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Covalent Bonding of Two Ag(I) Atoms to a Square-Planar Pt(II) Atom in $[Pt_3(S_2CNEt_2)_6Ag_2](ClO_4)_2$

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$[Pt(S_2CNEt_2)_2]$ reacts with $[AgClO_4]$ to form $[\{Pt_3(S_2CNEt_2)_6Ag_2\}(ClO_4)_2]$. Its crystal has an extended two-dimensional cationic lattice with an Ag-Pt-Ag arrangement [Pt-Ag = 2.932(2) Å and ∠Ag-Pt-Ag = 166.8(1)°] unsupported by covalently bridging ligands.

Only a few cluster complexes have been characterized to have a Pt(II)-Ag(I) bond unsupported by a covalent bridge.[1,2] Bonding interactions between Pt and Ag atoms have been a matter of arguments in complexes containing these metal atoms in neighboring positions supported by covalent bridges.[3,4] We report here that $[Pt(S_2CNEt_2)_2]$[5] (**1**) reacts with $[AgClO_4]$ (**2**) to form $[\{Pt_3(S_2CNEt_2)_6Ag_2\}(ClO_4)_2]$ (**3**). The crystal of **3** has an extended two-dimensional lattice with an Ag-Pt-Ag

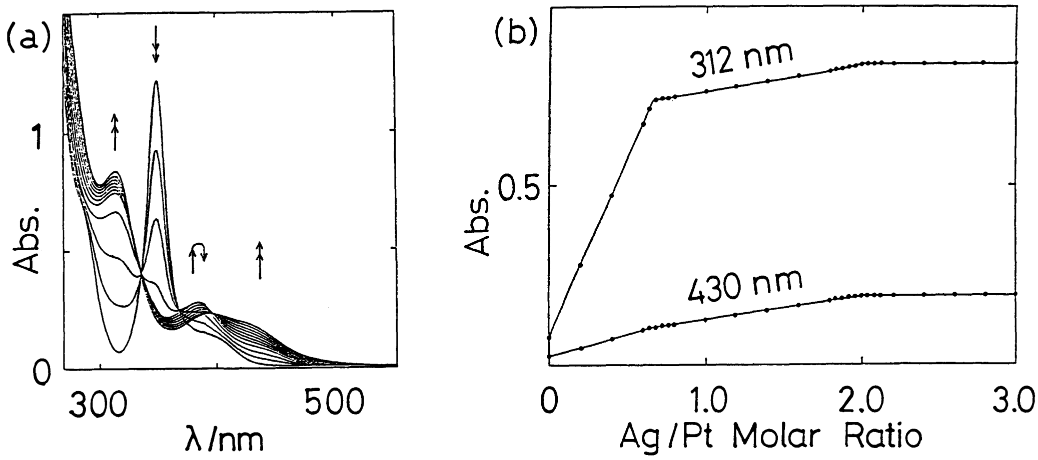

Fig. 1. The binding of 1 to Ag^+ in CH_2Cl_2. (a) 0.010 cm^3 each of a 0.100 mol/dm^3 solution of 2 in toluene was added successively into 100 cm^3 of a 50.0 $\mu mol/dm^3$ solution of 1 in CH_2Cl_2. The reaction was monitored with use of a 1-cm pathlength cell. (b) Plots of absorbances of the solution against the Ag/Pt molar ratio.

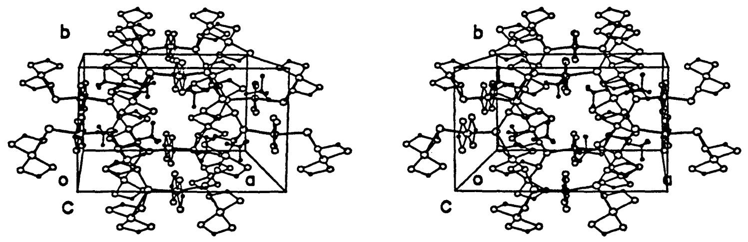

Fig. 2. Stereoview of the unit cell of 3. Diethylamino groups are omitted for clarity.

bonding unsupported by covalent bridges.

The reaction between **1** and Ag^+ was monitored on a spectrophotometer with successive addition of aliquots of a toluene solution of 2 into a CH_2Cl_2 solution of **1** at room temperature (Fig. 1a). Absorbances of the solution were plotted against the Ag/Pt molar ratio (Fig. 1b). Figure 1 shows that the reaction takes place in successive two steps.

