Synthesis, Spectroscopy and Excited-state Redox Properties of Novel Luminescent Trinuclear Three-co-ordinate Gold(I) Phosphine Complexes†

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Reaction of $[Au_3(dmmp)_2][ClO_4]_3$ with an excess of dmmp [bis(dimethylphosphinomethyl)methylphosphine] in methanol yielded $[Au_3(dmmp)_3][ClO_4]_3$ in almost quantitative yield. Excitation of a degassed acetonitrile solution of $[Au_3(dmmp)_3]^{3+}$ at $\lambda > 350$ nm resulted in intense phosphorescence ($\lambda_{em} = 625$ nm, $\tau_0 = 2.2 \pm 0.2$ μs). A comparison between the electronic absorption and emission spectra of $[Au_3(dmmp)_3]^{3+}$ and $[Au_2(dmpm)_3]^{2+}$ [dmpm = bis(dimethylphosphino)methane] has been made. The assignment of the lowest electronic excited state in the $(AuP_3)_n$ system has been suggested to be $^3[(d_{\delta^*})(p_\sigma)]$. The excited-state redox potentials of $[Au_3(dmmp)_3]^{3+*}$ and $[Au_2(dmpm)_3]^{2+*}$ have been determined through oxidative quenching experiments with a series of pyridinium acceptors of variable reduction potential.

Polynuclear d^{10} metal complexes have been shown to exhibit rich photophysical and photochemical properties.[1,2] Of particular interest is the nature of the lowest electronic excited states which serves to develop a better understanding of the luminescent properties of d^{10}–d^{10} systems. As part of our continuing efforts to elucidate the nature of the excited-state properties and to develop and design new luminescent materials, a novel luminescent trinuclear three-co-ordinate gold(I) phosphine complex has been synthesized. Herein we report the synthesis, spectroscopy, and excited-state redox properties of the complex $[Au_3(dmmp)_3]^{3+}$ [dmmp = bis(dimethylphosphinomethyl)methylphosphine]. The present work allows direct comparison of $[Au_3(dmmp)_3]^{3+}$ and its binuclear analogue,$[Au_2(dmpm)_3]^{2+}$[dmpm = bis(dimethylphosphino)methane], which would give further insight into the understanding of the luminescent properties of the d^{10}–d^{10} system.

Experimental

Bis(dimethylphosphinomethyl)methylphosphine (dmmp) and bis(dimethylphosphino)methane (dmpm) were purchased from Strem Chemicals. Potassium tetrachloroaurate and 2,2′-thiodiethanol were obtained from Aldrich. Acetonitrile (Mallinkrodt, ChromAR, HPLC grade) was distilled over calcium hydride and potassium permanganate before use. The pyridinium salts were prepared by refluxing the corresponding substituted pyridine with the appropriate alkylating reagent such as methyl iodide in acetone–ethanol (1 : 1 v/v) for 4 h, followed by metathesis in water using ammonium hexafluorophosphate and recrystallization from acetonitrile–diethyl ether.

Synthesis of Gold Complexes.—$[Au_2(dmpm)_2][ClO_4]_2$. This compound was prepared according to the published procedure.[1j,3] UV/VIS (MeCN): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 213 (11 500), 239 (5500), 269 (24 700) and 316(sh) (310).

$[Au_2(dmpm)_3][ClO_4]_2$. This compound was prepared according to the published procedure.[4] UV/VIS (MeCN): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 206 (35 000), 258 (21 500), 311 (1600) and 347 (sh) (1060).

$[Au_3(dmmp)_2][ClO_4]_3$. This compound was prepared according to the published procedure.[1c] UV/VIS (MeCN): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 218 (11 500), 242 (9490) and 315 (23 360).

