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Synthesis, X-ray structures, and photoluminescence of heterometal trinuclear Hg(II)–Pt(I) and tetranuclear Hg(II)–Pd(I) complexes

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ABSTRACT

A heterometallic trinuclear complex with monovalent platinum consisting of a [Pt₂Hg] cluster bridged by two μ₃-Cl atoms and another tetranuclear complex with monovalent palladium owning the structural core of open cubane-like [Hg₂Pd₂Cl₂]₂ framework were synthesized by self-assembly reactions.

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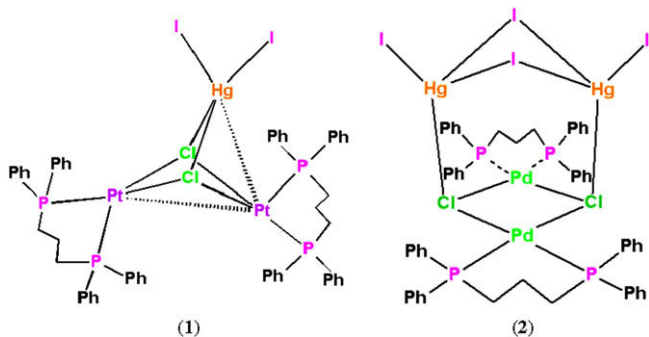
The selective, direct assembling of heterometal structures is a challenging area of synthetic chemistry that has numerous implications in optical properties [1], molecular magnetism [2], reactivity [3], and catalysis [4] requiring multiple metal sites as well as in bioinorganic chemistry [5]. The structural study of heterometal systems with heavy metal atoms including Pd, Pt, and Hg associating with each other have been gaining considerable attention [6]. Among these reported Pt–Hg or Pd–Hg heterometal systems, the oxidation states of both Pd and Pt are 0 and +2, and the electronic configurations for Pd(0) and Pt(0) are d¹⁰s⁰ and d⁹s¹, respectively, Pd(II) and Pt(II) d⁸s⁰. In contrast, there have been only limited reports of solid-state Pt–Hg or Pd–Hg heterometal structures with d⁹s⁰ electronic configuration of Pd(I) or Pt(I) in the literature. Finding convenient preparation of these heterometal complexes is still an interesting goal. In addition, both Pd(I) and Pt(I) complexes have important potential applications in organometallic catalysis [7a–7d] as a result of their ability to react with a wide range of substrates. Some structures of heterobimetallic complexes containing Pd(I) or Pt(I) have been reported [7e,7f]. We therefore are interested in developing systematic methods of preparing new heterometal cluster complexes with d⁹s⁰ electronic configuration of Pd(I) or Pt(I). Here we describe the simple syntheses, crystal structures and optical properties of heterometal trinuclear platinum–mercury cluster and tetranuclear palladium–mercury complex with d⁹ and d¹⁰ electronic configurations.

A yellow air-stable platinum–mercury cluster, [HgPt₂(dppp)₂(μ₃-Cl)₂](DMF)(H₂O) (**1**) (dppp = 1,3-bis(diphenylphosphine)propane), is synthesized directly by the reaction of H₂[PtCl₆](H₂O)₆ with HgI₂ and dppp ligand in ethanol–DMF–pyridine mixed solvent (see Appendix A. Supplementary materials). In the similar synthetic conditions, one-pot reaction of Pd(PPh₃)₂Cl₂, HgI₂, and AgCl in the presence of dppp ligand gives rise to a deep-red air-stable palladium–mercury complex, Hg₂Pd₂(μ₃-Cl)₂(dppp)₂L₄ (**2**) with the formation of colorless cubane-like structure Ag₄Cl₄(PPh₃)₄ [8] as a by-product. It is noteworthy that the use of other silver(I) halide such as AgBr or AgI instead of AgCl also affords **2** in similar yield with the generation of Ag₄X₄(PPh₃)₄ (X = Br[−] or I[−], respectively). Obviously, the formations of **1** and **2** involve Pd(II) or Pt(IV) reduction. While it is possible that PPh₃ or dppp is the only reducing agent in the reaction system, the solvent ethanol is most likely involved [9]. Reduction of Pt(IV) and Pd(II) complexes by alcohols has long been known [10]. Experimentally, the addition of other reducing agents, such as NaBH₄ or LiAlH₄, causes directly the formation of black palladium(0) or platinum(0) precipitation, because the corresponding reducing agent is not mild and the reaction is difficult to control.

