Synthesis and Structural Characterisation of Five-co-ordinate Copper(I) and Silver(I) 2,2′:6′,2″-Terpyridine Complexes*

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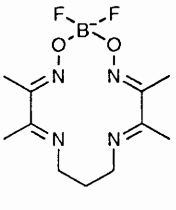
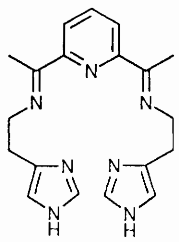
Five-co-ordinate copper(I) and silver(I) 2,2′:6′,2″-terpyridine (terpy) complexes of the type $[M(PPh_3)_2(terpy)]ClO_4$ (M = Cu or Ag) have been prepared by the reaction of terpy with either $[Cu(PPh_3)_2(MeCN)_2]ClO_4$ or $[Ag(PPh_3)_2]ClO_4$. The complexes have been characterised by spectroscopic methods and single-crystal X-ray diffraction analysis. In the crystal the complexes consist of discrete monomers of distorted trigonal-bipyramidal geometry, with the metal atoms co-ordinated to the distal terpyridine pyridyl rings [Cu–N 2.386(3), 2.535(4); Ag–N 2.614(2), 2.561(2)Å] in axial sites. The co-ordination spheres are completed by the binding of the central pyridyl nitrogen atoms [Cu–N(2) 2.102(3), Ag–N(2) 2.457(2) Å] and two PPh_3 phosphorus atoms, which together define the equatorial planes. The ^1H and $\{^1H\}$-^{13}C NMR spectra of $[Cu(PPh_3)_2(terpy)]ClO_4$ and $[Ag(PPh_3)_2(terpy)]ClO_4$ show that for each of the complexes the five-co-ordinate nature of the compounds is also retained in solution with the distal pyridyl rings being equivalent on the NMR time-scale.

In the solid state, the stereochemistry of mononuclear copper(I) and silver(I) complexes is dominated by four-co-ordinate species, but significant numbers of two- and three-co-ordinate compounds are also known.[1,2] In contrast five-co-ordinate copper(I) and silver(I) compounds are unusual, with six-co-ordination being unknown for copper(I) and rare for silver(I).[1,2] The small number of mononuclear five-co-ordinate copper(I) and silver(I) complexes reported to date occur with macrocyclic[3-5] or acyclic[6-8] ligands and the co-ordination geometry observed with these d^{10} metal centres may be a consequence of the geometrical constraints imposed by the nature of these ligands. For example the tetradentate macrocycle L^1 forms a square-pyramidal copper(I) complex [CuL^1(CO)][3] whereas the acyclic pentadentate ligand L^2 co-ordinates in a distorted trigonal-bipyramidal manner.[6] A pentagonal planar geometry is observed for the 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) complex with silver(I),[8] $[Ag(qpy)]PF_6$. To our knowledge there are no examples of five-co-ordinate copper(I) or silver(I) complexes involving only tri-, bi- or mono-dentate ligands. One such potentially tridentate ligand is 2,2′:6′,2″-terpyridine (terpy) which has been extensively studied in co-ordination chemistry.[9] In this paper we report the synthesis and characterisation of the five-co-ordinate copper(I) and silver(I) complexes with this ligand incorporating triphenylphosphine as co-ligand. The single-crystal X-ray structural analyses of $[M(PPh_3)_2(terpy)]ClO_4$ (M = Cu or Ag), together with spectroscopic data are presented.



L^1



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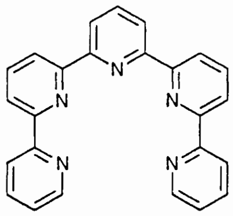

qpy

Results and Discussion

2,2′:6′,2″-Terpyridine reacts readily with $[Cu(PPh_3)_2(MeCN)_2]ClO_4$ or $[Ag(PPh_3)_2]ClO_4$ in dichloromethane–ethanol to yield $[Cu(PPh_3)_2(terpy)]ClO_4$ **1** and $[Ag(PPh_3)_2(terpy)]ClO_4$ **2** as yellow and colourless crystalline materials respectively. These compounds are stable in the solid state at room temperature and in air. However in solution complex **1** is oxidised over a period of 1–2 h in air to give a pale blue powder of, as yet, unknown composition. While the characterisation of both complexes by NMR spectroscopy, mass spectrometry and elemental analysis indicated the possibility of five-co-ordination, it was the single-crystal X-ray diffraction studies (see below) that showed that this was indeed the case.

The mass spectra (LSIMS) of compounds **1** and **2** exhibited only very weak peaks corresponding to the parent ions, $[M(PPh_3)_2(terpy)]^+$ (M = Cu or Ag), but a strong fragmentation pattern corresponding to the successive loss of ligands was observed. In each case the most intense signal corresponded to the $[M(terpy)]^+$ ion. The mass spectral data and the corresponding peak assignments are listed in Table 1.

The NMR specroscopic data (^1H and $\{^1H\}$-^{13}C) for compounds **1** and **2** are listed in Tables 2 and 3 respectively. Assignments were made on the basis of coupling considerations, chemical shift data, relative intensities and by comparison with the chemical shifts of the free ligand. Two-dimensional *J*-resolved ^1H, ^1H–^1H shift correlation and ^1H–^{13}C shift correlation spectra were recorded on the compounds to aid the assignments. Fig. 1 shows the labelling scheme used for the assignments.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

The ^{1}H NMR spectrum of compound **1** shows some broadening of resonances, even when samples were prepared under argon, probably due to decomposition to copper(II) species. The largest chemical shift difference in the ^{1}H NMR spectra on co-ordination of terpyridine to the Cu^{I} or Ag^{I} metal centres occurs for the protons H^{1} and H^{15} which are adjacent to the pyridyl nitrogens N^{1} and N^{3} respectively. These protons are shielded on co-ordination and exhibit shifts of 1.17 and 0.86 ppm to lower frequency for the copper(I) and silver(I) compounds respectively. The triphenylphosphine ligands exhibit two resonances in the ^{1}H NMR spectra for both compounds of relative intensity 6:24 which are attributable to the protons *para*- to the *ipso* carbon and *ortho*-, *meta*- to the *ipso* carbon respectively. For both complexes the $\{^{1}H\}$-^{13}C resonances of the pyridyl ring containing N^{1} are equivalent to those of the pyridyl ring containing N^{3}. Hence in solution at room temperature on the NMR time-scale, the distal rings of the terpyridine ligand are equivalent. Overall the NMR data point to the co-ordination of the terpyridine and triphenylphosphine ligands to the copper(I) and silver(I) ions in solution.

