Luminescent Metallomacrocycles from Gold(I) and Silver(I) Complexes of 2,7-Bis(diphenylphosphino)-1,8-naphthyridine (L) and Crystal Structure of $[Au_2KL_3][ClO_4]_3 \cdot CH_2Cl_2 \cdot 2MeOH \cdot 0.5H_2O$

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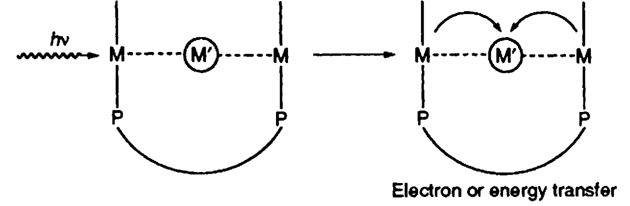
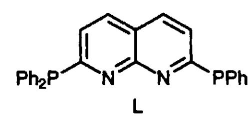
The synthesis and X-ray crystal structure of the $[Au_2KL_3]^{3+}$ [L = 2,7-bis(diphenylphosphino)-1,8-naphthyridine] complex which contains an encapsulated K^+ ion is described; both the $[Au_2KL_3]^{3+}$ and $[Ag_3L_3]^{3+}$ complexes are emissive in fluid solution with the latter being a powerful photooxidant.

Recent works from various groups have established the rich photo-physical and -chemical properties of polynuclear d^{10}-metal complexes, particularly those of Cu$^{\text{I}}$ [1] and Au$^{\text{I}}$,[2] which belong to new classes of inorganic luminophores. Our interests in this area have recently shifted to the design of luminescent metallomacrocycles from d^{10}-metal complexes with bridging pyridylphosphine ligands for the purpose of performing host–guest photochemistry.



In this context, Balch *et al.*[3] had reported some dinuclear complexes of Rh$^{\text{I}}$ and Ir$^{\text{I}}$ with bis(diphenylphosphino)-methylphenylarsine, which react with transition metal ions to give trimetallic complexes having intriguing spectroscopic and emission properties. Herein are described the preparation and photophysical properties of some complexes of Au$^{\text{I}}$ and Ag$^{\text{I}}$ with 2,7-bis(diphenylphosphino)-1,8-naphthyridine L. The dinuclear complex of Au$^{\text{I}}$ with L has been found to encapsulate K^+ to give a novel $[Au_2KL_3]^{3+}$ complex, which features an interesting example of a metallomacrocycle for encapsulation of alkali metal ions.



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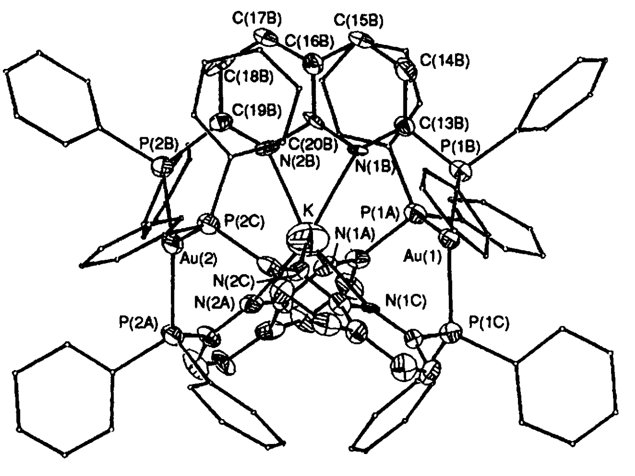
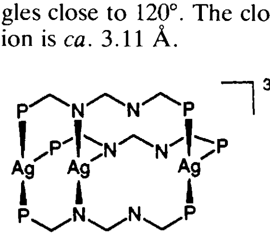


Fig. 1 A perspective view of the $[Au_2KL_3]^{3+}$ cation (bond lengths in Å, angles in °), Au(1)···K 3.615(5), Au(1)–P(1A) 2.395(4), Au(1)–P(1B) 2.366(3), Au(1)–P(1C) 2.365(3), Au(2)···K 3.575(5), Au(2)–P(2A) 2.357(3), Au(2)–P(2B) 2.368(3), Au(2)–P(2C) 2.370(4), K–N(1A) 2.549(10), K–N(2A) 2.487(10), K–N(1B) 2.507(10), K–N(2B) 2.482(10), K–N(1C) 2.477(10), K–N(2C) 2.500(10). P(1A)–Au(1)–P(1B) 114.52(12), P(1A)–Au–P(1C) 117.63, P(1B)–Au–P(1C) 126.17(12), N(1A)–K–N(2A) 54.5(3), N(1A)–K–N(1B) 99.8(3), N(1A)–K–N(2B) 103.6(3), Au(1)–K–Au(2) 177.11(15).