X-ray single-crystal diffraction analysis [11] reveals that the structural core of **1** can be viewed as a triangle arrangement of three metal atoms (Hg(1)–Pt(1)–Pt(2)) with two chloride ions functioning as μ₃-ligands capping the three metal ions, respectively (Scheme 1 and Fig. 1). The linear Cl–Cl is perpendicular to the plane of the Pt₂Hg triangle with which they form an angle of 180°. Each chlorine atom is displaced 1.568 Å from the triangle plane. The Pt···Pt distance of 3.1962(4) Å in **1** is in the higher range

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Scheme 1. Structures of the title complexes.

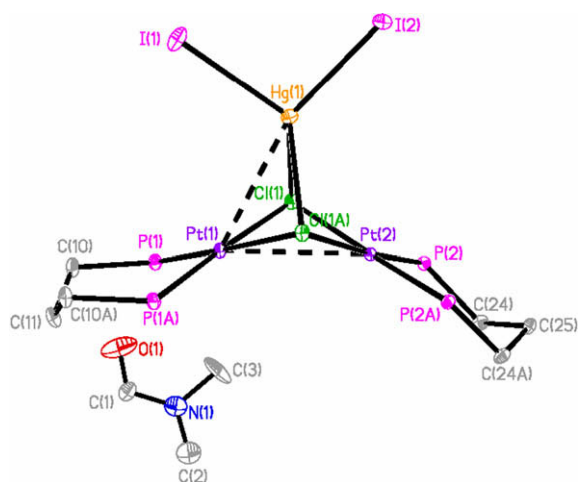


Fig. 1. View of the molecular structure of **1**. Phenyl groups, water molecule and all hydrogen atoms have been omitted for clarity. Ellipsoids enclose 40% of the electron density. Selected distances (Å): Pt(1)–P(1) 2.246(1), Pt(1)–Cl(1) 2.368(1), Pt(1)–Hg(1) 3.1744(4), Pt(1)–Pt(2) 3.1962(4), Hg(1)–Pt(2) 3.407(1), Pt(2)–P(2) 2.260(1), Pt(2)–Cl(1) 2.366(1), Hg(1)–Cl(1) 2.632(1), Hg(1)–I(1) 2.8103(6), Hg(1)–I(2) 2.7344(7).

of the values found for Pt–Pt single bonds [12], but shorter than the sum of van der Waals radii of Pt ($r_{vdw}(\text{Pt}) = 1.70 \text{ \AA}$) [13] and is suggestive of an intramolecular weak interaction between the two metal platinum centers. The Hg...Pt separations in the triangle are Hg(1)...Pt(1) = 3.1744(4) and Hg(1)...Pt(2) = 3.407(1) Å, respectively. The former Hg–Pt separation is fairly longer than the corresponding distances of 2.824 and 2.643 Å for the reported complexes [HgPt{Si(OMe)₃}Fe₂(CO)₆{Si(OMe)₃}(μ-dppm)₂] [14], Hg[Pt₃(2,6-Me₂C₆H₃NC)₆]₂ [15], respectively, but still comparable to those observed in other Hg–Pt clusters [15,16], possibly indicative of a weak metallophilic interaction. Whereas the latter is very close to the sum of the van der Waals radii for mercury ($r_{vdw}(\text{Hg}) = 1.73 \text{ \AA}$) [17] and platinum ($r_{vdw}(\text{Pt}) = 1.70 \text{ \AA}$) [13], which indicates little or no metallophilic interaction. The coordination geometry around the platinum(I) atoms is best described as an approximately square-planar arrangement coordinated by two P donors from dppp ligand and two μ₃-Cl ions (P(1)–Pt(1)–Cl(1A) = 173.77(4)°, P(2A)–Pt(2)–Cl(1) = 173.57(4)°, symmetry codes: A x, –y + 1/2, z), while the mercury(II) atom is four-coordinate, surrounded by two terminal I[–] ions and two μ₃-Cl[–] ions to form a slightly distorted tetrahedron. The Pt–Cl and Pt–P distances are essentially identical to those reported complexes [18]. The Hg–I and Hg–Cl bond lengths are in the ranges 2.7344(7)–2.8103(6) and 2.632(1) Å, respectively. To the best of our knowledge, **1** is the first report of Cl atoms bridging two Pt atoms and one Hg atom simultaneously.