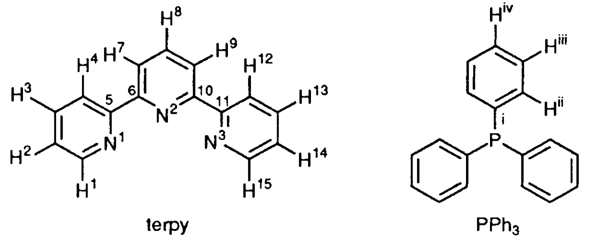


Fig. 1 Labelling schemes used for NMR assignments

Table 1 Mass spectral data for $[M(PPh_3)_2(terpy)]ClO_4$ (M = Cu or Ag)

	*m/z**	
Ionic species	M = Cu	M = Ag
$[M(PPh_3)_2(terpy)]^+$	820 (< 1)	864 (~ 1)
$[M(PPh_3)_2]^+$	587 (18)	631 (62)
$[M(PPh_3)(terpy)]^+$	558 (25)	602 (43)
$[M(PPh_3)]^+$	325 (16)	369 (49)
$[M(terpy)]^+$	296 (100)	340 (100)
$[PPh_3]^+$	262 (10)	262 (31)
$[terpy]^+$	—	233 (13)

* Based on ^{63}Cu and ^{107}Ag respectively. Relative intensities (%) are given in parentheses.

Table 2 ^{1}H NMR data for $[M(PPh_3)_2(terpy)]ClO_4$ (M = Cu or Ag)

	M = Cu		M = Ag	
	δ[a]	Δδ[b]	δ[a]	Δδ[b]
H^1, H^{15}	7.53 (br s)	−1.17	7.81−7.87 (m)	−0.86
H^2, H^{14}	*ca.* 7.07[c]	−0.26	*ca.* 7.10[c]	−0.23
H^3, H^{13}	7.72 (t, *J* 7.4)	−0.14	7.81–7.87 (m)	−0.02
H^4, H^{12}	8.02 (d, *J* 7.8)	−0.60	8.19 (d, *J* 8.2)	−0.43
H^7, H^9	8.21 (br s)	−0.25	8.25–8.27 (m)	−0.20
H^8		+0.25		+0.30
H^{ii}, H^{iii}	6.96–7.18 (m)		7.07–7.21 (m)	
H^{iv}	7.33–7.35 (m)		7.38 (t of d, *J* 7.2, 1.2)	

[a] In $CDCl_3$ at 25 °C (for assignments see Fig. 1); *J* values in Hz. [b] Δδ = δ(complex) − δ(free ligand). [c] Chemical shift estimated from two-dimensional ^{1}H–^{1}H shift correlation spectrum since resonance is obscured by PPh_3 resonances.

Molecular Structure of $[Cu(PPh_3)_2(terpy)]ClO_4$ **1**.—The molecular structure consists of a discrete monomer with an N_3P_2 donor set in a distorted trigonal-bipyramidal copper co-ordination geometry (Fig. 2). Positional parameters for the non-hydrogen atoms are given in Table 4, and selected bond lengths and angles in Tables 5 and 6 respectively. The trigonal plane is defined by atoms P(1), P(2) and N(2), with the copper atom lying out of the plane by 0.10 Å. The metal centre forms bonds of length 2.257(1), 2.289(1) and 2.102(3) Å to P(1), P(2) and N(2) respectively which lie within the range observed for a series of other copper(I) compounds [Cu–P 2.246(3)–2.295(3), Cu–N 1.999(9)–2.161(13) Å].[10–13] The metal atom also forms longer Cu–N bonds to the distal pyridyl nitrogens N(1) and N(3) of the terpy ligand [2.386(3) and 2.535(4) Å respectively], these distances being well outside the above Cu–N range. Thus the equatorial donor atom N(2) co-ordinates more strongly to the copper atom than do the two axial donor atoms N(1) and N(3). The angles subtended at the copper in the trigonal plane are 109.6(1), 121.5(1) and 128.3(1)° for N(2)–Cu–P(2), N(2)–Cu–P(1) and P(1)–Cu–P(2) respectively, two of these values showing some distortion from the ideal angle of 120° for a regular trigonal bipyramid. However the P(1)–Cu–P(2) angle is consistent with the P–Cu–P angles observed for tetrahedral bis(triphenylphosphine) copper(I) complexes, where angles of greater than 120° are found,[13] in part due to repulsions between the phenyl rings of the triphenylphosphine ligands.

Slightly longer axial copper–nitrogen bonds in comparison with those within the equatorial plane have been reported for a series of copper(II) terpyridine complexes.[14–17] In these, the central pyridyl nitrogen atoms have Cu–N bond lengths in the

Table 3 ^{13}C NMR data for $[M(PPh_3)_2(terpy)]ClO_4$ (M = Cu or Ag)

	M = Cu		M = Ag	
	δ[a]	Δδ[b]	δ[a]	Δδ[b]
C^1, C^{15}	149.2	+0.1	149.8	+0.7
C^2, C^{14}	124.6	+0.9	124.5	+0.8
C^3, C^{13}	138.0	+1.2	138.1	+1.3
C^4, C^{12}	123.3	+2.2	123.0	+1.9
C^5, C^{11} C^6, C^{10}	153.6, 154.3	−1.7, −1.9	153.7, 154.1	−1.6, −2.1
C^7, C^9	124.5	+3.6	123.3	+2.4
C^8	139.9	+2.0	140.0	+2.1
C^{i}	132.4 [*J*(PC) 25.4][c]	−4.7	132.0 [*J*(PC) 23.3][c]	−5.1
C^{ii}	133.2 [*J*(PC) 13.6]	−0.5	133.3 [*J*(PC) 15.6]	−0.4
C^{iii}	128.6 [*J*(PC) 7.8]	+0.1	128.9 [*J*(PC) 9.8]	+0.4
C^{iv}	130.0	+1.3	130.4	+1.7

[a] In $CDCl_3$ at 25 °C (for labelling see Fig. 1); *J* values in Hz. [b] Δδ = δ(complex) − δ(free ligand). [c] *J*(PC) for free PPh_3: 9.8 (C^{i}), 19.6 (C^{ii}), 7.9 Hz (C^{iii}).

