Complexes of Silver(I) with Bis(dialkyldithiocarbamato)platinum(II) as Ligand: Synthesis and Structures of $[Pt_3(S_2CNPr^i{}_2)_6Ag_2](BF_4)_2$ and $[Pt_3(S_2CNBu^n{}_2)_6Ag_2](ClO_4)_2$

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Bis(dialkyldithiocarbamato)platinum(II) complexes with Pr^i or Bu^n substituents on the dithiocarbamato ligands and Ag^I salts gave the complexes in the title with $^1J(^{195}Pt-^{107,109}Ag)$ of *ca.* 200 Hz indicating a Pt–Ag bonding interaction; their X-ray structures showed that they consist of two Ag atoms separated by *ca.* 3.0 Å surrounded by three molecules of the starting Pt complex.

Formation of heterometallic polynuclear complexes by reaction between Ag^I and d^8 complexes of the group 10 elements has attracted recent attention in the hope of finding new modes of ligation, new reagents and/or catalysts. A wide range of metal–metal interactions has been discovered in this and related classes of complexes:[1] an M–M′ bond[2,3] an M···M′ 'bonding interaction'[4] and no direct M–M′ bond.[5] We previously reported[6] the formation of $[Pt_3(S_2CNEt_2)_6Ag_2](ClO_4)_2$ **1**, the cationic part of which forms a two-dimensional polymer in the crystal. It dissolves in CH_2Cl_2 probably with the destruction of the polymeric structure, but the cationic species in solution still retains the composition $[Pt_3(S_2CNEt_2)_6Ag_2]^{2+}$. The structure in solution has remained unresolved. We report here the unprecedented structure of the discrete cationic complexes $[Pt_3(S_2CNPr^i{}_2)_6Ag_2](BF_4)_2$ **2** and $[Pt_3(S_2CNBu^n{}_2)_6Ag_2](ClO_4)_2$ **3**, which have a Pt···Ag 'bonding interaction' as evidenced by Pt–Ag nuclear spin–spin coupling.

Monitoring of the UV–VIS spectra of reaction mixtures of $[M(S_2CNR_2)_2]$ (M = Pt, Pd; R = Pr^n, Pr^i, Bu^n, cyclohexyl) and AgX (X = ClO_4, BF_4) showed spontaneous formation of $[M_3(S_2CNR_2)_6Ag_2]X_2$ and/or $[M(S_2CNR_2)_2Ag_2]X_2$ in CH_2Cl_2 depending on the ratio of reagents. The products were isolated by addition of hexane.

In contrast with **1** the X-ray structure† of the orange complex **2** showed that the cation is a discrete unit (Fig. 1). Pt(2) is on the crystallographic twofold axis. The three platinum units are located around the Ag···Ag axis which is a pseudo-threefold axis. Two diagonally related S atoms in each platinum complex are coordinated to separate Ag atoms: the

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† Complex **2** crystallized by slow diffusion of hexane into a dichloromethane solution, orthorhombic, *Pccn* (No. 56), a = 11.616(2), b = 29.844(2), c = 20.424(3) Å, V = 7080 Å^3, Z = 4, Mo-Kα radiation, $2\theta_{max}$ = 55°, 13543 reflections measured (two octants) on a Rigaku RASA-5R diffractometer (Governmental Industrial Research Institute, Nagoya), 3441 used [$F_o > 3\sigma(F_o)$], empirical absorption correction (psi scan), R = 0.075, R_w = 0.065.

Complex **3** crystallized by slow evaporation from a dichloromethane solution, orthorhombic, *Pbca* (No. 61), a = 31.244(7), b = 30.671(10), c = 17.291(3) Å, V = 16570 Å^3, Z = 8, Mo-Kα radiation, $2\theta_{max}$ = 55°, 19560 reflections measured on a Rigaku AFC-5R diffractometer (Institute for Molecular Science, Okazaki), 5002 used [$F_o > 5\sigma(F_o)$], absorption correction as a cylinder, R = 0.090, R_w = 0.099.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

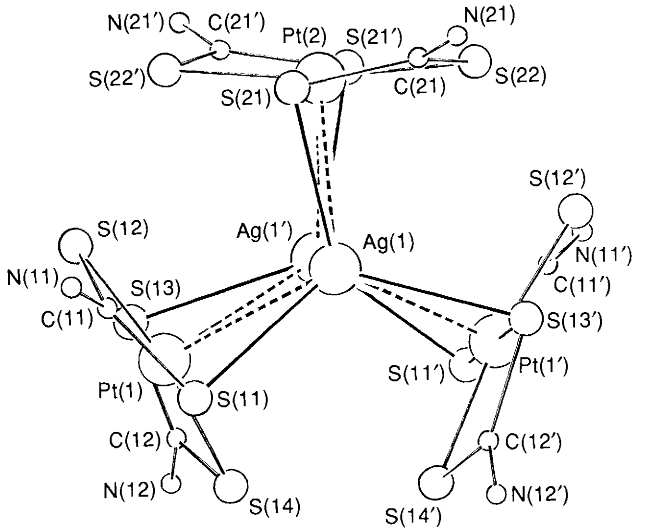

Fig. 1 Structure of $[Pt_3(S_2CNPr^i{}_2)_6Ag_2]^{2+}$ ion in **2** without alkyl groups for clarity. Important bond distances (Å) and angles (°) are as follows: Pt(1)–Ag(1), 2.905(2); Pt(1)–Ag(1'), 3.002(2); Pt(2)–Ag(1), 2.932(2); Ag(1)–Ag(1'), 2.964(2); average Pt–S 2.320(2); Ag(1)–S(11), 2.745(6); Ag(1)–S(13'), 2.724(6); Ag(1)–S(21), 2.717(6); S(11)–Pt(1)–S(13), 179.0(2); S(12)–Pt(1)–S(14), 171.4(2); S(21)–Pt(2)–S(21'), 179.3(2); S(22)–Pt(2)–S(22'), 171.2(2).

