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Cationic Five-Coordinate Pt^{II} Complexes as Donors in the Formation of Pt→Ag Dative Bonds

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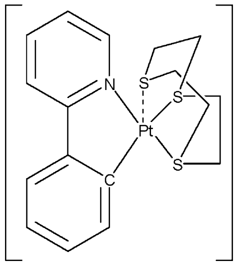
A unique trinuclear cluster containing two short Pt→Ag dative bonds was prepared and characterized crystallographically. Two monocationic orthometalated Pt^{II} complexes containing 2-phenylpyridine and the tridentate ligand 9S3 (1,4,7-trithiacyclononane) exhibit axial sulfur interactions with Pt as well as short dative bonds. The Pt→Ag dative bonding results in a dramatic shortening of the axial Pt–S distance in each Pt complex cation, relative to the mononuclear Pt complex. Evidence for Pt–Ag interactions in solution is also presented.

Transition-metal-mediated synthesis in supramolecular chemistry has played a key role in the assembly of extended structures that can be employed in nanoscale devices, crystal engineering, and other applications.[1] The use of metal−metal dative bonding to construct helical chains and other complex geometries is emerging, and intriguing metal−metal bonding interactions for this purpose are Pt^{II}→Ag^{I} dative bonds, which employ an occupied high-energy d$_{z^2}$ orbital on Pt^{II} as the donor orbital.[2] Our group and others have been interested in using Pt−S axial interactions in elongated square-pyramidal thiacrown complexes to investigate how the electronic environment changes as a result of the differences in the donor/acceptor properties of ancillary ligands coordinated to the Pt^{II}.[3] The cyclometalating ligand, 2-phenylpyridine (phpy), is known to enhance the electron-donating ability of Pt^{II} and thereby to assist in the formation of Pt→M dative bonds (Chart 1).[4]

Chart 1. Cation of Complex **1**



We therefore prepared the electron-rich Pt^{II}(phpy) heteroleptic complex with the thiacrown 1,4,7-trithiacyclononane (9S3) to probe the platinum's ability to function as a donor to the d^{10} ion Ag^{I} and to study the effects that Pt→Ag dative bonding would have upon the intramolecular structure of the Pt complex. We report the preparation and crystal structures of a trinuclear cluster [{Pt(phpy)(9S3)}$_2$Ag(CN$_3$CN)$_2$](PF$_6$)$_3$ (**1**) assembled with Pt^{II}→Ag^{I} dative bonds and its analogous mononuclear complex [Pt(phpy)(9S3)](PF$_6$) (**2**). We note that, although the Pt^{II}→Ag^{I} dative bonds were truncated by the axial thiacrowns, the potential is certainly demonstrated to build more complex materials via these types of units.

Compound **1** was prepared in an acetonitrile solution by reacting (μ-Cl)$_2$[Pt(phpy)]$_2$ with 2 equiv of AgPF$_6$ for 24 h at room temperature, followed by filtration of AgCl solid and the addition of 1 equiv of 9S3. Crystals were grown by diethyl ether diffusion into a solution of the reaction mixture.[5] Incomplete dechlorination of the Pt(phpy) dimer yielded **1**, an adduct of two [Pt(phpy)9S3]$^+$ cations with AgPF$_6$ that remained in acetonitrile. A sample of compound **2** was

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(5) Crystal data for **2**: C$_{38}$H$_{46}$N$_4$AgPt$_2$S$_6$·3PF$_6$·CH$_3$CN, monoclinic, space group $P2_1/n$, $a = 14.2016(14)$ Å, $b = 22.179(2)$ Å, $c = 17.2955(18)$ Å, $\alpha = 90°$, $\beta = 91.739(4)°$, $\gamma = 90°$, $V = 5545.1(9)$ Å^3, $Z = 4$, $D_{calcd} = 2.104$ Mg/m^3, $\mu = 5.899$ mm^{-1}, final R indices [$I > 2\sigma(I)$], R1 = 0.0475, wR2 = 0.1137, R indices (all data), R1 = 0.0559, wR2 = 0.1182.

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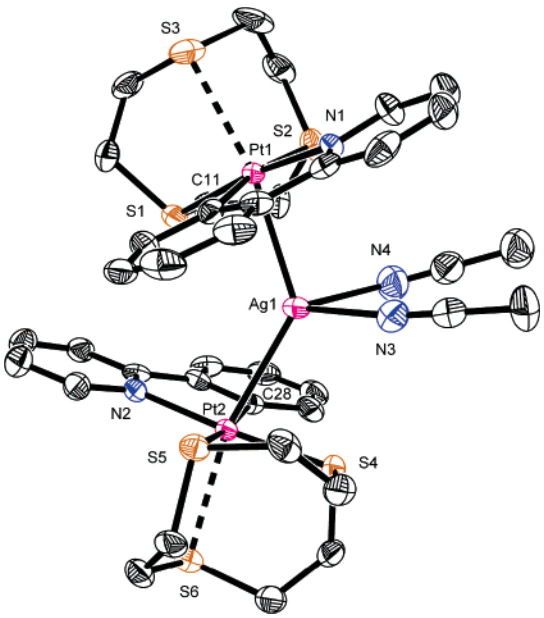

