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Microgels

A Water Soluble Diruthenium–Gold Organometallic Microgel**

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Selection of the combination of metal, ligand set, and spacer groups that are most appropriate to form a coordination complex with a desired function are of paramount importance in supramolecular chemistry. In particular, the establishment of reproducible methods to accomplish controlled self-organization of molecules to form polymers and homo- or heterometallic coordination aggregates is an important field of research.[1] Although important advances have already been made, few metallopolymers, which are one of the most exciting classes of functional materials, are water soluble. An important example of a water-soluble polymer is the polyferrocenylsilane-β-polyaminomethacrylate copolymer described by Manners and co-workers,[2] as part of their ongoing study on metallocene-based polymers.[3] Recent examples also include the water-soluble metallopolymer obtained by reaction of bipyridyl-appended poly(*p*-phenyleneethynylene) (PPEs) with metal ions in organic and aqueous solution.[4] Other examples of ligands that afford coordination polymers with various topologies and applications are ferrocenyl groups bearing bipyridine (bpy)[5] or carboxylate moieties.[6] A recent example of a non-water-soluble multimetallic polymer is $[Sm(H_2O)_5][Ru_2(bpy)_2(CN)_7]$, in which the CN ligands bridge the samarium and ruthenium metal centers.[7]

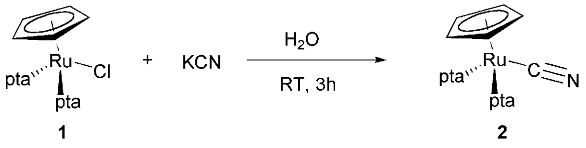
The first air-stable water-soluble multimetallic polymer that includes mixed P,N ligands as metal-coordinating spacers has been recently reported by us.[8] This heterobimetallic complex is based on two metal-containing moieties, $[CpRu]^+$ (Cp = cyclopentadienyl) and $[AgCl_2]^-$, and is bridged by the cagelike water-soluble monodentate phosphine 1,3,5-triaza-7-phosphaadamantane (pta) in an unprecedented P,N coordination mode. More recently, the synthesis of silver coordination polymers containing pta bridging molecules in a tridentate P,N,N′ coordination mode[9] has been reported and several examples of pta N coordination have been presented.[10] Therefore the pta molecule could be an excellent ligand from which to obtain water-soluble Ru–Au polymers which could have interesting and useful properties for a variety of applications such as magnetism,[11] nonlinear optics,[12] electrocatalysis,[13] photocatalysis,[14] photovoltaic,[15] template formation of ordered networks,[16] advanced electrode materials,[17] and conjugated coordination polymers.[18]

Herein, we describe the first water-soluble, air-stable heterobimetallic polymeric structure based on two metal-containing moieties $[CpRuCNRuCp]^+$ and $[Au(CN)_4]^-$, bridged by pta in the P,N coordination mode. Interestingly, this complex display gel-like properties[19] in water, specifically a thermally controlled volume transition. To the best of our knowledge, this is the first example of an coordination polymer network that is sensitive to its environment. The physical and chemical properties of this complex make it a promising material for industrial and biological applications, for example, smart catalysis, drug delivery, or chemical sensing.

The first strategy we attempted to obtain a water soluble Ru–Au polymer was similar to that used for the synthesis of $[\{CpRu(pta)_2(DMSO\text{-}\kappa S)\}\{AgCl_2\}]_\infty$.[8] The complex $[CpRuCl(pta)_2]$ (**1**) was reacted in a straightforward manner with $AuCl_3$ in water, EtOH, and DMSO, and in the presence of $NaBF_4$ and $NaCF_3SO_3$. This resulted in the swift formation of a stoichiometric amount of metallic gold.

