Inorg. Chem. **2005**, *44*, 3466–3472

Inorganic Chemistry
Article

# Metal–Metal Interactions in Platinum(II)/Gold(I) or Platinum(II)/Silver(I) Salts Containing Planar Cations and Linear Anions

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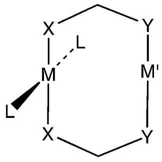
Received November 24, 2004

The salts $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$, $[Pt\{C(NHMe)_2\}_4][Ag_2(CN)_3][Ag(CN)_2]$, $[Pt(en)_2][Au(CN)_2]_2$, $[Pt(en)_2][Ag(CN)_2]_2$, and $[Pt(bipy)_2][Au(CN)_2]_2$ have been prepared by mixing solutions of salts containing the appropriate cation with solutions of $K[Au(CN)_2]$ or $K[Ag(CN)_2]$. Because the platinum atom in the cation is sterically protected, the structures of $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$ and $[Pt\{C(NHMe)_2\}_4][Ag_2(CN)_3][Ag(CN)_2]$ reveal no close metal–metal interactions. Colorless crystals of $[Pt(en)_2][Au(CN)_2]_2$ and $[Pt(en)_2][Ag(CN)_2]_2$ are isostructural and involve extended chains of alternating cations and anions that run parallel to the crystallographic *a* axis, along with isolated anions. In the chains, the metal–metal separations are relatively short: Pt···Au, 3.1799(3) Å; Pt···Ag, 3.1949(2) Å. In $[Pt(bipy)_2][Au(CN)_2]_2$, each cation has axial interactions with the anions through close Pt···Au contacts [3.1735(6) Å]. In addition, the anions are weakly linked through Au···Au contacts of 3.5978(9) Å. Unlike the previously reported Pt/Au complex $[Pt(NH_3)_4][Au(CN)_2]_2\cdot 1.5H_2O$, which is luminescent, none of the salts reported here luminesce.

## Introduction

Interactions between closed-shell $d^{10}$ metal centers, especially with gold(I), have attracted considerable experimental and theoretical attention.[1,2] Such interactions are necessarily weak and readily perturbed by local environmental effects. Similarly, the pseudo-closed-shell $d^8$ ions such as platinum(II) also show a proclivity to interact through weak Pt···Pt interactions. Such interactions are seen in dimeric complexes such as $Pt_2(P_2O_5H_2)_4]^{4-}$;[3] in the extended chain structures present in a variety of salts of $[Pt(CN)_4]^{2-}$;[4] and in double salts such as Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$.[5]

A number of heterobinuclear complexes that combine a $d^8$ metal center with a $d^{10}$ metal center also have been prepared. Most such complexes use bridging ligands that were designed to bring the two metals into close proximity.[6] The framework outlined in structure **1** shows a motif that is particularly well designed to allow the two metal centers to be placed in close proximity.[7−11] This motif provides for a planar, four-coordinate environment for the $d^8$ metal (M) and a linear, two-coordinate environment for the $d^{10}$ metal (M′). In addition, a number of other bridging ligand arrangements have been utilized to bring the two metal centers together.[12−15]



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In this paper, we explore an alternate strategy for the formation of situations in which a $d^8$ metal center and a $d^{10}$

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metal center might be combined. Here, we use simple ionic interactions to bring the two components together by examining the reactions of cationic $d^8$ platinum(II) complexes with anionic $d^{10}$ gold(I) and silver(I) complexes, $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$. As long as ligand exchange reactions can be avoided, this procedure should form salts of the type $[PtL_4][M(CN)_2]$. Yet will the products have the metal centers close together, or will they be widely separated?

An additional complication to this strategy arises from the ability of the $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ ions to self-associate through aurophilic or argentophilic interactions. Such interactions arise from a combination of relativistic and correlation effects[1] and generally result in metal−metal separations that are less than ∼3.5 Å.[16] The expected separation based on the van der Waals radii of the ion is 3.4 Å.[17] Whereas the majority of crystal structures of salts containing $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ show the linear anions surrounded by cations,[18] a number of examples are known where these anions self-associate, even though Coulombic repulsion needs to be overcome to allow such self-association. Cases where self-association of $[Au(CN)_2]^-$ is observed crystallographically include examples where the cation is a polypyridinium ion,[19] a transition metal complex,[20−23] or a secondary ammonium ion.[24] In many of these examples, hydrogen bonding of the nitrogen atoms of the anions with N−H functionalities on the cations occurs along with self-association. Argentophilic interactions between $[Ag(CN)_2]^-$ ions unsupported by additional ligands occur in $Tl[Ag(CN)_2]$.[25]

Recently, this laboratory reported that the reaction of $[Pt(NH_3)_4]Cl_2$ and $K[M(CN)_2]$ produced luminescent crystals of $[Pt(NH_3)_4][M(CN)_2]_2$. In this solid, the ions formed columns with continuous ···Au···Pt···Au···Au···Pt···Au··· chains that were cross-linked through additional Au···Au interactions.[26] Here, we report the synthesis and crystallographic characterization of new salts that have a variety of Pt···Au, Au···Au, and hydrogen-bonding interactions between the ionic components.

