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Gold(I) complex of 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy) as a metalloligand for encapsulation of metal ions. Crystal structures of $[AuCu(dpnapy)_3][ClO_4]_2$ and $[AuCd(dpnapy)_3][ClO_4]_3$

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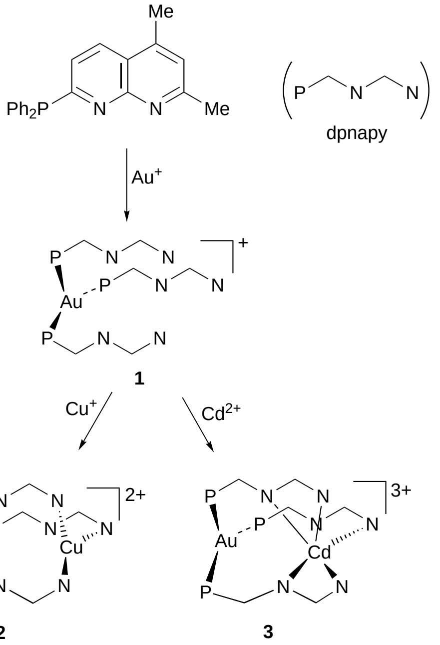
Reaction of dpnapy [dpnapy = 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine] with [Au(tht)Cl] (tht = tetrahydrothiophene) in dichloromethane afforded $[Au(dpnapy)_3]^+$, which shows a strong affinity towards Cu^I and Cd^{II} ions; crystal structures of $[AuCu(dpnapy)_3][ClO_4]_2$ and $[AuCd(dpnapy)_3][ClO_4]_3$ revealed that $[Au(dpnapy)_3]^+$ 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-naphthyridine[6] (dpnapy) to gold(I) to give $[Au(dpnapy)_3]^+$ **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 $\mathbf{2}[ClO_4]_2$ and $\mathbf{3}[ClO_4]_3$ were obtained by treating $\mathbf{1}[ClO_4]$ with a stoichiometric amount of $[Cu(CH_3CN)_4][ClO_4]$ and $Cd(ClO_4)_2$, respectively, in acetone. Recrystallisation of the crude products in acetonitrile–diethyl ether solution afforded red crystals of $\mathbf{2}[ClO_4]_2$ and yellow prisms of $\mathbf{3}[ClO_4]_3\cdot CH_3CN$.‡ The ^1H and ^{13}C 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 ^{31}P NMR spectra of cations **1**–**3** display a single resonance revealing that the three dpnapy ligands in the complexes are equivalent.

The structure of $\mathbf{1}[ClO_4]$ 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 $\mathbf{2}[ClO_4]_2$ and $\mathbf{3}[ClO_4]_3\cdot CH_3CN$ 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 $[Au(dpnapy)_3]^+$ unit binds to the Cu atom *via* three N_1 donors to give a face-to-face hetero-metallocycle. The Cu(1) atom adopts a distorted trigonal-planar co-ordination and the AuP_3 and CuN_3 planes are nearly parallel (dihedral angle of 3.5°). This



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

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‡ $\mathbf{1}[ClO_4]$: a mixture of [Au(tht)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 $\mathbf{1}[ClO_4]\cdot CH_3OH\cdot H_2O$: C, 58.59; H, 4.62; N, 6.12%).

$\mathbf{2}[ClO_4]_2$: a mixture of $\mathbf{1}[ClO_4]$ (1.3 g, 1 mmol) and $[Cu(CH_3CN)_4][ClO_4]$ (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 $\mathbf{2}[ClO_4]_2$: C, 53.33; H, 3.86; N, 5.65%).

$\mathbf{3}[ClO_4]_3$: a mixture of $\mathbf{1}[ClO_4]$ (1.3 g, 1 mmol) and $Cd(ClO_4)_2$ (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 $\mathbf{3}[ClO_4]_3\cdot CH_3CN$: C, 48.73; H, 3.61; N, 5.85%).

§ ^1H NMR (CD_3CN): δ 2-Me $\mathbf{1}[ClO_4]$, 2.69 (s); $\mathbf{2}[ClO_4]_2$, 2.79 (s); $\mathbf{3}[ClO_4]_3\cdot CH_3CN$, 2.75 (s). ^{13}C NMR (CD_3CN): δ 2-Me $\mathbf{1}[ClO_4]$, 25.1 (s); $\mathbf{2}[ClO_4]_2$, 26.1 (s); $\mathbf{3}[ClO_4]_3\cdot CH_3CN$, 25.9 (s). ^{31}P NMR (CD_3CN): δ $\mathbf{1}[ClO_4]$, 39.6 (s); $\mathbf{2}[ClO_4]_2$, 38.5 (s); $\mathbf{3}[ClO_4]_3\cdot CH_3CN$, 41.0 (s).

