0.30 × 0.20 × 0.10	0.25 × 0.15 × 0.09	0.16 × 0.09 × 0.04
formula weight	534.1	786.21	802.10
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2(1)/c$	$Pbcn$	$P\bar{1}$
a/Å	15.396(2)	15.3121(8)	8.3645(9)
b/Å	17.210(2)	14.7414(8)	9.0108(9)
c/Å	15.233(2)	18.801(1)	14.541(2)
α/deg	94.186(2)		93.831(2)
β/deg			94.604(2)
γ/deg			93.759(2)
V/Å^3	4025.4(7)	4243.8(4)	1087.2(2)
Z	8	8	2
D_c/g/cm^3	1.749	2.461	2.426
μ(Mo-Kα)/mm^{-1}	1.680	8.672	8.477
F(000)	2096	2960	740
θ range/deg	1.33 to 25.00	1.92 to 26.00	1.41 to 25.00
index ranges	−18, −20, −18 to 17, 18, 18	−17, −18, −23 to 18, 16, 23	−9, −10, −15 to 9, 9, 17
reflections collected	30190	33365	8329
unique reflections [R(int)]	7058 [R(int) = 0.1209]	4170 [R(int) = 0.0547]	3712 [R(int) = 0.0313]
completeness to θ	99.5%	100%	97.1%
data/restraints/params	7058/16/388	4170/0/254	3712/0/253
goodness-of-fit on F^2	1.078	1.029	0.999
R1 (reflns obsd) [$I > 2\sigma(I)$]	0.0748 (3355)	0.0292 (2929)	0.0335 (2978)
wR2 (all data)	0.2903	0.0845	0.0900

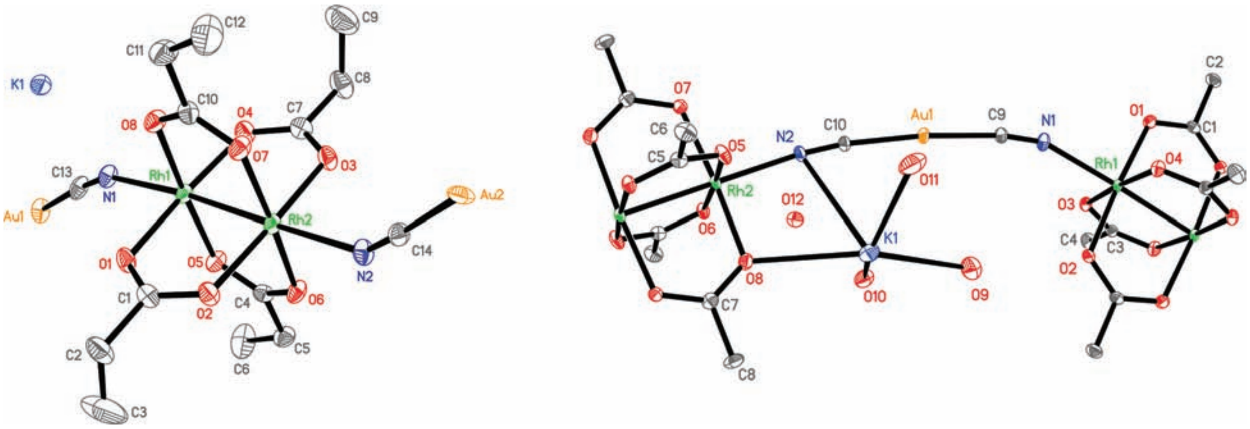

Figure 1. Thermal ellipsoid plots of **2** (left) and **3** (right) at 30% probability. Hydrogen atoms have been omitted for clarity.

