

## Gold(III) and Platinum(II) Polypyridyl Double Salts and a General Metathesis Route to Metallophilic Interactions

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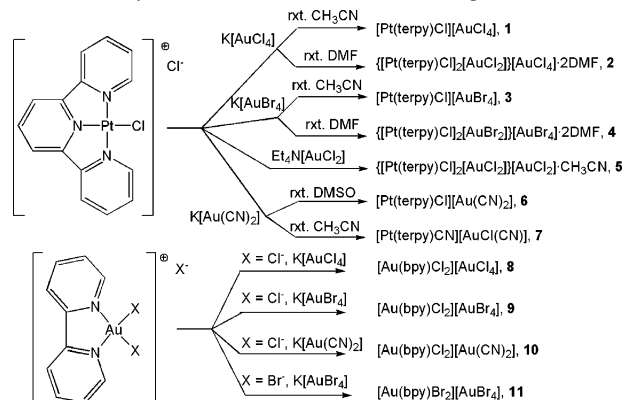
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Nine new double-salt compounds have been prepared and six crystal structures are reported that demonstrate a general metathesis route to double-salt compounds with metallophilic interactions. The compounds contain  $[\text{Pt}(\text{terpy})\text{X}]^+$  or  $[\text{Au}(\text{bpy})\text{X}_2]^+$  cations,  $\text{Au}^{\text{III}}$  or  $\text{Au}^{\text{I}}$  anions such as  $[\text{AuBr}_4]^-$  or  $[\text{AuCl}_2]^-$ , and are prepared in water and recrystallized from organic solvents. In all crystallographically characterized cases, there exist metallophilic interactions between cations and anions, demonstrating the power of this general route. In most cases, there exists an unbroken chain of metallophilic interactions through the crystal, forming single-atom-wide wires.

Metallophilic interactions<sup>1</sup> are increasingly appreciated as a type of closed-shell interaction that can be used deliberately to form metal–metal contacts. These interactions are observed between metals with  $d^{10}$  and  $d^8$  electron configurations.<sup>2</sup> Contacts between metals have particular potential in the field of molecular electronics.<sup>3</sup> Metal–metal contacts have inherently good energetic overlap and can be efficient conductors with an appropriately tailored electronic population.<sup>4</sup> Previously, much work had been done on linear chains of  $[\text{Pt}(\text{CN})_4]^{2-}$  anions, whose conductivity increases substantially upon partial oxidation of Pt with halogens.<sup>5</sup> Our goal is to make compounds with linear metal atom chains without noncoordinated ions.

We have developed a general metathetical approach to double-salt compounds that lead to metallophilic interactions and contain single-atom-wide wires extending to submillimeter length in the single-crystal form. Halide salts of polypyridyl-containing  $\text{Pt}^{\text{II}}$  or  $\text{Au}^{\text{III}}$  cations such as  $[\text{Pt}(\text{terpy})\text{Cl}]^+$  or  $[\text{Au}(\text{bpy})\text{X}_2]^+$  ( $\text{X} = \text{Cl}, \text{Br}$ ) are combined in water

Scheme 1. Syntheses of Double Salts with Metallophilic Interactions



with K salts of  $\text{Au}^{\text{III}}$  or  $\text{Au}^{\text{I}}$  anions such as  $[\text{AuCl}_4]^-$  or  $[\text{Au}(\text{CN})_2]^-$ , as depicted in Scheme 1. The metal-containing products precipitate rapidly and can be recrystallized from polar organic solvents.

These double salts have several design features that facilitate the formation of extended linear chains of metallophilic interactions while minimizing the number of possible electron-transfer paths. First, both the cation and anion can participate in the metal–metal contact formation such that all ions are part of the chain and leave no extra possible charge carriers. Second, both ions are chosen to have linear or planar geometries, namely,  $[\text{AuX}_2]^-$  anions, polypyridyl-containing cations, or  $[\text{AuX}_4]^-$  anions. No chelating ligands are used to bring the metal ions together.<sup>6</sup> Third, with singly charged cations and anions, rather than di-ionic<sup>7</sup>  $[\text{Pt}(\text{CNR})_4]^{2+}$  or  $[\text{PtX}_4]^{2-}$  ions, the compounds have sufficient solubility to be recrystallized under ambient conditions. Finally, anticipating future conductivity studies of these compounds, the choice of aprotic ligands (in contrast<sup>8</sup> to  $[\text{Pt}(\text{NH}_2\text{R})_4]^{2+}$ ) with limited potential for H bonding between ions or chains reduces the number of possible alternative electron-transfer paths.

