

Gold(I) complex of 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy) as a metalloligand for encapsulation of metal ions. Crystal structures of $[\text{AuCu}(\text{dpnapy})_3][\text{ClO}_4]_2$ and $[\text{AuCd}(\text{dpnapy})_3][\text{ClO}_4]_3$

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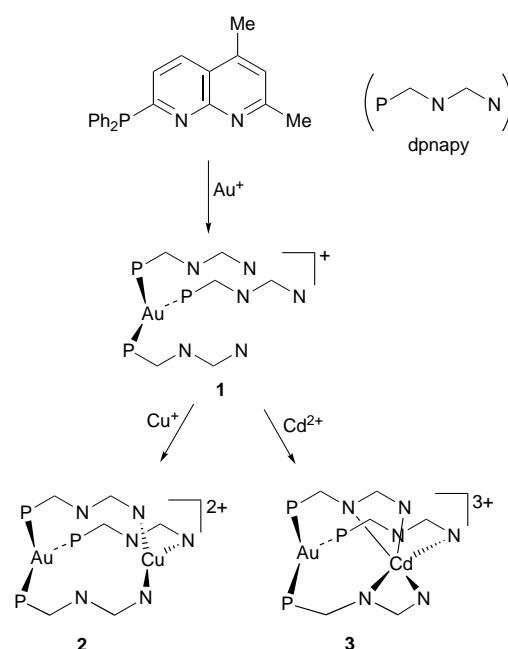
Reaction of dpnapy [dpnapy = 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine] with $[\text{Au}(\text{tht})\text{Cl}]$ (tht = tetrahydrothiophene) in dichloromethane afforded $[\text{Au}(\text{dpnapy})_3]^+$, which shows a strong affinity towards Cu^{I} and Cd^{II} ions; crystal structures of $[\text{AuCu}(\text{dpnapy})_3][\text{ClO}_4]_2$ and $[\text{AuCd}(\text{dpnapy})_3][\text{ClO}_4]_3$ revealed that $[\text{Au}(\text{dpnapy})_3]^+$ functions as a metalloligand with the three naphthyridyl groups positioned in a trigonal fashion.

The design of macropolycyclic ligands as receptor molecules that have binding sites positioned in a preferred geometry is an important area in molecular recognition and in host-guest chemistry. Examples of such ligand systems *e.g.* cryptands have been reported though their preparations are usually tedious.¹ In this context, we envisaged co-ordination of pyridylphosphine ligands to d^{10} metal ions *via* the phosphorus atoms which could direct the spatial arrangement of the pendant pyridyl groups. Consequently, this may lead to a new class of metalloligands for encapsulation of ions in a preferred geometry.² Whereas there are many tripodal ligands, such as 1,4,7-triazacyclononane and 1,1,1-tris(diphenylphosphinomethyl)ethane,^{3,4} which co-ordinate metal ions in a facial manner, examples of planar tridentate chelating ligands are scarce.⁵ Herein is described the co-ordination of 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine⁶ (dpnapy) to gold(I) to give $[\text{Au}(\text{dpnapy})_3]^+$ **1**, which has the three pendant naphthyridyl groups positioned in a trigonal arrangement.

Scheme 1 outlines the procedures for the preparation of cations **1–3**. Complexes **2** and **3** were obtained by treating **1** with a stoichiometric amount of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ and $\text{Cd}(\text{ClO}_4)_2$, respectively, in acetone. Recrystallisation of the crude products in acetonitrile–diethyl ether solution afforded red crystals of **2** and yellow prisms of **3**.[†] The ¹H and ¹³C NMR spectra of **1** show

that the 2-Me resonances are comparable to those of the free ligand whereas downfield shifts are observed for those of **2** and **3**.[§] These downfield shifts evidence the metal–naphthyridyl co-ordination. The ³¹P NMR spectra of cations **1–3** display a single resonance revealing that the three dpnapy ligands in the complexes are equivalent.