Table 4 Fractional atomic coordinates for [Cu(PPh$_3$)$_2$(terpy)]ClO$_4$ **1** with estimated standard deviations (e.s.d.s.) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	−0.221 50(3)	0.178 30(4)	0.235 76(2)	C(14)	−0.170 2(4)	0.505 9(3)	0.364 7(2)
Cl	0.253 46(12)	0.287 61(9)	0.542 55(7)	C(15)	−0.247 1(4)	0.454 6(2)	0.359 3(2)
P(1)	−0.144 86(7)	0.210 01(7)	0.331 61(5)	C(16)	−0.238 0(3)	0.365 5(3)	0.351 1(2)
P(2)	−0.375 31(7)	0.198 67(7)	0.208 69(5)	C(21)	−0.180 7(3)	0.156 4(3)	0.407 9(2)
O(1)	0.315(1)	0.330(1)	0.508(1)	C(22)	−0.224 1(3)	0.199 0(3)	0.458 0(2)
O(2)	0.163(1)	0.319(1)	0.519(1)	C(23)	−0.253 4(4)	0.153 0(4)	0.512 8(2)
O(3)	0.258(1)	0.301(1)	0.613(1)	C(24)	−0.237 5(4)	0.065 4(4)	0.517 3(3)
O(4)	0.281(1)	0.203(1)	0.522(1)	C(25)	−0.195 0(5)	0.022 6(4)	0.468 1(3)
O(11)	0.236(2)	0.195(1)	0.540(1)	C(26)	−0.165 1(4)	0.068 5(3)	0.413 2(3)
O(12)	0.168(1)	0.299(2)	0.544(1)	C(31)	−0.020 7(3)	0.185 1(3)	0.335 7(2)
O(13)	0.300(1)	0.310(1)	0.598(1)	C(32)	0.032 1(4)	0.186 6(4)	0.392 7(3)
O(14)	0.279(3)	0.341(3)	0.497(2)	C(33)	0.124 6(4)	0.165 0(4)	0.394 9(3)
N(1)	−0.143 7(2)	0.281 2(2)	0.168 7(1)	C(34)	0.164 9(4)	0.139 6(4)	0.338 2(4)
N(2)	−0.159 4(2)	0.104 4(2)	0.161 8(1)	C(35)	0.115 4(3)	0.138 7(4)	0.280 3(3)
N(3)	−0.261 0(3)	0.018 7(2)	0.254 1(2)	C(36)	0.022 1(3)	0.160 6(3)	0.278 3(2)
C(01)	−0.121 1(3)	0.364 6(3)	0.180 9(2)	C(41)	−0.414 7(3)	0.295 7(3)	0.162 0(2)
C(02)	−0.052 7(4)	0.408 7(3)	0.149 1(3)	C(42)	−0.376 7(3)	0.375 8(3)	0.182 4(2)
C(03)	−0.003 1(4)	0.364 2(4)	0.103 4(3)	C(43)	−0.406 1(4)	0.452 1(3)	0.152 4(3)
C(04)	−0.025 2(3)	0.278 4(3)	0.089 8(2)	C(44)	−0.472 6(4)	0.448 7(4)	0.100 5(3)
C(05)	−0.096 0(3)	0.239 8(3)	0.122 5(2)	C(45)	−0.508 7(4)	0.370 3(4)	0.080 6(3)
C(06)	−0.121 6(3)	0.146 9(3)	0.110 8(2)	C(46)	−0.480 7(3)	0.294 1(3)	0.111 4(2)
C(07)	−0.105 3(3)	0.105 5(3)	0.050 9(2)	C(51)	−0.452 7(3)	0.201 5(3)	0.278 3(2)
C(08)	−0.128 4(4)	0.018 2(4)	0.043 4(2)	C(52)	−0.546 6(3)	0.225 0(4)	0.270 4(3)
C(09)	−0.162 8(3)	−0.025 9(3)	0.095 6(2)	C(53)	−0.599 5(4)	0.230 0(4)	0.325 0(3)
C(010)	−0.176 9(3)	0.017 9(3)	0.154 9(2)	C(54)	−0.563 1(4)	0.212 8(4)	0.387 1(3)
C(011)	−0.211 7(3)	−0.028 8(3)	0.212 7(2)	C(55)	−0.473 0(4)	0.188 8(3)	0.394 9(3)
C(012)	−0.194 4(4)	−0.116 2(3)	0.224 5(3)	C(56)	−0.418 0(3)	0.182 5(3)	0.340 8(2)
C(013)	−0.229 6(4)	−0.155 7(3)	0.279 3(3)	C(61)	−0.414 4(3)	0.106 4(3)	0.158 3(2)
C(014)	−0.282 8(4)	−0.109 2(3)	0.319 2(2)	C(62)	−0.380 7(3)	0.096 8(3)	0.095 8(2)
C(015)	−0.298 2(4)	−0.023 6(4)	0.304 1(3)	C(63)	−0.399 5(4)	0.022 1(4)	0.059 3(3)
C(11)	−0.151 9(3)	0.326 8(3)	0.348 2(2)	C(64)	−0.450 6(5)	−0.043 8(4)	0.085 6(4)
C(12)	−0.074 3(3)	0.380 7(3)	0.353 2(2)	C(65)	−0.483 6(4)	−0.036 3(4)	0.146 9(4)
C(13)	−0.085 6(4)	0.469 3(3)	0.360 9(3)	C(66)	−0.467 9(4)	0.038 4(3)	0.183 1(3)

