Synthesis and X-ray crystal structure of a hexanuclear silver(I) complex with non-chelating tri- and tetra-dentate bridging *o*-(diphenylphosphino)benzoate ligands

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Single crystal X-ray analysis of the hexanuclear silver(I) complex $Ag_6[o\text{-}Ph_2P(C_6H_4CO_2)\text{-}O,P]_6$, synthesized by treatment of $Ag(CF_3SO_3)$ with $N(CH_2CH_2NH_2)_3$, 1,3-dicyclohexylcarbodiimide (DCC) and $o\text{-}Ph_2PC_6H_4(CO_2H)$ in 1:1:3:3 molar ratio in ethanol, shows that the complex is centrosymmetric and consists of three independent silver(I) centres linking together *via* non-chelating tri- and tetradentate bridging *o*-(diphenylphosphino)benzoate groups.

We have been interested in the preparation of diimino-, diamino- and diamido-diphosphine ligands and demonstrated that these ligands do indeed exhibit a very rich coordination chemistry.[1,2] Recently, we have extended our study to the preparation of polydentate ligands containing three iminophosphino groups and show that the heptadentate ligand $\{(o\text{-}Ph_2PC_6H_4)CH{=}NCH_2CH_2\}_3N$ can be prepared *via* template synthesis.[3] Here we report the result of our attempt to extend the template synthetic route for the preparation of the amidophosphino heptadentate ligand.

Treatment of $Ag(CF_3SO_3)$ with $N(CH_2CH_2NH_2)_3$, 1,3-dicyclohexylcarbodiimide (DCC) and $o\text{-}Ph_2PC_6H_4CO_2H$ in 1 : 1 : 3 : 3 molar ratio in refluxing ethanol affords, after work up, white crystals of stoichiometry $[Ag(o\text{-}Ph_2PC_6H_4CO_2)]_6$ **1**‡ in 10% yield. However, compound **1** could not be isolated from the reaction of $Ag(CF_3SO_3)$ with $o\text{-}Ph_2PC_6H_4CO_2H$ and 4-dimethylamino-pyridine (DMAP) in 1 : 1 : 1 molar ratio in the absence of DCC. The structure of **1** was established by X-ray crystallography. Crystals of $\mathbf{1}\cdot 2C_4H_8O\cdot C_6H_{14}$ suitable for X-ray diffraction study§ were grown by slow diffusion of hexane into a tetrahydrofuran solution of **1**. The molecular structure of **1** [Fig. 1(*a*)] shows that the hexameric system is embedded within an outer shell of aromatic rings formed by the phenyl rings of the phosphine and benzoate. The molecule is a centrosymmetric hexanuclear silver(I) complex with three independent Ag atoms linking together *via* the *o*-(diphenylphosphino)benzoate groups forming a $Ag_6[o\text{-}Ph_2P(C_6H_4CO_2)\text{-}O,P]_6$ cluster as shown in Fig. 2. The three independent Ag atoms in the asymmetric unit are four-coordinate and their coordination geometries can be described as highly distorted tetrahedra. The coordination environment of Ag(2) and Ag(3) are very similar. Both silver(I) centres are surrounded by two O atoms and one P atom from three different *o*-(diphenylphosphino)benzoate ligands and have a very long metal–metal distance [Ag(2)–Ag(3) 3.244(2) Å which is significantly shorter than the other two inter-silver distances; Ag(1)···Ag(2) 3.805, Ag(1)···Ag(3) 3.756 Å] between each other. The Ag(2)···Ag(3) distance is much longer than that (2.89 Å) found in metallic silver and is comparable to the long Ag–Ag distance [3.090(4) Å] in $[Ag_6L_2(HL)_2(H_2O)_4]$ (L = pyridine-2,3-dicarboxylate),[4] [3.194(2) Å] in $[Ag(\eta^2\text{-}O_2CMe)(\mu\text{-dppm})]_2$ (dppm = $Ph_2PCH_2PPh_2$),[5] and the interchain Ag–Ag distances [3.269(2) and 3.346(2) Å] in $[Ag_2L'_2(H_2O)]_n[ClO_4]_{2n}$ (L′ = trimethylammoniopropionate)[6] indicating a very weak metal–metal interaction. Ag(2) is approximately coplanar with O(1), O(6*) and P(2) [Ag(2)–O(1) 2.185(7), Ag(2)–O(6*) 2.411(8), Ag(2)–P(2) 2.376(4) Å] with a