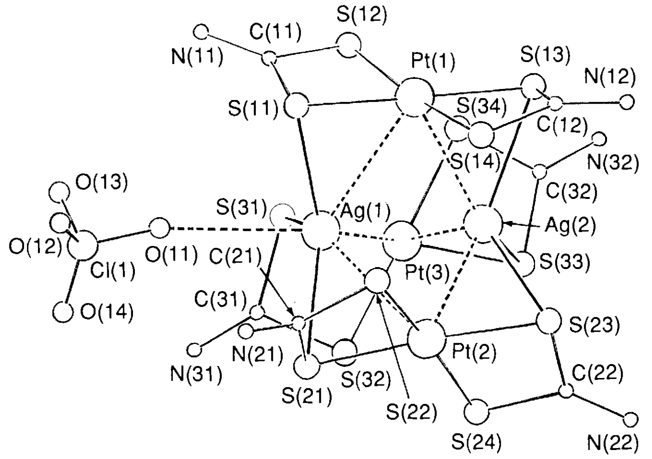

Fig. 2 Structure of $[Pt_3(S_2CNBu^n{}_2)_6Ag_2]^{2+}$ with the interacting ClO_4^- in **3**; alkyl groups omitted for clarity. Important bond distances (Å) and angles (°) are as follows: Pt(1)–Ag(1), 3.061(4); Pt(1)–Ag(2), 2.912(4); Pt(2)–Ag(1), 3.055(4); Pt(2)–Ag(2), 2.842(4); Pt(3)–Ag(1), 3.172(4); Pt(3)–Ag(2), 2.825(4); Ag(1)–Ag(2), 3.033(5); average Pt–S, 2.30(1); Ag(1)–S(11), 2.74(1); Ag(1)–S(21), 2.74(2); Ag(1)–S(31), 2.62(1); Ag(2)–S(13), 2.74(1); Ag(2)–S(23), 2.77(1); Ag(2)–S(33), 2.82(1); Ag(1)–O(11), 3.03(4); S(11)–Pt(1)–S(13), 178.1(4); S(12)–Pt(1)–S(14), 172.0(4); S(21)–Pt(2)–S(23), 176.0(5); S(22)–Pt(2)–S(24), 171.3(4); S(31)–Pt(3)–S(33), 179.0(4); S(32)–Pt(3)–S(34), 172.6(4).

Ag–S bond lengths are 2.717(6)–2.745(6) Å. The Pt atoms and the S atoms bound to the Ag atoms are closer to the Ag···Ag axis from the PtS_4 best planes by 0.08(1) and 0.06(1) Å, respectively. The Ag atoms are 0.78 Å closer to the central Pt_3 plane from the plane of three S atoms to which they are bound. The Ag···Ag distance is 2.964(2) Å and the Ag···Pt distances are 2.905(2)–3.002(2) Å. These distances are far shorter than the van der Waals contacts.[7] All these observations imply that each Ag atom is attracted by the Pt atoms and/or the other Ag atom. There are short intramolecular contacts between sulfur atoms [S(12)–S(22') 3.494(7) Å, S(14)–S(14') 3.263(9) Å].

The ^{195}Pt NMR spectrum of $[Pt_3(S_2CNBu^n{}_2)_6Ag_2](BF_4)_2$ **4** in CH_2Cl_2 at room temperature showed a signal at −3348 ppm *vs.* external H_2PtCl_6 in D_2O, 481 ppm deshielded from that of $[Pt(S_2CNBu^n{}_2)_2]$, as a 1 : 2 : 1 triplet (J 194 Hz) due to the two equivalent $^{107,109}Ag$ nuclei [both $I = 1/2$; the difference between $^1J(^{195}Pt–^{107}Ag)$ and $^1J(^{195}Pt–^{109}Ag)$ was not resolved]. This result as well as the similarity of the diffuse reflectance spectrum of powdered **2** and the solution spectra of **2** and **4** in CH_2Cl_2 suggests that the solution structures of the cations of these Pt_3Ag_2 complexes are similar to that of **2** in the crystal. Since the magnitude of ^1J(Pt–Ag) between the directly bonded atoms is in the range 370–820 Hz,[3,8] the coupling constant of **4** indicates the existence of moderate 'bonding interaction' between the Pt and Ag atoms.

The X-ray structure† of **3** showed that it also consists of discrete $[Pt_3(S_2CNBu^n{}_2)_6Ag_2]^{2+}$ units (Fig. 2), but it is distorted by coordination of ClO_4^- to one of its Ag atoms [Ag(1)–O(11) 3.03(4) Å]. The Pt–Ag distances involving Ag(1) are longer than those involving Ag(2) by 0.24(7) Å. The Ag–S bond lengths involving Ag(1) are shorter than those involving Ag(2) by *ca.* 0.08 Å. Ag(2) is 0.96 Å inside the plane of the three S atoms bound to it, whereas Ag(1) is only 0.48 Å inside. The ^{195}Pt NMR signal of **3** in CH_2Cl_2 was observed as a 1 : 2 : 1 broad triplet (J 200 Hz) at −3361 ppm at 223 K but as a broad singlet at room temperature. This indicates intermolecular exchange of the Ag ions probably promoted by coordination of the ClO_4^- ions.

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