dimensional compounds. We have also chosen $[Au(CN)_2]^-$ units to explore the possible existence of aurophilicity[12] in these complexes with presumably distant gold atoms. The $[Au(CN)_2]^-$ fragment could introduce luminescence as a new additional interesting property. Thus, we describe in this work the preparation and structural characterization of the starting compound $[Rh_2(O_2CEt)_4(H_2O)_2]$ (**1**) and two one-dimensional heterobimetallic polymers $K_n\{Rh_2(O_2CEt)_4[Au(CN)_2]\}_n$ (**2**) and $K_n\{Rh_2(O_2CMe)_4[Au(CN)_2]\}_n \cdot 4nH_2O$ (**3**). Some physical properties such as luminescence and electrical conductivity have also been measured.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes. The starting complex $[Rh_2(O_2CEt)_4(H_2O)_2]$ (**1**) was obtained by methatesis reaction of tetraacetatodirhodium(II) in excess of propionic acid, following a similar method to that described by Rempel et al.[13] The derivatives $K_n\{Rh_2(O_2CEt)_4[Au(CN)_2]\}_n$ (**2**) and $K_n\{Rh_2(O_2CMe)_4[Au(CN)_2]\}_n \cdot 4nH_2O$ (**3**) were obtained from $K[Au(CN)_2]$ and **1** or $[Rh_2(O_2CMe)_4(H_2O)_2]$, respectively.

The most characteristic bands of the infrared spectra (IR) present in these compounds are the O−C−O asymmetric and symmetric stretching vibrations of the carboxylate groups, showing in every case the typical bands corresponding to the bridging mode at 1583−1565 cm^{-1} (ν_{as}) and 1419−1412 cm^{-1} (ν_s).

The presence of the ν(CN) stretching vibration at 2144 cm^{-1} (for complex **2**) and 2162 cm^{-1} (for complex **3**) is indicative of the existence of coordinated CN$^-$, as confirmed by X-ray diffraction data.

Description of the Structures. The crystal structures of compounds **1**, **2**, and **3** have been determined by single crystal X-ray diffraction. A summary of the fundamental crystal and refinement data is given in Table 1.

The crystal structure of **1** shows dirhodium paddlewheel molecules with the axial positions occupied by water molecules (Supporting Information, Figure S1). The solid state arrangement is similar to that observed in the crystal structure of $[Rh_2(O_2CMe)_4(H_2O)_2]$.[14]

Compounds **2** and **3**, with formula $K_n\{Rh_2(O_2CEt)_4[Au(CN)_2]\}_n$ and $K_n\{Rh_2(O_2CMe)_4[Au(CN)_2]\}_n\cdot 4nH_2O$, respectively, display one-dimensional infinite chains. These chains are formed by dirhodium paddlewheel units with the axial positions occupied by bridging dicyanoaurate ligands (Figure 1). As Figure 2 depicts, the chains are nonlinear and have in common some structural parameters such as the wavy shape, very similar Rh—Rh distances [Rh1—Rh2 = 2.3949(7) Å in compound **2** compared to Rh1—Rh1 = 2.3920(12) Å and Rh2—Rh2 = 2.3965(12) Å in compound **3**] and C—Au—C angles [C13—Au1—C13 = 171.0(4)°, C14—Au2—C14 = 179.9(4)° for **2** and C10—Au1—C9 = 174.5(4)° for **3**]. Rh—N distances are slightly longer in the propionate derivative [2.240(6) and 2.304(6) Å in **2** and 2.207(7) and 2.229(7) Å in **3**], and Rh—N—C angles are also different [155.4(6) and 145.0(6)° in **2** compared to 173.0(7) and 158.4(8)° in **3**]. Figure 1 shows thermal ellipsoid plots of compounds **2** and **3**.

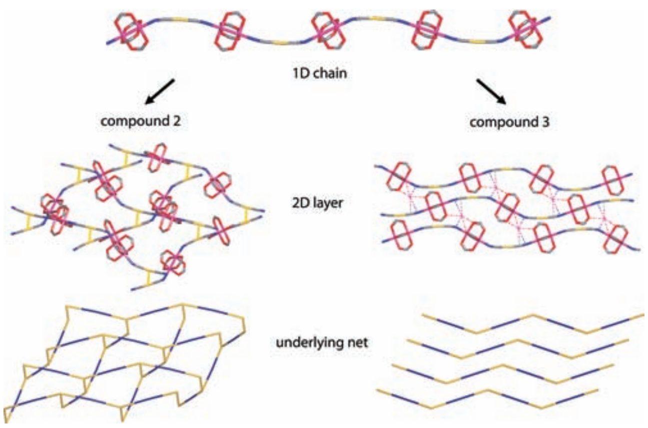

Figure 2. Schematic view of the two-dimensional arrangement of $\{Rh_2(O_2CR)_4[Au(CN)_2]\}_\infty$ chains, with double layers formed by aurophilic interactions in **2** (R = Et, left), and layers of parallel chains in **3** (R = Me, right) where no aurophilic interactions are present.

