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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.

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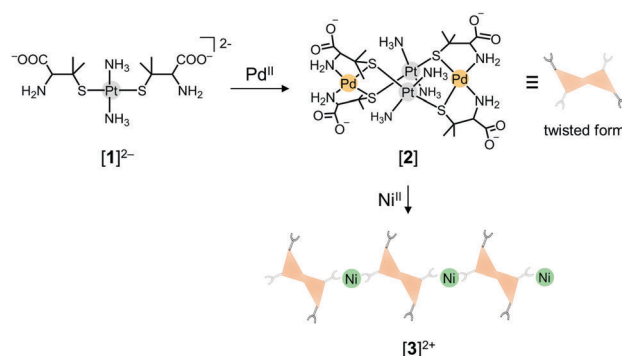
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Stepwise construction of a 1D heterotrimetallic coordination polymer containing all three group 10 metal ions via an ammineplatinum(II) metalloligand with D-penicillamine is reported. This system showed a significant enhancement in heterogeneous catalytic activity for electrochemical hydrogen evolution by the stepwise introduction of Pd^{II} and Ni^{II} into the Pt^{II} 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.[1] 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.[2] 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.[3] To overcome this problem, we have developed a metalloligand approach, in which a metal complex having several donor sites coordinates in a stepwise fashion to second and third metal ions to form the desired heterotrimetallic coordination compounds.[4–6] Previously, we showed that a linear-type Au^I complex, [Au(D-pen)$_2$]$^{3-}$ (D-H$_2$pen = D-penicillamine), in which an Au^I centre is linearly coordinated by two thiolato groups from two D-pen ligands, can serve as a multifunctional metalloligand by using coordinated thiolato and free amine and carboxylate groups, forming a variety of heterobimetallic and heterotrimetallic species.[6] For example, a cage-type metallosupramolecular compound that contains all

group 11 metal ions (Au^I, Ag^I, and Cu^{II}) has been synthesized by the stepwise reaction of [Au(D-pen)$_2$]$^{3-}$ with Ag$^+$ and Cu^{2+}.[6a] This was the first example of a heterotrimetallic coordination compound consisting of all group 11 metal ions. Other heterotrimetallic compounds that consist of all metal ions belonging to the same group have rarely been synthesized.[7] Recently, we found that a newly prepared Pt^{II} metalloligand with D-pen, trans-[Pt(NH$_3$)$_2$(D-pen)$_2$]$^{2-}$ ([1]$^{2-}$), in which the Au^I linker in [Au(D-pen)$_2$]$^{3-}$ is replaced by a trans-{Pt^{II}(NH$_3$)$_2$}$^{2+}$ moiety, also acts as a multifunctional metalloligand.[8] This finding prompted us to investigate the reactivity of [1]$^{2-}$ toward Pd^{2+} and Ni^{2+} to create a heterotrimetallic compound containing all group 10 metal ions (Pt^{II}, Pd^{II}, and Ni^{II}) in one molecule. Here, we report that [1]$^{2-}$ reacts with Pd(OAc)$_2$ to afford a Pt$_2^{II}$Pd$_2^{II}$ tetranuclear complex ([2]), which further reacts with NiCl$_2$ to produce a Pt$_2^{II}$Pd$_2^{II}$Ni^{II} coordination polymer ([3]Cl$_2$) (Scheme 1). Remarkably, [3]Cl$_2$ showed excellent catalytic activity for electrochemical hydrogen evolution compared with [1]$^{2-}$ 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(NH$_3$)$_2$(D-Hpen)$_2$] ([H$_2$1]) with Pd(OAc)$_2$ in H$_2$O gave an orange solution, from which yellow crystals ([2]) were isolated. The ^{1}H NMR spectrum of [2] displayed only a

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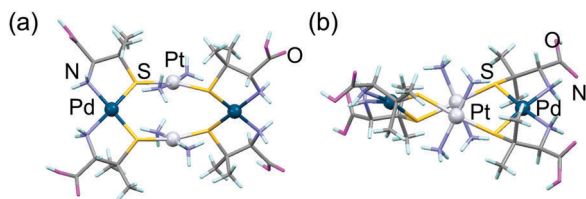

Scheme 1 Synthetic route of [2] and [3]$^{2+}$ via [1]$^{2-}$.