The formation of **2** is thought to involve dinuclear intermediate states, which undergo dimeric assemblies. A possible pathway for the reaction is shown in Scheme S1. The Pd(dppp)₂Cl₂ [19] (thought to be generated by the reaction of Pd(PPh₃)₂Cl₂ and dppp) as a common building fragment as well as a starting material has the tendency to form a rhomboidal fragment under the reduction conditions. The rhomboidal fragment could bind the other dinuclear iodo-bridged fragment [Hg₂I₄] to further form a cubane-like heterometallic complex as in **2** by the unit-construction method [20], a convenient method that uses reactive fragments as building blocks to obtain clusters. The molecular structure of **2** is illustrated in Fig. 2, which provides an atomic numbering scheme for important atoms. **2** consists of a planar Pd₂(dppp)₂Cl₂ core with out-of-plane Hg₂I₄ fragment linearly coordinated to the chlorine atoms in a *syn* orientation and the cluster skeleton can be viewed as a cubane-like [Hg₂Pd₂Cl₂I₂] (Scheme 1 and Fig. 2). In the planar Pd₂(dppp)₂Cl₂, each palladium(I) atom has a *cis*-quasi-square coordination geometry, with two phosphorus donors of dppp and two bridging chloride donors. The Pd–Cl distances (2.363 Å average) are in the region of those for the parent monomer Pd(dppp)Cl₂ (2.360 Å average). The Pd–P distances (2.281 Å average) are slightly shorter than those in Pd(dppp)Cl₂ (2.247 Å average). In the Hg₂I₄ fragment displaying a butterfly-shaped unit, each Hg(II) center lies in a distorted tetrahedral environment formed by two μ-I atoms (Hg–I bond distances ranging from 2.9898(8) to 3.0903(8) Å), one terminal I atom (Hg(1)–I(4) = 2.6415(6) Å and Hg(2)–I(3) = 2.6606(7) Å) and one μ₃-Cl atom (Hg(1)–Cl(2) = 2.425(2) Å and Hg(2)–Cl(1) = 2.428(2) Å). These bond lengths are consistent with those of the reported mercury(II) complexes [21]. The intramolecular Pd...Pd, Pd...Hg, and Hg...Hg distances in **2** are 3.428, 3.708 and 3.728 Å, respectively. These contacts are apparently longer than the van der Waals contact distances of two metal atoms, indicating no intramolecular weak interaction between the two metal palladium centers and no metallophilic interactions.

Recent interest in luminescent metal complexes has mostly focused on polynuclear Cu(I), Ag(I), and Au(I) complexes with d¹⁰ configurations, which stems from the tendency of these metal ions to form clusters and aggregates as a result of weak metal–metal interactions [22] and a number of these aggregates exhibit rich luminescence behavior in the solid state at ambient temperature

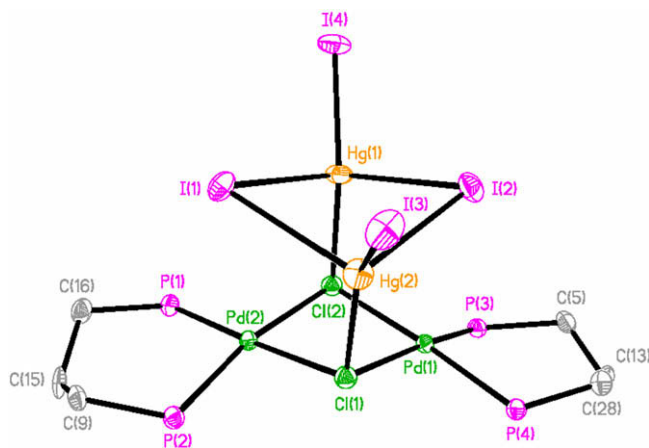


Fig. 2. View of the molecular structure of **2**. Phenyl groups and all hydrogen atoms have been omitted for clarity. Ellipsoids enclose 40% of the electron density. Selected distances (Å): Hg(1)–Cl(2) 2.425(2), Hg(1)–I(1) 3.0681(6), Hg(1)–I(2) 2.9898(8), Hg(1)–I(4) 2.6415(6), Hg(2)–Cl(1) 2.428(2), Hg(2)–I(1) 3.0903(8), Hg(2)–I(2) 3.0278(7), Hg(2)–I(3) 2.6606(7), Pd(1)–P(3) 2.271(2), Pd(1)–P(4) 2.284(2), Pd(1)–Cl(1) 2.367(2), Pd(1)–Cl(2) 2.362(2), Pd(2)–P(1) 2.288(2), Pd(2)–P(2) 2.281(2), Pd(2)–Cl(1) 2.370(2), Pd(2)–Cl(2) 2.354(2).