The ligand L was prepared by the method developed by Ziessel.[4] Reaction of an equimolar amount of L and Au$^{\text{I}}$, generated *in situ* by the reduction of $K[AuCl_4]$ with 2,2-thioethanol in methanol for 30 min at room temp. gave a yellow solution. Addition of $LiClO_4$ to the solution precipitated $[Au_2KL_3][ClO_4]_3$ **1** as a yellow crystalline solid. Similar reaction of $AgClO_4$ with L in CH_2Cl_2–MeOH gave $[Ag_3L_3][ClO_4]_3$ **2** in high yield. Crystals of **1** and **2** were obtained by diffusion of diethyl ether into dichloromethane–methanol solutions and their structures were determined by X-ray crystal analysis.† Fig. 1 shows a perspective view of the $[Au_2KL_3]^{3+}$ cation. The structure features an interesting example of a metallocryptand with an encapsulated K^+ ion. As in $[K(phen)_3]^+$ (phen = 1,10-phenanthroline),[5] the K^+ ion, which binds to the three naphthyridine moieties, is six-coordinate. The measured K^+–N distances which range from 2.477(10) to 2.549(10) Å are significantly shorter than those of 2.800(6)–2.893(5) Å found in the unconstrained $[K(phen)_3]^+$ complex[5] and 2.74–2.81(1) Å in the macrocyclic K^+ complex of 7,16,21,26-tetraoxa-1,4,10,13-tetraazatricyclo-[11.5.5.5.^{4,10}]octacosane.[6] Such short K^+–N distances indicate a strong binding of the encapsulated K^+ ion by the three naphthyridine moieties. The coordination polyhedron of the K^+ ion is distorted trigonal-prismatic with an average twist angle of 25° and chelate bite [N(1A)–K–N(2A)] of 54.7°. Each Au$^{\text{I}}$ is in a trigonal-planar geometry with the P–Au–P angles close to 120°. The Au(I)···K^+ separations are 3.615(5) and 3.575(5) Å. The Au–K–Au axis is close to linearity. The structure of **2** has been established by a partial X-ray crystal analysis. Due to the large amount of co-crystallised solvent and the small crystal size, the *R* value is high.

Nevertheless, **2** can be interpreted as having the following structure. All the three Ag$^{\text{I}}$ are three-coordinate with P–Ag–P and N–Ag–N angles close to 120°. The closest intramolecular Ag···Ag separation is *ca.* 3.11 Å.



Both **1** and **2** show room temp. emission upon photoexcitation of the complexes at 300–400 nm. Their spectroscopic and emission properties together with that of the free ligand are listed in Table 1. As shown in Fig. 2, the emission of **1** is at lower energy than that of **2**. No metal–metal bonded excited state is expected for these two complexes. Because the emission of **1** is at lower energy than that of **2** and the free ligand, it is tentatively assigned to come from a MLCT [Au →

Table 1 The photophysical properties of L and complexes **1** and **2** in different degassed solvents at room temperature

Compound	Solvent	UV–VIS λ_{max}/nm ($10^{-4}\ \varepsilon_{max}$/ $dm^3\ mol^{-1}\ cm^{-1}$	Emission λ_{max}/nm	Lifetime τ/μs	Quantum yield
Free ligand	CH_2Cl_2	258 (2.65), 358(1.15)	440	<10 ns	0.014
1	CH_2Cl_2	258(9.20), 316(2.64), 368(1.57)	625	0.1	0.04
	MeCN	258(6.63), 316(1.92), 368(1.30)	500(sh), 625	0.1	0.04
2	CH_2Cl_2	258(9.00), 367(1.82)	550	2.7	0.002
	MeCN	258(9.20), 367(2.09)	550	5.0	0.013
	Solid	—	550	—	—