Fig. 1 (a) Top and (b) side views of the molecular structure of $[H_42]^{4+}$.

Fig. 2 1D chain heterotrimetallic structure in $[3]^{2+}$.

single set of signals (δ 1.43, 1.56, and 3.35 ppm) due to D-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†).[9] The elemental analytical data of [2] were in agreement with a neutral formula containing $[1]^{2-}$ and Pd^{II} in a 1:1 ratio. Single crystals of [2] suitable for X-ray crystallography were obtained as the protonated form, $[H_42]Cl_4$. The asymmetric unit of $[H_42]Cl_4$ contains one complex cation and four chloride anions, besides solvated water molecules. As shown in Fig. 1, the complex cation has an S-bridged Pt$^{II}_2$Pd$^{II}_2$ tetranuclear structure in $[Pd_2Pt_2(NH_3)_4(D\text{-}Hpen)_4]^{4+}$, consisting of two metalloligands with protonated carboxyl groups ($[H_21]$) and two Pd^{II} atoms. Each of the two metalloligands span two Pd^{II} atoms in a bis(bidentate-N,S) mode, such that each Pd^{II} centre has a square planar geometry with a cis-N_2S_2 donor set (av. Pd–N: 2.084 Å, Pd–S: 2.272 Å). The Pt$\cdots$Pt distance in $[H_42]^{4+}$ is 3.300 Å, indicating the lack of an intramolecular Pt$\cdots$Pt interaction.[10] Each NH$_3$ ligand is hydrogen-bonded with a D-pen thiolato group (av. $N_{NH_3}\cdots S$ = 3.46 Å), which appears to stabilize the Pt$^{II}_2$Pd$^{II}_2$ structure in [2]. Here, it should be noted that the ^{1}H NMR spectral features of the reaction solution are the same as those of isolated [2] (Fig. S1, ESI†), indicating that only a single isomer with two cis-[PdN$_2$S$_2$] planes is selectively formed by the reaction of $[H_21]$ with Pd^{2+}. This result is different from the corresponding reaction of $[Au(D\text{-}pen)_2]^{3-}$ with Pd^{2+}, which produced a mixture of cis and $trans$ isomers of $[Au_2Pd_2(D\text{-}pen)_4]^{2-}$.[6c] The overall structure of $[H_42]^{4+}$ resembles that of the cis isomer of $[Au_2Pd_2(D\text{-}pen)_4]^{2-}$. However, all of the bridging S atoms in $[H_42]^{4+}$ have the R configuration and form a twisted Pt$^{II}_2$Pd$^{II}_2$S$_4$ framework with a D_2 molecular symmetry (Fig. 1). In contrast, cis-$[Au_2Pd_2(D\text{-}pen)_4]^{2-}$ has two S and two R configurational bridging S atoms, forming a boat-like framework with a C_2 symmetry.[6c] While a number of S-bridged M$_2$M$_2'$ tetranuclear complexes with two MN$_2$S$_2$ square-planes have been prepared and structurally characterized,[11] the formation of the twisted form is rare. Molecular model examinations revealed that, in $[H_42]^{4+}$, there exist steric repulsions between the NH$_3$ ligand and the methyl group of a D-pen ligand in the $trans$ isomer and the boat and chair forms of the cis isomer (Fig. S3, ESI†).