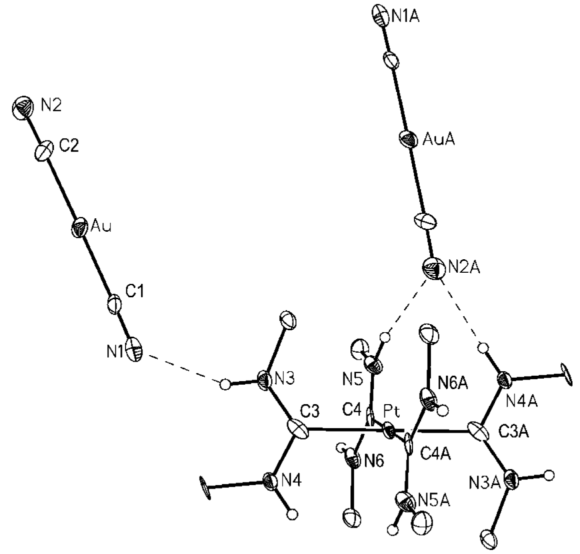

**Figure 1.** View of $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$ with 50% thermal contours. This view shows the hydrogen bonded contacts of one cation with neighboring anions. Selected interatomic distances (Å): Au−C1, 1.985(8); Au−C2, 2.000(8); N1−C1, 1.1155(11); N2−C2, 1.125(11); Pt−C3, 2.060(8); Pt−C4, 2.048(8); C3−N3, 1.316(10); C3−N4, 1.337(9); C4−N5, 1.333(10); C4−N6, 1.337(9). Selected interatomic angles (deg): C1−Au−C2, 177.7(3), Au−C1−N1, 178.4(7); Au−C2−N2, 177.6(8); C3−Pt−C4, 88.4(3); C3−Pt−C4A, 91.6(3), N3−C3−N4, 117.7(7); N5−C4−N6, 116.9(7).

## Results

**$[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$.** Colorless crystals of $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$ were obtained by mixing a solution of $[Pt\{C(NHMe)_2\}_4](PF_6)_2$ in methanol with a solution of $K[Au(CN)_2]$ in water. The infrared spectrum of these crystals shows $\nu$(CN) at 2143 $cm^{-1}$ and bands at 3289 and 3343 $cm^{-1}$ due to the N−H groups.

The asymmetric unit of $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$, as determined by an X-ray crystal structure, consists of an anion in a general position and one-half of a cation with its platinum atom residing on a crystallographic center of symmetry. Figure 1 shows a drawing of one cation and neighboring anions with their dimensions given in the figure caption. The structure of the cation is similar to that reported earlier for $[Pt\{C(NHMe)_2\}_4](PF_6)_2$.[27] The positioning of the carbene ligands nearly perpendicular to the $PtC_4$ plane provides steric shielding of the platinum ion. Consequently, there is no direct Pt···Au interaction in this salt. The closest contact between the platinum and gold centers is 5.136 Å.

The closest contact between $[Pt\{C(NHMe)_2\}_4]^{2+}$ and $[Au(CN)_2]^-$ involves hydrogen bonds between the N−H groups of the carbene ligands and the cyano groups of the anions. These contacts connect a single cation to four different anions in its vicinity as seen in Figure 1, although to conserve space only two of these are shown in the drawing.

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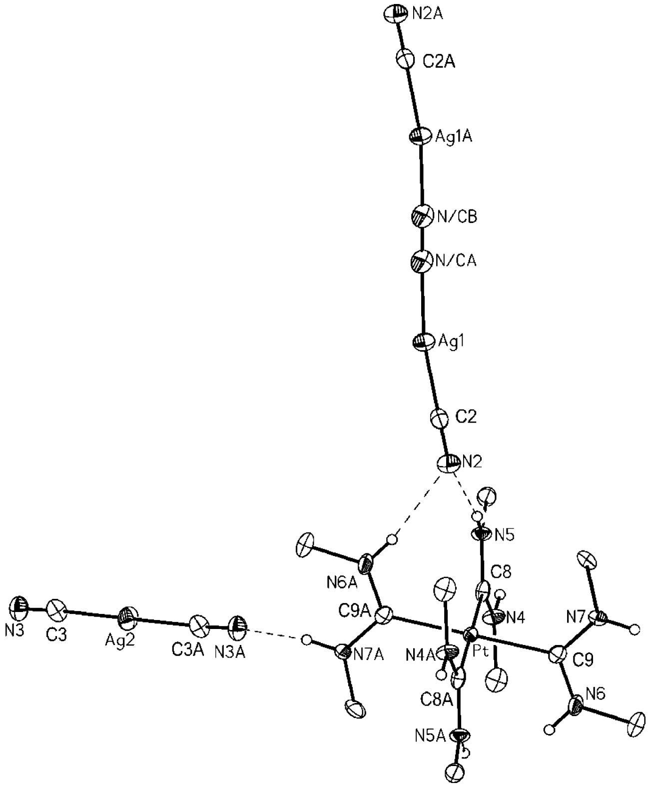

**Figure 2.** View of [Pt{C(NHMe)$_2$}$_4$][Ag$_2$(CN)$_3$][Ag(CN)$_2$] with 50% thermal contours. This view shows the hydrogen-bonded contacts of one cation with the two types of neighboring anions. Selected interatomic distances (Å): Ag1−N/CA, 2.070(4); Ag1−C2, 2.051(5); N/CA−N/CB, 1.154(9); N2−C2, 1.150(6); Pt−C8, 2.043(4); Pt−C9, 2.048(5). Selected interatomic angles (deg): N/CA−Ag−C2, 177.7(6); Ag−N/CA−N/CB, 177.7(6); Ag1−C2−N2, 176.0(5); C8−Pt−C9, 88.98(17).

