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# New Structural Features of Unsupported Chains of Metal Ions in Luminescent $[(NH_3)_4Pt][Au(CN)_2]_2\cdot 1.5(H_2O)$ and Related Salts

**Matthias Stender, Rochelle L. White-Morris, Marilyn M. Olmstead, and Alan L. Balch***

*Department of Chemistry, University of California, Davis, California 95616*

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Luminescent $[(NH_3)_4Pt][Au(CN)_2]_2\cdot 1.5(H_2O)$, which forms from aqueous solutions of $[(NH_3)_4Pt]Cl_2$ and $K[Au(CN)_2]$, crystallizes with extended chains of the two ions with multiple close Pt···Au (3.2804(4) and 3.2794(4) Å) and Au···Au (3.2902(5), 3.3312(5), and 3.1902(4) Å) contacts. Nonluminescent $[(NH_3)_4Pt][Ag(CN)_2]_2\cdot 1.4(H_2O)$ is isostructural with $[(NH_3)_4Pt][Au(CN)_2]_2\cdot 1.5(H_2O)$. Treatment of $[(NH_3)_6Ni]Cl_2$ with $K[Au(CN)_2]$ forms $[(NH_3)_2Ni][Au(CN)_2]_2$ in which the $[Au(CN)_2]^-$ ions function as nitrile ligands toward nickel, which assumes a six-coordinate structure with trans $NH_3$ ligands. The $[Au(CN)_2]^-$ ions self-associate into linear columns with close Au···Au contacts of 3.0830(5) Å, and pairs of gold ions in these chains make additional but longer (3.4246(5) Å) contacts with other gold ions.

One-dimensional chains of metal ions have attracted considerable interest recently.[1] Such chains can exhibit a number of remarkable properties such as the solvoluminescence seen for the columnar stacks of gold ions in $Au_3(MeN{=}COMe)_3$,[2] the vapochromic behavior seen in the platinum chains in salts such as $[(RNC)_4Pt][Pt(CN)_4]$,[3] and semiconducting properties seen in a modified form of Magnus' green salt, $[(NH_3)_4Pt][PtCl_4]$.[4] Here we report the formation and structures of some new, unsupported chains of metal ions which have added complexity due to additional metal−metal bonding that creates more intricate networks of metal ions. These structures have been constructed from $[Au(CN)_2]^-$ or $[Ag(CN)_2]^-$ building blocks. Such cyanometalates are well-known to form complex, three-dimensional networks.[5] Aurophilic attractions, which bring gold(I) centers closer than 3.6 Å,[6−8] are found in a number of salts that combine complex metal cations with $[Au(CN)_2]^-$.[9−12]

Addition of an aqueous solution of $[(NH_3)_4Pt]Cl_2$ (48.0 mg (0.13 mmol) in 2 mL of water) to a solution of $K[Au(CN)_2]_2$ (50.1 mg (0.25 mmol) in 2 mL of water) produces the immediate formation of a colorless precipitate which was removed by filtration. After standing for 2 days, colorless blocks of $[(NH_3)_4Pt][Au(CN)_2]_2\cdot 1.5(H_2O)$ (**1**) (IR, $\nu(CN) = 2149, 2140\ cm^{-1}$) were collected in 90% yield from the filtrate. The structure of this solid as determined by single crystal X-ray diffraction is shown in Figure 1.[13] The asymmetric unit consists of one $[(NH_3)_4Pt]^{2+}$ ion, two $[Au(CN)_2]^-$ ions, and two water molecules, one of which has 0.50 site occupancy. The two $[Au(CN)_2]^-$ ions are situated above and below the plane of the $[(NH_3)_4Pt]^{2+}$ ion, and the Pt···Au distances (3.2804(4) and 3.2794(4) Å) are indicative of a degree of bonding between these metal centers. For comparison, in Magnus' green salt, $[(NH_3)_4Pt][PtCl_4]$, where a $[(NH_3)_4Pt]^{2+}$ ion is surrounded by two $[PtCl_4]^{2-}$ ions, the Pt···Pt distance is 3.25 Å.[14] The $[Au(CN)_2][(NH_3)_4Pt][Au(CN)_2]$ unit in **1** also resembles that of

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* To whom correspondence should be addressed. E-mail: albalch@ucdavis.edu.

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(13) Crystal data for $[(NH_3)_4Pt][Au(CN)_2]_2\cdot 1.5(H_2O)$ (**1**): $C_4H_{15}Au_2N_8O_{1.5}Pt$, $M = 788.26$, monoclinic, space group $P2_1/n$, $a = 7.4655(8)$ Å, $b = 13.4429(14)$ Å, $c = 13.9910(14)$ Å, $\beta = 102.371(3)°$, $V = 1371.5(2)$ Å$^3$, $\mu(\text{Mo K}\alpha) = 31.516\ mm^{-1}$, $Z = 4$, $T = 90(2)$ K, 15482 reflns collected, 3382 unique ($R_{int} = 0.0349$), $R_w(F^2)$ was 0.053 (all data), conventional R1 for 2962 reflns with $I > 2\sigma I$ with 159 params was 0.024.