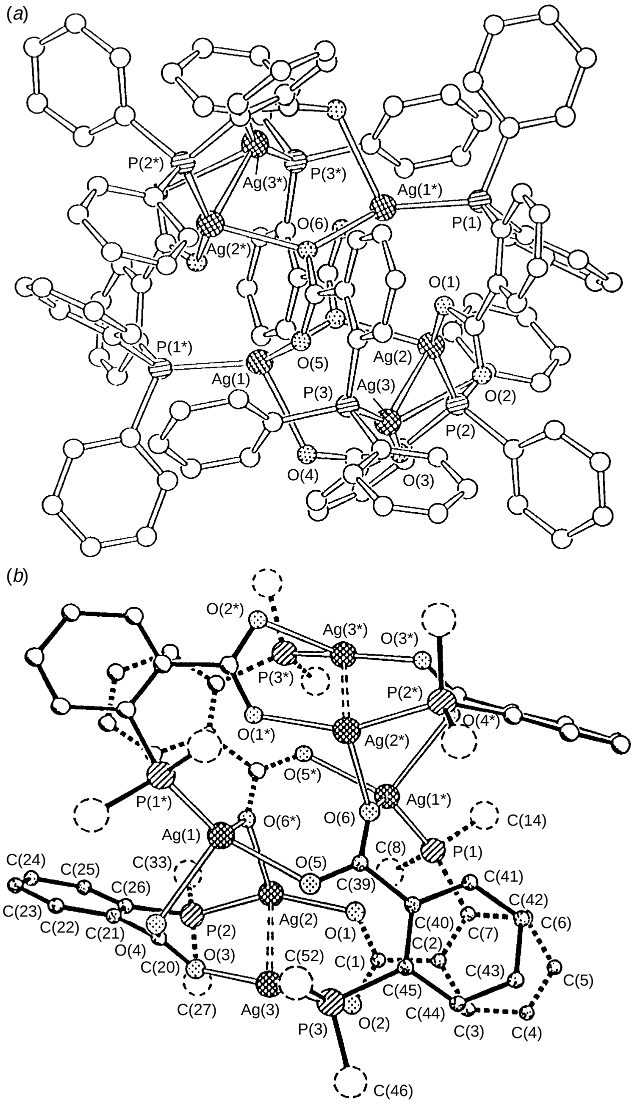

Fig. 1 (*a*) Overall molecular geometry of compound **1**. For clarity, the hydrogen atoms are omitted. (*b*) A perspective drawing of **1** with the phenyl rings of the PPh_2 groups each represented by a circle with broken outline. Selected bond lengths (Å) and angles(°): Ag(2)–Ag(3) 3.244(2), Ag(1)–P(1*) 2.381(4), Ag(2)–P(2) 2.376(4), Ag(3)–P(3) 2.378(4), Ag(1)–O(4) 2.598(9), Ag(1)–O(5) 2.261(9), Ag(1*)–O(6) 2.394(9), Ag(2)–O(1) 2.185(9), Ag(2*)–O(6) 2.411(9), Ag(3)–O(2) 2.619(9), Ag(3)–O(3) 2.176(9), P(1*)–Ag(1)–O(4) 108.8(2), P(1*)–Ag(1)–O(5) 129.5(2), P(1*)–Ag(1)–O(6*) 130.5(2), O(4)–Ag(1)–O(5) 100.4(3), O(4)–Ag(1)–O(6*) 87.9(3), O(5)–Ag(1)–O(6*) 89.9(3), O(1)–Ag(2)–O(6*) 98.6(3), P(2)–Ag(2)–O(6*) 108.0(2), Ag(3)–Ag(2)–P(2) 106.0(1), P(2)–Ag(2)–O(1) 152.8(2), O(2)–Ag(3)–P(3) 93.1(2), O(2)–Ag(3)–O(3) 105.4(3), O(3)–Ag(3)–P(3) 161.2(3), Ag(2)–Ag(3)–P(3), 134.6(1).