A second strategy, in which the $[Au(CN)_4]^-$ moiety (which is very stable under a wide variety of conditions)[20] was used, was then tested. The reaction of **1** with $K[Au(CN)_4]$ led to the partial reduction of gold together with the formation of several new species. A careful analysis of the reaction products suggested that the presence of the chloride ion in **1** could give rise to the formation of unstable gold species which finally decompose to metallic gold. To avoid the presence of the chloride ion in the reaction, the complex $[RuCp(CN)(pta)_2]$ (**2**) was prepared by substitution of **1** with KCN at room temperature in water (Scheme 1).

Slow crystallization of a diluted H_2O solution of $[Ru(CN\text{-}\kappa C)Cp(pta)_2]$ (**2**) in air give colorless crystals suitable for X-ray diffraction.[21] The X-ray crystal structure of complex **2** shows that it is a mononuclear complex in the solid state and is similar to **1**, except that the chloride ligand has been



Scheme 1. Formation of **2** by substitution of Cl^- in **1** by CN^- ions.

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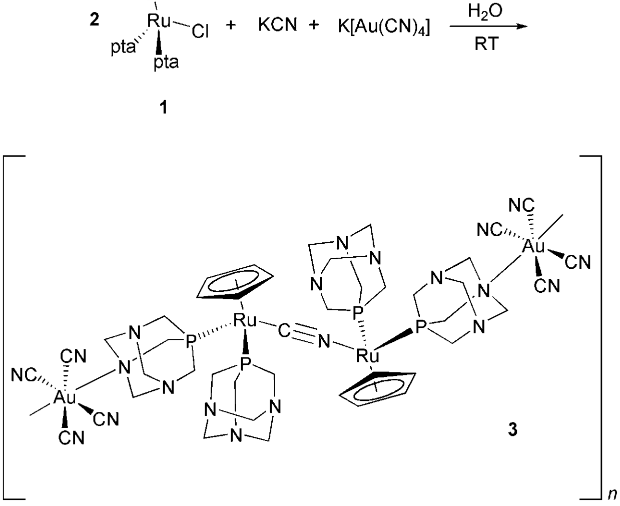
substituted by cyanide. The Ru–CN bond length (2.012(6) Å) is similar to that found for Cp-Ru complexes containing coordinated CN ligands.[22]

No reaction between complex **2** and $K[Au(CN)_4]$ in water at 100 °C was observed, but also no elemental gold was produced. Several new strategies were tested, all of which used $[Au(CN)_4]^-$. The reaction of **1** with **2** and $K[Au(CN)_4]$ (1:1:1) in water gave a mixture containing only two main compounds. The most abundant (79 %) species was separated by recrystallization from DMSO. This was shown to be the air-stable water-soluble trimetallic polymer complex $[\{Cp(pta)_2Ru\text{-}\mu\text{-}CN\text{-}RuCp(pta)_2\}\{Au(CN)_4\}]_\infty$ (**3**). This complex can also be obtained by reaction of **1** with KCN and $K[Au(CN)_4]$ in water at room temperature (Scheme 2). The second method is more convenient as it involves only one reaction step and produces complex **3** in a higher yield than the first method.



Scheme 2. Synthesis of the organometallic polymer **3**.

Complex **3** is air stable both in the solid state and solution and is water soluble (3.5 mg mL^{-1} at 25°C) without decomposition. The FTIR spectrum of **3** shows absorption bands for both Au–CN (2185 cm^{-1}) and Ru–CN (2097 cm^{-1}) coordination. The band assigned to the Au–CN signal is found at a frequency similar to that of other complexes containing the $[Au(CN)]^-$ ion.[20,23] The Ru–CN stretching frequency is 37 cm^{-1} higher than that of the CN ligand in the complex **2** (2060 cm^{-1}). In general, the IR absorption of bridging CN groups is higher than that of the parent mononuclear CN complexes.[24] Intense sharp absorption bands are also observed (3549 and 3380 cm^{-1}), which could indicate the presence of an extensive hydrogen-bond network between water molecules and the nitrogen atoms ($OH\text{–}N_{pta}$, $OH\text{–}N_{NCAu}$). The $^{31}P\{^1H\}$ NMR spectrum of **3** (in D_2O) shows two singlets at $\delta = -19.21$ and -21.82 ppm. These signals can be assigned to two magnetically inequivalent pta ligands bonded to ruthenium atoms, although no coupling is observed between the two ligands. The ^1H NMR spectrum supports this assignment as signals are observed at $\delta = 4.80$ and 4.95 ppm, each integrating to five protons, which could be assigned only to the Ru-Cp ligands.[25] Unfortunately **3** was not sufficiently soluble in D_2O to obtain a $^{13}C\{^1H\}$ NMR spectrum. Crystals of **3** suitable for X-ray diffraction were obtained by recrystallization from DMSO.[26] The X-ray crystal structure shows that **3** is a linear chain polymer in the solid state, formed from alternating $[CpRu(\mu\text{-}CN)RuCp]^+$ moieties and $[Au(CN)_4]^-$ anions with bridging pta ligands as tethering units between the two metal aggregates ($d_{Ru\cdots Au} =$ 7.09(1) Å, Figure 1, selected bond lengths and angles are provided in the Supporting Information).