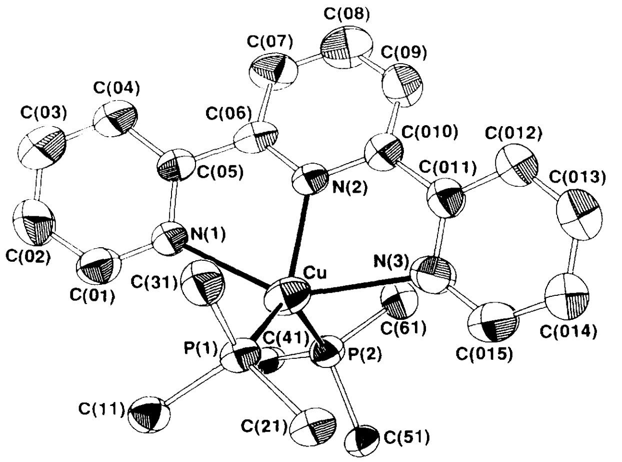
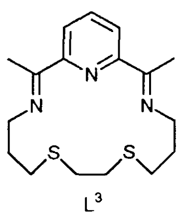


Fig. 2 Thermal ellipsoid diagram for [Cu(PPh$_3$)$_2$(terpy)]ClO$_4$ **1** drawn at the 50% probability level. Only the *ipso* carbons of the PPh$_3$ rings are included for clarity



L^3

range 1.923(5)–1.957(6) Å, whereas the distal pyridyl nitrogens have the longer Cu–N distances of 2.029(5)–2.059(6) Å. The radius of the Cu^I ion is expected to be only slightly larger than that of Cu^{II} (< 0.05 Å).[1] Although conclusions drawn from size comparisons of the 3d^9 Cu^{II} and 3d^{10} Cu^I ions should be made with caution, it is noted that the longer Cu–N(2) distance of 2.102(3) Å observed for the central pyridine nitrogen in compound **1**, compared with those reported for copper(II) terpyridine compounds is consistent with the increase in ionic radii in going from Cu^{II} to Cu^I. However the increase in the Cu–N distances for the distal nitrogens, N(1) and N(3), in **1** is as much as 0.5 Å, an increase which cannot simply be attributed to the larger radius of Cu^I. This observation of long axial copper–nitrogen bonds has also been reported for a series of pentadentate ligands which form distorted trigonal-bipyramidal five-co-ordinate copper(I) complexes.[4,6,7] Where the ligand is the macrocycle formed from the condensation reaction of 2,6-diacetylpyridine with 1,10-diamino-4,7-dithiadecane, L^3,[4] it has been suggested that it is too large for the Cu^I ion and as a result the ligating atoms in the equatorial plane are tightly bound with the remaining donor atoms fitting in as best they can. However in the complex [CuL^2]BF$_4$[6] and the related complex [CuL^4]BF$_4$ [L^4 = 2,6-bis(1-{[2-(2-pyridyl)ethyl]imino}ethyl)pyridine],[7] the acyclic ligands do not possess this degree of conformational rigidity yet long axial bonds are still observed. The significant number of trigonal-planar three co-ordinate copper(I) complexes now characterized[1] suggests that the electronic requirements of the Cu^I ion can be satisfied by this stereochemistry. Thus it appears that if a trigonal-bipyramidal five-co-ordination is demanded by the ligand bound to copper(I), a distorted geometry will result with the equatorial bond lengths being at the upper end of the range expected for trigonal copper(I) complexes[1] and the axial bond lengths being significantly longer.

The terpyridine ligand in complex **1** is non-planar with angles of 27.5° between the pyridyl ring containing nitrogen N(1) and that containing N(2), and of 31.3° between the pyridyl ring containing N(2) and that containing N(3). In contrast the

Table 5 Selected bond lengths (Å) for $[M(PPh_3)_2(terpy)]ClO_4$ (M = Cu or Ag) with e.s.d.s. in parentheses

	M = Cu	M = Ag		M = Cu	M = Ag
P(1)–M	2.257(1)	2.492(1)	C(03)–C(04)	1.376(8)	1.388(5)
P(2)–M	2.289(1)	2.525(1)	C(04)–C(05)	1.371(6)	1.382(4)
N(1)–M	2.386(3)	2.614(2)	C(05)–C(06)	1.484(6)	1.498(3)
N(2)–M	2.102(3)	2.457(2)	C(06)–C(07)	1.397(6)	1.378(4)
N(3)–M	2.535(4)	2.561(2)	C(07)–C(08)	1.383(8)	1.378(4)
N(1)–C(01)	1.337(6)	1.348(3)	C(08)–C(09)	1.364(7)	1.370(5)
N(1)–C(05)	1.341(5)	1.331(4)	C(09)–C(010)	1.398(6)	1.396(4)
N(2)–C(06)	1.353(5)	1.349(3)	C(010)–C(011)	1.476(6)	1.470(4)
N(2)–C(010)	1.353(5)	1.354(3)	C(011)–C(012)	1.380(6)	1.390(4)
N(3)–C(011)	1.333(6)	1.341(3)	C(012)–C(013)	1.378(8)	1.388(4)
N(3)–C(015)	1.331(7)	1.336(3)	C(013)–C(014)	1.339(8)	1.349(5)
C(01)–C(02)	1.374(8)	1.372(4)	C(014)–C(015)	1.361(7)	1.382(4)
C(02)–C(03)	1.371(9)	1.361(5)			

Table 6 Selected bond angles (°) for $[M(PPh_3)_2(terpy)]ClO_4$ (M = Cu or Ag) with e.s.d.s. in parentheses