$[Au_3(dmmp)_3][ClO_4]_3$. The perchlorate salt was prepared by treating a stirred suspension of $[Au_3(dmmp)_2][ClO_4]_3$ (100 mg) in methanol (20 cm^3) under nitrogen with an excess of dmmp which was added dropwise to give a clear yellow solution. The solvent volume was reduced by rotary evaporation. Addition of diethyl ether to the solution gave a yellow precipitate of $[Au_3(dmmp)_3][ClO_4]_3$. Recrystallization by vapour diffusion of diethyl ether into an acetonitrile solution gave yellow octahedrally shaped microcrystals of $[Au_3(dmmp)_3][ClO_4]_3$ (Found: C, 17.50; H, 3.65; Cl, 7.25. Calc. for $C_{21}H_{57}Au_3Cl_3O_{12}P_9$: C, 17.05; H, 3.85; Cl, 7.20%). UV/VIS (MeCN): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 217 (25 025), 301 (31 910), 380 (sh) (2430).

Physical Measurements and Instrumentation.—The UV/VIS spectra were obtained on a Milton Roy Spectronic 3000 diode array spectrophotometer, and steady-state emission spectra on a Spex Fluorolog 111 spectrofluorometer. Elemental analyses of the new complex were performed by Butterworth Laboratories Ltd. Emission-lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10 Hz, G-resonator). Luminescence decay signals were recorded on a Tektronix model 2430 digital oscilloscope, and analysed using a program for exponential fits. All solutions for photophysical studies were rigorously degassed with no fewer than four freeze–pump–thaw cycles. Luminescence quenching experiments were monitored by time-resolved (lifetime) emission measurements, and data were treated by a Stern–Volmer fit as described by $\tau_0/\tau = 1 + k_q\tau_0[Q]$, where τ_0 and τ are the respective excited-state lifetimes in the absence and in the presence of quencher Q, k_q is the bimolecular quenching rate constant, and [Q] is the concentration of the quencher.

Results and Discussion

Reaction of $[Au_3(dmmp)_2][ClO_4]_3$ with an excess of dmmp in methanol gave a clear yellow solution, from which yellow octahedrally shaped crystals of $[Au_3(dmmp)_3][ClO_4]_3$ could be obtained in almost quantitative yield, and which were characterized by elemental analyses and electronic absorption spectroscopy. Attempts to obtain single crystals for X-ray crystal analysis were unsuccessful owing to their twinned nature.

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

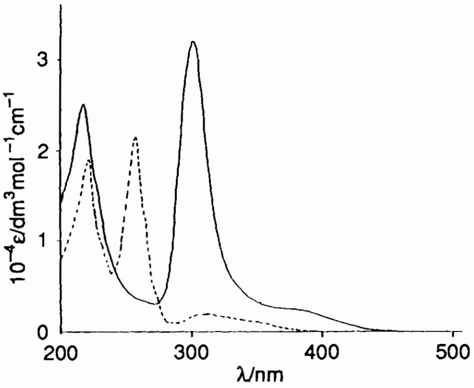

Fig. 1 Electronic absorption spectra of $[Au_3(dmmp)_3][ClO_4]_3$ (——) and $[Au_2(dmpm)_3][ClO_4]_2$ (– – – –) in acetonitrile at 25 °C