Not only are there no direct Pt···Au interactions in [Pt{C(NHMe)$_2$}$_4$][Au(CN)$_2$]$_2$, but the anions are also widely separated so that there are no short Au···Au contacts in this salt either.

Samples of [Pt{C(NHMe)$_2$}$_4$][Au(CN)$_2$]$_2$ are not luminescent at room temperature and at 77 K.

**[Pt{C(NHMe)$_2$}$_4$][Ag$_2$(CN)$_3$][Ag(CN)$_2$].** Colorless crystals of [Pt{C(NHMe)$_2$}$_4$][Ag$_2$(CN)$_3$][Ag(CN)$_2$] were obtained in a fashion similar to the procedure used to make [Pt{C(NHMe)$_2$}$_4$][Au(CN)$_2$]$_2$. However, the product differs in that two different anions, [Ag(CN)$_2$]$^-$ and [Ag$_2$(CN)$_3$]$^-$, are present. Figure 2 shows a drawing of the cation and the adjacent anions that are hydrogen bonded to the N−H groups of the cation. The two different anions are nearly linear, as expected. The bridging cyano group in [Ag$_2$(CN)$_3$]$^-$ is disordered, as it is in [(dien)Cu(NC)Ag(CN)}]$_2$[Ag$_2$(CN)$_3$]-[Ag(CN)$_2$].[28] The [Ag$_2$(CN)$_3$]$^-$ ion is hydrogen bonded to the N−H groups of a pair of the carbene ligands, and the [Ag(CN)$_2$]$^-$ ion is hydrogen bonded to the N−H group of one ligand.

As in [Pt{C(NHMe)$_2$}$_4$][Au(CN)$_2$]$_2$, the steric constraints of the cation preclude any direct Pt···Ag interactions in [Pt{C(NHMe)$_2$}$_4$][Ag$_2$(CN)$_3$][Ag(CN)$_2$]. The anions are also widely separated. Consequently there are no direct Ag···Ag interactions in this salt.

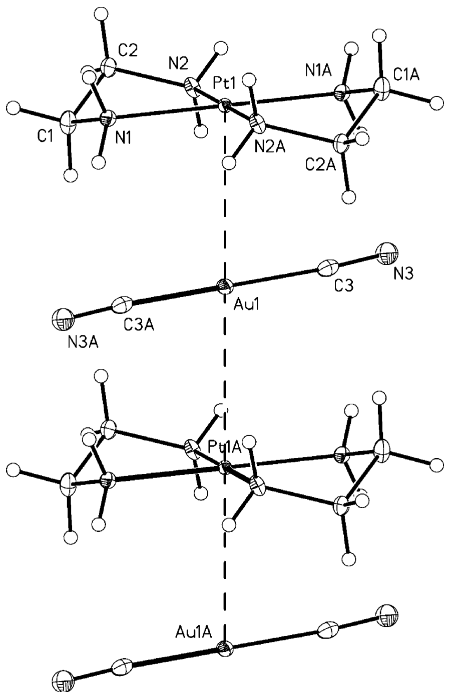

**Figure 3.** View of the extended chain of alternating cations and anions in crystalline [Pt(en)$_2$][Au(CN)$_2$]$_2$ with 50% thermal contours. Selected interatomic distances (Å): Pt1···Au1, 3.1799(3); Pt1−N1, 2.061(4); Pt1−N2, 2.048(4); Au1−C3, 1.990(5), Au2−C4, 1.986(5). Selected interatomic angles for [Pt(en)$_2$][Au(CN)$_2$]$_2$ (deg): N1−Pt1−N2, 82.99(15); N1−Pt1−N2A, 97.01(15). Crystals of [Pt(en)$_2$][Ag(CN)$_2$]$_2$ have a similar structure. Selected interatomic distances for [Pt(en)$_2$][Ag(CN)$_2$]$_2$ (Å): Pt1···Ag1, 3.1950(2); Pt1−N1, 2.060(2); Pt1−N2, 2.049(2); Ag1−C3, 2.070(3); Ag−C4, 2.067(3) Å. Selected interatomic angles (deg): N1−Pt1−N2, 82.99(9); N1−Pt1−N2A, 97.01(9).

No luminescence has been detected from [Pt{C(NHMe)$_2$}$_4$][Ag$_2$(CN)$_3$][Ag(CN)$_2$].

**[Pt(en)$_2$][Au(CN)$_2$]$_2$.** Mixing a solution of [Pt(en)$_2$]Cl$_2$ in water with an aqueous solution of K[Au(CN)$_2$] produced colorless crystals of [Pt(en)$_2$][Au(CN)$_2$]$_2$. The infrared spectrum of these crystals shows $\nu$(CN) at 2136 and 2144 cm$^{-1}$ and bands at 3109, 3211, 3248, and 3292 cm$^{-1}$ due to the N−H groups.

