Metal–Metal Interaction in Polynuclear Silver(I) Complexes: Spectroscopy, Luminescent Properties and X-Ray Crystal Structure of $[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]^+$ [dppp = bis(diphenylphosphinophenylphosphine)]

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The $[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]^+$ complex displays $^1(d_{\sigma^*} \rightarrow p_\sigma)$ transition at 288 nm and solid state photoluminescence at 467 nm; the Ag–Ag distances are 2.943–3.014 (2) Å.

The study of metal–metal interaction and luminescent properties of polynuclear d^{10} metal clusters has been recently receiving much attention.[1–6] The interaction between two d^{10} metal ions in close proximity has been investigated by various methods. On the experimental side, Gray and coworkers studied the electronic spectroscopy of emissive Pd^0 and Pt^0 dimers.[2] As in the case of the d^8–d^8 system, these workers assigned the intense lowest energy transition to be $^1(d_{\sigma^*} \rightarrow p_\sigma)$, which is regarded to be a fingerprint for metal–metal interaction. Similar $^1(d_{\sigma^*} \rightarrow p_\sigma)$ transition has also been reported in polynuclear Au^I such as $[Au_2(dppm)_2]^{2+}$ [dppm = bis(diphenylphosphino)methane].[3b, 5a,b, 7] However, related spectroscopic studies on polynuclear Ag^I complexes are sparse. Recently, Cotton and coworkers[4] reported their studies on $Ag_2(form)_2$ (form = *N,N'*-di-*p*-tolyformamidinate). Based on the results of SCF-X_α-SW calculations, it was suggested that their is little or no metal–metal interaction and assignment of the $^1(d_{\sigma^*} \rightarrow p_\sigma)$ transition in this silver dimer is complicated by the intense intraligand transitions. Herein is described the structure and spectroscopic properties of a new

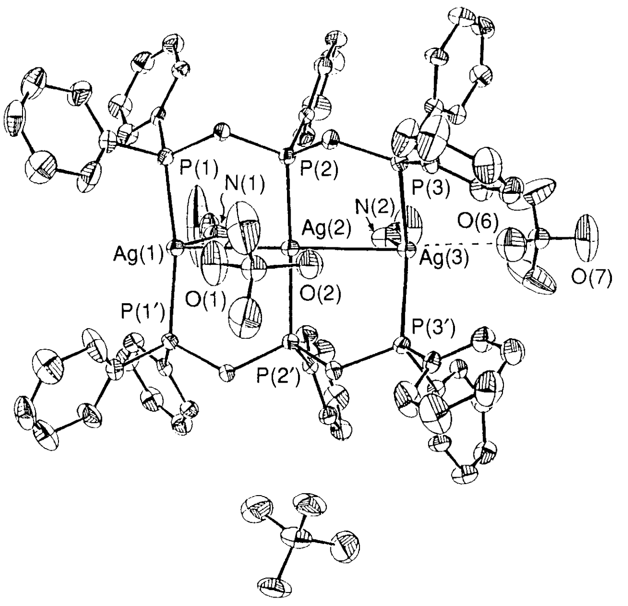

Fig. 1 ORTEP plot of the $[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]^+$ cation with atom numbering. Selected bond distances (Å) and angles (°): Ag(1)–Ag(2) 2.943(2), Ag(2)–Ag(3) 3.014(2), Ag(1)–P(1) 2.420(3), Ag(2)–P(2) 2.397(3), Ag(3)–P(3) 2.447(3), Ag(1)–N(1) 2.552(16), Ag(3)–N(2) 2.425(16), Ag(1)–O(1) 3.231(14), Ag(2)–O(2) 3.119(13), Ag(2)–O(1) 3.212(15), Ag(3)–O(2) 3.489(12), Ag(3)–O(6) 2.762(13); Ag(1)–Ag(2)–Ag(3) 175.33(7), P(3)–Ag(3)–P(3′) 137.91(12), P(2)–Ag(2)–P(2′) 169.28(13), P(1)–Ag(1)–P(1′) 161.24(12), N(1)–Ag(1)–Ag(2) 75.1(4), N(2)–Ag(3)–Ag(2) 68.3(4), O(6)–Ag(3)–N(2) 86.4(5), P(3)–Ag(3)–O(6) 98.97(14), P(2)–Ag(2)–O(2) 84.84(8), P(1)–Ag(1)–O(1) 83.78(8).

