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A short platinum to silver dative bond and its application in the construction of extended structures: syntheses and structures of $Ag_2[Pt(ox)_2]{\cdot}2H_2O$ and $[Ag(H_2O)]_2[Ag_2(CF_3SO_3)_4][Pt(acac)_2]_2$

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Two new coordination polymers, $Ag_2[Pt(ox)_2]{\cdot}2H_2O$ (ox = oxalate) and $[Ag(H_2O)]_2[Ag_2(CF_3SO_3)_4][Pt(acac)_2]_2$, which are formed by short platinum to silver dative bonds, were synthesized and structurally characterized.

In recent years, the synthesis of coordination compounds with extended structures has attracted much attention from the view point of nano-scale science, supramolecular chemistry, crystal engineering, and solid state properties (chemistry).[1,2] Weak interactions such as hydrogen-bonding,[2] charge transfer interactions,[3] and weak metal–metal homonuclear bonding[4] as well as strong chemical bonds have been used to make such systems. The present study has been undertaken to explore the construction of an extended structure using metal–metal dative bonds.

It has been shown that the occupied d_{z^2} orbital in a d^8 transition metal ion with square-planar coordination geometry acts as a potential donor to another metal ion (M) to form a dative $M(d^8)$–M bond. A few examples of a Pt^{II}–M dative bond have been reported.[5–8] In the published literature on Pt^{II}–M dative bonds, no one has focused on making an extended structure. We report, here, three-dimensional (3-D) structures of $Ag_2[Pt(ox)_2]{\cdot}2H_2O$ **1** (ox = oxalate) and two-dimensional structures (2-D) of $[Ag(H_2O)]_2[Ag_2(CF_3SO_3)_4][Pt(acac)_2]_2$ **2**, which were constructed through the formation of a relatively short Pt–Ag bond.

The colorless compound **1** was prepared by the slow diffusion of aqueous solutions containing $K_2[Pt(ox)_2]$ and $[Ag(py)_2]$-CF_3SO_3, and characterized by X-ray crystallography.† Compound **1** has a stacked 2-D layer structure (Fig. 1). The 2-D layer is composed of $[Pt(ox)_2]^{2-}$, water, and a silver ion, which are connected by three types of Ag–O bond [Fig. 1(a)].‡ The stacking of the layer is depicted in Fig. 1(b) and (c). There are two interlayer interactions. One is a Pt to Ag dative bond and the other is a water O(3)-to-Ag coordination bond. The platinum in $[Pt(ox)_2]^{2-}$ coordinates to two silver ions at its two axial sites with a relatively short Pt–Ag distance of 2.943(1) Å. In view of the separation, it is evident that weak Pt to Ag dative bonds are formed. Although the silver–water coordination bond [2.502(9) Å] exists between layers, the platinum to silver dative bond undoubtedly plays a significant role in the interlayer interaction.

Complex **2** was prepared by slow evaporation of a nitromethane solution containing $[Pt(acac)_2]$ and $AgCF_3SO_3$ in a 1 : 2 molar ratio.§ The structure of **2** is described as a 2-D sheet comprised of three units, $[Ag(H_2O)]$, $[Ag_2(CF_3SO_3)_4]$, and $[Pt(acac)_2]$. The repeating unit is shown in Fig. 2(a) and (b). There is an inversion center at the midpoint of two Ag(1) ions. Two of the silver ions, Ag(1) and Ag(1′), are quadruply bridged by triflates in a "μ-triflate-*O*,*O*′" fashion. The $[Ag_2(CF_3SO_3)_4]$ moiety has the so called "lantern" type structure. The two terminal $[Pt(acac)_2]$ units are connected to this $[Ag_2(CF_3SO_3)_4]$ moiety through the $[Ag(H_2O)]$ groups. The repeating units are further connected to each other by the Ag(1)–Pt bond to form the 2-D sheet [Fig. 2(c)]. The Ag(1)–Pt bond distance is 2.814(1) Å, and is shorter than that in **1**. It is obvious that the Pt to Ag dative bonds, shown by filled bonds in Fig. 2(c), play a primary role in making the sheet structure and it should be emphasized that the Ag(1)–Pt bond in **2** essentially does not have any other supporting interactions. There is no obvious interlayer interaction. The shortest interlayer contacts are the F · · · F contacts of 2.95(1) and 2.89(2) Å. This is consistent with the fact that the crystal of **2** has a cleavage plane.