To create a heterotrimetallic coordination compound containing all group 10 metal ions (Pt^{II}, Pd^{II}, and Ni^{II}), [2] was reacted with NiCl$_2$ in water. This reaction gave a clear green solution, from which yellow crystals of $[3]Cl_2$ were obtained. X-ray fluorescence analyses indicated the presence of Pt, Pd, and Ni atoms in $[3]Cl_2$, and its elemental analytical data were consistent with a formula containing [2] and NiCl$_2$ in a 1:1 ratio. The IR spectrum of $[3]Cl_2$ showed a strong
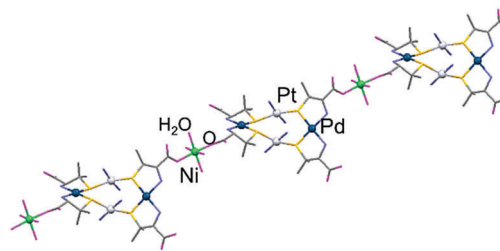
absorption band at 1640 cm^{-1}, indicating the presence of deprotonated carboxylate groups (Fig. S2, ESI†).[9] The structure of $[3]Cl_2$ was established by a single-crystal X-ray diffraction study. The asymmetric unit of $[3]Cl_2$ contains one $[Pd_2Pt_2(NH_3)_4(D\text{-}pen)_4]$ molecule, one Ni^{II} ion, and two chloride anions, besides solvated water molecules. As shown in Fig. 2, the overall structure of the Pt$^{II}_2$Pd$^{II}_2$ tetranuclear molecule in $[3]Cl_2$ is essentially the same as that of $[H_42]Cl_4$. However, the four carboxyl groups of the Pt$^{II}_2$Pd$^{II}_2$ molecule in $[3]Cl_2$ are deprotonated, consistent with the IR spectral feature. In addition, two of these groups each coordinate to a Ni^{II} ion to form a cationic 1D chain structure in $[\{Ni(H_2O)_4\}\{Pd_2Pt_2(NH_3)_4(D\text{-}pen)_4\}]^{2+}$ (Fig. 2). Note that $[3]Cl_2$ is the first example of a structurally characterized coordination compound with all three group 10 metal ions. In $[3]^{2+}$, each Ni^{II} ion is bound by four aqua ligands and two carboxylate groups in a $trans$ octahedral geometry (av. Ni–O$_{COO^-}$: 2.064 Å, Ni–O$_{water}$: 2.093 Å). The chloride ions are not involved in the coordination and are located between the Pt$^{II}_2$Pd$^{II}_2$Ni^{II} chains, forming hydrogen bonds with ammine groups and water molecules (av. Cl$\cdots N_{NH_3}$: 3.29 Å, Cl$\cdots$O$_{water}$: 3.09 Å, Fig. S3, ESI†).

The catalytic property of $[3]Cl_2$ in the solid state was electrochemically investigated, and the results were compared with those of $[H_21]$ and [2]. The linear sweep voltammetry of a solid sample of $[3]Cl_2$, attached to the surface of a glassy carbon electrode (0.07 cm^2), in H$_2$O/CH$_3$CN (v/v = 1/9) containing 0.1 M LiClO$_4$ 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).[12] However, a solid sample of $[H_21]$ 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,[13] the activity of which drastically increases in the following order: $[H_21] < [2] < [3]Cl_2$. During the voltammetric scans, the evolution of bubbles from the electrode surface was observed for [2] and $[3]Cl_2$. The bubbles were analyzed using gas chromatography (GC) and found to be H$_2$ gas (Fig. S5, ESI†). Such an evolution of bubbles, as well as a current increase, was not detected when absolute CH$_3$CN was used as the solvent instead of H$_2$O/CH$_3$CN (Fig. S6, ESI†). Thus, [2] and $[3]Cl_2$ catalyze the electrochemical reduction of water to produce H$_2$ gas. These are relatively few examples of coordination compounds that exhibit a heterogeneous catalytic activity for H$_2$ gas evolution on an electrode surface.[14] Considering that $[H_21]$ is significantly less active for catalytic reduction of water
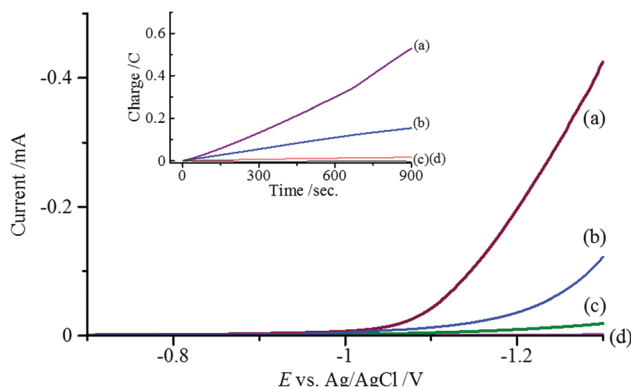
Fig. 3   Linear sweep voltammograms of (a) [**3**]Cl$_2$, (b) [**2**], and (c) [H$_2$**1**] attached to a glassy carbon electrode (0.07 cm^2), and (d) a bare glassy carbon electrode, in H$_2$O–CH$_3$CN (v/v = 1/9) containing 0.1 M LiClO$_4$. The scan rate is 0.01 V s^{-1}. Inset: charge build-up *versus* time in extended potential-controlled electrolysis experiments at an applied potential of −1.20 V.