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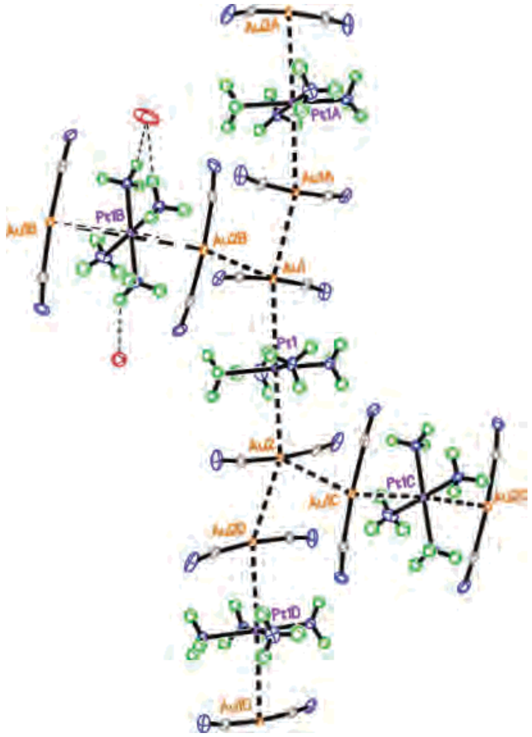

**Figure 1.** View of the structure of $[(NH_3)_4Pt][Au(CN)_2]_2{\cdot}1.5(H_2O)$ (**1**), which shows three Au−Pt−Au units arranged in a chain and two Au−Pt−Au units that intersect from the side. Selected interatomic distances (Å): Pt···Au1, 3.2804(4); Pt···Au2, 3.2794(4); Au1···Au1A, 3.2602(5); Au1···Au2B, 3.1902(4); Au2···Au2D, 3.3312(5); Pt−N1, 2.041(5); Pt−N2, 2.057(6); Pt−N3, 2.056(6); Pt−N4, 2.059(6); Au1−C1, 1.988(7); Au1−C2, 1.989(8); Au2−C3, 1.977(8); Au2−C4, 1.986(7); Selected interatomic angles (deg): Au1−Pt−Au2, 174.040(10); Pt−Au1−Au2B, 114.597(10); Pt−Au1−Au1A, 160.015(13); Pt−Au2−Au2D, 158.030(13); Pt−Au2−Au1C, 113.734(10); Au1A−Au1−Au2B, 85.242(11); Au1C−Au2−Au2D, 87.786(11); C1−Au1−C2, 175.2(3); C3−Au2−C4, 174.3(3). The oxygen atoms of the water molecules surrounding Pt1B are shown, but all other oxygen atoms have been omitted for clarity. Crystals of $[(NH_3)_4Pt][Ag(CN)_2]_2{\cdot}1.4(H_2O)$ are isostructural with **1**. Selected interatomic distances (Å): Pt···Ag1, 3.252(3); Pt···Ag2, 3.258(3); Ag1···Ag1A, 3.339(5); Ag1···Ag2B, 3.095(3); Ag2···Ag2D, 3.410(3); Pt−N1, 2.02(2); Pt−N2, 2.02(3); Pt−N3, 2.05(2), Pt−N4, 2.02(2); Ag1−C1, 2.07(3); Ag1−C2, 2.10(3); Ag2−C3, 2.01(3); Ag2−C4, 2.06(3). Selected interatomic angles (deg): Ag1−Pt−Ag2, 172.13(7); Pt−Ag1−Ag2B, 111.65(8); Pt−Ag1−Ag1A, 158.85(12); Pt−Ag2−Ag2D, 151.80(10); Pt−Ag2−Ag1C, 111.32(8); Ag1A−Ag1−Ag2B, 88.39(10); Ag1C−Ag2−Ag2D, 92.43(11); C(1)−Ag(1)−C(2), 177.2(12); C3−Ag2−C4, 174.1(13).

$Tl_2[Pt(CN)_4]$, which has two $Tl^+$ ions situated above and below the plane of the $[Pt(CN)_4]^{2-}$ ion with a Pt···Tl distance of 3.140(1) Å.[15] However, in **1** these $[Au(CN)_2]$-$[(NH_3)_4Pt][Au(CN)_2]$ units are arranged into chains through short Au···Au interactions (Au1···Au1A, 3.2902(5) Å; Au2···Au2B, 3.3312(5) Å). These distances are consistent with significant aurophilic attraction between the $[Au(CN)_2]^-$ ions.[11,12] Additional cross-linking of these chains occurs through further Au···Au interactions (Au1···Au2B, 3.1902(4) Å). Thus, both Au1 and Au2 are connected to two other Au centers and to a $[(NH_3)_4Pt]^{2+}$ unit. As expected from a database study, the Au1···Au2B separation, which involves nearly staggered $[Au(CN)_2]^-$ ions, is shorter that the Au1···Au1A and Au2···Au2B separations, which involve pairs of $[Au(CN)_2]^-$ ions in nearly eclipsed arrangements.