Figure 1. Structure of [{Pt(phpy)(9S3)}$_2${Ag(NCCH$_3$)$_2$}]$^{3+}$ in **1**. Relevant bond lengths (Å) and angles (deg): Pt1−Ag1, 2.7557(6); Pt2−Ag1, 2.7659(6); Pt1−S1, 2.2621(17); Pt1−S2, 2.3779(18); Pt1−S3, 2.6870(18); Pt1−N1, 2.063(6); Pt1−C11, 2.021(7); Pt2−S4, 2.2712(17); Pt2−S5, 2.3569(18); Pt2−S6, 2.7461(19); Pt2−N2, 2.046(6); Pt2−C28, 2.025(7); Ag1−N3, 2.417(7); Ag1−N4, 2.480(8); S3−Pt1−Ag1, 166.17(4); S6−Pt2−Ag1, 168.78(5); Pt1−Ag1−Pt2, 132.27(2); N4−Ag1−N3, 79.0(3).

prepared in an acetonitrile solution by reacting (μ-Cl)$_2$[Pt(phpy)]$_2$ with 2 equiv of 9S3 at room temperature for 24 h. Crystals of compound **2** were grown by evaporation of an acetonitrile solution of **2**.[6]

An ORTEP drawing of [{Pt(phpy)(9S3)}$_2$Ag(CN$_3$CN)$_2$]$^{3+}$ in **1** is shown in Figure 1. Compound **1** consists of two [Pt(phpy)(9S3)]$^+$ units complexed to a Ag$^+$ ion via short Pt→Ag dative bonds. Two acetonitrile ligands complete the distorted tetrahedral environment of the Ag ion. The two Pt^{II}→Ag^I bonds present in **1** are short [Pt1−Ag1, 2.7557(6) Å; Pt2−Ag1, 2.7659(6) Å], indicating strong bonding between the formally cationic Pt metal complexes and the cationic Ag center. The lack of stereochemical preference by Ag^I allows for the bent ligation of the acetonitrile ligands [Ag1−N3−C35 angle, 161.7(8)°; Ag1−N4−C37 angle, 137.0(8)°] to accommodate the steric demands imposed by the dative-bonded Pt complexes.

The only three other structures with completely unsupported Pt→Ag dative bonds[7] include either formally anionic or neutral Pt complexes as donors, in contrast to the cationic donor complexes presented here. Complexes of the form [{Pt(L)$_2$}$_2${Ag(acetone)$_2$}]$_n$(ClO$_4$)$_{2n}$ have short unsupported Pt→Ag dative bonds [L = phpy, Pt−Ag, 2.6781(9) Å; L = 2-(2-thienyl)pyridine, Pt−Ag, 2.6746(7) Å] employing neutral Pt complexes as donors.[2] Short unsupported Pt→Ag dative bonds in the complex [Pt(C$_6$F$_5$)$_3$(tht)Ag(PPh$_3$)] [Pt−Ag, 2.639(2) Å] utilize anionic Pt complexes as donors.[8] The lack of any Ag interactions other than the Pt−Ag bonds indicates that the structure of **1** is a rare example of simple "pure" Pt−Ag dative bonds.

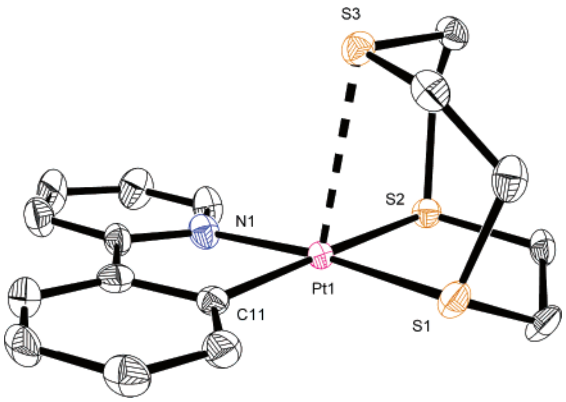

Figure 2. Structure of [Pt(phpy)(9S3)]$^+$ in **2**. Relevant bond lengths (Å) and angles (deg): Pt1−S1, 2.2641(16); Pt1−S2, 2.3544(16); Pt1−S3, 2.9518(17); Pt1−N1, 2.050(6); Pt1−C11, 2.031(6).