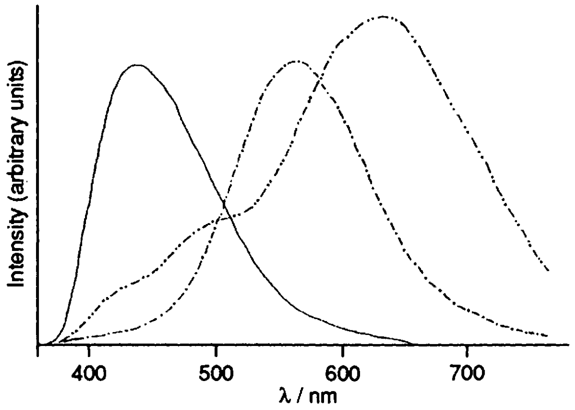


Fig. 2 Emission spectrum of L in dichloromethane (—), **1** in CH_2Cl_2 (–··–··–) and **2** (–·–·–) in MeCN at room temp. Excitation at 330–370 nm.

π*(L)] excited state. For **2** the emission is likely to be intraligand in nature. Although **1** has a relatively short emission lifetime, the emission of **2** has a lifetime of 5.0 μs in acetonitrile at room temp. Preliminary studies showed that this long-lived emission is reductively quenched by substituted aromatic hydrocarbons.

We acknowledge support from The University of Hong Kong, National Science Foundation of Taiwan and The Hong Kong Research Grants Council.

Received, 21st June 1994; Com. 4/03753G

Footnote

† *Crystal data*: **1**, $C_{96}H_{72}Au_2Cl_3KN_6O_{12}P_6{\cdot}CH_2Cl_2{\cdot}2CH_3OH{\cdot}0.5H_2O$, $M = 2385.31$, monoclinic, space group $C2/c$, $a = 27.266(17)$, $b = 28.527(7)$, $c = 26.819(1)$ Å, $\beta = 111.56(4)°$, $V = 19401(13)$ Å^3, $\lambda = 0.7107$ Å, $Z = 8$, $D_c = 1.633\ g\ cm^{-3}$, crystal dimensions 0.30 × 0.30 × 0.50 mm, μ(Mo-Kα) = 34.1 cm^{-1}, $F(000) = 9496$. X-Ray diffraction data were collected on a Nonius CAD4 diffractometer using the ω-2θ scan mode with $2\theta_{max} = 45°$ at the National Taiwan University. The unit cell dimensions were obtained from 25 reflections. The structure was solved by the Patterson method and refined by least squares analysis. The last least squares cycle was calculated with 208 atoms, 1136 parameters and 8548 reflections ($I_o > 2\sigma I_o$) out of 12648 reflections; $R = 0.050$, $R' = 0.051$, $w^{-1} = \sigma^2(F)$. The final Fourier difference map showed residual extrema in the range of 1.46 to −1.64 e A^{-3}.

2, $C_{96}H_{72}Ag_3Cl_3N_6O_{12}P_6{\cdot}3H_2O{\cdot}5CH_2Cl_2$, $M = 2596.97$, monoclinic, space group $P2_1/c$, $a = 17.066(3)$, $b = 23.500(5)$, $c = 28.224(9)$ Å, $\beta = 94.38(2)°$, $V = 11286(5)$ Å^3, $\lambda = 0.7107$ Å, $Z = 4$, $D_c = 1.528\ g\ cm^{-3}$, crystal dimensions 0.25 × 0.30 × 0.30 mm, μ(Mo-Kα) = 9.6 cm^{-1}, $F(000) = 5232$. Data collection and structural refinement were performed as for **1**. The last least squares cycle was calculated with 226 atoms, 606 parameters and 4888 reflections ($I > 2\sigma I_o$) out of 14730 reflections; $R = 0.112$, $R' = 0.103$, $w^{-1} = \sigma^2(F)$. Although the R values are slightly high due to the large amount of co-crystallised solvents (5 dichloromethane and 3 water molecules), the distances and angles of cation appear to be reasonable with chemically equivalent parameters agreeing well. The final Fourier difference map showed residual extrema in the range of 1.490 to −0.810 e A^{-3}.

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

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