Despite the similarities in $\{Rh_2(O_2CR)_4[Au(CN)_2]\}_\infty$ chains in both polymeric compounds, the supramolecular arrangement of the chains is very different. Compound **2** displays alternating layers of parallel chains in the [101] and [-101] crystallographic directions. Aurophilic interactions parallel to the *b* axis between gold atoms can be found (Figure 2, right) where the pairs of gold atoms involved in these interactions belong to chains from adjacent layers and are separated 3.328 Å. For a given d^{10}-metal complex, the presence of metal—metal distances that are shorter than the sum of the van der Waals radii is commonly used as a characteristic identifier for metallophilic interactions. In gold(I)—gold(I) interactions, this value is 3.6 Å, and these attractive aurophilic interactions, which have an order of magnitude strength similar to hydrogen bonding, appear for a wide range of distances (2.8—3.5 Å).[12] Taking into account both coordination bonds and aurophilic interactions, the resulting structure can be described as a stacking of double layers parallel to the *ac* plane. The topological simplification of the structure considering Au atoms as nodes gives rise to an underlying bidimensional 3-connected uninodal plane net with point symbol $8^2\cdot 10$.

As stated above, the solid state arrangement of compound **3** also shows chains with formula $\{Rh_2(O_2CR)_4[Au(CN)_2]\}_\infty$ and very similar structural parameters. In this structure, however, all of the chains follow the same crystallographic direction, namely [21—1], and are located in sheets parallel to the *bc* plane (Figure 2, right). The resulting $\{K\text{-}\{Rh_2(O_2CMe)_4[Au(CN)_2]\}\cdot 4H_2O\}_\infty$ layers are joined through hydrogen bonds involving uncoordinated water molecules located between these layers, and also through van der Waals interactions. Au atoms are too far apart in this arrangement to give rise to aurophilic interactions (Au—Au distance of 8.365 Å for Au atoms located in the same layer and 7.457 Å for Au atoms in adjacent layers).

A remarkable difference between the structures of compounds **2** and **3** is the presence of water molecules: compound **2** is anhydrous whereas complex **3** has four crystallization water molecules, although both complexes were prepared by the same experimental procedure. Thus, in complex **2**, the potassium cations are surrounded by three oxygen atoms belonging to three carboxylate ligands, and three nitrogen atoms from bridging C≡N groups (Supporting Information, Figure S2). These interactions join neighbor layers, and the resulting position of the chains favors the Au—Au interactions to give rise to the resulting double layers. However, in complex **3** the potassium cations are surrounded by three oxygen atoms from water molecules (O9, O10, and O11), three oxygen atoms belonging to carboxylate ligands, one nitrogen atom from a CN group, and one triple bond from a CN group (Supporting Information, Figure S3). In this case, potassium cations join adjacent chains of the same layer, and hydrogen bonds involving the fourth uncoordinated water molecule join different layers. These interactions determine the parallel arrangement of the chains preventing Au—Au approaches.

In summary, the change of a methyl by an ethyl group in the carboxylate ligand does not have any influence in the formation of the $\{Rh_2(O_2CR)_4[Au(CN)_2]\}_\infty$ one-dimensional chains. However, the arrangement of the polymeric chains drastically changes with the nature of the alkyl substituent and with the presence/absence of water molecules.