The Pt−S axial interactions with the S atoms of 9S3 trans to the Pt−Ag bonds are also relatively short [Pt1−S3, 2.6870(18) Å; Pt2−S6, 2.7461(19) Å]. The axial Pt−S bonds are only slightly tilted from the normal to the mean-square plane containing the immediate coordination sphere around Pt (S3−Pt1 plane normal, 8.7°; S6−Pt2 plane normal, 11.7°). The Pt−Ag bonds are somewhat tilted from the normal to the mean-square plane containing the immediate coordination sphere around Pt (Ag1−Pt1 plane normal, 15.6°; Ag1−Pt2 plane normal, 12.7°). The axial S−Pt−Ag angles [S3−Pt1−Ag1, 166.17(4)°; S6−Pt2−Ag1, 168.78(5)°] deviate from 180° because of steric concerns at the Ag atom. The unique combination of the strong field ligand carbon donor phpy paired with the ability of the strong field and axially coordinating ligand 9S3 to enrich the electron density of the Pt d$_{z^2}$ orbital enables these cationic/cationic dative bonds to form. Besides its electron-donating ability, the axial Pt−S interaction of the 9S3 truncates the cluster at three metal centers, preventing the formation of polymeric structures previously constructed using Pt−Ag dative bonds.[2a]

Each Pt complex donor cation in the structure of **1** possesses metal-based chirality because the mixed C/N ligation of phpy destroys mirror and 2-fold symmetry perpendicular to the square plane and the axial Pt−S interaction destroys mirror symmetry within the coordination plane. Each trinuclear cluster contains an example of both enantiomers. Each Pt complex donor in **1** also has a chiral component of the 9S3 conformation, but only one chiral configuration of 9S3 is observed. The structure of **2** exhibits the same chirality. In solution, however, the 9S3 ligands of this cation are fluxional, as indicated by ^{1}H and ^{13}C NMR.

Comparison with the structure of compound **2** (ORTEP drawing of [Pt(phpy)(9S3)]$^+$ in **2**; Figure 2) reveals that the axial S interaction in the absence of the Ag$^+$ ion is significantly longer [Pt1−S3, 2.9518(17) Å] and typical of

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[6] Crystal data for **1**: C$_{17}$H$_{20}$NS$_3$Pt·PF$_6$, orthorhombic, space group *Pbca*, $a = 11.944(2)$ Å, $b = 12.122(2)$ Å, $c = 28.012(6)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 4055.5(14)$ Å^3, $Z = 8$, $D_{\text{calcd}} = 2.210$ Mg/m^3, $\mu = 7.366$ mm^{-1}, final R indices [$I > 2\sigma(I)$], R1 = 0.0422, wR2 = 0.0803, R indices (all data), R1 = 0.0470, wR2 = 0.0819.

[7] Completely unsupported Pt−Ag dative bonds are defined as having no ligands bridging Pt and Ag, no Ag interactions with other ligands attached to Pt, and no additional M−M interactions.

[8] Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 2556.

other Pt−S distances observed in Pt(9S3) complexes.[3] The presence of the Pt→Ag dative bonds draws the electron-donating trans S closer to the Pt by over 0.20 Å. This is consistent with the d_{z^2} orbital bringing the axial S closer to replenish the electron density donated to the Ag^+ ion. The axial Pt−S bonds are slightly tilted from the normal to the mean-square plane containing the immediate coordination sphere around Pt (S3−Pt1 plane normal, 11.1°). Much smaller changes are observed in the equatorial Pt−S, Pt−N, and Pt−C bond lengths of the two structures.

The presence of Pt→Ag dative bonds in solution is supported by ^{195}Pt NMR spectra, cyclic voltammetry, and UV−vis measurements. Compound **2** shows a ^{195}Pt NMR resonance at −3787 ppm in a DMSO-d_6 solution (vs K_2PtCl_6 in D_2O). Upon the addition of excess $AgPF_6$, a ^{195}Pt NMR signal at −3582 ppm is observed.[9] This downfield shift is consistent with the formation of Pt→Ag dative bonds in solution because the electron density at Pt is diminished upon bonding with the Ag^+ ion. Cyclic voltammetry measurements of a solution of **2** show an irreversible oxidation at +0.377 V (vs Fc/Fc$^+$; see the Supporting Information). On the basis of the assignment of similar complexes with diimines, this oxidation is assigned as a Pt$^{II/III}$ couple. Upon the addition of excess Ag^+ ion to a solution of **2**, one irreversible process is observed, now shifted to +0.517 V. Assignment of this irreversible oxidation as the Pt$^{II/III}$ couple suggests that the Pt center is more electron-poor upon the addition of Ag^+ because a dative bond is formed in solution. In a dilute acetonitrile solution, the addition of $AgPF_6$ to **2** shows no changes in the UV−vis spectrum. However, in a concentrated acetonitrile solution, the lowest energy feature in the electronic spectrum of **2** (assigned as a Pt → phpy metal-to-ligand charge-transfer band, 370 nm) upon the addition of excess $AgPF_6$ shifts to lower energy (380 nm) and increases in intensity by 50%.

Studies are underway to examine other d^{10} metals as acceptors in the formation of cation/cation dative bonds with complex **2**, as well as the effects of modifying the donor/acceptor properties of the cyclometalating moiety.

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Supporting Information Available: Experimental details and characterization, tables of crystallographic data, ^{195}Pt NMR spectra, UV−vis spectra, and cyclic voltammograms for compund **2**, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Reference 2a reports a downfield ^{195}Pt NMR chemical shift of approximately 400 ppm in a Pt(phpy) complex capable of forming two Pt−Ag interactions per Pt complex. The downfield shift we observe of about 200 ppm is consistent with a Pt complex that can only involve one Pt−Ag interaction per Pt complex.