The structure of [Pt(en)$_2$][Au(CN)$_2$]$_2$ has been determined by single-crystal crystallography. The asymmetric unit consists of one-half of a cation and two separate half-anions. The platinum and gold atoms all reside on centers of symmetry. Figure 3 shows the extended chains of alternating cations and anions (involving anion **1**) that run parallel to the crystallographic *a* axis. Within these chains, the Pt···Au distance is 3.1799(3) Å. The anion is shifted from an eclipsed orientation with regard to the N−Pt−N bonds in the cation so that the C3−Au1−C3A unit is turned by 16.2(2)° away from the N1−Pt1−N1A unit.

The cations have a planar geometry that is entirely consistent with prior structural data on related salts.[29] The anions are strictly linear because of the crystallographic symmetry. In addition to the anion that makes up the extended chains, there is another anion (anion 2) that is not involved in any Pt···Au or Au···Au interactions. The relative

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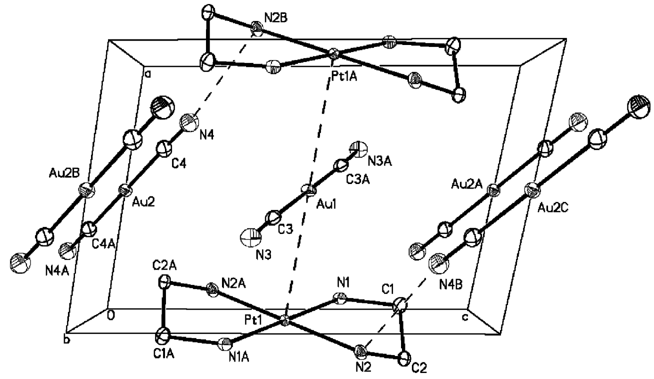

**Figure 4.** Drawing of the unit cell for $[Pt(en)_2][Au(CN)_2]_2$ with 50% thermal contours. The unit cell for $[Pt(en)_2][Ag(CN)_2]_2$ is similar.

locations of these components are given in Figure 4, which shows the unit cell of the salt. Anion 2 is located on the center of the *a* axis edges of the cell. Consequently, the separation of the gold atoms in adjacent pairs of anion 2 is long, 6.3598(6) Å. Anion 2 forms hydrogen bonds between the nitrogen atoms and protons on N2 of two different cations. This interaction allows anion 2 to span two different chains that run parallel to the crystallographic *a* axis.

Samples of $[Pt(en)_2][Au(CN)_2]_2$ are nonluminescent at room temperature and at 77 K.

**$[Pt(en)_2][Ag(CN)_2]_2$.** Colorless crystals of $[Pt(en)_2][Ag(CN)_2]_2$, which were obtained by mixing aqueous solutions of $[Pt(en)_2]Cl_2$ and $K[Ag(CN)_2]$, are isostructural with $[Pt(en)_2][Au(CN)_2]_2$. Thus, the structural features are similar to those of $[Pt(en)_2][Au(CN)_2]_2$. Selected bond distances and angles are given in the caption to Figure 3. Within the stacks of alternating cations and anions in $[Pt(en)_2][Ag(CN)_2]_2$, the Pt···Ag separation [3.1949(2) Å] is slightly longer than the Pt···Au separation [3.1799(3) Å] in $[Pt(en)_2][Au(CN)_2]_2$. The Ag−C separations in $[Pt(en)_2][Ag(CN)_2]_2$ are longer than the Au−C separations in $[Pt(en)_2][Au(CN)_2]_2$. These observations are consistent with recent reports indicating that Ag(I) is larger than Au(I).[30]

Like $[Pt(en)_2][Au(CN)_2]_2$, $[Pt(en)_2][Ag(CN)_2]_2$ is not luminescent.

**$[Pt(bipy)_2][Au(CN)_2]_2$.** Yellow crystals of $[Pt(bipy)_2][Au(CN)_2]_2$ were produced by mixing a solution of $K[Au(CN)_2]$ in acetonitrile with a solution of $[Pt(bipy)_2](BF_4)_2$ in acetonitrile. The infrared spectrum of these crystals shows $\nu$(CN) at 2137 $cm^{-1}$.

The asymmetric unit consists of one-half of a cation in a special position with the platinum atom located at a center of symmetry and an entire anion in a general position. A drawing of the entire $[Pt(bipy)_2][Au(CN)_2]_2$ unit is shown in Figure 5. The cation has the expected four-coordinate geometry with the addition of axial interactions with the anions through Pt···Au contacts. The Pt···Au distance is 3.1735(6) Å.

The $[Pt(bipy)_2]^{2+}$ ion can display two types of distortions: bowed, where the two pyridine rings are bent toward each other, or twisted, where the two pyridine rings are rotated about the central C−C bond in opposite directions. These ligand distortions allow the ortho protons on adjacent ligands to avoid direct contact. As is evident in Figure 5, the bipy ligands in the cation are not planar but are bowed. The $[Pt(bipy)_2]^{2+}$ ions in $[Pt(bipy)_2]$(7,7,8,8-tetracyanoquinodimethane monoanion$)_2$,[31] in $[Pt(bipy)_2]$(7,7,8,8-tetracyanoquinodimethane monoanion dimer),[32] and in $[Pt(bipy)_2](F_3CSO_3)_2$[33] all have the centrosymmetric bowing that is seen in $[Pt(bipy)_2][Au(CN)_2]_2$. This type of distortion allows the platinum atom to retain its usual planar coordination by the four nitrogen atoms of the ligands. In contrast, in $[Pt(bipy)_2](NO_3)_2\cdot H_2O$, the pyridine rings in each ligand are twisted by 7.5°, and the two ligands are arranged so that the dihedral angle between the least-squares planes of the two bipy ligands is 24.0(3)°.[34] As a consequence, the platinum atom in this salt has a slight distortion toward tetrahedral coordination.