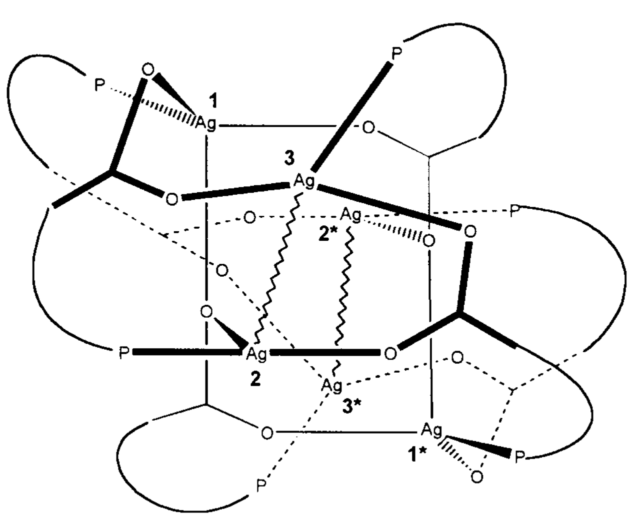

Fig. 2 $Ag_6[o\text{-}Ph_2P(C_6H_4CO_2)\text{-}O,P]_6$ cluster

deviation of 0.108 Å and equatorial bond angles [O(1)–Ag(2)–O(6*) 98.6(3), P(2)–Ag(2)–O(6*) 108.0(2), and P(2)–Ag(2)–O(1) 152.8(2)°] summing to *ca.* 360°. Ag(3) is *ca.* 0.250 Å above the least-squares plane formed by O(2), O(3) and P(3) [Ag(3)–O(2) 2.619(9), Ag(3)–O(3) 2.176(9), Ag(3)–P(3) 2.378(4) Å] with equatorial bond angles [O(2)–Ag(3)–P(3) 93.1(2), O(2)–Ag(3)–O(3) 105.4(3), O(3)–Ag(3)–P(3) 161.2(3)°] summing to *ca.* 360°. However, if one considers the long Ag–O [Ag(2)–O(6*) 2.411(8), Ag(3)–O(2) 2.619(9)] and Ag(2)–Ag(3) distances as insignificant and non-interacting, with the large P(2)–Ag(2)–O(1) [152.8(2)°] and P(3)–Ag(3)–O(3) [161.2(3)°] angles, Ag(2) and Ag(3) may be described as two-coordinate. Ag(1) is surrounded by three carboxylato-O atoms and a P atom from four different *o*-(diphenylphosphino)benzoate ligands [Ag(1)–O(4) 2.598(9), Ag(1)–O(5) 2.261(9), Ag(1)–O(6*) 2.394(9), Ag(1)–P(1*) 2.381(4) Å]. The coordination geometry of Ag(1) is highly distorted from tetrahedral with the Ag atom lying only 0.418 Å above the least-squares plane of O(5), O(6*) and P(1*) and the bond angles ranging from 89.9(3) to 130.5(2)°. The Ag–P distances are normal and comparable to the Ag–P distances [2.363(4), 2.390(4) Å] in $[Ag_2(\mu\text{-}O_2CMe\text{-}O,O')(\mu\text{-}O_2CMe\text{-}O)(dppm)]_2$[5] and [2.342(4)–2.378(5) Å] in $[(C_{12}H_6O_4)_2(Ph_3PAg)_4]$ ($C_{12}H_6O_4$ = 1,8-naphthalenedicarboxylate).[7]