Luminescence Properties. Gold(I) complexes have been among the most prominent luminescent transition-metal coordination compounds. The luminescence in most Au(I) compounds is attributed to d^{10}-d^{10} closed-shell aurophilic interactions.[15] The term "aurophilicity" is now widely used to describe various kinds of Au—Au interactions within and between gold compounds and appears to be operative between closed-shell gold centers in the formal oxidation state Au^+ (with the valence electronic configuration $5d^{10}$) and in the linearly two-coordinated state. The low coordination number is an important prerequisite since it minimizes steric repulsions between ligands in the aggregates.[16] The energy associated with this aurophilic interaction has been calculated to be 21—46 kJ/mol, which is of the order of the dissociation energy of a hydrogen bond, and the Au(I) centers must be separated by less than 3.6 Å (twice the van der Waals radius for gold).[17]

Compound $K_n\{Rh_2(O_2CEt)_4[Au(CN)_2]\}_n$ (**2**) shows rich blue luminescent properties. At room temperature, excitation of powder solid samples at λ = 360 nm produces a broad intense emission with a maximum peak at 475 nm in the characteristic range of other $[Au(CN)_2]^-$ based coordination polymers.[18] In a scan using different excitation wavelengths, only with $\lambda = 360$ nm was significant emission found. The powder emission spectrum of **2** is shown in Figure 3. As mentioned above, its structure shows one-dimensional infinite chains with a disposition that displays Au···Au interchain distances of 3.328 Å. It has been established that Au···Au distances play an important role on the luminescent properties, showing the emission energy a red-shift when the Au···Au separation decreases.[19] So, if we compare luminescent properties of **2** with $K[Au(CN)_2]$, whose crystal structure consists of layers of linear chains of $[Au(CN)_2]^-$ where gold atoms are arranged in two-dimensional sheets[20] (Au···Au interlayer distances of 3.64 Å), and where the K^+ ions connect the layers through N atoms, a significant red-shift is observed in **2** (λ_{em} = 475 nm) compared to $K[Au(CN)_2]$ (λ_{em} = 390 nm).[18a] In accordance with previous studies[15b] the observed band must be the result of an Au-centered emission originated by the overlap of filled d orbitals and empty p orbitals on the Au(I) cations involved in the aurophilic bond.[15b,16]

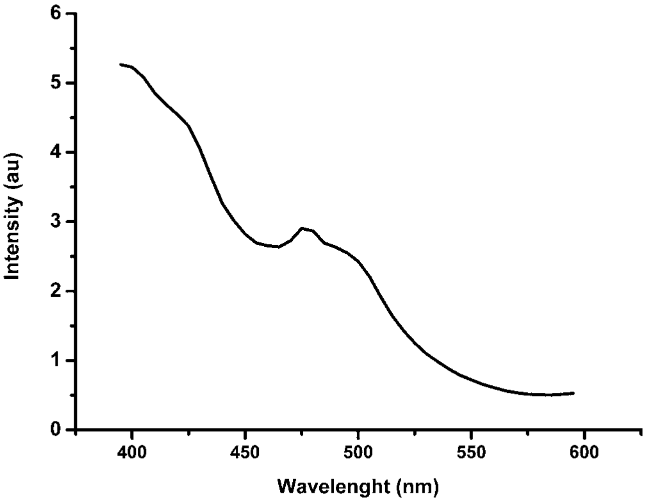

Figure 3. Emission spectrum of **2** in the solid state at λ_{exc}= 360 nm.

Compound **3**, with very long Au···Au distances (8.365 Å for Au atoms located in the same sheet, and 7.457 Å for Au atoms from adjacent layers), does not show luminescent properties because these distances do not allow Au···Au aurophilic interactions.

Electrical Properties. It is well-known that electrical conductivity of classical covalent polymers has attracted the interest of many researchers in materials science. However, the study of this property in coordination polymers has been little explored. On the basis of recent results, and also motivated for the high potential of coordination polymers toward nanotechnological applications,[21] this trend is being reversed.[22] Conductivity measurements in one-dimensional paddlewheel complexes with metal−ligand cores as linkers are really scarce, and only two examples of rhodium derivatives can be found in the literature, in particular $[Rh_2(acam)_4]^+$ with K_2MCl_4 (M = Pd, Pt) as infinite $(\text{-Rh-Rh-Cl-M-Cl-})_n$ chains. In those cases, the conductivity values measured at room temperature in pressed pellets[7] are around 10^{-7} S cm^{-1}. Primarily, the different electrical behaviors can be distinguished by looking at the room temperature value of the conductivity (which is approximately, in the range 10^0−10^5 S cm^{-1} for metals, 10^{-10}−10^0 S cm^{-1} for semiconductors and below about 10^{-10} S cm^{-1} for insulators). Therefore, two probe direct current (DC) electrical conductivity measurements at 300 K were performed in several single crystals of complexes **2** and **3**. These measurements with applied electrical voltages in the range −10 to 10 V show conductivity values of about 10^{-10} and 10^{-6} S cm^{-1} for compounds **2** and **3**, respectively, suggesting a semiconducting behavior. This behavior is confirmed by conductivity measurements as a function of the temperature in the range 300−400 K showing a decrease of the resistivity with increasing temperature that follows quite closely the classical Arrhenius law, $\rho = \rho_0 \exp(E_a/kT)$ in the temperature range where the sample could be measured (378−400 K) (Supporting Information, Figure S4). A close look at this plot shows a slight concavity in the experimental data that may be attributed to different sources: (i) a possible small contribution of the K^+ ions (ionic conductivity), (ii) a possible saturation effect, since the measured resistance values are close to our equipment limit, and (iii) the possible existence of other conductivity mechanism operating at high temperatures, such as interchain hopping, leading to a variable range hopping mechanism.