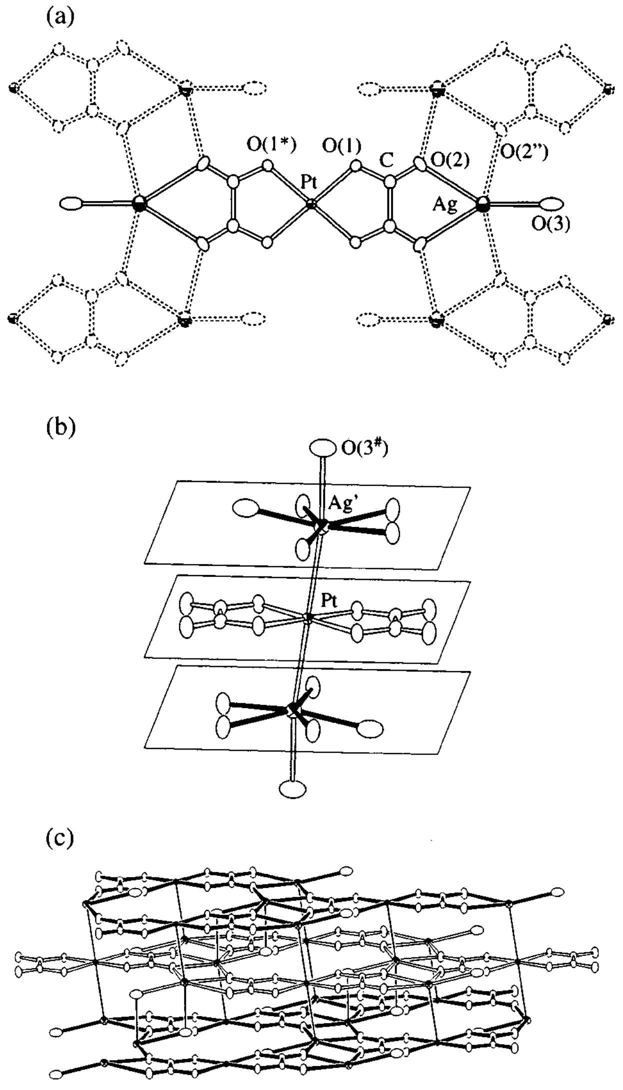

Fig. 1 ORTEP[10] drawings of $Ag_2[Pt(ox)_2]{\cdot}2H_2O$ **1**. (a) Structure of 2-D sheet (50% probability). The repeating unit is shown in solid bonds; (b) and (c) piled layer structure. Relevant bond lengths (Å): Pt–Ag′ 2.943(1), Pt–O(1) 2.003(4), Ag–O(2) 2.559(5), Ag–O(2″) 2.632(6), Ag–O(3) 2.424(8), Ag′–O(3#) 2.502(9) Å. (Key to symmetry operation: ′ = −*x*, −*y*, 1 − *z*; ″ = −1/2 − *x*, 1/2 − *y*, 1 − *z*; # = 1 + *x*, *y*, *z*; * = −*x*, *y*, −*z*).