trinuclear Ag^I complex $[Ag_3(dppp)_2]^{3+}$ [dppp = bis(diphenylphosphinomethylphosphine], which can be considered as a model for luminescent Ag^I clusters.[6b]

Reaction of $AgCF_3SO_3$ with 2/3 equimolar quantity of dppp ligand in dichloromethane at room temperature afforded $[Ag_3(dppp)_2](CF_3SO_3)_3$. The perchlorate salt was obtained by the metathesis reaction with $LiClO_4$ in methanol. Colourless crystalline solid $[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]ClO_4{\cdot}(Et_2O)_2$ was obtained by vapour diffusion of diethyl ether into acetonitrile. Its ^{31}P NMR spectrum in CD_2Cl_2 shows two broad signals at δ 17.0 and 11.3 (relative to H_3PO_4). The structure of the silver complex has been established by X-ray crystallography.† Fig. 1 shows the ORTEP plot of the complex cation with atom numbering. It consists of three non-equivalent silver ions bridged by a pair of *trans* dppp ligands. The three silver atoms, two perchlorate ions and two acetonitrile molecules are located at the crystallographic mirror. Two ClO_4^- ions weakly interact with the silver atom. The one that lies close to Ag(2) has Ag–O distances ranging from 3.119(13) [Ag(2)–O(2)] to 3.489(12) Å [Ag(3)–O(2)], reflecting that the interaction involved is non-bonded electrostatic in nature. The other ClO_4^- ion can be considered as weakly coordinated to Ag(3) because of the Ag(3)–O(6) distance of 2.762(13) Å. There are three different Ag–P distances: Ag(1)–P(1) 2.420(3), Ag(2)–P(2) 2.397(3) and Ag(3)–P(3), 2.447(3) Å. These distances, match closely those values found in $[Ag_3(dppm)_3Br_2]Br$ [2.42(1)–2.47(1) Å][8] and $[Ag_2(dppm)_2(NO_3)_2]$ [2.417(2)–2.436(2) Å][9]. The three P–Ag–P bonds deviate from linearity in different degrees. The P(1)–Ag(1)–P(1′) and P(2)–Ag(2)–P(2′) angles are 161.24(12) and 169.28(13)°, respectively, which contrast sharply with that of 137.91(12)° for P(3)–Ag(3)–P(3′). Such differences in bond angles are due to the presence of acetonitrile molecules, which coordinate to Ag(1) and Ag(3), with the Ag(1)–N(1) and Ag(3)–N(2) distances being 2.552(16) and 2.425(16) Å, respectively, and to a ClO_4^- ion which coordinates to Ag(3). This is similar to the case of $[Ag_2(dppm)_2(NO_3)_2]$[9] where the nitrate ions coordinate to silver with the shortest $Ag–O(NO_3)$ distance being 2.410 Å.[9] The Ag(3) atom has the strongest interaction with acetonitrile and ClO_4^- and hence it could be considered as four-coordinated. The intramolecular Ag(1)–Ag(2) and Ag(2)–Ag(3) distances are 2.943(2) and 3.014(2) Å respectively. These values, however, are shorter than those found in $[Ag_2(dppm)_2(NO_3)_2]$ (3.085 Å)[9] and $[Ag_3(dppm)_3Br_2]Br$ [3.362(3)–3.192(3) Å][8], indicating the possibility of weak metal–metal interaction in this trinuclear Ag^I complex. Unlike the related $[Au_3(dmmp)_2]^{3+}$ [dmmp = bis(dimethylphosphinomethyl)methylphosphine] where the Au–Au–Au angle is 136.26(4)°,[5] the measured Ag–Ag–Ag angle of 175.33(7)° is close to the ideal value of 180° expected for rectilinear geometry. The coordination geometry of the dppp ligand is normal.[11]