As indicated above, the dirhodium units of the zigzag chains in both compounds are very similar and, therefore, the differences in the electrical conductivity must be due to differences in the interdimer interactions that generate the chain. A careful analysis of these interactions show that the Rh−N bond distances are shorter in compound **2** (2.208 and 2.229 Å) than in **3** (2.240 and 2.305 Å), suggesting that compound **2** should be a better conductor. Albeit the Rh−N−C bond angles are significantly larger in compound **3** (173.05° and 158.46° in **3** compared to 155.47 and 144.94° in **2**) yielding a much better overlap of the molecular orbitals and, consequently, a better conductivity value in compound **3**, in agreement with the experimental measurements. Unfortunately, in both compounds the absence of an almost linear arrangement of the dirhodium units along the chains prevents the presence of a high conductivity and a metallic behavior.

■ CONCLUSIONS

In this work we have been able to prepare two of the very scarce examples of dirhodium carboxylato complexes containing metallic spacing groups. We have shown that the arrangement of the fragments in the solid state is strongly influenced by the equatorial ligands and the presence or absence of water molecules in the complex. Interestingly, minor differences in the aliphatic fragment of the carboxylate ligand have given rise to different arrangements in the solid state and resulting properties: compound **2** (R = Et), with aurophilic interactions, displays rich blue luminescent properties, while complex **3** (R = Me), in which the disposition of Au atoms prevents these interactions, does not show luminescence. Compounds **2** and **3** are electrical semiconductors with room temperature conductivities of about 10^{-10} and 10^{-6} S cm^{-1}. These values can be well correlated with the structural features showing a better overlap between the dirhodium and the dicyanoaurate units in compound **3** with larger Rh−N−C angles (closer to linearity) than in **2**.

■ EXPERIMENTAL SECTION

General Procedures. KBr, $RhCl_3{\cdot}xH_2O$, carboxylic acids and solvents were purchased and used as received. The dirhodium(II) acetate used in this report was obtained by a method previously described.[13]

IR spectra were recorded on a PerkinElmer spectrum 100 spectrophotometer using a universal ATR sampling accessory.

Elemental Analyses were carried out by the Microanalytical Service of the Complutense University of Madrid.

Luminescence excitation and emission spectra of the solid compounds were recorded at 298 K with a JASCO FP-6500 spectrofluorometer using a diode laser with emission at 360 nm (50 mW) and a sample holder developed for powders.

Preliminary direct current (DC) electrical conductivity measurements were performed on several different single crystals of compounds **2** at 300 K and in the temperature range 300−400 K for compound **3** with the two contacts method. The contacts were made with platinum wires (25 μm diameter) using graphite paste. The samples were measured with an electrical current with voltages form +10 to −10 V.

X-ray Data Collection and Structure Refinement. Data collection for all compounds was carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) operating at 50 kV. In all cases, data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. In all cases, each exposure was of 20 s covered 0.3 in ω. The cell parameters were determined and refined by a least-squares fit of all reflections. The first 100 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. A semiempirical absorption correction was applied for all cases.