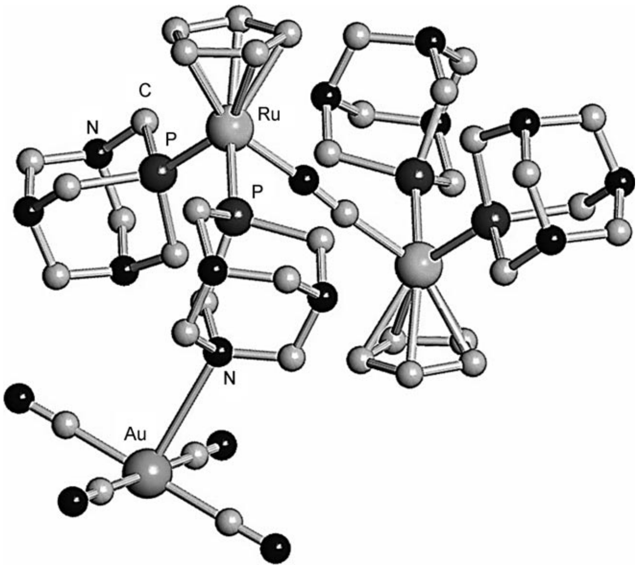


Figure 1. X-ray crystal structure of **3** (repeating unit).

The $[CpRu(\mu\text{-}CN)RuCp]^+$ moiety contains two ruthenium atoms linked by a disordered CN ligand (73/27 %) between both metal atoms. The Cp and pta ligands are aligned in opposite directions as imposed by the *i* symmetry element on the C≡N bond. The coordination geometry around the ruthenium atoms is more regular, with the $Ru\text{–}Cp_{(centroid)}$ distance (1.868 Å) slightly larger than that found for $[CpRuCl(pta)_2]$ (1.846 Å),[27] while the Ru–P separation (average: 2.2618(8) Å) is consistent with that found in the few other Ru–pta derivatives that have been studied by X-ray diffraction.[22,25] This is the second known compound in which the pta acts as a bidentate ligand,[8] bonded in this case to a ruthenium with the conventional lone pair of electrons of the phosphorus atom and to the gold atom of the tetracyanogold(III) moiety by one of the three nitrogen atoms (N3) contained in the adamantane cage (Figure 2).

The $[Au(CN)_4]^-$ center bridges two $[(pta)_2CpRu(\mu\text{-}CN)RuCp(pta)_2]^+$ units, giving a somewhat distorted octahedron with the N3-Au1-N3B angle opened up to about 180° and the average N-Au-CN angle to be approximately 94° (C2C-Au1-N3 = 96.55°; C1C-Au1-N3 = 92.56°). The average Au–CN distance is 1.999 Å, which is in the range of reported limits for the Au–CN distance (1.995 and 2.004 Å).[20,22,23] The $Au\text{–}N_{pta}$ distance (2.985(3) Å) is longer than that found for other diamino–gold complexes (2.13 Å)[22] but is shorter than