	M = Cu	M = Ag		M = Cu	M = Ag
P(1)–M–P(2)	128.3(1)	121.8(1)	N(1)–M–N(3)	146.1(1)	130.0(1)
P(1)–M–N(1)	97.1(1)	104.4(1)	N(2)–M–N(3)	72.0(1)	66.3(1)
P(1)–M–N(2)	121.5(1)	134.7(1)	M–N(1)–C(01)	129.7(3)	122.8(2)
P(1)–M–N(3)	100.7(1)	101.1(1)	M–N(1)–C(05)	110.5(3)	115.7(2)
P(2)–M–N(1)	104.2(1)	105.3(1)	M–N(2)–C(06)	118.8(3)	122.1(1)
P(2)–M–N(2)	109.6(1)	103.2(1)	M–N(2)–C(010)	121.2(2)	119.4(2)
P(2)–M–N(3)	86.9(1)	96.3(1)	M–N(3)–C(010)	107.7(3)	114.4(1)
N(1)–M–N(2)	74.1(1)	65.1(1)	M–N(3)–C(015)	132.6(3)	121.5(1)

non-planarity of the entire ligand is much less evident in the copper(II) terpyridine compounds $[Cu(terpy)(H_2O)(C_4O_4)]\cdot H_2O$, $[Cu_2(terpy)_2(H_2O)_2(C_4O_4)][ClO_4]_2$, $[Cu(terpy)(NCO)(H_2O)]NO_3$ and $[Cu(terpy)(NCO)(H_2O)]PF_6$,[18,19] where angles between pyridyl rings are much smaller (in range 0.65–3.29°). Only small deviations from planarity are observed when terpyridine is co-ordinated to other first-row transition metals,[20] but for the larger d^{10} Hg^{II} ion complexes $[Hg(CF_3)_2(terpy)]$[21] and $[HgMe(teterpy)]NO_3$[22] (teterpy = 4,4′,4″-triethyl-2,2′:6′,2″-terpyridine) the angles between the distal pyridyl rings and the central pyridyl ring are in the range 15.4–21.5°. The deviations from planarity in the terpyridine ligands of these latter mercury(II) complexes appear to be necessary to accommodate the longer metal–nitrogen bonds [2.26(2)–2.70(2) Å] observed in these compounds. Similarly the non-planar conformation of the terpyridine in compound **1** arises from the need for the ligand to accommodate the longer Cu–N bonds to the distal nitrogens, N(1) and N(3).

Molecular Structure of $[Ag(PPh_3)_2(terpy)]ClO_4$ **2**.—The molecular structure of complex **2** is similar to that of **1**, with distorted trigonal-bipyramidal co-ordination geometry for the metal and an N_3P_2 set of donor atoms (Fig. 3). Positional parameters for non-hydrogen atoms are given in Table 7, and selected bond lengths and angles in Tables 5 and 6 respectively. The trigonal plane is defined by atoms P(1), P(2) and N(2), with the metal centre displaced by 0.08 Å from it. Axial bonds are formed between the silver atom and the distal nitrogens N(1) and N(3). The silver–phosphorus bonds Ag–P(1) and Ag–P(2), are 2.492(1) and 2.525(1) Å long respectively, which lie within the range of distances observed [2.467(2)–2.556(1) Å] for $[AgCl(PPh_3)_n]$ (where n = 2 or 3).[23,24] The metal centre forms a bond of length 2.457(2) Å to the nitrogen of the central pyridyl ring, N(2). This value is in accord with the silver–nitrogen distances observed for the five-co-ordinate ligand in $[Ag(qpy)]PF_6$[2.439(13)–2.479(23) Å][8] but longer than the value of 2.317(9) Å observed for the equatorial Ag–N distance in the silver(I) complex of the macrocyclic ligand L^3.[4] As was observed for complex **1**, longer axial bonds are formed to the nitrogen atoms N(1) and N(3) of the distal pyridyl rings, with bond lengths of 2.614(2) and 2.561(2) Å respectively. Both the Ag–N(1) and Ag–N(2) distances are significantly longer than those observed in the five-co-ordinate silver(I) complex $[Ag(qpy)]PF_6$, but the Ag–N(3) bond length does not differ significantly from the silver–nitrogen distance of 2.570(5) Å found in $[Ag(PPh_3)_2(py)Br]$ (py = pyridine).[25] The Ag–N(1) bond length is however significantly shorter than the axial silver–nitrogen interactions of 2.7408(10) Å reported for a binuclear six-co-ordinate silver(I) compound.[26]

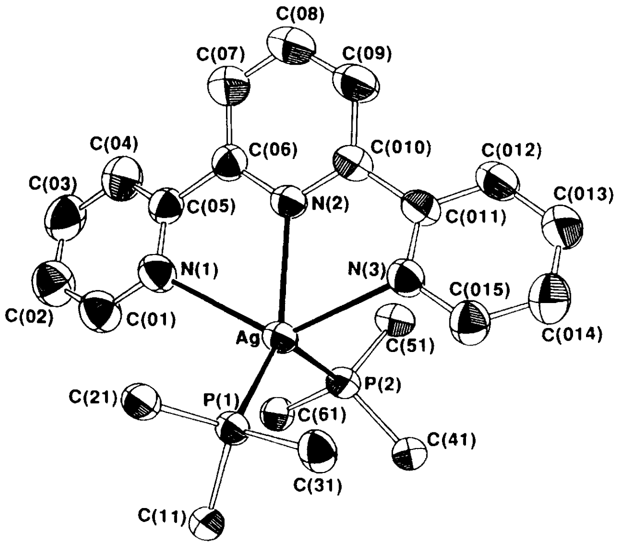


Fig. 3 Thermal ellipsoid diagram for $[Ag(PPh_3)_2(terpy)]ClO_4$ **2** drawn at the 50% probability level. Only the *ipso* carbons of the PPh_3 rings are included for clarity

