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A platinum(II)–palladium(II)–nickel(II) heterotrimetallic coordination polymer showing a cooperative effect on catalytic hydrogen evolution

The first example of a heterotrimetallic coordination polymer containing all three group 10 metal ions was created. This compound shows a significant enhancement in heterogeneous hydrogen evolution by the stepwise introduction of Pd$^{II}$ and Ni$^{II}$ to the Pt$^{II}$ metalloligand.

As featured in:

**A platinum(II)–palladium(II)–nickel(II) heterotrimetallic coordination polymer showing a cooperative effect on catalytic hydrogen evolution**

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Stepwise construction of a 1D heterotrimetallic coordination polymer containing all three group 10 metal ions via an ammineplatinum(II) metalloligand with γ-penicillamine is reported. This system showed a significant enhancement in heterogeneous catalytic activity for electrochemical hydrogen evolution by the stepwise introduction of Pd⁰ and Ni⁰ into the Pt¹ metalloligand.

In recent years, heterometallic coordination compounds have received increased attention because the incorporation of different kinds of metal ions into one molecule often leads to an intriguing cooperative effect on physical and chemical properties, such as magnetism, emission, and catalysis. To date, many examples of ‘heterobimetallic’ compounds that show some cooperative effect on their properties have been reported. However, reports on a cooperative effect for ‘heterotrimetallic’ species are still relatively uncommon. This is owing to a lack of rational synthetic methods to incorporate three different kinds of metal ions into a single molecule; most of the heterotrimetallic coordination compounds have been synthesized via one-pot reactions in which three kinds of metal ions are self-assembled with organic and/or inorganic ligands under specific conditions. To overcome this problem, we have developed a metalloligand approach, in which a metal ligand under specific conditions acts as a multifunctional metalloligand. This finding prompted us to investigate the reactivity of [Au(γ-pen)]⁺ toward Pd²⁺ and Ni²⁺ to create a heterotrimetallic compound containing all group 10 metal ions (Pt⁰, Pd⁰, and Ni⁰) in one molecule. Here, we report that [Au(γ-pen)]⁺ reacts with Pd(OAc)₂ to afford a Pt²⁺Pd²⁺ tetranuclear complex ([2]), which further reacts with NiCl₂ to produce a Pt²⁺Pd²⁺Ni²⁺ coordination polymer ([3]Cl₂) (Scheme 1). Remarkably, [3]Cl₂ showed excellent catalytic activity for electrochemical hydrogen evolution compared with [1]¹⁻ and [2], indicating a significant enhancement of the catalytic activity due to the incorporation of all three group 10 metal ions in one molecule. To our knowledge, such a cooperative effect on catalytic activity has not been reported.

The reaction of [Pt(NH₃)₂(γ-Hpen)]⁺ ([H₂1]) with Pd(OAc)₂ in H₂O gave an orange solution, from which yellow crystals ([2]) were isolated. The ¹H NMR spectrum of [2] displayed only a

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single set of signals (δ 1.43, 1.56, and 3.35 ppm) due to ν-pen ligands in the complex, indicative of its high symmetrical structure (Fig. S1, ESI†). The presence of a deprotonated carboxyl group in [2] was implied by its IR spectrum that shows a strong band at 1600 cm⁻¹ (Fig. S2, ESI†). The elemental analytical data of [2] were in agreement with a neutral formula containing [1] and Pd in a 1:1 ratio. Single crystals of [2] suitable for X-ray crystallography were obtained as the protonated form, [H₂]Cl₂. The asymmetric unit of [H₂]Cl₂ contains one complex cation and four chloride anions, besides solvated water molecules. As shown in Fig. 1, the complex cation has an S-bridged Pd⁵Pd⁵ tetranuclear structure in [Pd₂P₄(C₅O₄)₄(D-Hpen)₄]⁺, consisting of two metalloligands with protonated carboxyl groups ([H₂I] and two Pd⁵ atoms. Each of the two metalloligands span two Pd⁵ atoms in a bis(bidentate-N,S) mode, such that each Pd⁵ centre has a square planar geometry with a cis-N₂S₂ donor set (av. Pd-N: 2.084 Å, Pd-S: 2.272 Å). The Pt···Pt distance in [H₂I] is 3.300 Å, indicating the lack of an intramolecular Pt···Pt interaction. Each NH₃ ligand is hydrogen-bonded with a ν-pen thioloate group (av. N-NH₃: 3.29 Å), which appears to stabilize the Pd⁵C₄S₄ octahedral geometry (av. Ni–OCOO: 2.064 Å, Ni–Owater: 2.093 Å). The chloride ions are not involved in the coordination and are located between the Pd⁵Pd⁵Ni⁴ chains, forming hydrogen bonds with ammine groups and water molecules (av. Cl···N₅H₄: 3.29 Å, Cl···Owater: 3.09 Å, Fig. S3, ESI†).