The electronic absorption spectra of $[Au_3(dmmp)_3][ClO_4]_3$ and $[Au_2(dmpm)_3][ClO_4]_2$ in acetonitrile exhibit similar absorption patterns and are shown in Fig. 1. By analogy to the well established pattern in d^8–d^8 species[5] and previous work on related d^{10}–d^{10} systems,[1,4b,6] the intense 301 nm absorption band of $[Au_3(dmmp)_3][ClO_4]_3$ and the 258 nm band of $[Au_2(dmpm)_3][ClO_4]_2$ are attributed to the spin-allowed $d_{\sigma^*} \longrightarrow p_\sigma$ transition. This has also been suggested by Mason and co-workers[4b] for the assignment of transitions in the binuclear $[Au_2(dmpm)_3]^{2+}$ complex. The red shift of the transition energy from binuclear to trinuclear species (0.69 eV) is in accordance with the assignment of the $d_{\sigma^*} \longrightarrow p_\sigma$ transition, since increasing the number of P_3Au units causes a rise in the energy of the d_{σ^*} orbital, and hence narrowing of the d_{σ^*}–p_σ gap. Similar red shifts in the $d_{\sigma^*} \longrightarrow p_\sigma$ transition have also been observed in the two-co-ordinate polynuclear d^{10} gold(I) system[1c] and in other polynuclear d^8 systems.[7] For comparison, the red shift of the $^1(d_{\sigma^*} \longrightarrow p_\sigma)$ transition energy from $[Au_2(dmpm)_2]^{2+}$ to $[Au_3(dmmp)_2]^{3+}$ is 0.67 eV. Another noteworthy feature is that the red shift in the $^1(d_{\sigma^*} \longrightarrow p_\sigma)$ transition energies on going from the three-co-ordinate to the corresponding two-co-ordinate species ($[Au_2(dmpm)_3]^{2+}$ *vs.* $[Au_2(dmpm)_2]^{2+}$, 0.20 eV; $[Au_3(dmmp)_3]^{3+}$ *vs.* $[Au_3(dmmp)_2]^{3+}$, 0.18 eV) is similar. This red shift is probably attributed to the greater $Au^I \cdots Au^I$ repulsion, and hence further $Au \cdots Au$ contacts, between the more electron-rich metal centres in the three-co-ordinate species as well as the greater $6p_{\sigma(z)}(Au)$–$3d_{\pi^*}(P)$ interaction in the two-co-ordinate species which causes the lowering of the p_σ orbital energy and a red shift in the $d_{\sigma^*} \longrightarrow p_\sigma$ transition energy. (Here the Au–Au axis is taken as the z axis, the P–Au–P axis as the x axis; and $3d_{\pi^*}(P)$ is the empty $3d_{xz}$ orbital of phosphorus in the two-co-ordinate system.) The weaker low-energy absorption bands at 311 and 347 nm in $[Au_2(dmpm)_3]^{2+}$ and 380 nm in $[Au_3(dmmp)_3]^{3+}$ are assigned as transitions to spin–orbit states of predominantly triplet parentage. It is likely that they correspond to the spin-forbidden $d_{\sigma^*} \longrightarrow p_\sigma$ and $d_{\delta^*} \longrightarrow p_\sigma$ transitions which occur at similar energies. With reference to previous work on the two-co-ordinate system, the $d_{\delta^*} \longrightarrow p_\sigma$ transition energy should be relatively insensitive to the number of AuP_3 units present.[1c]

Excitation of degassed acetonitrile solutions of $[Au_3(dmmp)_3]^{3+}$ and $[Au_2(dmpm)_3]^{2+}$ at $\lambda > 350$ nm at room temperature results in long-lived intense luminescence: $[Au_3(dmmp)_3]^{3+}$, $\lambda_{em} = 625$ nm ($\tau_0 = 2.2 \pm 0.2$ μs); $[Au_2(dmpm)_3]^{2+}$, $\lambda_{em} = 588$ nm ($\tau_0 = 0.85 \pm 0.10$ μs) (Fig. 2). The photophysical data are summarized in Table 1. The relatively small difference in emission energies upon changing the number of AuP_3 units (0.13 eV), and the very large Stokes shift between the $d_{\sigma^*} \longrightarrow p_\sigma$ transition energies and the emission energies suggest that the lowest emitting electronic states are unlikely to be derived from the $(d_{\sigma^*})^1(p_\sigma)^1$ triplet, but rather from the $(d_{\delta^*})^1(p_\sigma)^1$ triplet. The excitation spectra of $[Au_2(dmpm)_3]^{2+}$ and $[Au_3(dmmp)_3]^{3+}$ in degassed acetonitrile exhibit excitation maxima at 370 and 390 nm, respectively, the energy separation of which is 0.17 eV. It is likely that the 370 nm band in $[Au_2(dmpm)_3]^{2+}$ and the 390 nm band in $[Au_3(dmmp)_3]^{3+}$ correspond to the $(d_{\delta^*})^1(p_\sigma)^1$ origin for the emission.