The synthesis reactions proceed in time of mixing at room temperature (see the Supporting Information) and are re-

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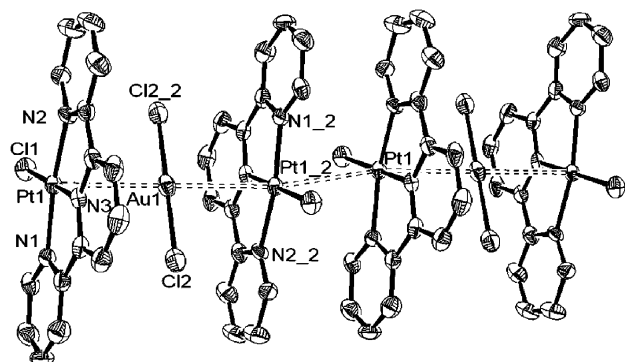
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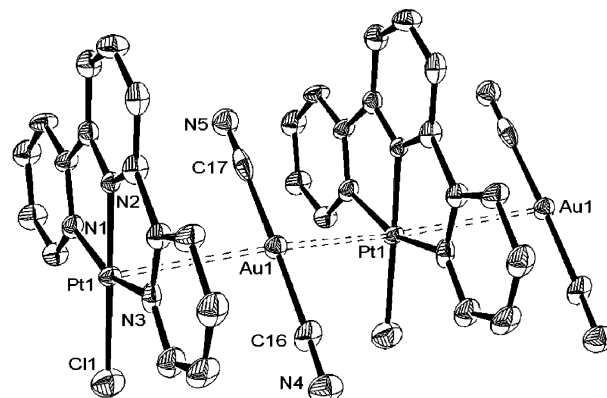


**Figure 1.** ORTEP of two  $\{[Pt(terpy)Cl_2][AuCl_2]\}^+$  cations from **2**. H atoms are not shown for clarity. Selected distances (Å) and angles (deg): Pt1–Au1, 3.284(1); Au1–Cl2, 2.268(2); Pt1–Pt1<sub>2</sub>, 3.447(1); Au1–Pt1<sub>2</sub>–Pt1, 170.58(3).

crystallized from polar, aprotic media including dimethylformamide (DMF),  $CH_3CN$ , or dimethyl sulfoxide. Recrystallization of  $[Pt(terpy)Cl][AuCl_4]$  (**1**) from  $CH_3CN$  gave analytically pure material, but the yellow needles were too thin for X-ray crystallography with a Mo  $K\alpha$  source. Recrystallization from DMF led to red crystals of the new salt  $\{[Pt(terpy)Cl_2][AuCl_2]\}[AuCl_4 \cdot 2DMF]$  (**2**), in which some of the  $Au^{III}$  ions have been reduced to  $Au^I$  by the solvent. The crystal structure of **2** in Figure 1 reveals an infinite chain of  $\{[Pt(terpy)Cl_2][AuCl_2]\}^+$  cations. An  $[AuCl_2]^-$  anion is bound between two  $[Pt(terpy)Cl]^+$  cations, within which there is a unique  $Au \cdots Pt$  distance of 3.284(1) Å. The Pt1–Au1–Pt1<sub>2</sub> angle is constrained crystallographically to be linear, and the Au1–Pt1<sub>2</sub>–Pt1 angle is 170.58(3)°. The intercation Pt1–Pt1<sub>2</sub> distance is 3.447(1) Å, consistent with other such crystallographically characterized Pt $\cdots$ Pt pairings in  $[Pt(terpy)Cl]^+$  systems.<sup>9–14</sup> The  $[AuCl_4]^-$  anion maintains the charge balance but does not exhibit any metallophilic interactions, consistent with previous observations<sup>15</sup> that more electron-rich metal centers, i.e.,  $Au^I$  vs  $Au^{III}$ , are more likely to be observed in metallophilic contact. The DMF solvent molecule also exhibits no close contacts to any other species.

An analogous bromide derivative,  $[Pt(terpy)Cl_2][AuBr_2][AuBr_4] \cdot 2DMF$  (**4**), has been prepared similarly. This compound is isostructural with the chloride analogue and exhibits a slightly longer  $Au \cdots Pt$  distance of 3.318(1) Å.