than [**2**] and [**3**]Cl$_2$, the catalytic reaction mainly occurs at the Pd^{II} centre of the [Pd(D-pen)$_2$]$^{2-}$ square-planes. It has been proposed that Pd is the best alternative to Pt in catalytic systems for H$_2$ evolution.[15] However, examples reporting catalytic hydrogen evolution are limited to several homogeneous catalytic systems,[16] and this is the first Pd^{II} coordination system that evidences heterogeneous catalytic H$_2$ evolution.

To evaluate the H$_2$ evolution rate, potential-controlled electrolyses were 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 [H$_2$**1**] < [**2**] < [**3**]Cl$_2$, which is in parallel with the voltammetric results (Fig. 3). The turnover frequency (TOF) of H$_2$ (mol H$_2$/mol cat) was calculated to be 3.73, 18.2, and 34.4 mol min^{-1} cm^{-2} for [H$_2$**1**], [**2**], and [**3**]Cl$_2$, respectively. The GC analysis indicated that the amount of H$_2$ gas generated during the electrolysis using [**2**] and [**3**]Cl$_2$ was 1.56 μmol and 2.88 μmol, respectively. From these values, the Faraday efficiencies for [**2**] and [**3**]Cl$_2$ were calculated to be 81% and 100%, respectively, indicating that no side redox reaction occurs during the electrolysis for [**3**]Cl$_2$. 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**]Cl$_2$, the D-pen carboxylate group coordinates to a Ni^{II} centre, which might lead to an increase of the Lewis acidity around a Pd^{II} catalytic centre.[18]

In summary, we showed that the metalloligand *trans*-[Pt(NH$_3$)$_2$-(D-pen)$_2$]$^{2-}$ ([**1**]$^{2-}$) reacts with Pd^{II} to afford an S-bridged Pt$_2^{II}$Pd$_2^{II}$ complex, [Pd$_2$Pt$_2$(NH$_3$)$_4$(D-pen)$_4$] ([**2**]), which exclusively forms a twisted isomer consisting of *cis*-[Pd(D-pen)$_2$]$^{2-}$ planes. This coordination behaviour is due to the presence of two NH$_3$ ligands bound to each Pt^{II} centre, exerting non-bonding steric and NH$\cdots$S hydrogen bonding interactions. Complex [**2**] acts as an O-donating metalloligand to Ni^{II} to create a Pt$_2^{II}$Pd$_2^{II}$Ni^{II} coordination polymer, [{Ni(H$_2$O)$_4$}{Pd$_2$Pt$_2$(NH$_3$)$_4$(D-pen)$_4$}]Cl$_2$ ([**3**]Cl$_2$), 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 Pd^{II} and Ni^{II} centres with [**1**]$^{2-}$, 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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18 A solid sample of $Ni(CH_3COO)_2 4H_2O$, which has essentially the same octahedral *trans*-$[Ni(RCOO)_2(H_2O)_4]$ structure as that in [**3**]Cl_2, 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 Ni^{II} center in [**3**]Cl_2 also acts as an active site for the electrochemical hydrogen evolution.