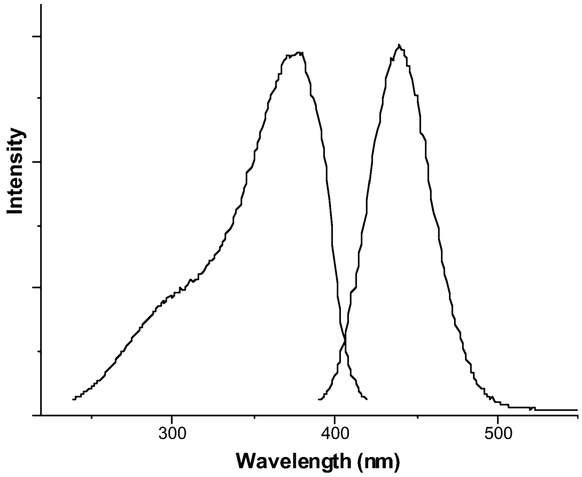

**Figure 2.** Emission (right with excitation at 353 nm) and excitation (left monitored for emission at 443 nm) spectra of crystals of $[(NH_3)_4Pt][Au(CN)_2]_2{\cdot}1.5(H_2O)$ at 77 K.

Finally, water molecules are hydrogen-bonded to the $NH_3$ groups of the platinum cation in two different fashions.

Similarly, addition of an aqueous solution of $[(NH_3)_4Pt]Cl_2$ to an aqueous solution of $K[Ag(CN)_2]$ produces colorless blocks of $[(NH_3)_4Pt][Ag(CN)_2]_2{\cdot}1.4(H_2O)$ (**2**). $[(NH_3)_4Pt][Ag(CN)_2]_2{\cdot}1.4(H_2O)$ is isostructural with the gold analogue (**1**).[16] Selected interatomic distances and angles for **2** are given in the caption to Figure 1. Comparison of the interatomic distances in $[(NH_3)_4Pt][Ag(CN)_2]_2{\cdot}1.4(H_2O)$ (**2**) with those in its gold analogue (**1**) shows, as expected from Schmidbaur's earlier studies,[17] that the Ag−X distances are longer that the corresponding Au−X distances. The exception to this statement involves the Ag1···Ag2B separation (3.095(3) Å) which is shorter than the corresponding Au1···Au2B distance (3.1902(4) Å). Attempts to prepare similar materials by mixing aqueous solutions of $[(NH_3)_4Pd]Cl_2$ with aqueous solutions of $K[Au(CN)_2]$ or $K[Ag(CN)_2]$ produced only amorphous powders.

Crystals of $[(NH_3)_4Pt][Au(CN)_2]_2{\cdot}1.5(H_2O)$ are nonluminescent at room temperature but become luminescent upon cooling. Figure 2 shows the emission and excitation spectra for this salt at 77 K. A broad, unstructured emission is observed at 443 nm. The emission spectrum is independent of the excitation wavelength over the range 300−370 nm. In contrast, crystals of $[(NH_3)_4Pt][Ag(CN)_2]_2{\cdot}1.4(H_2O)$ are nonluminescent at both room temperature and at a 77 K. Consequently, the emission from $[(NH_3)_4Pt][Au(CN)_2]_2{\cdot}1.5(H_2O)$ is likely to originate in the close proximity of the $[Au(CN)_2]^-$ ions and possibly their interaction with the platinum ion. The luminescence of aggregates of $[Au(CN)_2]^-$ ions has received considerable study.[18−20]

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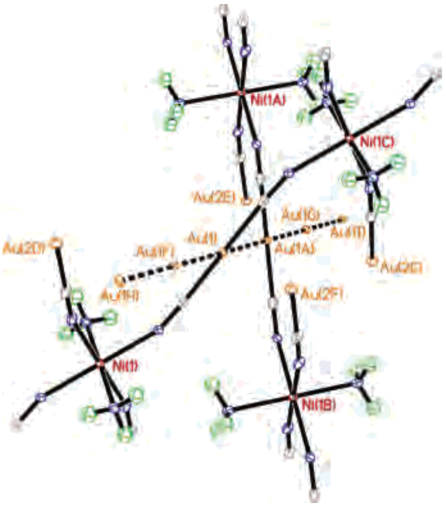