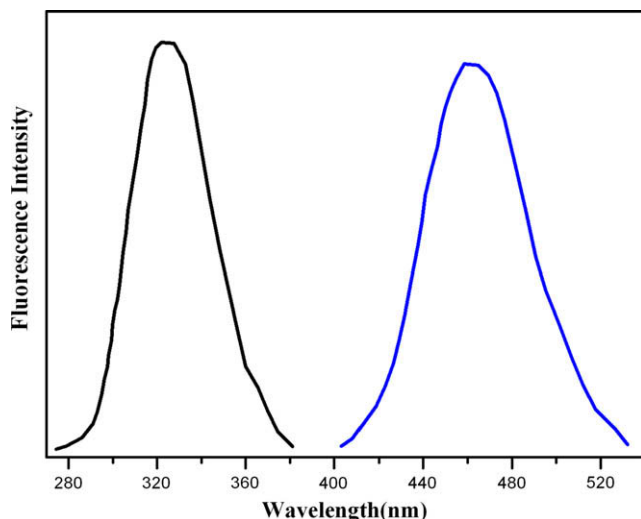


Fig. 3. Solid-state excitation and emission spectra of **1** at room temperature. Black line (left): excitation spectrum; blue line (right): emission spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[23]. In contrast, the luminescent properties of heterometallic complexes in the d^9/d^{10} system have received rare attention. **1** and **2** are stable in air and insoluble in water and most organic solvents, so as to no additional measurements of luminescence in solution could be performed. Interestingly, **1** shows strong blue fluorescent emission band in the solid state at 460 nm upon photo-excitation at 325 nm at room temperature (Fig. 3). The emission may be tentatively assigned as ligand-to-metal–metal charge transfer (LMMCT) character [24] that mix with metal-centered states which are modified by Pt(I)···Pt(I)···Hg(II) interactions. Unlike in **1**, no photoluminescence is observed in **2**. The possible reason is that no metalophilic interactions exist in **2**.

In summary, we report a facile synthesis of two heterometallic complexes with d^9 and d^{10} electronic configurations, namely, $[\text{HgPt}_2(\mu_3\text{-Cl})_2\text{I}_2(\text{dppp})_2](\text{DMF})(\text{H}_2\text{O})$ and $\text{Hg}_2\text{Pd}_2(\mu_3\text{-Cl})_2\text{I}_4(\text{dppp})_2$. These complexes illustrate the success of our synthetic strategy to design a series of d^9/d^{10} heterometallic systems. Furthermore, this class of complexes is revealed to be good potential luminescent materials.

Acknowledgments

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Appendix A. Supplementary materials

CCDC 687024 and 687026 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.08.017.

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- [11] Crystal data for **1**: empirical formula $\text{C}_57\text{H}_{61}\text{NO}_2\text{Cl}_2\text{P}_4\text{I}_2\text{HgPt}_2$, $M_r = 1831.42$, monoclinic, space group $P2_1/m$ (No. 12), $a = 11.0433(2)$, $b = 14.8811(2)$, $c = 18.0227(3)$ Å, $\beta = 97.375(1)$, $V = 2937.28(8)$ Å³, $T = 173(2)$ K, $Z = 2$, $D_c = 2.071$ g cm⁻³, $\mu(\text{MoK}\alpha) = 8.650$ mm⁻¹, $F(000) = 1724$, 18,543 reflections measured, 5926 unique ($R_{\text{int}} = 0.0371$) which were used in all calculations. Refinement converged as a final $R = 0.0259$ ($wR_2 = 0.0566$) for 4631 observed reflections [$I > 2\sigma(I)$]. Crystal data for **2**: $\text{C}_{54}\text{H}_{52}\text{Cl}_2\text{Hg}_2\text{I}_4\text{P}_4\text{Pd}_2$, $M_r = 2017.32$, orthorhombic, space group $P2_12_12_1$, $a = 14.5357(3)$, $b = 16.7723(3)$, $c = 24.3133(4)$ Å, $V = 5927.5(2)$ Å³, $T = 173$ K, $Z = 4$, $D_c = 2.261$ g cm⁻³, $\mu(\text{MoK}\alpha) = 8.077$ mm⁻¹, $F(000) = 3736$, 22,181 reflections measured, 10,172 unique ($R_{\text{int}} = 0.0336$) which were used in all calculations. Refinement converged as a final $R = 0.0288$ ($wR_2 = 0.0443$) for 4631 observed reflections [$I > 2\sigma(I)$]. Crystal data were measured on a Bruker SMART 2000 CCD diffractometer using the ω scan mode with MoK α radiation $\lambda = 0.71073$ Å. These structures were solved by direct methods and refined anisotropically on F^2 (G.M. Sheldrick, SHELXS-97 and SHELXL97, University of Göttingen, Germany, 1997).
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