The catalytic property of [3]Cl₂ in the solid state was electrochemically investigated, and the results were compared with those of [H₂I] and [2]. The linear sweep voltammetry of a solid sample of [3]Cl₂, attached to the surface of a glassy carbon electrode (0.07 cm²), in H₂O/CH₃CN (v/v = 1/9) containing 0.1 M LiClO₄ displayed a sharp current increase at an onset potential of −0.98 V (vs. Ag/AgCl). A similar but lower current increase was also observed for a solid sample of [2] at −1.10 V (Fig. 3). However, a solid sample of [H₂I] showed only a slight current increase at −1.15 V. Since the control experiment using a bare glassy carbon electrode under the same conditions did not show any current increase until reaching −1.5 V, this observation is indicative of a catalytic reduction, the activity of which drastically increases in the following order: [H₂I] < [2] < [3]Cl₂. During the voltammetric scans, the evolution of bubbles from the electrode surface was observed for [2] and [3]Cl₂. The bubbles were analyzed using gas chromatography (GC) and found to be H₂ gas (Fig. S5, ESI†). Such an evolution of bubbles, as well as a current increase, was not detected when absolute CH₃CN was used as the solvent instead of H₂O/CH₃CN (Fig. S6, ESI†). Thus, [2] and [3]Cl₂ catalyze the electrochemical reduction of water to produce H₂ gas. These are relatively few examples of coordination compounds that exhibit a heterogeneous catalytic activity for H₂ gas evolution on an electrode surface. Considering that [H₂I] is significantly less active for catalytic reduction of water.
than [2] and [3]Cl₂, the catalytic reaction mainly occurs at the Pdᴵᴵ centre of the [Pd(n-pen)]²⁺ square-planes. It has been proposed that Pd is the best alternative to Pt in catalytic systems for H₂ evolution.¹⁵ However, examples reporting catalytic hydrogen evolution are limited to several homogeneous catalytic systems,¹⁶ and this is the first Pdᴵᴵ coordination system that evidences heterogeneous catalytic H₂ evolution.

To evaluate the H₂ evolution rate, potential-controlled electrolysis was carried out under the same conditions as those of the voltammetric experiments. At an applied potential of −1.20 V, the rate of Coulomb charge increased in the order [H₂,1] < [2] < [3]Cl₂, which is in parallel with the voltammetric results (Fig. 3). The turnover frequency (TOF) of H₂ (mol H₂/mol cat) was calculated to be 3.73, 18.2, and 34.4 mol min⁻¹ cm⁻² for [H₂,1], [2], and [3]Cl₂, respectively. The GC analysis indicated that the amount of H₂ gas generated during the electrolysis using [2] and [3]Cl₂ was 1.56 μmol and 2.88 μmol, respectively. From these values, the Faraday efficiencies for [2] and [3]Cl₂ were calculated to be 81% and 100%, respectively, indicating that no side redox reaction occurs during the electrolysis for [3]Cl₂. It has been shown that the increase of Lewis acidity around the reaction centre promotes the efficiency of an electrocatalytic hydrogen evolution.¹⁷ In [3]Cl₂, the n-pen carboxylate group coordinates to a Niᴵᴵ centre, which might lead to an increase of the Lewis acidity around a Pdᴵᴵ catalytic centre.¹⁸

In summary, we showed that the metalloligand trans-[Pt(NH₃)₂Cl₂(n-pen)]²⁻ ([I]⁻) reacts with Pdᴵ to afford an S-bridged Pdᴵᴵ complex, [Pd₂Pt₂(NH₃)₄(n-pen)] [2]), which exclusively forms a twisted isomer consisting of cis-[Pd(n-pen)]²⁺ planes. This coordination behaviour is due to the presence of two NH₃ ligands bound to each Pdᴵᴵ centre, exerting non-bonding steric and NH···S hydrogen bonding interactions. Complex [2] acts as an O-donating metalloligand to Niᴵ to create a Niᴵᴵ[Pd(NH₃)₄(n-pen)]Cl₃, ([II]Cl₃), which is the first example of a structurally characterized heterotrimetallic coordination compound with all three group 10 metal ions in one molecule. Due to the stepwise combination of Pdᴵ and Niᴵ centres with [I]⁻, the electrocatalytic water reduction was largely enhanced by heterogeneous activity, demonstrating a significant cooperative effect due to metal ions belonging to the same group, for the first time.

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Notes and references


¹⁸ The overpotentials at 10 mA cm⁻² were 0.79 V and 0.69 V for [2] and [3]Cl₂, respectively.

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18 A solid sample of Ni(CH₃COO)₂·4H₂O, which has essentially the same octahedral trans-[Ni(RCOO)₂(H₂O)₄] structure as that in [3]Cl₂, does not show any catalytic activity for electrochemical hydrogen evolution under the same conditions (Fig. S7, ESI†). This result seems to exclude the hypothesis that the Ni²⁺ center in [3]Cl₂ also acts as an active site for the electrochemical hydrogen evolution.