When Ag^+ was added into the solution of **1**, the absorption peak at 347 nm due to **1** diminished accompanied with the appearance of new peaks at 313 and 383 nm. Isosbestic points were observed at 334 and 366 nm. A sharp flection was detected in the absorbance dependence on the Ag/Pt ratio at Ag/Pt = 2.0/3.0 in Fig. 1b. The reaction can be represented as Eq 1.

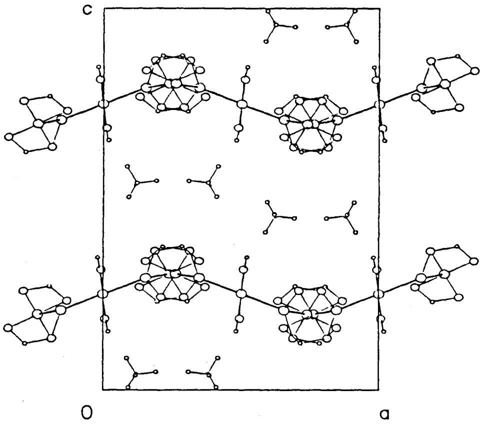

Fig. 3. Projection of the unit cell of 3 onto the ac-plane. Diethylamino groups are omitted for clarity.

$$3Pt(S_2NEt_2)_2 + 2AgClO_4 = [Pt_3(S_2CNEt_2)_6Ag_2](ClO_4)_2 \qquad (1)$$

Further addition of Ag^+ induced reaction of 3 to form a new complex. In this process, the peaks due to 3 at 313 and 383 nm were shifted to 312 and 395 nm, respectively. A new shoulder appeared at 430 nm. Isosbestic points were observed at 330 and 396 nm. The second flection in Fig. 1b was observed at the Ag/Pt molar ratio of 2.0/1.0, suggesting formation of $[\{Pt(S_2CNEt_2)_2Ag_2\}(ClO_4)_2]$.

Orange-yellow micro-crystals of 3 were prepared by reaction of 1 and 2 in CH_2Cl_2 in the molar ratio of 3 : 2 (yield = 73%, isolated).6)

The crystal structure of 3 was obtained with an analysis of X-ray diffractions of an orange-yellow 0.3 × 0.25 × 0.05 mm^3 single-crystal grown from a CH_2Cl_2 solution by slow evaporation of the solvent.7) Figures 2 and 3 show the arrangement of atoms in the unit cell. The crystal is an alternate pile of extended two-dimensional lattices of $[Pt_3(S_2CNEt_2)_6Ag_2]_x^{2x+}$ and anionic layers containing ClO_4^-. All the atoms in the cationic lattice are covalently connected (vide infra).

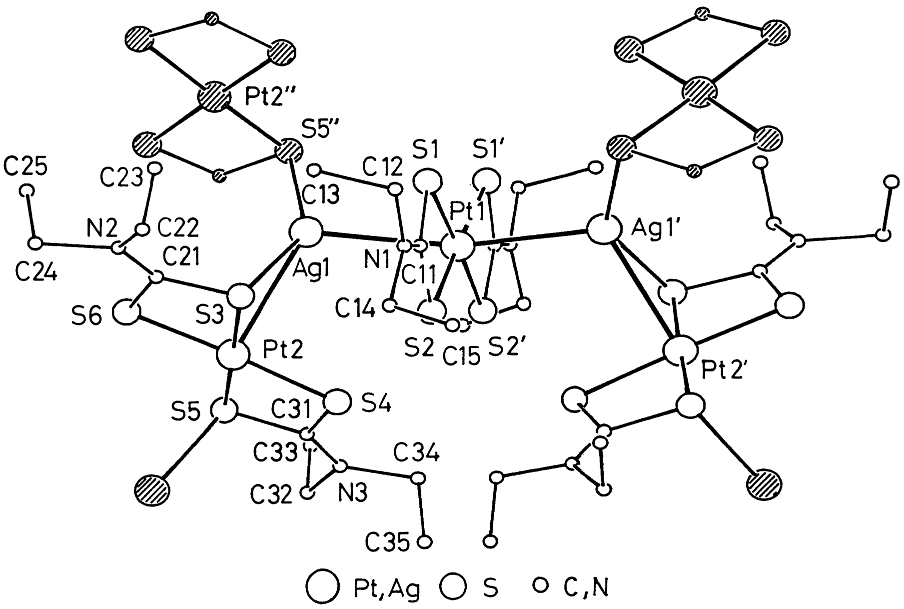

Fig. 4. $[Pt_3(S_2CNEt_2)_6Ag_2]^{2+}$ unit with two extra $Pt(S_2C)_2$ groups (hatched) and two extra Ag atoms (hatched) to show the connections between neighboring units. All atoms are represented by arbitrary circles.