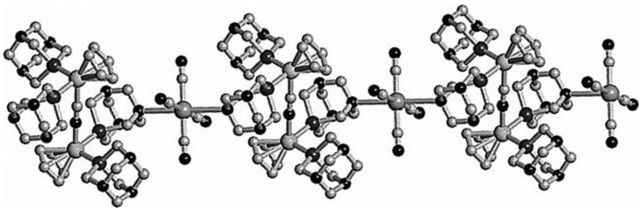


Figure 2. X-ray crystal structure of **3** showing the bidimensional arrangement.

the sum of the van der Waals radii for gold and nitrogen (3.21 Å)[28] and similar to that (2.963(13) Å) found in [Cu(dmeda)$_2$Au(CN)$_4$][Au(CN)$_4$] (dmeda = *N*,*N'*-dimethylethylenediamine).[23c] X-ray crystal structures of gold compounds with an octahedral geometry are rare and no examples of octahedral gold complexes containing CN ligands have been reported.[22]

The bridging pta ligand, of which N coordination to a transition metal is uncommon, is much more intriguing.[9,10] The coordination of the [Au(CN)$_4$]$^-$ unit to the nitrogen atom N3 in pta does not significantly affect the structural features of the cage in comparison with other Ru(pta) complexes.[25,29] It is interesting to note that all attempts to obtain polymers from the monomer **1** led to **3** but not to the expected [{Cp(pta)$_2$Ru(CN-κC)}{Au(CN)$_4$}]$_\infty$ in which a monomeric ruthenium moiety [CpRu(CN-κC)(pta)$_2$] is linked to [Au(CN)$_4$]$^-$.

The Ru$_2$–Au chains in **3** form a 3D array by electrostatic interactions and hydrogen bonds between the [(pta)$_2$CpRu(μ-CN)RuCp(pta)$_2$]$^+$ and [Au(CN)$_4$]$^-$ units, with an interchain separation of the metal ions of 8.119 Å (Figure 3). The 2D arrays are stacked in the lattice by a hydrogen-bonding network of water molecules, which bridge the [Au(CN)$_4$]$^-$ anion by the nitrogen atoms of one layer and the N1 and N6 atoms of the pta units in two different adjacent layers (Figure 3). The shortest hydrogen contacts between atoms in contiguous layers were found to be 2.723(2) Å (O1–O2), 2.815(3) Å (O1–N6), 2.839(3) Å (O1–N1) and 2.944(4) Å (O2–N2C), which are longer than a hydrogen bond but shorter than the sum of their van der Waals radii.[28] The hydrogen bond is strong enough to prevent protonation of the uncoordinated pta nitrogen atoms.[30] The Cp groups alternate their positions within adjacent layers to minimize their steric hindrance.[31]

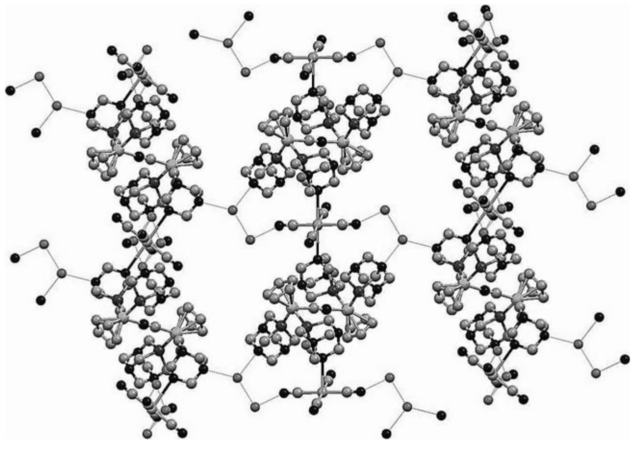


Figure 3. X-ray crystal structure of **3** showing the hydrogen-bonding network connecting the polymeric chains via the pta nitrogen atom of adjacent chains and to the [Au(CN)$_4$]$^-$ nitrogen atom.