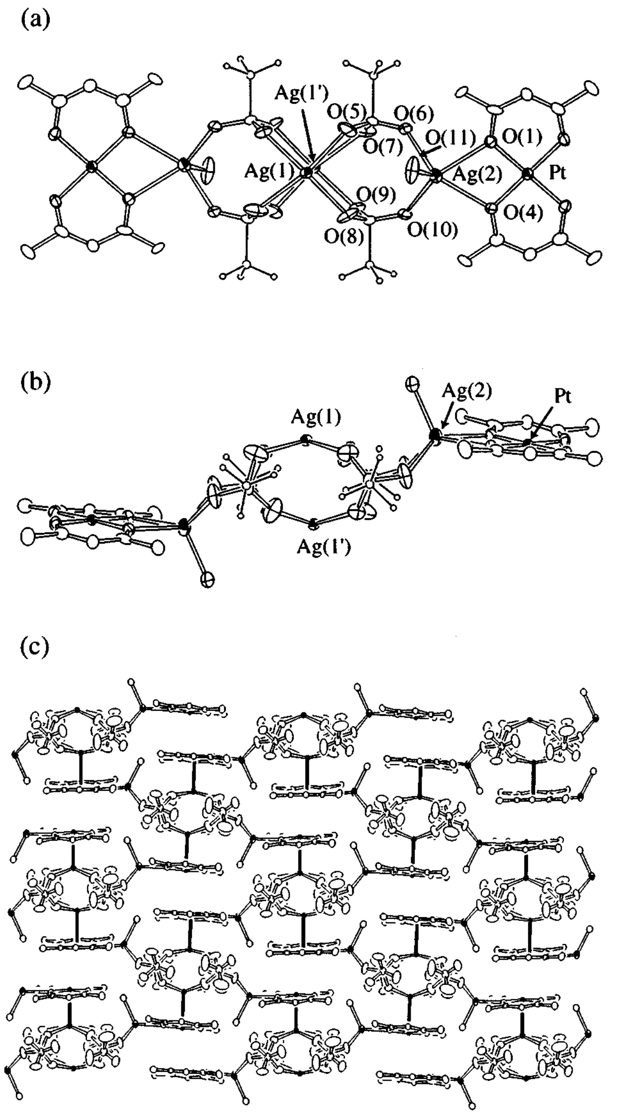

Fig. 2 ORTEP[10] drawings of $[Ag(H_2O)]_2[Ag_2(CF_3SO_3)_4][Pt(acac)_2]_2$ **2**. (a) Top view of repeating unit (20% probability, atoms of CF_3 moieties are drawn as small circle for clarity); (b) side view of repeating unit; (c) 2-D layer structure. Relevant bond lengths (Å): Pt–Ag 2.814(1), Pt–O(1) 1.968(9), Pt–O(2) 1.985(9), Pt–O(3) 1.982(9), Pt–O(4) 1.976(8), Ag(1)–O(5) 2.41(1), Ag(1)–O(8) 2.40(1), Ag(1')–O(7) 2.52(1), Ag(1')–O(9) 2.38(1), Ag(2)–O(1) 2.557(9), Ag(2)–O(4) 2.575(9), Ag(2)–O(6) 2.52(1), Ag(2)–O(10) 2.47(1), Ag(2)–O(11) 2.28(1). (Key to symmetry operation: ' = −*x*, −*y*, −*z*.)

The Pt–Ag distances in **1** [2.943(1) Å] and in **2** [2.814(1) Å] are relatively short, and the latter, especially, is below the sum of the metal radii (2.83 Å).¶ These short distances indicate the formation of Pt–Ag bonds. These short metal–metal dative bonds give rise to the 3-D and 2-D structures in **1** and **2**.

Comparison of the Pt–Ag distances in **1** and **2** shows that the platinum in **2** makes a stronger metal–metal dative bond than that in **1**. The reason may be attributed to the following two factors. One is that platinum in **2** coordinates to only one silver whereas in **1** it coordinates to two silver ions; in the latter the electron pair in the d_{z^2} orbital is shared between the two axial sites. The other reason is the ligand field strength of the ligand coordinated to the platinum. Possibly, the ligand field strength of acetylacetonate ion coordinated to Pt^{2+} is stronger than that of oxalate ion, and the stronger donation of the $acac^-$ ligand may cause an increase in the electron density of the d_{z^2} orbital to make a stronger metal–metal dative bond.

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Notes and references

† Preparation of complex **1**. An aqueous solution of $K_2[Pt(ox)_2]$ (5 mg in 3 cm^3) and $[Ag(py)_2]CF_3SO_3$ (4 mg in 3 cm^3) were allowed to slowly diffuse in an H-tube at ambient temperature. Colorless crystals of $Ag_2[Pt(ox)_2]\cdot 2H_2O$ were obtained after 1 week. Crystal data: **1** = $PtAg_2C_4H_4O_{10}$, $M = 623$, monoclinic, space group $C2/m$ (no. 12), $a = 9.745(2)$, $b = 7.913(1)$, $c = 6.954(1)$ Å, $\beta = 117.05(1)°$, $V = 477.6(1)$ Å^3, $Z = 2$, $\mu = 18.64$ mm^{-1}, $T = 293$ K. With the use of 585 unique reflections [$I > 3\sigma(I)$] out of 625 reflections, the final R and R_w values were 0.024 and 0.030.

‡ The asymmetric unit consists of six non-hydrogen atoms with unprimed labeling except for hydrogens. Crystallographic $2/m$ symmetry exists at Pt atoms: a crystallographic C_2 axis passes through Pt and bisects the O(1)–Pt–O(1*) angle; there exists a mirror plane perpendicular to the $[Pt(ox)_2]$ plane which passes through Pt, Ag and O(3).

§ Preparation of complex **2**. $[Pt(acac)_2]$ (4 mg) and $AgCF_3SO_3$ (5 mg) were dissolved in nitromethane (3 cm^3) and the solution was slowly evaporated in a refrigerator for 1 week. Colorless crystals of $[Ag(H_2O)]_2[Ag_2(CF_3SO_3)_4][Pt(acac)_2]_2$ were collected. Crystal data: **2** = $Pt_2Ag_4C_{24}H_{32}O_{22}F_{12}S_4$, $M = 1850$, monoclinic, space group $P2_1/n$ (no. 14), $a = 13.039(7)$, $b = 12.287(3)$, $c = 15.000(3)$ Å, $\beta = 102.90(2)°$, $V = 2342(1)$ Å^3, $Z = 2$, $\mu = 7.86$ mm^{-1}, $T = 293$ K. With the use of 2985 unique reflections [$I > 3\sigma(I)$] out of 5872 reflections, the final R and R_w values were 0.046 and 0.037. CCDC reference number 186/1301. See http://www.rsc.org/suppdata/dt/1999/273/ for crystallographic files in .cif format.

¶ The Cambridge Structural Database[9] shows a total of 27 complexes having a Pt^{II}-to-Ag dative bond shorter than 2.82 Å. All the complexes, however, have a pentahalogenophenyl ligand attached to Pt, and one *ortho* halogen atom of each C_6X_5 group makes a close contact (2.75–2.90 Å) with the silver ion. The interaction can possibly facilitate an attractive force that contributes to the shortening of the Pt–Ag bonds. Some of these complexes also have a bridging hydride, chloride, or thioether between Pt and Ag other than the dative bond.

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