The same  $\{[Pt(terpy)Cl_2][AuCl_2]\}^+$  cations with virtually identical interactions have also been observed in the crystal structure of  $[Pt(terpy)Cl][AuCl_2]$  (**5**; see the Supporting Information), which has one  $[AuCl_2]^-$  counterion per  $\{[Pt(terpy)Cl_2][AuCl_2]\}^+$  cation. The  $Au \cdots Pt$  distance is 3.268(1) Å, the Pt $\cdots$ Pt interaction distance is 3.453(1) Å, the Pt–



**Figure 2.** ORTEP of two asymmetric units of **6**. Selected distances (Å): Pt1–Au1, 3.349(1); Pt1–N1, 2.023(9); Pt1–N2, 1.929(9); Pt1–N3, 2.046(10); Pt1–Cl1, 2.296(4); Au1–Cl16, 1.997(13); Au1–Cl17, 2.004(17). Selected angles (deg): Pt1–Au1–Pt1, 147.83(3); Cl16–Au1–Cl17, 176.6(6); N1–Pt1–N3, 161.0(4); N2–Pt1–Cl1, 179.0(3).

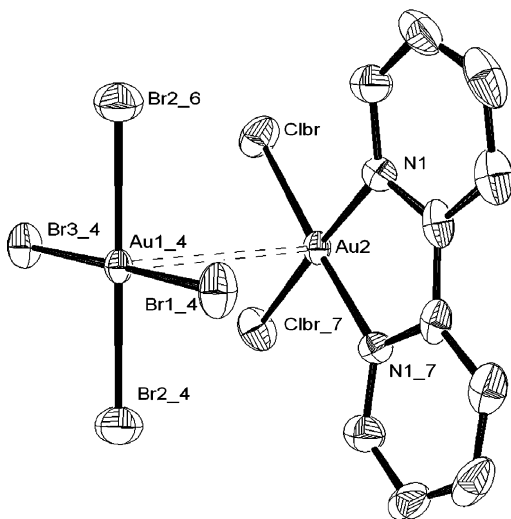
Au–Pt angle is constrained again crystallographically to be linear, and the Au–Pt–Pt angle is 165.10(3)°. There is also one molecule of  $CH_3CN$  in the structure. The structures of **2** and **4** show the exclusion of  $Au^{III}$ -containing anions from the metallophilic chain of atoms, but intriguingly in **5** half of the  $Au^I$ -containing  $[AuCl_2]^-$  anions are not part of the chain. Computational studies are underway to explore in detail the energetic factors involved.<sup>16</sup>

A compound with the same  $[Pt(terpy)Cl]^+$  cation and only metallophilically bonded  $Au^I$  anions is exemplified by  $[Pt(terpy)Cl][Au(CN)_2]$  (**6**), shown in Figure 2. The unique Pt $\cdots$ Au distance is 3.349(1) Å, and the Pt1–Au1–Pt1 angle is noticeably nonlinear at 147.83(3)° because of the steric pressure of a terpyridine group in the adjacent unit cell (see the Supporting Information). No solvent is present in the crystal, and the  $\{Pt \cdots Au\}_\infty$  repeat forms an infinite chain through the crystal. It is notable that the metallophilic contacts in **6** form preferentially over bridging cyanide ligands between the Au and Pt atoms. The IR  $C \equiv N$  stretch is observed at 2139  $cm^{-1}$ .

Recrystallization of **6** from hot  $CH_3CN$  gave the isomeric compound  $[Pt(terpy)(CN)[AuCl(CN)]]$  (**7**), which has also been characterized crystallographically<sup>17</sup> and shown to be very similar to **6**. Both UV–vis and IR data (2139 and 2132  $cm^{-1}$ ) are consistent with the presence of two different cyanide binding modes, although the X-ray structure of **7** suggests some disorder in the anionic ligands. Because no extra anions are present during the recrystallization, it is likely that the exchange is incomplete and different crystals have slightly different occupancies. This report is the first crystallographic characterization of either the cation or anion, although the cation has been reported and spectroscopically characterized previously.<sup>18,19</sup> The monodentate ligand ambiguity prevents a publishable structure from being reported, but the structure of **7** is very similar to that of **6** including a Pt–Au distance of  $\sim 3.34$  Å and the Pt–Au–Pt angle again is bent at  $\sim 152^\circ$ .

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**Figure 3.** ORTEP of **9**. Selected distances (Å) and angles (deg): Au2...Au1\_4, 3.518(1); Au–Cl,Br, 2.2975(17); Au2–Au1\_4–Br3\_4, 97.41(3).

Metathetic syntheses with the  $[\text{Au}(\text{bpy})\text{X}_2]^+$  cations ( $\text{X} = \text{Cl}, \text{Br}$ ) have also been carried out. The exogenous halide anions were readily exchanged with metal-containing anions such as  $\text{K}[\text{AuBr}_4]$  to give  $[\text{Au}(\text{bpy})\text{Cl}_2][\text{AuBr}_4]$  (**9**). The compounds  $[\text{Au}(\text{bpy})\text{Cl}_2][\text{AuCl}_4]$  (**8**) and  $[\text{Au}(\text{bpy})\text{Br}_2][\text{AuBr}_4]$  (**11**) have been previously reported<sup>20,26</sup> with preliminary spectroscopic<sup>21</sup> but no structural characterization.