Despite the similarity in overall co-ordination geometry between compounds **1** and **2** there is a larger range of metal–nitrogen distances observed for the former [2.102(3)–2.535(4) Å] than for the latter [2.457(2)–2.614(2) Å]. At the same time complex **2** exhibits a greater distortion from ideal trigonal-bipyramidal geometry with the three angles lying in the equatorial plane, P(1)–Ag–P(2), P(1)–Ag–N(2) and P(2)–Ag–N(2), observed at 121.8(1), 134.7(1) and 103.2(1)° respec-

Table 7 Fractional atomic coordinates for [Ag(PPh$_3$)$_2$(terpy)]ClO$_4$ **2** with e.s.d.s. in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ag	0.065 63(2)	0.208 92(1)	0.253 06(1)	C(16)	−0.015 5(4)	0.246 6(2)	−0.057 0(2)
Cl	−0.512 17(8)	0.277 46(4)	0.732 63(4)	C(21)	0.218 6(2)	0.151 3(2)	0.042 5(2)
P(1)	0.124 65(6)	0.231 21(4)	0.098 93(3)	C(22)	0.192 0(3)	0.062 3(2)	0.068 5(2)
P(2)	−0.143 53(6)	0.264 12(4)	0.319 38(4)	C(23)	0.252 2(4)	−0.004 1(2)	0.026 0(2)
O(1)	−0.557 4(4)	0.313 3(2)	0.656 2(2)	C(24)	0.340 4(2)	0.018 4(2)	−0.040 9(2)
O(2)	−0.604 4(3)	0.285 8(2)	0.802 0(2)	C(25)	0.369 8(3)	0.106 0(2)	−0.066 1(2)
O(3)	−0.378 1(3)	0.328 0(2)	0.752 7(2)	C(26)	0.309 4(3)	0.173 7(2)	−0.025 2(2)
O(4)	−0.497 3(4)	0.186 5(2)	0.718 5(3)	C(31)	0.233 5(3)	0.340 9(2)	0.084 3(2)
N(01)	0.019 9(2)	0.033 6(1)	0.269 1(1)	C(32)	0.373 9(3)	0.350 9(2)	0.110 7(2)
N(02)	0.182 0(2)	0.153 4(1)	0.376 3(1)	C(33)	0.452 8(4)	0.436 4(3)	0.111 4(2)
N(03)	0.250 0(2)	0.328 6(1)	0.324 6(1)	C(34)	0.398 7(6)	0.510 8(3)	0.089 1(3)
C(01)	−0.077 0(3)	−0.021 3(2)	0.222 4(2)	C(35)	0.262 2(5)	0.500 5(2)	0.061 1(3)
C(02)	−0.136 2(3)	−0.105 8(2)	0.247 5(2)	C(36)	0.179 8(4)	0.415 0(2)	0.058 3(2)
C(03)	−0.098 3(4)	−0.134 7(2)	0.324 8(3)	C(41)	−0.174 7(3)	0.374 9(2)	0.285 7(2)
C(04)	0.000 4(4)	−0.079 3(2)	0.374 4(2)	C(42)	−0.093 0(3)	0.417 1(2)	0.221 6(2)
C(05)	0.060 0(3)	0.003 3(2)	0.343 1(2)	C(43)	−0.108 8(4)	0.502 4(2)	0.195 9(3)
C(06)	0.170 2(3)	0.064 6(2)	0.392 8(2)	C(44)	−0.210 2(4)	0.546 5(2)	0.233 8(3)
C(07)	0.253 0(3)	0.030 6(2)	0.451 7(2)	C(45)	−0.291 3(4)	0.504 6(2)	0.296 7(3)
C(08)	0.351 3(4)	0.089 8(2)	0.496 9(2)	C(46)	−0.273 6(3)	0.421 2(2)	0.323 5(2)
C(09)	0.363 6(3)	0.180 6(2)	0.482 9(2)	C(51)	−0.141 3(3)	0.280 1(2)	0.435 9(2)
C(010)	0.278 5(2)	0.211 0(2)	0.421 3(2)	C(52)	−0.037 6(4)	0.344 2(3)	0.470 4(2)
C(011)	0.289 1(2)	0.307 6(2)	0.403 1(2)	C(53)	−0.026 0(4)	0.361 1(3)	0.557 5(2)
C(012)	0.334 0(3)	0.374 1(2)	0.464 9(2)	C(54)	−0.122 3(5)	0.312 5(3)	0.611 2(2)
C(013)	0.338 4(3)	0.464 3(2)	0.444 8(2)	C(55)	−0.225 0(4)	0.245 7(3)	0.578 0(2)
C(014)	0.302 3(3)	0.485 3(2)	0.365 2(2)	C(56)	−0.234 5(3)	0.229 9(2)	0.490 5(2)
C(015)	0.259 6(3)	0.416 0(2)	0.306 6(2)	C(61)	−0.305 7(3)	0.187 2(2)	0.295 9(2)
C(11)	−0.027 0(3)	0.236 6(2)	0.029 7(2)	C(62)	−0.304 0(3)	0.095 6(2)	0.311 3(2)
C(12)	−0.158 1(3)	0.230 4(2)	0.068 8(2)	C(63)	−0.420 7(3)	0.032 0(2)	0.290 6(2)
C(13)	−0.274 3(3)	0.238 1(2)	0.019 5(2)	C(64)	−0.537 0(3)	0.058 3(2)	0.255 0(2)
C(14)	−0.262 0(4)	0.250 0(2)	−0.067 0(3)	C(65)	−0.537 9(3)	0.148 2(2)	0.239 6(2)
C(15)	−0.135 6(5)	0.254 4(3)	−0.106 2(2)	C(66)	−0.423 8(3)	0.210 0(2)	0.260 6(2)

tively, values which show a greater spread than do their counterparts in complex **1** [128.3(1), 121.5(1), 109.6(1)°]. Moreover the angles between the axial donors [N(1), N(3)] and the two equatorial phosphorus atoms [*viz*. P(1)–Ag–N(1), P(1)–Ag–N(3), P(2)–Ag–N(1), P(2)–Ag–N(3)] at 104.1(1), 101.1(1), 105.3(1) and 96.3(1)° respectively are greater than the corresponding angles in **1** [97.1(1), 100.7(1), 104.2(1), 86.9(1)°]. Of particular interest is the very significant decrease in angles between the nitrogen donors in the terpyridine ligand [N(1)–Ag–N(2), N(2)–Ag–N(3) and N(1)–Ag–N(3) at 65.1(1), 66.3(1) and 130.0(1)° respectively in **2** in comparison with the corresponding angles observed in complex **1** of 74.1(1), 72.0(1) and 146.1(1)°]. These effects probably result from the longer Ag–N bond lengths observed and the greater flexibility in the co-ordination capabilities of silver(I). As was observed in the copper(I) complex **1**, in complex **2** the terpyridine ligand is non-planar with an angle of 24.2° between the pyridyl ring containing atom N(1) and that containing atom N(2), and an angle of 28.1° between this latter ring and that containing the nitrogen atom N(3).