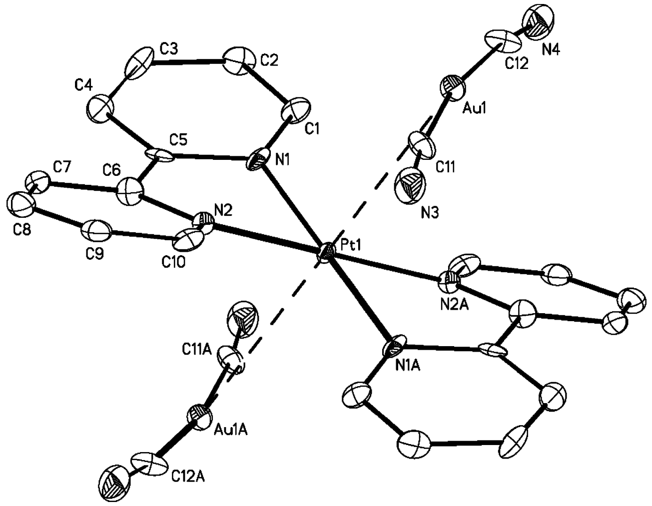

**Figure 5.** View of the structure of $[Pt(bipy)_2][Au(CN)_2]_2$ with 50% thermal contours which shows the interactions of two of the anions with the cation. Selected interatomic distances: Pt1···Au1, 3.1735(6); Au1···Au1A, 3.5978(9); Pt1−N1, 2.026(7) Å; Pt1−N2, 2.044(8); Au1−C11, 1.988(10), Au1−C12, 1.980(10) Å. Selected interatomic angles for $[Pt(en)_2][Au(CN)_2]_2$; N1−Pt1−N2, 79.3(3); N1−Pt1−N2A, 100.7(3).

Figure 6 shows a view of the structure that reveals that the anions also weakly interact to form an extended, bent chain. The Au···Au separation is rather long, 3.5978(9) Å, but it is significant to note that the cyano groups are bent away from each other so that the gold atoms represent the closest contacts between the anions. The C11−Au1−C12 angle involved in this bending is 171.3(4) Å.

No luminescence has been observed from $[Pt(bipy)_2][Au(CN)_2]_2$. The absorption spectrum of $[Pt(bipy)_2][Au(CN)_2]_2$ in a potassium bromide pellet shows maxima at 320 and 400 nm. Similar features at 320 and 400 nm are

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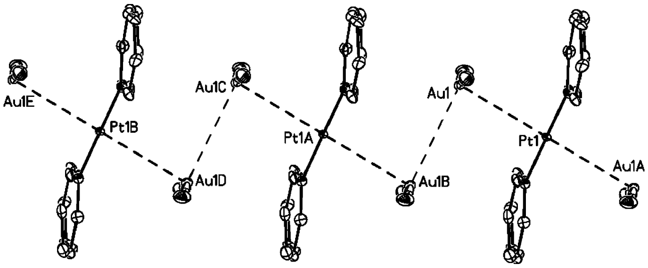

**Figure 6.** View of the extended structure of $[Pt(bipy)_2][Au(CN)_2]_2$ with 50% thermal contours including the interactions of adjacent anions. The Au1⋯Au1B distance is 3.5978(9) Å.

seen in the absorption spectrum of $[Pt(bipy)_2](BF_4)_2$. Thus, the Pt⋯Au contacts do not produce a detectable alteration the spectrum of the platinum cation.

**Infrared Spectra.** The infrared spectra of the new salts are reported in the Experimental Section. All show sharp bands for $\nu$(CN) that exhibit only modest variations from compound to compound. For $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$, $\nu$(CN) occurs at 2143 $cm^{-1}$, whereas $KAu(CN)_2$ has $\nu$(CN) at 2141 $cm^{-1}$.[35] Despite the presence of two different anions, $[Pt\{C(NHMe)_2\}_4][Ag_2(CN)_3][Ag(CN)_2]$ exhibits only a single $\nu$(CN) at 2136 $cm^{-1}$. For comparison, $KAg(CN)_2$ has $\nu$(CN) at 2140 $cm^{-1}$.[36] The two different anions in $[Pt(en)_2][Au(CN)_2]_2$ and in $[Pt(en)_2][Ag(CN)_2]_2$ produce two different $\nu$(CN) values in each salt: 2136, 2144 $cm^{-1}$ for $[Pt(en)_2][Au(CN)_2]_2$ and 2126, 2134 $cm^{-1}$ for $[Pt(en)_2][Ag(CN)_2]_2$. For $[Pt(bipy)_2][Au(CN)_2]_2$, $\nu$(CN) occurs at 2137 $cm^{-1}$.

## Discussion

The five new salts prepared here show a range of metal−metal interactions. In $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$ and $Pt\{C(NHMe)_2\}_4][Ag_2(CN)_3][Ag(CN)_2]$, there are no close metal−metal interactions between any of the components. The lack of interaction of the platinum atom in the cation with the gold atoms is clearly a result of the presence of four bulky carbene ligands that deny access to the platinum atom.