We tentatively select the $[Pt_3(S_2CNEt_2)_6Ag_2]^{2+}$ unit in Fig. 4 as a building brick. It has C_2 symmetry. The symmetry axis coincides with the line bisecting the valence angle of S1-Pt1-S1'. Each of Pt1 and Pt2 is surrounded by four sulfur atoms in a square-planar geometry with normal bond lengths and bond angles. The Pt1-Ag1 bond length is 2.932(2) Å. This bond is tilted toward S1: Ag1-S1 = 3.028(5), Ag1-S2 = 3.391(5), Ag1-S1' = 4.112(6), and Ag1-S2' = 4.278(6) Å. Since these Ag-S distances are far greater than the sum of the covalent radii of both atoms (2.56 Å),[8] we propose that both Ag1 and Ag1' are covalently bonded to Pt1. The Ag1-Pt1-Ag1' bond angle is 166.8(1)°. Note that in CH_2Cl_2 solution of **3** there exists only one species formed from **1** and **2** in the molar ratio of 3 to 2 without detectable equilibrium of dissociation into mononuclear species as shown in Fig. 1. To our knowledge, this is the first example of a covalently-bonded Ag-Pt-Ag arrangement unsupported by covalent bridges. Since both Ag1 and Ag1' share the $d(z^2)$ lone-pair on Pt1 from the both side of the S_4Pt basal plane, the Pt-Ag distance is longer than that observed for $Pt(C_6F_5)_3(SC_4H_8)Ag(PPh_3)$ (2.637 Å).[1a] In the latter complex, a Pt atom is bonded to a single Ag atom. The present Pt1-Ag1 distance is the longest one among the reported values of definite Pt-Ag covalent bonds.[1,2] The Ag1-S1 distance is too long for a covalent bond, but it is slightly shorter than the sum of the ionic radius of Ag^+ and the van der Waals radius of S (3.11 Å).[8] The contact of S1 to Ag1 suggests that this sulfur atom weakly supports the Ag1-Pt1 bond.

Pt2 and Ag1 are separated by 3.045(2) Å. S3 is bridging between these atoms: Pt2-S3 = 2.328(5), Ag1-S3 = 2.546(6) Å, and ∠Pt2-S3-Ag1 = 77.2(2)°. Since the Pt2-Ag1 distance is only 0.11 Å longer than the covalent bond-length for Pt1-Ag1, we suppose there exists bonding interaction between the former pair of metal atoms. The covalent linkage between the neighboring $[Pt_3(S_2CNEt_2)_6Ag_2]^{2+}$ units is supplied by the Ag1-S5'' bond [2.479(5) Å] and its crystallographic equivalents. All the covalent bonds from Pt1, Pt2, S3 and S5'' to Ag1 and the dative interaction from S1 toward Ag1 are supplied by π electrons of $Pt(S_2CNEt_2)_2$ moieties. We suppose Pt-Ag and Ag-S covalent bonds have stabilized the otherwise less-stable stacked structure of alternatingly-charged layers.

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6) Elemental anal. Found: C, 19.29; H, 3.18%. Calcd for $C_{30}H_{60}N_6O_8S_{12}Cl_2Ag_2Pt_3$: C, 19.07; H, 3.20%.

7) Crystal data: $C_{30}H_{60}N_6O_8S_{12}Cl_2Ag_2Pt_3$, Orthorhombic, Pbcn, a = 17.166(2) Å, b = 11.261(2) Å, c = 28.631(2) Å, V = 5534.6(10) Å^3, Z = 4, D(calcd) = 2.268 g cm^{-3}, μ = 89.06 cm^{-1}, R = 0.081 and R_w = 0.071 for 4304 independent reflections.

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