The structure of **1** has been established by X-ray crystal analysis. However, the high *R'* value of the structure precludes a detailed discussion. Nevertheless the structure reveals that the Au atom adopts a trigonal-planar geometry. The dpnapy ligands are P-monodentate with three naphthyridyl moieties radiating from the Au atom to form a void. In this context, the Au atom can be viewed as a template to fix the ligating sites of the naphthyridyl rings. The crystal structures of complexes **2** and **3** have been determined by X-ray analyses and perspective views of the complex cations are depicted in Figs. 1 and 2.[¶] In both complexes, the Au atom retains a trigonal-planar geometry with P–Au–P angles and Au–P distances comparable to those in **1**. For **2**, the $[\text{Au}(\text{dpnapy})_3]^+$ unit binds to the Cu atom *via* three N₁ donors to give a face-to-face hetero-metallocycle. The Cu(1) atom adopts a distorted trigonal-planar co-ordination and the AuP₃ and CuN₃ planes are nearly parallel (dihedral angle of 3.5°). This



Scheme 1 Preparation of complexes **1–3**

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[‡] $[\text{ClO}_4]^-$: a mixture of $[\text{Au}(\text{tht})\text{Cl}]$ (tht = tetrahydrothiophene) (0.32 g, 1 mmol) and dpnapy (1.0 g, 3 mmol) in dichloromethane (25 ml) was stirred for 1 h at room temperature. Metathesis of the product with LiClO_4 (0.11 g, 1 mmol) in methanol afforded pale yellow microcrystals of **1** (0.69 g, 52%) (Found: C, 58.20; H, 4.62; N, 6.22. Calc. for $[\text{Au}(\text{ClO}_4)]\cdot\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$: C, 58.59; H, 4.62; N, 6.12%).

$2[\text{ClO}_4]_2^-$: a mixture of **1** ($[\text{ClO}_4]^-$) (1.3 g, 1 mmol) and $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ (0.33 g, 1 mmol) in acetone (25 ml) was stirred for 1 h at room temperature. The solvent was removed *in vacuo*. The crude product was recrystallized by diffusion of diethyl ether into an acetonitrile solution to afford red crystals (0.92 g, 62%) (Found: C, 54.02; H, 3.80; N, 5.55. Calc. for $2[\text{ClO}_4]_2^-$: C, 53.33; H, 3.86; N, 5.65%).

$3[\text{ClO}_4]_3^-$: a mixture of **1** ($[\text{ClO}_4]^-$) (1.3 g, 1 mmol) and $\text{Cd}(\text{ClO}_4)_2$ (0.31 g, 1 mmol) in acetone (25 ml) was stirred for 1 h at room temperature. The solvent was removed *in vacuo*. The crude product was recrystallized by diffusion of diethyl ether into an acetonitrile solution to afford yellow crystals (0.83 g, 51%) (Found: C, 48.11; H, 3.80; N, 5.65. Calc. for $3[\text{ClO}_4]_3^- \cdot \text{CH}_3\text{CN}$: C, 48.73; H, 3.61; N, 5.85%).

[§] ¹H NMR (CD_3CN): δ 2-Me $[\text{ClO}_4]^-$, 2.69 (s); $2[\text{ClO}_4]_2^-$, 2.79 (s); $3[\text{ClO}_4]_3^- \cdot \text{CH}_3\text{CN}$, 2.75 (s). ¹³C NMR (CD_3CN): δ 2-Me $[\text{ClO}_4]^-$, 25.1 (s); $2[\text{ClO}_4]_2^-$, 26.1 (s); $3[\text{ClO}_4]_3^- \cdot \text{CH}_3\text{CN}$, 25.9 (s). ³¹P NMR (CD_3CN): δ $[\text{ClO}_4]^-$, 39.6 (s); $2[\text{ClO}_4]_2^-$, 38.5 (s); $3[\text{ClO}_4]_3^- \cdot \text{CH}_3\text{CN}$, 41.0 (s).

