A Helical Metal−Metal Bonded Chain via the Pt→Ag Dative Bond

Tadashi Yamaguchi,* Fumie Yamazaki, and Tasuku Ito*

Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578, Japan

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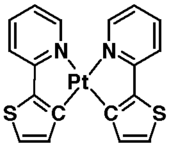
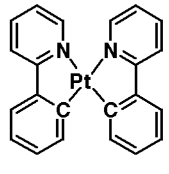
In recent years, the synthesis of coordination compounds with extended structures has attracted much attention from the viewpoint of nanoscale science, crystal engineering, and solid-state properties.[1] We have demonstrated that a metal−metal dative bond is a useful connector for preparing metal complex assemblages, where the extended structures were constructed by metal−metal dative bonds and normal coordination bonds.[2] In this study, we have prepared metal−metal bonded chain complexes by means of a $\mathrm{Pt^{II}}\rightarrow\mathrm{Ag^+}$ dative bond using [Pt(phpy)$_2$] and [Pt(thpy)$_2$] (Hphpy = 2-phenylpyridine, Hthpy = 2-(2-thienyl)pyridine), and report a novel helical 1-D chain complex and a linear pentanuclear complex with alternating $\mathrm{Pt^{II}}$ and $\mathrm{Ag^+}$ ions. The carbon-coordinated platinum complexes, [Pt(phpy)$_2$] and [Pt(thpy)$_2$], were used for the following reason. It has been shown from the molecular orbital scheme for the $\mathrm{Pt^{II}}\rightarrow$M dative bond that the stronger dative bond will be formed as the d_{z^2} level of the platinum moves higher in energy, and that this will occur when platinum is placed in a strong ligand field exerted by carbon donor ligands such as phpy or thpy.[3]



***cis*-[Pt(thpy)$_2$]**



***cis*-[Pt(phpy)$_2$]**

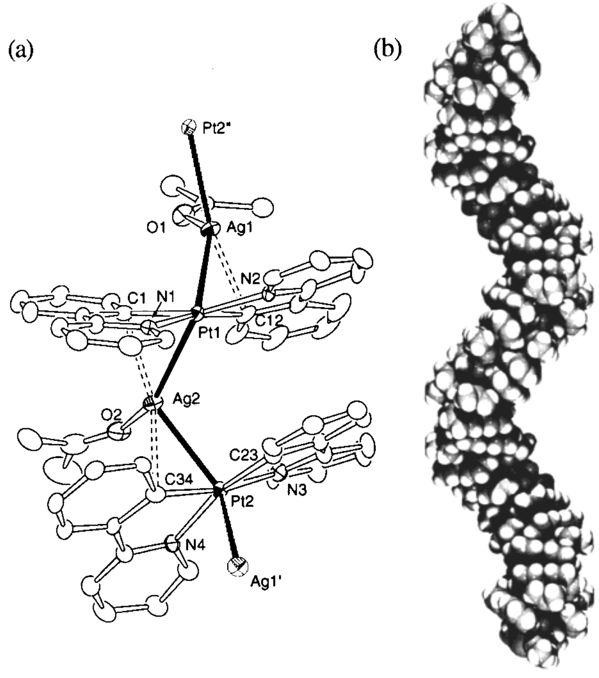


Figure 1. Structure of $[\{\mathrm{Pt(phpy)_2}\}_2\{\mathrm{Ag(acetone)}\}_2]_n^{2n+}$ in **1**: (a) asymmetric unit and (b) helical chain structure. Relevant bond lengths (Å) and angles (deg): Pt(2)−Ag(1′) = 2.6781(9), Pt(2)−Ag(2) = 2.7959(9), Pt(1)−Ag(1) = 2.8121(9), Pt(1)−Ag(2) = 2.8004(9), Pt(1)−N(1) = 2.111(8), Pt(1)−N(2) = 2.136(9), Pt(1)−C(1) = 2.062(11), Pt(1)−C(12) = 1.99(1), Pt(2)−N(3) = 2.113(8), Pt(2)−N(4) = 2.128(8), Pt(2)−C(23) = 2.020(9), Pt(2)−C(34) = 2.032(11), Ag(1)−O(1) = 2.419(9), Ag(1)−C(12) = 2.364(10), Ag(2)−O(2) = 2.373(9), Ag(2)−C(1) = 2.437(9), Ag(2)−C(34) = 2.536(9); Ag(1)−Pt(1)−Ag(2) = 113.89(3), Ag(1′)−Pt(2)−Ag(2) = 129.51(3), Pt(1)−Ag(1)−Pt(2″) = 132.96(4), Pt(1)−Ag(2)−Pt(2) = 115.62(3).