Experimental

All reactions were routinely performed under dinitrogen using standard Schlenk techniques. The compounds [Cu(PPh$_3$)$_2$(MeCN)$_2$]ClO$_4$ and [Ag(PPh$_3$)$_2$]ClO$_4$ were prepared according to literature procedures.[10,27] 2,2′:6′,2″-Terpyridine (Aldrich) was used as supplied. Nuclear magnetic resonance spectra were recorded on a JEOL GX270W spectrometer and infrared spectra on a BIORAD FTS-40 instrument as Nujol mulls between KBr discs. Mass spectra were obtained using a Varian VG70-250S double focussing magnetic sector mass spectrometer by the method of liquid secondary ion mass spectrometry (LSIMS) at the Horticulture and Food Research Institute of New Zealand Limited, Palmerston North. Samples were dissolved in CH$_2$Cl$_2$ with *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were carried out using standard techniques by the Campbell Microanalytical Laboratory, University of Otago.

Preparation of [Cu(PPh$_3$)$_2$(terpy)]ClO$_4$ **1**.—2,2′:6′,2″-Terpyridine (47 mg, 0.2 mmol) dissolved in CH$_2$Cl$_2$ (5 cm^3) was added to [Cu(PPh$_3$)$_2$(MeCN)$_2$]ClO$_4$ (154 mg, 0.2 mmol) in the same solvent (15 cm^3). The solution immediately turned yellow. Ethanol (40 cm^3) was added and the solution heated under a brisk flow of dinitrogen until small yellow crystals began to form. The solution was allowed to cool to room temperature and the product was collected by vacuum filtration, washed with a small volume of cold ethanol and dried *in vacuo*. Yield: 122 mg (66%) (Found: C, 66.30; H, 4.60; N, 4.60. Calc. for $C_{51}H_{41}ClCuN_3O_4P_2$: C, 66.50; H, 4.50; N, 4.55%); IR (cm^{-1}) 1095vs ν(ClO$_4^-$).

Preparation of [Ag(PPh$_3$)$_2$(terpy)]ClO$_4$ **2**.—2,2′:6′,2″-Terpyridine (47 mg, 0.2 mmol) dissolved in CH$_2$Cl$_2$ (5 cm^3) was added to [Ag(PPh$_3$)$_2$]ClO$_4$ (146 mg, 0.2 mmol) dissolved in CH$_2$Cl$_2$–ethanol (1:4, 25 cm^3). The resulting colourless solution was heated under a brisk flow of dinitrogen until the volume was approximately 15 cm^3. The solution was then allowed to cool to room temperature. The white crystalline product which formed was collected by vacuum filtration, washed successively with a small volume of cold ethanol, then diethyl ether and dried *in vacuo*. Yield: 134 mg (69%) (Found: C, 63.25; H, 4.25; N, 4.05. Calc. for $C_{51}H_{41}AgClN_3O_4P_2$: C, 63.45; H, 4.30; N, 4.35%); IR (cm^{-1}) 1095vs ν(ClO$_4^-$).

Crystal Structure Determination of (2,2′:6′,2″-*Terpyridine*-κ^3N,N′,N″)*bis*(*triphenylphosphine*-κP)*copper*(I) *Perchlorate* **1**.—Yellow crystals of complex **1** were obtained by slow evaporation of an ethanol–dichloromethane solution.

Crystal data. $C_{51}H_{41}ClCuN_3O_4P_2$, M = 920.9, monoclinic, space group $P2_1/c$, a = 14.430(3), b = 15.282(3), c =

20.294(3) Å, $\beta = 91.97(1)°$, $U = 4472.6$ Å^3 (from least-squares refinement of the setting angles of 25 reflections; $13.9 \leqslant \theta \leqslant 15.9°$), Mo-K$\alpha$ radiation, $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 1.367$ g cm^{-3}, $F(000) = 1904$, μ(Mo-Kα) = 6.7 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD-4 diffractometer at 290 K, ω–2θ scan mode with graphite-monochromated Mo-Kα radiation, ω scan angle $(1.0 + 0.34 \tan \theta)°$, fixed scan speed 1.65° min^{-1}, 6116 reflections measured ($0.0 \leqslant \theta \leqslant 22.5°$, $+h$, $+k$, $\pm l$). The intensities of three standard reflections were monitored every hour of X-ray exposure time and showed no significant loss of intensity. Of the reflections measured, 5566 were unique [merging $R_{\text{int}} = 0.015$ after data corrected for Lorentz and polarisation effects and absorption correction applied (maximum and minimum transmission factors = 0.999, 0.979)] giving 4062 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$.

Structure analysis and refinement. Structure solution was by a combination of Patterson and Fourier techniques. Full-matrix least-squares refinement with anisotropic thermal motion assumed for all non-hydrogen atoms. Some disorder was noted for the oxygen atoms of the perchlorate group and site occupancies of 0.6 and 0.4 were chosen for O(1)–O(4) and O(11)–O(14) respectively. These values were based on a consideration of thermal parameters. Hydrogen atoms in calculated positions (C–H 0.96 Å). At convergence R and R' were 0.042 and 0.051 respectively for the 614 parameters refined. The weighting function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = [\sigma^2(F_o) + 0.021\,75 F_o{}^2]$.