In $[Pt(en)_2][Au(CN)_2]_2$, linear chains of alternating cations and anions form with a Pt⋯Au distance of 3.1799(3) Å. This separation is somewhat longer than the Pt⋯Au separations in discrete binuclear complexes such as $[PtAu(\mu$-{bis(dicyclohexylphosphino)methane}$_2(CN)_2]^+$ [Pt⋯Au, 2.954(1) Å],[7] $[PtAu\{\mu$-bis(diphenylphosphino)methane$\}_2(CN)_2]^+$ [Pt⋯Au, 3.045(2) Å],[37] and $[PtAu\{\mu$-bis(diphenylphosphino)methane$\}_2(C{\equiv}CPh)_2]^+$ [Pt⋯Au, 2.910(1) Å][38] that have the ligand-bridged structure **1**. However, the Pt⋯Au separation in $[Pt(en)_2][Au(CN)_2]_2$ is shorter than the sum of the van der Waals radii for these metal ions, which is 3.47 Å.[39] The linear chains of alternating gold and platinum atoms in $[Pt(en)_2][Au(CN)_2]_2$ contrasts with the more complex arrangement previously observed in $[Pt(NH_3)_4][Au(CN)_2]_2\cdot 1.5(H_2O)$, where both Pt⋯Au and Au⋯Au contacts are found. In $[Pt(NH_3)_4][Au(CN)_2]_2\cdot 1.5(H_2O)$, each platinum atom is surrounded by two anions with Pt⋯Au separations [3.2804(4) and 3.2794(4) Å] that are somewhat longer than the Pt⋯Au separation in $[Pt(en)_2][Au(CN)_2]_2$. The $[Au(CN)_2][Pt(NH_3)_4][Au(CN)_2]$ units in $[Pt(NH_3)_4][Au(CN)_2]_2\cdot 1.5(H_2O)$ are arranged into chains through close Au⋯Au contacts [3.2902(5) and 3.3312(5) Å]. Additionally, cross-linking of these chains occurs through further aurophilic interactions with an Au⋯Au separation of 3.1902(4) Å. The fact that $[Pt(en)_2][Au(CN)_2]_2$ is nonluminescent reinforces our earlier conclusion that the luminescence of $[Pt(NH_3)_4][Au(CN)_2]_2\cdot 1.5(H_2O)$ arises from the close aurophilic interactions between the anions in this solid. It is also interesting to note that both $[PtAu(\mu$-{bis(dicyclohexylphosphino)methane}$_2(CN)_2]^+$ and $[PtAu\{\mu$-bis(diphenylphosphino)methane$\}_2(CN)_2]^+$, with shorter Pt⋯Au separations, are luminescent.[7,34]

The structure of $[Pt(bipy)_2][Au(CN)_2]_2$ consists of a Au⋯Pt⋯Au unit formed from a cation surrounded by two anions with a Pt⋯Au separation of 3.1735(6) Å. This distance is similar to the Pt⋯Au separation in $[Pt(en)_2][Au(CN)_2]_2$. The Au⋯Pt⋯Au units are connected by additional Au⋯Au interactions [3.5978(9) Å] that are considerably longer than those found in $[Pt(NH_3)_4][Au(CN)_2]_2\cdot 1.5(H_2O)$.

To put the present work into a larger context, there are several d$^8$ platinum(II) salts in which planar cations and anions combine to form extended chains with significant Pt⋯Pt interactions. The best and longest-known is Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, which forms columns of alternating cations and anions with a Pt⋯Pt separation of 3.25 Å.[5,40] A number of variations on this structural motif are known in which the substituents on the amine or the ligands in the anion vary.[41] The double salts of the type $[Pt(CNR)_4][Pt(CN)_4]$ also form columns in which anions and cations alternate and the platinum centers are brought into close proximity.[42] A number of these are vapochromic, that is, they change color when exposed to the vapors of volatile organic compounds. Examples in which ionic d$^8$ metal complexes associate via Coulombic interactions with other metal complexes with different electronic configurations are less common. There is one other example of a mixed-metal complex formed through interactions between d$^8$ and d$^{10}$ ions. The salt $Ag_2[Pt(O_2C_2O_2)_2]\cdot 2H_2O$ has two silver ions positioned above and below the platinum atom of the anion with a Pt⋯Ag separation of 2.943(1) Å.[43] This Pt⋯Ag separation