Yellow crystals of $[\{\mathrm{Pt(phpy)_2}\}_2\{\mathrm{Ag(acetone)}\}_2]_n(\mathrm{ClO_4})_{2n}\cdot n$ acetone (**1**) were obtained by slow evaporation of an acetone solution containing [Pt(phpy)$_2$][4] and Ag(ClO$_4$) in a 1:1 molar ratio for 1 week. The structure of the cation in **1**[5] is a helical chain consisting of an alternating stack of [Pt(phpy)$_2$] and [Ag(acetone)] units connected by a Pt→Ag dative bond (Figure 1). Since the helical chain has a crystallographic 6_1 axis and two sets of the platinum and silver units exist in the asymmetric unit, one cycle of the helix is comprised of $\mathrm{Pt_{12}Ag_{12}}$. The helix is ca. 23 Å in diameter and 41.608 Å in pitch. Since the space group $P6_1$ is chiral, the crystal specimen used in the X-ray study contains only the right-handed screw helices. The grooves of the helices are mutually occupied by adjacent helices. The Pt−Ag bond distances are within the range of 2.6781(9) to 2.8121(9) Å, and are shorter than the sum of the metallic radii of platinum and silver (2.83 Å), indicating the formation of a strong Pt→Ag dative bond. The [Pt(phpy)$_2$] unit coordinates to silver atoms on both sides of the coordination plane. This is in contrast to the structure of [{Pt(phpy)$_2$}{Cd(cyclen)}](ClO$_4$)$_2$ [3] in which the platinum unit coordinates to $\mathrm{Cd^{2+}}$ on only one side. In the helical structure (Figure 1), the silver is weakly coordinated by a carbon atom of the phpy ligand bound to the platinum (dotted bonds, Ag−C = 2.364(10)−2.536(9) Å). Since the Ag−C bonds are roughly perpendicular to the aromatic ring of phpy (66.2−73.2°), the interactions would be similar to a donor (π-electron of the aromatic ring)/acceptor ($\mathrm{Ag^+}$) bond like those in $\mathrm{Ag(ClO_4)\cdot C_6H_6}$ and related complexes.[6] As well, this interaction is absent in [{Pt(phpy)$_2$}{Cd(cyclen)}](ClO$_4$)$_2$.[3] The Ag−C interactions, however, do not support the Pt→Ag dative bonds since no Ag−C interaction exists at the shortest Pt→Ag dative bond (Pt(2)−Ag(1′) = 2.6781(9) Å).[7] On the contrary, the Ag−C interaction makes the Pt→Ag bonds longer by pulling the silver atom toward the aromatic ring. Thus, the helical chain is made up mainly by metal−metal dative bonds. The shortest Pt→Ag bond (2.6781(9) Å) is comparable to that in [Pt(C$_6$F$_5$)$_3$(tht)Ag(PPh$_3$)] (2.639(2) Å),[8] which is the shortest Pt→Ag dative bond known thus far. It has been reported, however, that weak Ag−F interactions support the Pt−Ag bond

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(2) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Chem. Soc., Dalton Trans.* **1999**, 273.

(3) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **1999**, *121*, 7405.

(4) Chassot, L.; Muller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249.

(5) Crystal data for **1**: yellow prismatic, hexagonal space group $P6_1$ (No. 169), $a = 14.8050(6)$ Å, $c = 41.608(3)$ Å, $V = 7898.1(6)$ Å^3, $Z = 6$; $R1 = 0.041$, $wR2 = 0.104$, GOF = 0.748.