A summary of the fundamental crystal and refinement data is given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXL-97).[23] All non-hydrogen atoms were refined anisotropically with the exception of several propyl C-atoms for **1** which were refined isotropically. In compound **1** some of the C-atoms from the alkyl chains were refined using geometric restraints and variable common C−C distances.

All hydrogen atoms were included in their calculated positions and refined riding on the respective carbon atoms.

Further crystallographic details for the structure reported here may be obtained from the Cambridge Crystallographic Data Center, on quoting the depository numbers CCDC 832982, 832986, and 832987.

Synthesis of $[Rh_2(O_2CEt)_4(H_2O)_2]$ (1). To a water/methanol (1:1) solution (40 mL) of dirhodium(II) acetate (0.400 g, 0.905 mmol), 3 mL (40.09 mmol) of propionic acid was added. The suspension was stirred for 4 h at 100 °C and then the solvents were removed in a rotary vacuum evaporator and the solid was washed with hexane and filtered off. To the obtained solid, 1 mL of propionic acid was added in 40 mL of a water−methanol solution (1:1) and the suspension was stirred for 4 h at 100 °C. The solvents were removed afterward in a rotary vacuum evaporator, and the obtained solid was washed with hexane, filtered off and dried under vacuum.

Clear green crystals were obtained by slow evaporation from a methanol solution at room temperature. Yield: 249 mg (51.9%). The compound can be manipulated in air without appreciable decomposition for a long period of time.

Elemental analysis calcd (%) for $C_{12}H_{24}O_{10}Rh_2$: C, 26.98; H, 4.5. Found(%): C, 26.92; H, 4.9. IR(cm^{-1}): 2976(w), 2941(w), 2879(w), 1566(s), 1523(m), 1461(m), 1415(vs), 1370(m), 1297(m), 1242(m), 1071(m), 1015(w), 892(m), 805(m), 746(m), 710(m), 676(s).

Synthesis of $K_n\{Rh_2(O_2CEt)_4[Au(CN)_2]\}_n$ (2). To an aqueous solution (15 mL) of dirhodium(II) propionate (0.053 g, 0.1 mmol), 0.029 g (0.1 mmol) of $K[Au(CN)_2]$ was added, (pH = 4.5). The suspension was stirred for 5 h at 25 °C and then filtered off. Yield: 50 mg (63.3%). Clear violet crystals were obtained by slow evaporation of the filtrate at room temperature. Yield: 26 mg (33%).

The powder diffraction patterns of both fractions show that the crystals and the powder are the same complex. Total yield: 76 mg (96.3%) Elemental analysis: Calcd (%) for $C_{14}H_{20}O_8N_2AuKRh_2$: C, 21.39, H, 2.56, N, 3.56. Found (%): C, 21.85, H, 2.71, N, 3.96

IR (cm^{-1}): 2984(w), 2144(w), 1578(m), 1532(w), 1463(s), 1419(s), 1356(s), 1301(m), 1083(w), 890(w), 812(w), 678(s).

Synthesis of $K_n\{Rh_2(O_2CMe)_4[Au(CN)_2]\}_n\cdot 4nH_2O$ (3). To an aqueous solution (15 mL) of dirhodium(II) acetate (0.100 g, 0.226 mmol), (pH = 6.7), 0.065 g (0.226 mmol) of $K[Au(CN)_2]$ was added. The suspension was stirred for 2 h at 25 °C and then filtered off. Yield: 81 mg (44.2%). Clear red crystals were obtained by slow evaporation of the filtrate at room temperature. Yield (crystals): 30 mg (17.3%). The powder diffraction patterns of both fractions show that the crystals and the powder are the same complex. Total yield: 111 mg (61.5%). Elemental analysis calcd (%) for $C_{10}H_{20}O_{12}N_2AuKRh_2$: C, 14.97; H, 2.51. N, 3.49, Found(%): C, 14.64, H, 2.83, N, 3.58.

IR(cm^{-1}): 3554(m), 3497(m), 3407(m), 2167 (m), 1644(m), 1574(s), 1413(s), 1350(m), 1046(m), 703(s).

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic file (CIF) for **1**−**3**, thermal ellipsoid drawing of complex **1**, and additional text and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Dr. F. A. Urbanos, deceased May 28, 2011.

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