Dynamic light scattering[32] was used to check polymer self-assembly on the colloidal length scale. The polymer does not dissociate in water, retains its polymeric structure, and associates to form stable microparticles. The scattered-intensity autocorrelation function[33] shows stable particles of average size (2295 ± 197) nm, (2373 ± 134) nm, and (2384 ± 253) nm, after 0, 3, and 7 days, respectively (data correspond to complex **3** at 25 °C). The presence of microparticles was confirmed by direct optical microscopy[34] (see inset in Figure 4).

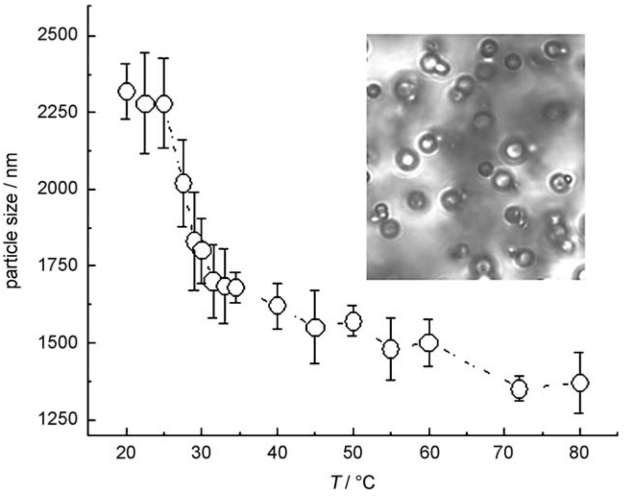


Figure 4. Plot of particle diameter against temperature in the temperature-controlled swelling of the Ru$_2$–Au microgel. The optical microscopy picture of the microparticles in aqueous dispersion is shown as inset.

The microparticles reversibly swell or shrink (the swelling may be cycled) in response to external temperature changes, as illustrated in Figure 4. A sharp but continuous volume transition is observed at a temperature of about 30 °C. Complex **3** is therefore a thermosensitive inorganic microgel. This feature is similar to that observed for organic poly-*N*-isopropylacrylamide (poly-NIPAM) microgels.[35]

It is well known that microgels exist in an equilibrium form when no net transfer of solvent takes place across the microgel–solvent interface, the critical parameters being polymer solubility, network elasticity, and mesh charge. The microgel size can be tuned by temperature variation, a feature related to the solubility of the polymer, which alters the hydrophobic or hydrophilic nature of the interactions within the polymer.[36,37]

We propose that the volume transition observed for the [{Cp(pta)$_2$Ru(μ-CN)RuCp(pta)$_2$}{Au(CN)$_4$}]$_\infty$ inorganic microgel arises from the hydrophilic and hydrophobic character of pta and cyclopentadiene units, respectively. Below the transition temperature, the particles are swollen because of the high solubility of pta.[9] The nitrogen atoms of pta are bridged through extensive hydrogen bonding with water molecules. In addition, water molecules form clusters around the hydrophobic Cp ligands. Above the transition temperature, the water–amine hydrogen bonds are disrupted, the attractive hydrophobic interactions between polymer chains become dominant, and the polymer chains collapse, expelling water from the particles. The deswelling process is therefore entropically driven, as a consequence of the disordering of hydrogen-bonded water molecules. This mechanism has been previously identified as being responsible for the volume transition of thermosensitive cross-linked organic microgels.[38]

Macromolecular chains of organometallic species assembled to form supramolecular structures by an extensive network of hydrogen bonding interactions are rare;[39] systems such as **3**, which incorporate half-sandwich cyclopentadienyl units and phosphines, have not been reported to date. Additionally, this coordination polymer represents the first example of a water-soluble organometallic macromolecule with additional swelling–deswelling characteristics.

Experiments are under way to isolate new water-soluble Ru–Au polymers and to verify the P,N coordination ability of pta with other transition-metal moieties as well as to establish the conductivity, electrochemical behavior, biological activity, and the chemical behavior in water of the new heteropolymetallic polymer.