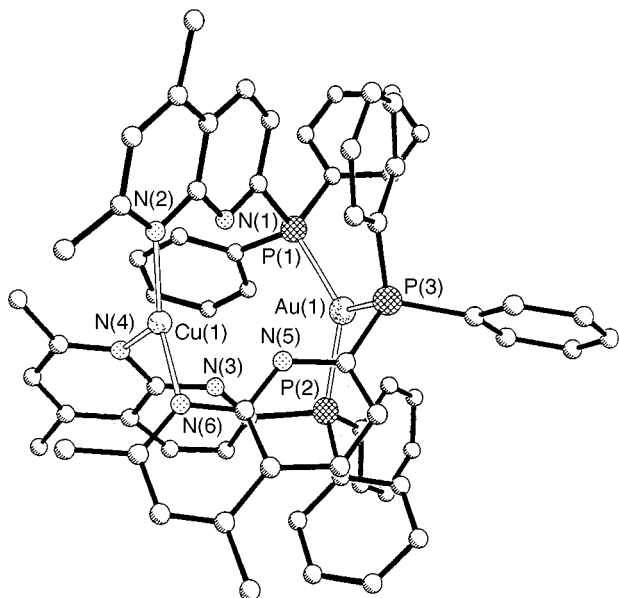


Fig. 1 A perspective view of complex cation **2**. Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.363(3), Au(1)–P(2) 2.367(3), Au(1)–P(3) 2.367(3), Cu(1)–N(2) 2.025(8), Cu(1)–N(4) 2.029(9), Cu(1)–N(6) 2.045(8); P(1)–Au(1)–P(2) 120.6(1), P(2)–Au(1)–P(3) 115.8(1), P(1)–Au(1)–P(3) 120.5(1), N(2)–Cu(1)–N(4) 126.9(4), N(2)–Cu(1)–N(6) 119.3(4), N(4)–Cu(1)–N(6) 110.8(4)

features an interesting face-to-face d^{10} – d^{10} hetero-bimetallic complex. Complex **3** is a rare hetero-bimetallic Au^I – Cd^{II} complex, in which the Cd atom is captured by $[Au(dpnpy)_3]^+$ through co-ordination to three naphthyridyl moieties. The co-ordination polyhedron of the Cd atom is distorted trigonal-prismatic, with a chelate bite $[N(1)–Cd–N(2)]$ of $56.83(3)^\circ$. In both **2** and **3**, a view down the Au–M axis (M = Cu or Cd) shows that the Au–P and M–N bonds are staggered with respect to each other. The P–Au...M–N torsional angles range from 53.1 to 60.4° , which are near to 60° required for a perfectly staggered conformation. The Au...Cu and Au...Cd separations of 4.469 and 3.745 Å respectively suggest no metal–metal interaction.

The spectroscopic data of complexes **1**–**3** are summarized in Table 1. Their UV/VIS absorption spectra are characterized by an absorption band at 320 – 360 nm (**1**: 325 , **2**: 320 , **3**: 360 nm), which is assigned to the $d(Au) \rightarrow \pi^*(dpnpy)$ MLCT transition. For complex **2**, a low energy absorption tail from 420 – 450 nm has been observed, which is attributed to the $d(Cu) \rightarrow \pi^*(dpnpy)$ MLCT transition. The red shift in the $d(Au) \rightarrow \pi^*(dpnpy)$ transition from **1** to **3** is due to the lowering of the π^* energy of the naphthyridyl rings through co-ordination to Cd^{II} . Upon excitation at 360 nm, complex **1** $[ClO_4]$ displays a low energy emission at 560 nm, which is tentatively assigned to the