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(7) The closest Ag−C contact between Pt(2) and Ag(1′) units is Ag(1)−C(34) = 2.85(1) Å.

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in [Pt(C_6F_5)$_3$(tht)Ag(PPh$_3$)]. As a result of the Ag−C interaction in **1**, the Pt→Ag bond is tilted by 24.8−44.1° from the normal to the mean square plane around the platinum, whereas the corresponding tilt in the Cd complex is 13.0°.[3] Around the platinum, a geometry distortion is also observed with dihedral angles between the ligand planes of 26.5(2)° and 22.9(1)° for Pt(1) and Pt(2), respectively. This distortion is a consequence of Ag−C interaction as well as steric repulsion between *ortho* protons of the ligands. The distortions make the Pt(1) and Pt(2) units chiral where the two Pt units have different chirality. There are $\pi-\pi$ stack interactions between the phpy ligands of adjacent Pt units across an Ag unit. The interactions are operating along the chain in such a way that one phpy ligand on a platinum interacts with the above ligand and the other the below ligand.[9] The interplane distances are 3.49 and 3.50 Å for Pt(1)···Pt(2) and Pt(1)···Pt(2′), respectively. The helical structure originates from the $\pi-\pi$ stack between the phpy ligands which connect the chiral Pt units.

In contrast to [Pt(phpy)$_2$], [Pt(thpy)$_2$][10] afforded, in a similar reaction with Ag$^+$, a discrete linear pentanuclear complex [{Pt(thpy)$_2$}$_3${Ag(acetone)}$_2$](ClO$_4$)$_2$·acetone (**2**). The structure of the complex cation of **2**[11] consists of a similar alternating stack of [Pt(thpy)$_2$] and [Ag(acetone)] units connected by a Pt→Ag dative bond as in **1**, but in this case, the chain terminates at platinum sites giving a Pt−Ag−Pt−Ag−Pt pentanuclear cluster (Figure 2). The Pt−Ag bond distances of 2.6746(7)−2.8083(6) Å indicate again formation of a strong Pt→Ag dative bond. The Ag−C(π) interactions are also observed in **2** at three of four Pt−Ag bonds (dotted bonds, Ag−C = 2.438(7)−2.558(7) Å). The Pt(1)−Ag(1) bond, without the Ag−C(π) interactions,[12] is again the shortest (2.6746(7) Å) as in **1**. The orientation of the aromatic ligand planes in **2** is similar to that in **1**.[13] Although **2** is a discrete pentanuclear complex, it interacts with adjacent complexes by weak Pt···Pt stacking interactions to form a 1-D chain (Figure S1). The Pt···Pt separation of 3.2787(4) Å is relatively short as compared with that of the mononuclear platinum complexes with aromatic ligands possessing a Pt···Pt interaction.[14]

Neither **1** nor **2** showed ^{195}Pt NMR in acetone-d_6 solution. It appears that the compounds dissociate in solution to give an equilibrium mixture of some species with different Pt/Ag combination, and they are converted mutually on the ^{195}Pt NMR time scale. The ^{195}Pt NMR spectrum of [Pt(phpy)$_2$] with excess Ag(ClO$_4$) shows a signal at −1529 ppm (vs K$_2$PtCl$_4$ in D$_2$O in acetone-d_6)[15] and at −1928 ppm without Ag(ClO$_4$). Similarly, in the presence of an excess of Ag(ClO$_4$), [Pt(thpy)$_2$] shows the ^{195}Pt NMR signal at −1797 ppm in acetone-d_6,[15] whereas in the absence of Ag(ClO$_4$) the signal appears at −2204 ppm. These low-field shifts suggest the formation of a Pt→Ag dative bond and are caused by the decrease in electron density of the Pt center upon coordination to Ag$^+$.