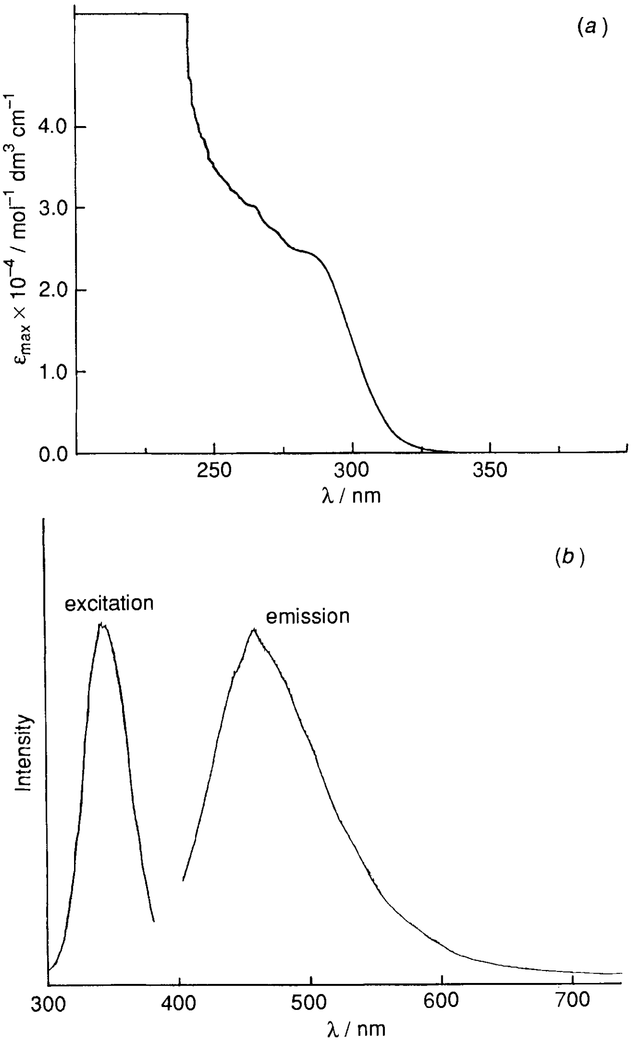

Fig. 2 (*a*) UV–VIS absorption spectrum (in CH_2Cl_2) and (*b*) solid state emission spectrum (room temp.; excitation, 300 nm) of $[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]^+$

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† *Crystal data*: $Ag_3P_6C_{76}H_{84}O_{14}Cl_3N_2$, M_r = 1865.29, orthorhombic, space group, *Pbcm*, *a* = 10.639(6), *b* = 27.256(6), *c* = 28.380(4) Å, *V* = 8229(5) Å^3, *Z* = 4, D_c = 1.506 g cm^{-3}, μ(Mo-Kα) = 0.97 mm^{-1}, *F*(000) = 3752, no. of parameters (p) 493, no. of unique reflections 5538, no. of reflections with $I > 3\sigma(I)$ 2796, R_F = 0.049, R_w = 0.046. Raw intensities collected on a Nonius CAD4 fully automated four-circle diffractometer (graphite-monochromatized Mo-Kα radiation) using the ω-2θ scan mode. All data reduction and structure refinement were performed using the NRCC-SDP-VAX packages. The structure was solved by the Patterson method and refined by least-squares analysis. 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.

Figs. 2(*a*) and 2(*b*) show the electronic absorption and emission spectra of the title silver complex measured at room temperature. In dichloromethane, an intense absorption is found at 288 nm with $\epsilon_{max} = 2.53 \times 10^4$ dm^3 mol^{-1} cm^{-1}. This absorption would not arise from intraligand transition since the absorptivity of the free ligand (λ_{max} is at 253 nm) at 288 nm is about 2.48×10^3 dm^3 mol^{-1} cm^{-1}. The possibility of this band to be a pure Ag → P metal-to-ligand charge transfer (MLCT) such as those occurring in the mononuclear $[Ag(PR_3)_2]^+$ is also excluded. This is because $[Au(PR_3)_2]^+$ does not show significant absorption at wavelength longer than 250 nm[10] and hence the Ag → P MLCT transition in $[Ag(PR_3)_2]^+$ should occur at a higher energy than 250 nm. Thus it is reasonable to assign the 288 nm absorption in the title silver complex to be due to the spin-allowed $^1(d_{\sigma*} \rightarrow p_{\sigma})$ transition. It should be stressed that this is the first identification of such a transition in trimeric silver(I) complexes. As expected, this transition is blue-shifted from the related $[Au_3(dmmp)_2]^{3+}$ [5a] probably because of the larger d-p energy gap for silver than for gold. At room temperature, the complex displays intense solid state photoluminescence with emission maximum at 467 nm upon excitation at 300–400 nm [Fig. 2(*b*)]. Such emission could also be observed in a dichloromethane solution of $[Ag_3(dppp)_2](CF_3SO_3)_3$. The room temperature lifetime of the emission is 11.2 μs (solid sample, first-order decay), suggesting that the emitting state is a spin-triplet excited state.

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