**Figure 3.** View of the structure of $[(NH_3)_2Ni][Au(CN)_2]_2$ (**3**) which emphasizes the location of the linear chain of $[Au(CN)_2]^-$ ions. Selected interatomic distances (Å): Au1···Au1A, 3.0829(5); Ni−N1 2.082(4), Ni−N2, 2.089(4); Ni−N3, 2.098(4); Au1−C1, 1.999(5); Au2−C2, 1.981(5). Selected interatomic angles (deg): Au1F−Au1−Au1A, 180; C1−Au1−C1A, 180; C2−Au2−C2A, 177.6(3); N1−Ni−N2, 92.81(17); N1−Ni−N2A, 87.19(16); N1−Ni−N3, 87.61(15).

Addition of an aqueous solution of $K[Au(CN)_2]$ to an aqueous solution of the substitutionally labile $[(NH_3)_6Ni]Cl_2$ produces colorless to light yellow crystals of $[(NH_3)_2Ni][Au(CN)_2]_2$ (**3**) (IR, $\nu$(CN) = 2174 cm$^{-1}$).. The structure of **3** as determined by X-ray crystallography is shown in Figure 3.[21] The asymmetric unit consist of two gold ions, one nickel ion, two cyanide ions, and an ammonia molecule. The Au1 and Ni atoms sit at crystallographic centers of symmetry, while Au2 sits on a crystallographic 2-fold axis. The solid contains a primary, linear chain of staggered $[Au(CN)_2]^-$ ions with a short Au1···Au1A distance of 3.0830(5) Å. This portion of the chain is similar to one found in $[Cu(en)Au(CN)_2][Au(CN)_2]$ which also involves a strictly linear arrangement of staggered $[Au(CN)_2]^-$ units with a longer, but still short, Au1···Au1A distance of 3.1405(2) Å.[9] The $[Au(CN)_2]^-$ ions function as nitrile ligands toward nickel. Each nickel ion is surrounded by four $[Au(CN)_2]^-$ ions and by two trans amine ligands. The Ni−N distances, 2.084(4), 2.089(4), and 2.098 Å, are all similar and are consistent with those in the six-coordinate complex, [Ni(tris(2-aminoethyl)amine)NCAuCN][Au(CN)$_2$], which range in length from 2.05(2) to 2.14(1) Å.[22] In addition to the short Au···Au contacts along the main chain shown in Figure 3, there are secondary interactions of Au2 atoms with the main chain of Au1 atoms that are not emphasized in this figure. Figure 4 shows that each Au2 atom makes pairwise contact with the main chain with Au1···Au2 distances of 3.4246(5) Å. This is a unique structural arrangement for a chain of Au(I) centers ions. The proximity of these additional Au(I) complexes along the primary chain is noteworthy, since the self-association involves units that are formally anionic.

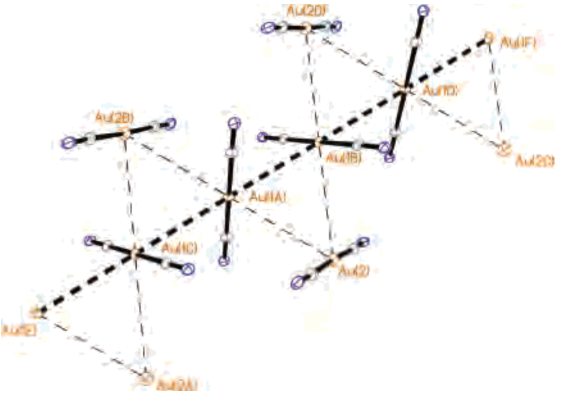

**Figure 4.** View of **3** showing the linear chain of Au1 atoms with an Au···Au distance of 3.0830(5) Å and the positions of Au2 atoms which make pairwise contact with the linear chain through a longer Au1···Au2 distance of 3.4246(5) Å. For clarity, some of the cyano ligands have been omitted.

Variations in the emission spectra obtained from the $[Au(CN)_2]^-$ ion in different environments including concentrated solutions and crystalline hosts suggest that a group of different aggregated forms of this ion can exist.[17−19] The structure shown in Figure 4 shows a new pattern of aggregation for the $[Au(CN)_2]^-$ ion and Au(I) complexes in general and demonstrates that self-association can involve more that the formation of just dimers, trimers, and simple extended chains. Such variations in the structures of aggregates of Au(I) complexes are significant in regard to the substantial changes in the luminescence that arise when solutions of Au(I) complexes are frozen or concentrated.[19,20,23,24] However, with a paramagnetic Ni(II) ion present, the salt (**3**) is nonluminescent at room temperature and at 77 K.

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**Supporting Information Available:** X-ray crystallographic file (CIF) including tables of crystallographic details, atomic coordinates, anisotropic thermal parameter, and interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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