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**Table 1.** Crystallographic Data for Salts of $[Au^{I}(CN)_2]^-$ and $[Ag^{I}(CN)_2]^-$

| | $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$ | $[Pt\{C(NHMe)_2\}_4][Ag_2(CN)_3][Ag(CN)_2]$ | $[Pt(en)_2][Au(CN)_2]_2$ | $[Pt(en)_2][Ag(CN)_2]_2$ | $[Pt(bipy)_2][Au(CN)_2]_2$ |
|---|---|---|---|---|---|
| color/habit | colorless needle | colorless needle | colorless needle | colorless needle | yellow plate |
| formula | $C_{16}H_{32}Au_2N_{12}Pt$ | $C_8H_{16}Ag_2N_8Pt$ | $C_8H_{16}Au_2N_8Pt$ | $C_8H_{16}Ag_2N_8Pt$ | $C_{24}H_{16}Au_2N_8Pt$ |
| fw | 981.56 | 635.12 | 813.31 | 635.12 | 1005.47 |
| crystal system | monoclinic | triclinic | triclinic | triclinic | triclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 8.919(5) | 6.3899(4) | 6.3598(6) | 6.3599(4) | 7.0515(13) |
| $b$, Å | 15.424(7) | 6.9793(5) | 6.9603(7) | 6.9793(5) | 9.2481(14) |
| $c$, Å | 10.074(5) | 8.9383(6) | 9.0333(9) | 8.9383(6) | 9.2728(18) |
| $\alpha$, deg | 90 | 89.0260(10) | 88.311(2) | 89.0260(10) | 75.077(2) |
| $\beta$, deg | 107.047(15) | 79.6310(10) | 79.576(2) | 79.6310(10) | 77.247(5) |
| $\gamma$, deg | 90 | 73.7160(10) | 74.306(2) | 73.7160(10) | 79.743(6) |
| $V$, Å$^3$ | 1325.0(11) | 376.15(4) | 378.53(6) | 376.15(4) | 565.16(17) |
| $Z$ | 2 | 1 | 1 | 1 | 1 |
| $T$, °C | 90(2) | 90(2) | 90(2) | 90(2) | 90(2) |
| $\lambda$, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $\rho$, g/cm$^3$ | 2.460 | 2.804 | 3.568 | 2.804 | 2.954 |
| $\mu$, mm$^{-1}$ | 16.338 | 11.851 | 28.547 | 11.851 | 19.152 |
| R1$^a$ (obsd data) | 0.052 | 0.015 | 0.021 | 0.015 | 0.035 |
| wR2$^a$ (all data, $F^2$ refinement) | 0.140 | 0.039 | 0.050 | 0.039 | 0.092 |

[a] $R1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$; $wR2 = \sqrt{(\Sigma[w(F_o^2 - F_c^2)^2])/(\Sigma[w(F_o^2)^2])}$.

is shorter than the Pt···Ag separation in $[Pt(en)_2][Ag(CN)_2]_2$. A similar structural unit is found in $Tl_2[Pt(CN)_4]$, which involves the interaction of a $d^8$ complex with two closed-shell $s^2$ ions.[44] The complex has a pseudo-octahedral structure with two equivalent thallium ions positioned above and below the planar anion with a short Pt···Tl separation of 3.140 (1) Å. The nature of the Pt···Tl bonding in this complex has been examined in a series of computational studies.[45,46]

The interactions between the metal centers in the salts considered here are likely to result from a combination of Coulombic and metallophillic interactions. For example, in $Tl_2[Pt(CN)_4]$, computations have indicated that the Pt···Tl bonding consists of an ionic component that accounts for 87% of the attraction and a covalent, metallophillic interaction that accounts for the remaining 13% of the bonding interaction.[43] Additionally, theoretical studies have shown that interaction of the thallium ion with the adjacent nitrile groups of neighboring complexes diminishes the strength of the Pt···Tl bond.[44] In [Cu(1,1′-bis(2-pyridal)octamethylferrocene)][$CuCl_2$], the Cu···Cu contact is short, 2.810 Å,[47] but calculations show that the attraction comes entirely from Coulombic factors and not from metallophilic interactions.[48] Further computational studies are needed to sort out the varying contributions from Coulombic and metallophilic interactions in the new salts reported here.

## Experimental Section

**Materials.** Samples of $[Pt(en)_2]Cl_2$, $K[Au(CN)_2]$, and $K[Ag(CN)_2]$ were obtained from Strem Chemicals and used as received. $[Pt\{C(NHMe)_2\}_4](PF_6)_2$ was prepared as described previously.[49] $[Pt(bipy)_2](BF_4)_2$ was prepared by a known route.[50]

**Preparation of Compounds. (i) $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$.** A filtered solution of 10 mg (0.018 mmol) of $[Pt\{C(NHMe)_2\}_4](PF_6)_2$ in 1.0 mL of methanol was added dropwise to a solution of 10 mg (0.035 mmol) of potassium dicyanoaurate in 1.0 mL of water. The colorless reaction mixture was transferred to a 5-mm-diameter tube and left undisturbed. After 3 days of slow evaporation of the solvent, colorless needles of the product that were suitable of X-ray analysis formed. After removal from the mother liquor, 8 mg (48% yield) of the colorless product was obtained. Infrared spectrum (cm$^{-1}$): 527 m, 640 sh, 674 sh, 700 m, 980 w, 1032 sh, 1129 w, 1189 m, 1308 m, 1361 m, 1454 m, 1524 sh, 1576 sh, 2143 sh [$\nu$(CN)], 2941 w, 3289 vs [$\nu$(N−H)], 3343 vs [$\nu$(N−H)].