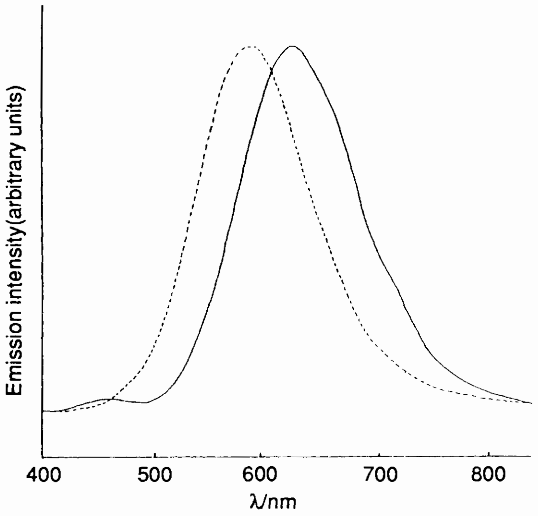

Fig. 2 Emission spectra of $[Au_3(dmmp)_3][ClO_4]_3$ (——) and $[Au_2(dmpm)_3][ClO_4]_2$ (– – – –) in degassed MeCN at 25 °C

The phosphorescence of $[Au_3(dmmp)_3]^{3+*}$ and $[Au_2(dmpm)_3]^{2+*}$ are found to be quenched by a number of electron acceptors. Excitation of the gold(I) complexes in the presence of methyl viologen (1,1′-dimethyl-4,4′-bipyridinium hexfluorophosphate, $dmbipy^{2+}2PF_6^-$) in degassed acetonitrile at 355 nm results in transient absorptions with maxima at 395 and 600 nm, typical of the $dmbipy^+$ radical cation.[8] The electron transfer nature of the reaction is suggested to be as in equations (1) and (2).

$$[Au_2(dmpm)_3]^{2+*} + dmbipy^{2+} \longrightarrow [Au_2(dmpm)_3]^{3+} + dmbipy^+ \quad (1)$$

$$[Au_3(dmmp)_3]^{3+*} + dmbipy^{2+} \longrightarrow [Au_3(dmmp)_3]^{4+} + dmbipy^+ \quad (2)$$

The phosphorescent states of $[Au_3(dmmp)_3]^{3+*}$ and $[Au_2(dmpm)_3]^{2+*}$ in acetonitrile also undergo facile electron-transfer quenching with pyridinium acceptors. In order to understand further the electron-transfer reactivity of the $^3[(d_{\delta^*})^1(p_\sigma)^1]$ excited state of the gold(I) complexes, a study of electron-transfer quenching by a series of pyridinium acceptors of variable reduction potential was undertaken. The quenching rate constants are summarized in Tables 2 and 3. Excited-state redox potentials of $E[Au_3(dmmp)_3{}^{4+/3+*}] = -1.7(1)$ V *vs.* saturated sodium chloride calomel electrode (SSCE) [$\lambda = 1.00(10)$ eV, $RT\ln K\kappa\nu = 0.50(10)$ V *vs.* SSCE] and $E[Au_2(dmpm)_3{}^{3+/2+*}] = -1.6(1)$ V *vs.* SSCE [$\lambda = 1.05(10)$ eV, $RT\ln K\kappa\nu = 0.57(10)$ V *vs.* SSCE] have been obtained by three-parameter, non-linear least-squares fits to equation (3)[9] where k_q' is the rate constant corrected for diffusional