Of the three independent carboxylate groups, two behave as bidentate and one as tridentate ligands. The coordination modes of the two bidentate carboxylate ligands are very similar. Both of them coordinate unsymmetrically to two different silver atoms with a short and a long Ag–O bond in a *syn*–*syn* bridging mode. For the carboxylato group C(2)C(1)O(1)O(2), the Ag(2)–O(1) distance [2.185(9) Å] is significantly shorter than that of Ag(3)–O(2) [2.619(9) Å] with comparable C–O distances [C(1)–O(2) 1.24(1), C(1)–O(1) 1.28(1) Å]. Similarly, for the carboxylato group C(21)C(20)O(3)O(4), the Ag(3)–O(3) distance [2.176(9) Å] is significantly shorter than that of Ag(1)–O(4) [2.598(9) Å] with similar C–O distances [C(20)–O(3) 1.26(1), C(20)–O(4) 1.24(1) Å]. The carboxylato group C(40)C(39)O(5)O(6) coordinates to three different Ag atoms with Ag–O [Ag(1)–O(5) 2.261(9), Ag(2*)–O(6) 2.411(9), Ag(1*)–O(6) 2.394(9) Å] and C–O [C(39)–O(5) 1.22(1), C(39)–O(6) 1.27(1) Å] distances comparable to those observed in $[Ag_2(\mu\text{-}O_2CMe\text{-}O,O')(\mu\text{-}O_2CMe\text{-}O)(dppm)]_2$ [Ag–O, 2.232(11)–2.485(10), C–O 1.238(21)–1.278(19) Å],[5] resulting a tridentate carboxylato-μ-*O,O′*;μ-*O,O* mode.

Unlike previous reported *o*-(diphenylphosphino)benzoate metal complexes in which the ligand behaves as a bidentate chelating ligand,[8,9] the *o*-(diphenylphosphino)benzoate-*O,P* ligands in **1** do not exhibit chelation with any Ag atom, neither do the carboxylato-*O,O′* groups, instead, both groups connect with different Ag atoms at different coordinating sites.

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Notes and References

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‡ $[Ag(o\text{-}Ph_2PC_6H_4CO_2)]_6{\cdot}2C_4H_8O{\cdot}C_6H_{14}$ ($\mathbf{1}{\cdot}2C_4H_8O{\cdot}C_6H_{14}$): white crystals, mp > 300 °C. Found: C, 56.6; H, 4.3. Calc. for $C_{128}H_{114}P_6O_{14}Ag_6$: C, 56.7; H, 4.2%. IR (cm^{-1}, in KBr): 3058w, 2976w, 2932w, 2854w, 2128w, 1597vs, 1577vs, 1556vs, 1481m, 1360vs, 1287m, 1260m, 1097m, 1061m, 1028w, 841m, 757vs, 696vs, 535m, 510m. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 10.6 (br) and 15.0 (br). ^1H NMR ($CDCl_3$): δ 7.25–7.69 (br, m).

§ *Crystal data*: $\mathbf{1}{\cdot}2C_4H_8O{\cdot}C_6H_{14}$: $C_{114}H_{84}P_6O_{12}Ag_6{\cdot}2C_4H_8O{\cdot}C_6H_{14}$, M_w = 2709.35, triclinic, space group $P\bar{1}$ (no. 2), a = 14.973(2), b = 15.635(3), c = 14.740(3) Å, α = 116.77(1)°, β = 107.71(1)°, γ = 71.87(1)°, U = 2872(1) Å^3, Z = 1, $F(000)$ = 1366, D_c = 1.566 g cm^{-3}, μ = 11.46 cm^{-1}. Crystal dimensions: 0.10 × 0.20 × 0.27 mm. Intensity data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å) using ω–2θ scans ($2\theta_{max} \leqslant 45°$) at room temperature. The data were corrected for Lorentz, polarization effects and absorption correction using ψ-scan method resulting in transmission factors ranging from 0.8482 to 1.0000. A total of 7503 (R_{int} = 0.066) unique reflections were measured; 3183 of these had $I \geqslant 3\sigma(I)$ and were considered to be observed. The structure was solved by direct methods (SIR92)[10] and refined by full matrix least-squares analysis to give R = 0.047, wR = 0.047. Silver and phosphorus atoms were refined anisotropically and the rest of the non-hydrogen atoms were refined isotropically. Hydrogen atoms were generated in their idealized positions (C–H bond fixed at 0.95 Å) and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were assigned appropriate isotropic thermal parameters and included in the structure factor calculations but not in the refinement. All calculations were performed on a Silicon-Graphics computer using program package Texsan from MSC.[11] CCDC 182/774.

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