Experimental Section

Complex **2** was obtained as colorless microcrystals by addition of a solution of [RuClCp(pta)$_2$] (**1**) (40 mg, 0.078 mmol) in H_2O (3 mL) to a solution of KCN (7 mg, 0.107 mmol) in H_2O (1 mL). After 1 hour the resulting mixture was filtered, the solvent removed and the wet white powder dissolved in EtOH (0.5 mL). Addition of Et_2O (10 mL) produced a white precipitate which was filtered, washed with Et_2O (4 × 3 mL) and dried under vacuum. Yield: 0.035 g, 90 %. Solubility at 25°C: 280 mg cm^{-3}. Elemental analysis calcd (%) for $C_{18}H_{29}N_7P_2Ru$ (507.10): C, 42.60; H, 5.76; N, 19.33; found: C, 42.42; H, 5.91; N, 19.06;. IR (KBr): $\nu = 2060$ cm^{-1} (C≡N). ^{1}H NMR (300.13 MHz, 23 °C, TMS, D_2O): $\delta = 3.94$ (m, 6H, NCH_2P), 4.47 (s, 6H, NCH_2N), 4.96 ppm (s, 5H, Cp). ^{31}P{^{1}H} NMR (121.49 Mz, 23 °C, 85 % H_3PO_4, D_2O): $\delta = -19.46$ ppm (s, pta).

Complex **3** was obtained by two different procedures.

Method A: K[Au(CN)$_4$] was prepared by reaction of Na[AuCl$_4$]·xH$_2$O (50 % Au, 35 mg, 0.088 mmol) and KCN (23 mg, 0.352 mmol) in H_2O (1 mL). This was added, with additional KCN (5 mg, 0.08 mmol) to a solution of [RuClCp(pta)$_2$] (80 mg, 0.155 mmol) in H_2O (5 mL) and the resulting solution was kept at 90 °C for 5 min, cooled to room temperature and filtered. The solvent was removed under vacuum to give a yellow powder, which was dissolved in DMSO (1 mL). Yellow crystals suitable for X-ray diffraction were obtained after 2 weeks.

Method B: A solution of K[AuCN$_4$] (prepared as described in method A) in H_2O (1 mL), to a solution of [RuCp(CN)(pta)$_2$] (39 mg, 0.077 mmol) and [RuClCp(pta)$_2$] (40 mg, 0.077 mmol) in H_2O (5 mL). After stirring at 90 °C for 20 min, the volume of solvent was reduced to 0.5 mL. Addition of acetone (10 mL) gave **3** as a yellow powder which was filtered, washed with acetone (2 × 1.5 mL), vacuum dried, and recrystallized from DMSO (0.5 mL). The resulting yellow microcrystals were filtered, washed with water (1 mL), EtOH (2 × 1 mL) and Et_2O (2 × 1 mL). Yield: (Method A) 0.060 g, 57 %; (Method B) 0.052 g, 49 %. Solubility at 25°C: 3.5 mg cm^{-3}. Elemental analysis calcd (%) for $C_{39}H_{66}AuN_{17}O_4P_4Ru_2$ (1361.22): C, 34.38; H, 4.89; N, 17.49; Found C, 33.95; H, 5.23; N, 17.03. IR (KBr): $\tilde{\nu} = 3549$, 3380 cm^{-1} (OH−N$_{pta}$), ν(OH−N$_{NCAu}$); $\tilde{\nu} = 2185$ cm^{-1} (C≡N); $\tilde{\nu} = 2097$ cm^{-1} (μ-C≡N). ^{1}H NMR (300.13 MHz, 23 °C, TMS, D_2O): $\delta = 3.86$ (m, NCH_2P), 3.97 (m, NCH_2P), 4.48 (m, NCH_2N), 4.80 (s, Cp), 4.95 ppm (s, Cp). ^{31}P{^{1}H} NMR (121.49 Mz, 23 °C, 85 % H_3PO_4, D_2O): $\delta = -19.21$ (s, pta), −21.82 ppm (s, pta).

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