$$\left(\frac{RT}{F}\right)\ln k_q' = \left(\frac{RT}{F}\right)\ln K\kappa\nu - \frac{\lambda}{4}\left(1 + \frac{\Delta G}{\lambda}\right)^2 \quad (3)$$

effects, $K = k_d/k_{-d}$ which is approximately 1–2 $dm^3\,mol^{-1}$, k_d is the diffusion-limited rate constant in acetonitrile which is taken to be $1.0 \times 10^{10}\ dm^3\,mol^{-1}\,s^{-1}$, κ is the transmission coefficient, ν is the nuclear frequency, and λ is the reorganization energy for electron transfer, and ΔG, the standard free energy change of the reaction which is given by equation (4) for oxidative

Table 1 Photophysical data of $[Au_3(dmmp)_3][ClO_4]_3$ and $[Au_2(dmpm)_3][ClO_4]_2$ in degassed acetonitrile at room temperature with comparison to the related two-co-ordinate complexes

Complex	λ_{abs}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm	τ_0/μs
$[Au_3(dmmp)_3][ClO_4]_3$	217 (25 025), 301 (31 910), 380 (sh) (2430)	625	2.2 ± 0.2
$[Au_2(dmpm)_3][ClO_4]_2$	206 (35 000), 258 (21 500), 311 (1600), 347 (sh) (1060)[a]	588	0.85 ± 0.10
$[Au_3(dmmp)_2][ClO_4]_3$[b]	218 (11 500), 242 (9490), 315 (23 360)	467	1.6 ± 0.2
		580	7.0 ± 0.5
$[Au_2(dmpm)_2][ClO_4]_2$[b]	213 (11 500), 239 (5500), 269 (24 700), 316 (sh) (310)	455	1.2 ± 0.2
		555	2.8 ± 0.2

[a] Ref. 4(*b*). [b] Ref. 1(*c*).

Table 2 Rate constants for the quenching of $[Au_2(dmpm)_3]^{2+*}$ by pyridinium acceptors in acetonitrile (0.1 mol dm^{-3} NBu_4PF_6) at 25 °C

Quencher[a]	$E(A^{+/0})$[b]/ V *vs.* SSCE	k_q/dm^3 mol^{-1} s^{-1}	k_q'[c]/dm^3 mol^{-1} s^{-1}	ln k_q'
4-Cyano-*N*-methylpyridinium	−0.67	4.66×10^9	8.71×10^9	22.89
4-Methoxycarbonyl-*N*-methylpyridinium	−0.78	1.94×10^9	2.41×10^9	21.60
4-Aminoformyl-*N*-ethylpyridinium	−0.93	1.53×10^9	1.80×10^9	21.31
3-Aminoformyl-*N*-methylpyridinium	−1.14	3.08×10^8	3.17×10^8	19.57
N-Ethylpyridinium	−1.36	4.40×10^7	4.42×10^7	17.60
4-Methyl-*N*-methylpyridinium	−1.49	1.80×10^6	1.80×10^6	14.40

[a] All the compounds are hexafluorophosphate salts. [b] Ref. 10, SSCE = saturated sodium chloride calomel electrode. [c] See ref. 9.

Table 3 Rate constants for the quenching of $[Au_3(dmmp)_3]^{3+*}$ by pyridinium acceptors in acetonitrile (0.1 mol dm^{-3} NBu_4PF_6) at 25 °C

Quencher[a]	$E(A^{+/0})$[b]/ V *vs.* SSCE	k_q/dm^3 mol^{-1} s^{-1}	k_q'[c]/dm^3 mol^{-1} s^{-1}	ln k_q'
4-Methoxycarbonyl-*N*-methylpyridinium	−0.78	1.96×10^8	1.99×10^8	19.11
4-Aminoformyl-*N*-ethylpyridinium	−0.93	1.77×10^8	1.81×10^8	19.01
3-Aminoformyl-*N*-methylpyridinium	−1.14	2.34×10^7	2.35×10^7	16.97
N-Ethylpyridinium	−1.36	6.08×10^6	6.08×10^6	15.62
4-Methyl-*N*-methylpyridinium	−1.49	5.10×10^5	5.10×10^5	13.14

[a] All the compounds are hexafluorophosphate salts. [b] Ref. 10. [c] See ref. 9.