**(ii) $[Pt\{C(NHMe)_2\}_4][Ag_2(CN)_3][Ag(CN)_2]$.** A filtered solution of 100 mg (0.16 mmol) of $[Pt\{C(NHMe)_2\}_4](PF_6)_2$ in 1.0 mL of methanol was added dropwise to a solution of 100 mg (0.50 mmol) of potassium dicyanoargentate in 0.5 mL of water in a 5-mm-diameter tube. The colorless reaction mixture was left undisturbed. After 4 days of slow evaporation of the solvent, a few colorless plates of the product formed. They were removed from the mother liquor to yield 3.2 mg (3%) of product. These crystals were suitable for collection of X-ray diffraction data. Infrared spectrum (cm$^{-1}$): 532 m, 675 sh, 740 w, 980 w, 1032 sh, 1129 w, 1189 m, 1309 m, 1362 m, 1452 m, 1527 sh, 1577 sh, 2136 m [$\nu$(CN)], 2939 w, 3286 vs [$\nu$(N−H)], 3310 vs [$\nu$(N−H)].

**(iii) $[Pt(en)_2][Au(CN)_2]_2$.** A solution of 121 mg (0.420 mmol) of $K[Au(CN)_2]$ in 2 mL of water was added to a solution of 80 mg (0.21 mmol) of $[Pt(en)_2]Cl_2$ in 2 mL of water. Colorless needles suitable for X-ray crystallography precipitated over the course of 2 days. The precipitate was collected and washed successively with water, ethanol, and ether to yield 102 mg (60%) of the product. Infrared spectrum (cm$^{-1}$): 757 m, 821 m, 899 w, 1020 w, 1589 sh, 1127 m, 1152 sh, 1275 w, 1304 sh, 1322 m, 1367 sh, 1446 sh, 1454 sh, 1589 sh, 1610 sh, 2136 sh [$\nu$(CN)], 2144 vs [$\nu$(CN)], 3109 vs [$\nu$(N−H)], 3211 m [$\nu$(N−H)], 3248 vs [$\nu$(N−H)], 3292 vs [$\nu$(N−H)]

**(iv) $[Pt(en)_2][Ag(CN)_2]_2$.** A solution of 87 mg (0.44 mmol) of $K[Ag(CN)_2]$ in 1.5 mL of water was added to a solution of 83 mg

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(0.22 mmol) of $[Pt(en)_2]Cl_2$ in 1 mL of water. Colorless needles suitable for crystallography formed upon standing overnight. The crystals were collected by filtration and washed successively with water, ethanol, and ether to yield 102 mg (88%) of the product. Infrared spectrum ($cm^{-1}$): 759 m, 830 m, 898 m, 1031 w, 1053 sh, 1133 w, 1157 sh, 1235 w, 1277 w, 1307 m, 1324 m, 1369 m, 1447 sh, 1456 sh, 1592 sh, 1617 m, 2126 sh [$\nu$(CN)], 2134 sh [$\nu$(CN)], 3082 vs [$\nu$(N−H)], 3242 vs [$\nu$(N−H)], 3288 vs [$\nu$(N−H)]

**(v) $[Pt(bipy)_2][Au(CN)_2]_2$.** A solution of 30 mg (0.10 mmol) of $K[Au(CN)_2]$ in 2 mL of acetonitrile was added dropwise to a solution of 34 mg (0.050 mmol) of $[Pt(bipy)_2](BF_4)_2$ in 6 mL of acetonitrile. A yellow precipitate immediately formed. The precipitate was collected by filtration and washed with acetonitrile to yield 45 mg (90%) of yellow platelets. X-ray diffraction quality plates were grown by layering a slurry of the reaction mixture over dimethyl sulfoxide. Yellow plates of the product slowly formed in this mixture. Infrared spectrum ($cm^{-1}$): 720 sh, 772 sh, 816 w, 1036−1129 vs br, 1155 m, 1162 m, 1428 m, 1450 sh, 1499 w, 1609 sh, 2137 sh [$\nu$(CN)], 3029 m, 3048 m, 3060 m, 3098 w, 3119 w

**Physical Measurements.** Infrared spectra were recorded as pressed KBr pellets on a Matteson Galaxie Series FTIR 3000 spectrometer. Electronic absorption spectra were recorded using a Hewlett-Packard 8450A diode array spectrophotometer.

**X-ray Crystallography and Data Collection.** The crystals were removed from the glass tubes in which they were grown together with a small amount of mother liquor and immediately coated with a hydrocarbon oil on the microscope slide. Suitable crystals were mounted on glass fibers with silicone grease and placed in the cold dinitrogen stream of a Bruker SMART CCD with graphite-monochromated Mo K$\alpha$ radiation at 90(2) K. No decay was observed in 50 duplicate frames at the end of each data collection. Crystal data are given in Table 1.

The structures were solved by direct methods and refined using all data (based on $F^2$) using the software of SHELXTL 5.1. A semiempirical method utilizing equivalents was employed to correct for absorption.[51] Hydrogen atoms were added geometrically and refined with a riding model.

**Acknowledgment.** We thank the Petroleum Research Fund (Grant 37056-AC) for support. The Bruker SMART 1000 diffractometer was funded in part by NSF Instrumentation Grant CHE-9808259.

**Supporting Information Available:** X-ray crystallographic file in CIF format for $[Pt\{C(NHMe)_2\}_4][Au(CN)_2]_2$, $[Pt\{C(NHMe)_2\}_4][Ag_2(CN)_3][Ag(CN)_2]$, $[Pt(en)_2][Au(CN)_2]_2$, $[Pt(en)_2][Ag(CN)_2]_2$, and $[Pt(bipy)_2][Au(CN)_2]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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