Crystal Structure Determination of (2,2′:6′,2″-*Terpyridine*-κ^{3}N,N′,N″)*bis*(*triphenylphosphine*-κP)*silver*(I) *Perchlorate* **2**.—Colourless crystals of complex **2** were obtained by slow evaporation of an ethanol–dichloromethane solution.

Crystal data. $C_{51}H_{41}AgClN_3O_4P_2$, $M = 965.2$, triclinic, space group $P\bar{1}$, $a = 9.706(2)$, $b = 14.993(5)$, $c = 15.614(6)$ Å, $\alpha = 91.30(3)$, $\beta = 90.08(2)$, $\gamma = 99.08(2)°$, $U = 2243.0$ Å^3 (from the least-squares refinement of the setting angles of 25 reflections; $13.5 \leqslant \theta \leqslant 16.6°$), Mo-K$\alpha$ radiation, $\lambda = 0.710\,73$ Å, $Z = 2$, $D_c = 1.429$ g cm^{-3}, $F(000) = 988$, μ(Mo-Kα) = 6.2 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD-4 diffractometer at 290 K, ω–2θ scan mode with graphite-monochromated Mo-Kα radiation, ω scan angle $(1.0 + 0.34 \tan \theta)°$, variable scan speed 1.1–8.2° min^{-1}, 8393 reflections measured ($0 \leqslant \theta \leqslant 25°$, $+h$, $\pm k$, $\pm l$). The intensities of three standard reflections were monitored every hour of X-ray exposure time and showed no significant loss of intensity. Of the reflections measured, 7367 were unique [merging $R_{\text{int}} = 0.030$ after data corrected for Lorentz and polarisation effects and absorption correction applied (maximum and minimum transmission factors = 0.999, 0.857)] giving 6829 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$.

Structure analysis and refinement. Structure solution was by a combination of Patterson and Fourier techniques. Full-matrix least squares refinement with anisotropic thermal motion assumed for all non-hydrogen atoms. Hydrogen atoms in calculated positions (C–H 0.96 Å). At convergence R and R' were both 0.043 for the 578 parameters refined. The weighting function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = [\sigma^2(F_o) + 0.024\,11 F_o{}^2]$.

For both structures computations were performed with the SDP-PLUS [28] package and SHELX 76 [29] program.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

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References

1 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, pp. 533–774.
2 R. J. Lancashire, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, pp. 775–859.
3 R. R. Gagne, J. L. Allison, R. S. Gall and C. A. Koval, *J. Am. Chem. Soc.*, 1977, **99**, 7170.
4 M. G. B. Drew, C. Cairns, S. G. McFall and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 2020.
5 S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. B. Othman and N. B. Mason, *J. Chem. Soc., Chem. Commun.*, 1977, 167.
6 J. A. Goodwin, G. A. Bodager, L. J. Wilson, D. M. Stanbury and W. R. Scheidt, *Inorg. Chem.*, 1989, **28**, 35.
7 J. A. Goodwin, D. M. Stanbury, L. J. Wilson, C. W. Eigenbrot and W. R. Scheidt, *J. Am. Chem. Soc.*, 1987, **109**, 2979.
8 E. C. Constable, M. G. B. Drew, G. Forsyth and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1988, 1450.
9 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.
10 P. F. Barron, J. C. Dyason, L. M. Engelhardt, P. C. Healy and A. H. White, *Aust. J. Chem.*, 1985, **38**, 261.
11 L. M. Engelhardt, C. Pakawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 125.
12 J. Díez, M. P. Gamasa, J. Gimeno, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, 1987, 1275.
13 E. W. Ainscough, E. N. Baker, M. L. Brader, A. M. Brodie, S. L. Ingham, J. M. Waters, J. V. Hanna and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1991, 1243.
14 T. Rojo, M. Vlasse and D. Beltrán-Porter, *Acta. Crystallogr., Sect C*, 1983, **39**, 194.
15 M. I. Arriortua, J. L. Mesa, T. Rojo, T. Debaerdermaeker, D. Beltrán-Porter, H. Stratemeier and D. Reinen, *Inorg. Chem.*, 1988, **27**, 2976.
16 J. V. Folgado, E. Coronado, D. Beltrán-Porter, T. Rojo and A. Fuertes, *J. Chem. Soc., Dalton Trans.*, 1989, 237.
17 T. Rojo, A. Garcia, J. L. Mesa, M. I. Arriortua, J. L. Pizzaro and A. Fuertes, *Polyhedron*, 1989, **8**, 97.
18 X. Solans, M. Aguiló, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 775.
19 T. Rojo, R. Cortes, L. Lezama, J. L. Mesa, J. Via and M. I. Arriortua, *Inorg. Chim. Acta*, 1989, **165**, 91.
20 B. N. Figgis, E. S. Kucharski and A. H. White, *Aust. J. Chem.*, 1983, **36**, 1527.
21 B. Kamenar, B. Korpar-Čolig, A. Hergold-Brundić and Z. Popović, *Acta. Crystallogr., Sect. B*, 1982, **38**, 1593.
22 A. J. Canty, N. Chaichit, B. M. Gatehouse, E. E. George and G. Hayhurst, *Inorg. Chem.*, 1981, **20**, 2414.
23 A. Cassel, *Acta Crystallogr., Sect. B*, 1981, **37**, 229.
24 A. Cassel, *Acta. Crystallogr., Sect. B*, 1979, **35**, 174.
25 L. M. Engelhardt, P. C. Healy, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1989, **42**, 907.
26 S. M. Nelson, S. G. McFall, M. G. B. Drew and H. B. Othman, *J. Chem. Soc., Chem. Commun.*, 1977, 370.
27 R. Uson, L. A. Oro and J. A. Cabeza, *J. Organomet. Chem.*, 1983, **247**, 105.
28 Enraf-Nonius Structure Determination Package, SDP, Enraf-Nonius, Delft, 1985.
29 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination and Refinement, University of Cambridge, 1976.

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