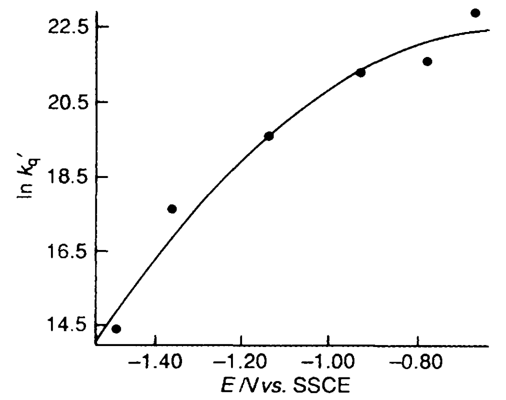

Fig. 3 Plot of ln k_q' *versus* $E(A^{+/0})$ for the electron-transfer quenching of $[Au_2(dmpm)_3]^{2+*}$ by pyridinium acceptors in degassed acetonitrile: (•) experimental; (——) calculated

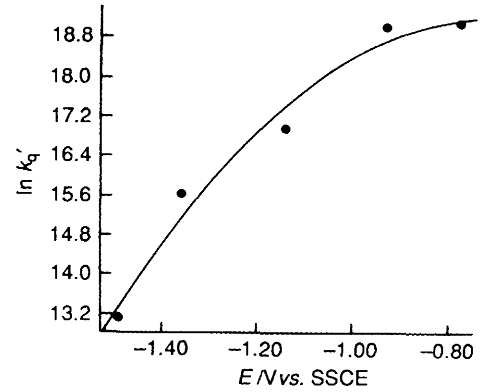

Fig. 4 Plot of ln k_q' *versus* $E(A^{+/0})$ for the electron-transfer quenching of $[Au_3(dmmp)_3]^{3+*}$ by pyridinium acceptors in degassed acetonitrile: (•) experimental; (——) calculated

$$\Delta G = E^\circ[Au^{(n+1)+/n+*}] - E^\circ(Q^{+/0}) + \omega_p - \omega_r \quad (4)$$

quenching, where ω_r and ω_p are work terms for bringing reactants or products to the mean separation for reaction. The work term associated with bringing the gold(I) complex and a pyridinium acceptor is 0.01–0.03 eV. This contribution is neglected in the analysis of the electron-transfer rate data. Figs. 3 and 4 show the theoretical fits. The close agreement between the theoretical curve with the experimental data is in accordance with the fact that the photoreactions are outer-sphere electron transfer in nature. Interestingly, the estimated λ values for both the $[Au_3(dmmp)_3]^{3+}$ and $[Au_2(dmpm)_3]^{2+}$ systems are similar, and are comparable to that found for the reaction between the $^3(d_{\delta^*}p_\sigma)$ states of the two-co-ordinate gold(I) species and pyridinium acceptors.[1c]

Attempts to use the spectroscopic and electrochemical properties of $[Au_2(dmpm)_3]^{2+}$ and $[Au_3(dmmp)_3]^{3+}$ to establish the excited-state reduction potentials, $E^\circ[Au_2(dmpm)_3{}^{3+/2+*}]$ and $E^\circ[Au_3(dmmp)_3{}^{4+/3+*}]$, were unsuccessful. The cyclic voltammograms show only an irreversible ligand-centred oxidation wave at potentials > +1.0 V *vs.* Ag–$AgNO_3$ in MeCN (0.1 mol dm^{-3} NBu_4PF_6). Thus an estimation of the excited-state reduction potential by this method is impossible.

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