Whereas  $[\text{Au}(\text{bpy})\text{Cl}_2][\text{AuCl}_4]$  is bright yellow and  $[\text{Au}(\text{bpy})\text{Br}_2][\text{AuBr}_4]$  is brown, crystals of **9** are reddish-maroon. In the solid state, the cation and anion are paired face-to-face in the crystal with a  $\text{Au}\cdots\text{Au}$  distance of 3.518(1) Å, consistent with a metallophilic interaction, as shown in Figure 3. The other axial coordination site of the Au cation interacts weakly with the  $[\text{AuBr}_4]^-$  anion at 3.361(1) Å (pictured in the Supporting Information).

Notably, the geometry of the two square-planar metal centers is staggered. Computational studies that found attractive  $\text{Au}^{\text{III}}\cdots\text{Au}^{\text{III}}$  interactions used models with eclipsed conformers,<sup>2</sup> but the steric bulk of the halide anions favors a staggered conformation in **9** and **11a** (see below). Such  $\text{Au}^{\text{III}}\cdots\text{Au}^{\text{III}}$  interactions have been given theoretical support<sup>2</sup> and experimental confirmation<sup>22</sup> in  $(\text{Me}_4\text{N})[\text{Au}(\text{N}_3)_4]$  only relatively recently.

Crystallographic data has been obtained for two polymorphs of **11**. In  $[\text{Au}(\text{bpy})\text{Br}_2][\text{AuBr}_4]$  (**11a**), another highly unusual  $\text{Au}^{\text{III}}\cdots\text{Au}^{\text{III}}$  interaction is seen. The structure is not of publishable quality but is very similar to that of **9**.<sup>23</sup> The distance between cationic and anionic Au atoms is  $\sim 3.54$  Å, comparable to the average interanionic distance of 3.54 Å within the metallophilic chains in  $\{[\text{Au}(\text{N}_3)_4]^- \}_\infty$ .<sup>22</sup> On the opposite side of the cation, the Au1 atom is  $\sim 3.38$  Å away

from a Br atom in another anion; thus, the  $\text{Au}\cdots\text{Au}$  contacts do not continue throughout the crystal. Another polymorph of  $[\text{Au}(\text{bpy})\text{Br}_2][\text{AuBr}_4]$  (**11b**) shows no metallophilic interactions but only distant interaction on both sides of the cationic  $\text{Au}^{\text{III}}$  atom with a Br atom from the  $[\text{AuBr}_4]^-$  anion at 3.497(1) Å. The energetic difference between these two polymorphs is likely quite small because they are obtained from the same solvent under the same conditions.

A double salt with  $\text{Au}^{\text{III}}-\text{Au}^{\text{I}}$  ions has also been prepared, namely,  $[\text{Au}(\text{bpy})\text{Cl}_2][\text{Au}(\text{CN})_2]$  (**10**). Crystals suitable for X-ray diffraction were not obtained, but the elemental analysis data are consistent with the proposed stoichiometry. The IR stretch of the bound cyanide ligand,  $2218\text{ cm}^{-1}$ , suggests a bridging binding mode to Au without a metallophilic interaction of the  $[\text{Au}(\text{CN})_2]^-$  anion in **10** as observed in **6**, but IR data are not always a reliable determinant in such cases.<sup>24</sup>

Solution UV–vis spectra of these new double-salt compounds, **1–7**, **9**, and **10**, as well as those for **8** and **11**, are provided in the Supporting Information. They are dominated by the UV polypyridine  $\pi-\pi^*$  and visible metal–polypyridine metal-to-ligand charge-transfer transitions commonly observed for such compounds.<sup>25</sup> The spectrum of each double salt is qualitatively similar to a superposition of the component metal-containing ion spectra.

This metathetical approach with water-soluble starting materials clearly provides an abundance of new compounds with expected and unexpected solid-state connectivity. Ambient and low-temperature luminescence properties of these compounds are being investigated, and studies are also underway to partially oxidize the  $\text{Au}^{\text{I}}$  centers in the  $\text{Pt}^{\text{II}}-\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}-\text{Au}^{\text{I}}$  systems to create systems with electrons delocalized along the metal–metal vectors.

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**Supporting Information Available:** X-ray crystallographic information<sup>27,28</sup> for compounds **2**, **4–7**, **9**, **11a**, and **11b** in tabular summary (except for **7** and **11a**) and CIF format, ORTEP representations of **4** and **5**, packing diagrams for **6** and **11b**, UV–vis spectra, and experimental details for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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