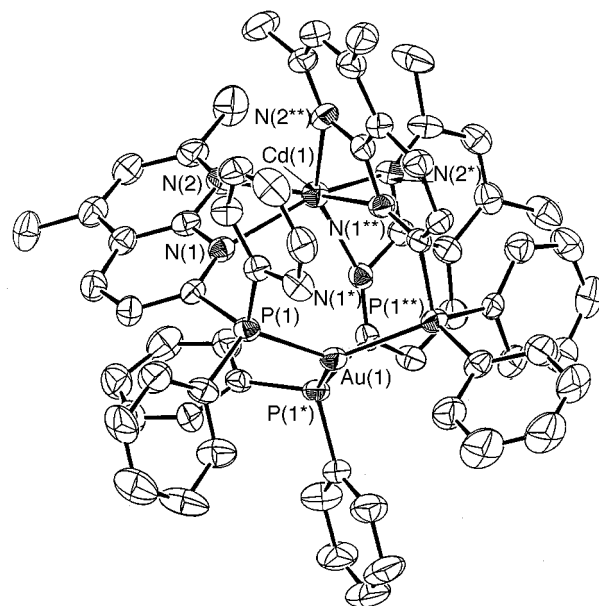


Fig. 2 A perspective view of complex cation **3**. Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.362(3), Cd(1)–N(1) 2.438(9), Cd(1)–N(2) 2.288(9); P(1)–Au(1)–P(1*) 118.69(3), N(1)–Cd(1)–N(1*) 100.5(2), N(1)–Cd(1)–N(2) 56.8(3), N(1)–Cd(1)–N(2*) 101.0(3), N(1)–Cd(1)–N(2**) 151.3(3), N(1*)–Cd(1)–N(2*) 56.8(3), N(1*)–Cd(1)–N(2**) 101.0(3), N(1**)–Cd(1)–N(2**) 56.8(3), N(2)–Cd(1)–N(2*) 106.7(2)

Table 1 Spectroscopic data for complexes **1**–**3** in degassed acetonitrile at room temperature

Complex	λ_{abs}/nm ($\epsilon_{max}/cm^{-1} M^{-1}$)	λ_{em}/nm (excitation 360 nm)	$\tau/\mu s$
1	268 (54 710), 325 (21 570)	560	0.96
2	264 (46 730), 320 (29 460), 435 (sh, 14 400)	530	—
3	268 (55 320), 318 (16 300), 360 (12 080)	606	0.71

$d(Au) \rightarrow \pi^*(dpnpy)$ MLCT excited state. Interestingly, co-ordination of Cu^I to $[Au(dpnpy)_3]^+$ in cation **2** results in a shift of the MLCT emission to 530 nm, which may be attributable to an admixture of two excited states of similar energy, $d(Au) \rightarrow \pi^*(dpnpy)$ and $d(Cu) \rightarrow \pi^*(dpnpy)$. In cation **3**, co-ordination of Cd^{II} to $[Au(dpnpy)_3]^+$ lowers the energy of the $d(Au) \rightarrow \pi^*(dpnpy)$ excited state and hence the MLCT emission is red shifted to a longer wavelength, 606 nm.

Acknowledgements

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$[2[ClO_4]_3]$: $C_{66}H_{57}AuCl_2CuN_6O_8P_3$, $M = 1486.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.795(1)$, $b = 16.092(1)$, $c = 16.491(1)$ Å, $\alpha = 87.75(1)$, $\beta = 62.93(1)$, $\gamma = 65.31(1)$, $U = 3331.7(4)$ Å³, $Z = 2$, $\mu(Mo-K\alpha) = 27.28$ cm⁻¹, crystal dimensions $0.20 \times 0.20 \times 0.18$ mm, $T = 293$ K, $F(000) = 1492$, no. of unique reflections = $10\ 333$, no. of reflections with $I \geq 2\sigma(I) = 9505$, no. of variables = 829 , $R = 0.079$, $R' = 0.088$, goodness of fit = 1.22 .

$3[ClO_4]_3 \cdot CH_3CN$: $C_{68}H_{60}AuCdCl_3N_7O_{12}P_3$, $M = 1675.9$, trigonal, space group $P\bar{3}$ (no. 147), $a = 13.873(1)$, $c = 21.611(2)$ Å, $U = 3602.1(3)$ Å³, $Z = 2$, $\mu(Mo-K\alpha) = 25.78$ cm⁻¹, crystal dimensions $0.15 \times 0.10 \times 0.30$ mm, $T = 301$ K, $F(000) = 1672$, reflections measured = 4662 , no. of unique reflections = 4258 , no. of reflections with $I \geq 3\sigma(I) = 2806$, no. of variables = 301 , $R = 0.055$, $R' = 0.075$, goodness of fit = 2.13 . Singly starred (*) atoms have coordinates at $(1 - y, 1 + x - y, z)$ and doubly starred (**) atoms have coordinates at $(y - x, 1 - x, z)$.

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