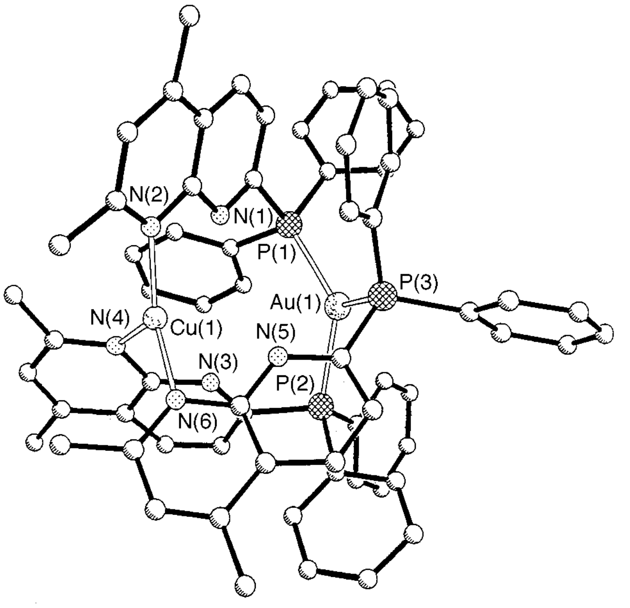

Fig. 1 A perspective view of complex cation **2**. Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.363(3), Au(1)–P(2) 2.367(3), Au(1)–P(3) 2.367(3), Cu(1)–N(2) 2.025(8), Cu(1)–N(4) 2.029(9), Cu(1)–N(6) 2.045(8); P(1)–Au(1)–P(2) 120.6(1), P(2)–Au(1)–P(3) 115.8(1), P(1)–Au(1)–P(3) 120.5(1), N(2)–Cu(1)–N(4)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

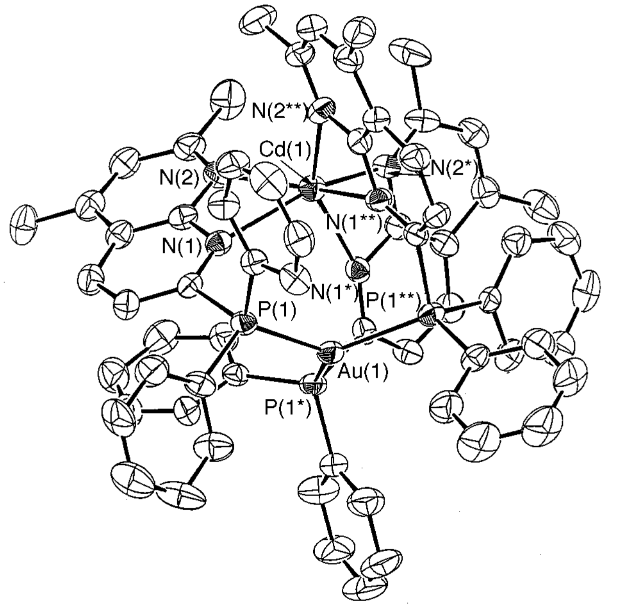

Fig. 2 A perspective view of complex cation **3**. Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.362(3), Cd(1)–N(1) 2.438(9), Cd(1)–N(2) 2.288(9); P(1)–Au(1)–P(1*) 118.69(3), N(1)–Cd(1)–N(1*) 100.5(2), N(1)–Cd(1)–N(2) 56.8(3), N(1)–Cd(1)–N(2*) 101.0(3), N(1)–Cd(1)–N(2**) 151.3(3), N(1*)–Cd(1)–N(2*) 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 (ε_{max}/cm^{-1} M^{-1})	λ_{em}/nm (excitation 360 nm)	τ/μs
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

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 $[Au(dpnapy)_3]^+$ 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)°. 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) $\longrightarrow$ π*(dpnapy) MLCT transition. For complex **2**, a low energy absorption tail from 420–450 nm has been observed, which is attributed to the d(Cu) $\longrightarrow$ π* (dpnapy) MLCT transition. The red shift in the d(Au) $\longrightarrow$ π* (dpnapy) 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 d(Au) $\longrightarrow$ π*(dpnapy) MLCT excited state. Interestingly, co-ordination of Cu^{I} to $[Au(dpnapy)_3]^+$ 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) $\longrightarrow$ π*(dpnapy) and d(Cu) $\longrightarrow$ π*(dpnapy). In cation **3**, co-ordination of Cd^{II} to $[Au(dpnapy)_3]^+$ lowers the energy of the d(Au) $\longrightarrow$ π*(dpnapy) excited state and hence the MLCT emission is red shifted to a longer wavelength, 606 nm.

Acknowledgements

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References

1 J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
2 S. J. Shieh, D. Li, S. M. Peng and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 195; R. H. Uang, C. K. Chan, S. M. Peng and C. M. Che, *J. Chem. Soc., Chem. Commun.*, 1994, 2561.
3 F. A. Cotton and B. Hong, *Prog. Inorg. Chem.*, 1992, **40**, 179.
4 P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **35**, 329.
5 C. M. Hartshorn and P. J. Steel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2655, and refs. therein.
6 M. Grassi, G. D. Munno, F. Nicolo and S. L. Schiavo, *J. Chem. Soc., Dalton Trans.*, 1992, 2367.

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¶ **2**$[ClO_4]_2$: $C_{66}H_{57}AuCl_2CuN_6O_8P_3$, $M = 1486.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.795(1)$, $b = 16.092(1)$, $c = 16.491(1)$ Å, $\alpha = 87.75(1)$, $\beta = 62.93(1)$, $\gamma = 65.31(1)$, $U = 3331.7(4)$ Å^3, $Z = 2$, μ(Mo-Kα) = 27.28 cm^{-1}, crystal dimensions 0.20 × 0.20 × 0.18 mm, $T = 293$ K, $F(000) = 1492$, no. of unique reflections = 10 333, no. of reflections with $I \geqslant 2\sigma(I) = 9505$, no. of variables = 829, $R = 0.079$, $R' = 0.088$, goodness of fit = 1.22.

3$[ClO_4]_3$·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, $U = 3602.1(3)$ Å^3, $Z = 2$, μ(Mo-Kα) = 25.78 cm^{-1}, crystal of dimensions 0.15 × 0.10 × 0.30 mm, $T = 301$ K, $F(000) = 1672$, reflections measured = 4662, no. of unique reflections = 4258, no. of reflections with $I \geqslant 3\sigma(I) = 2806$, 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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