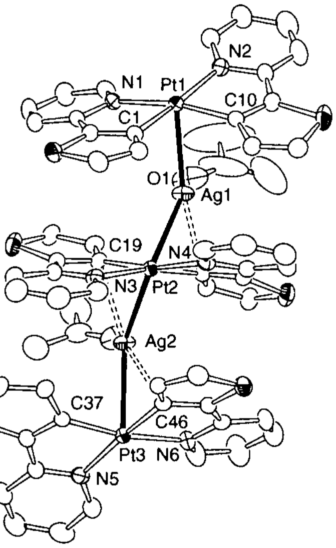

Figure 2. ORTEP drawing of [{Pt(thpy)$_2$}$_3${Ag(acetone)}$_2$]$^{2+}$ in **2**. Relevant bond lengths (Å) and angles (deg): Pt(1)−Ag(1) = 2.6746(7), Pt(2)−Ag(1) = 2.7711(7), Pt(2)−Ag(2) = 2.8083(6), Pt(3)−Ag(2) = 2.7425(6), Pt(1)−N(1) = 2.157(6), Pt(1)−N(2) = 2.148(6), Pt(1)−C(1) = 2.009(8), Pt(1)−C(10) = 2.004(7), Pt(2)−N(3) = 2.135(6), Pt(2)−N(4) = 2.142(6), Pt(2)−C(19) = 2.006(7), Pt(2)−C(28) = 2.007(7), Pt(3)−N(5) = 2.142(6), Pt(3)−N(6) = 2.157(6), Pt(3)−C(37) = 2.001(7), Pt(3)−C(46) = 2.010(7), Ag(1)−O(1) = 2.532(8), Ag(1)−C(28) = 2.438(7), Ag(2)−O(2) = 2.471(7), Ag(2)−C(19) = 2.558(7), Ag(2)−C(46) = 2.541(7); Ag(1)−Pt(2)−Ag(2) = 115.9792), Pt(1)−Ag(1)−Pt(2) = 135.53(3), Pt(2)−Ag(2)−Pt(3) = 140.19(2).

Compound **1** is a 1-D chain bound by relatively short metal−metal bonds. Even though the metallic radius of Ag is larger than that of Pt, the Pt−Ag distances in **1** (2.6781(9) to 2.8121(9) Å) are somewhat shorter than those in the conductive 1-D chain compound, K$_2$Pt(CN)$_4$·Br$_{0.3}$ (KCP) and its analogue (2.87−2.96 Å).[16] In contrast to KCPs, **1** should be an insulator. Partial oxidation of **1**, however, may lead to conductivity. The conductometry of these compounds is now under investigation.

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Supporting Information Available: Tables of crystallographic data, experimental conditions, atomic positional and thermal parameters, and interatomic distances and bond angles for **1** and **2**, and stacking view of **2** (PDF) as well as an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The stacking operates mutually between the pyridine ring of one ligand and the phenyl ring of the neighboring ligand.

(10) Chassot, L.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814.

(11) Crystal data for **2**: orange prismatic, monoclinic space group $P2_1/n$ (No. 14), a = 16.7243(9) Å, b = 23.973(1) Å, c = 16.9345(9) Å, β = 90.625(1)°, V = 6789.2(5) Å^3, Z = 4; $R1$ = 0.033, $wR2$ = 0.084, GOF = 0.630.

(12) The Ag−C contacts are Ag(1)−C(1) = 2.779(6) Å and Ag(1)−C(10) = 2.920(8) Å.

(13) The Pt−Ag bond is tilted by 24.3−39.6° from the normal to the mean square plane around the platinum. The dihedral angles between the two ligands on the platinum atoms are 13.64, 18.19, and 13.81° for Pt(1), Pt(2), and Pt(3), respectively.

(14) Connick, W. B.; Marsh, R. E.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 913.

(15) Experiments varying the Pt:Ag molar ratio and following the UV−vis absorption intensity in solution suggest that the main species is a trinuclear PtAg$_2$ complex when an Ag:Pt ratio is more than 3.

(16) Miller, J. S., Ed. *Extended Linear Chain Compounds*; Plenum Press: New York, 1982; Vol. 1.