Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 12.* Structural Studies of Some Bis(methyl-substituted pyridine)-copper(I) and -silver(I) Nitrates and Perchlorates †

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The crystal structure of a number of bis(monodentate pyridine base)-copper(I) and -silver(I) nitrate and perchlorate salts have been established at 295 K by single-crystal X-ray diffraction methods; the use of sterically hindered nitrogen bases enables the characterisation of these metal ions in a basically linear two-co-ordinate co-ordination environment. Crystals of bis(2,6-dimethylpyridine)copper(I) perchlorate, (1), are monoclinic, space group $C2/c$, with a = 15.175(6), b = 8.151(3), c = 13.227(10) Å, β = 99.26(4)°, Z = 4; R was 0.045 for N_{O} = 724 independent 'observed' reflections. The cation lies with the copper atom on a crystallographic inversion centre; Cu–N = 1.936(5) Å and N–Cu–N = 180°. Crystals of bis(2,6-dimethylpyridine)copper(I) nitrate, (2), are monoclinic, space group $P2_1/n$, with a = 12.774(3), b = 14.252(4), c = 8.373(4) Å, β = 93.56(3)°, Z = 4; R = 0.051 for N_{O} = 1 203. Cu–N = 1.966(5), 1.956(5) Å and N–Cu–N = 165.9(2)°; there are close approaches to the copper atom from 'bidentate' nitrate oxygen atoms at 2.506(7), 2.518(7) Å. Crystals of bis(2,4-dimethylpyridine)copper(I) perchlorate, (3), are orthorhombic, space group $Fdd2$, with a = 29.69(1), b = 10.007(5), c = 11.285(4) Å, Z = 8; R = 0.060 for N_{O} = 291. The cation symmetry is 2 with Cu–N = 1.86(1) Å and N–Cu–N = 170(1)°. Crystals of bis(2,6-dimethylpyridine)silver(I) perchlorate, (4), are tetragonal, space group $I4_1/acd$, with a = 15.234(3) Å, c = 14.428(6) Å, Z = 8; R = 0.041 for N_{O} = 423. The cation symmetry is 2 with Ag–N = 2.166(4) Å and N–Ag–N = 180.0°. Bis(2,6-dimethylpyridine)silver(I) nitrate, (5), is isomorphous with the copper(I) analogue (2): a = 13.235(3), b = 14.280(3), c = 8.284(3) Å, β = 94.54(2)°; R = 0.037 for N_{O} = 1 288. Ag–N = 2.192(6), 2.182(6) Å, with N–Ag–N = 169.3(2)°; Ag–O(NO_3) = 2.715(8), 2.663(7) Å.

A widespread belief in regard to the stereochemical properties of elements with the d^{10} electronic configuration is typified by the statement from a reputable standard text [1] that: 'Ag$^{\mathrm{I}}$ and Au$^{\mathrm{I}}$, along with Cu$^{\mathrm{I}}$ and Hg$^{\mathrm{II}}$ show a pronounced tendency to exhibit linear two-fold co-ordination'; *ds* hybridization effects [2] are often invoked as a rationalization of this presumed trend. However, the results of extensive structural studies on complexes of Ag$^{\mathrm{I}}$ and Cu$^{\mathrm{I}}$ show that for both cations, and particularly for Cu$^{\mathrm{I}}$, two-co-ordination is relatively rare, being limited to complexes with ligands which are primarily σ-bonding and non-polarizable [3–19] or polarizable ligands which are sterically demanding.[20–22] Both cations most commonly exhibit four-co-ordinate 'tetrahedral' stereochemistries, often achieved by complex oligomerization or polymerization processes.

The influence of ligands with bulky substituent groups on the co-ordination number of Cu$^{\mathrm{I}}$ and Ag$^{\mathrm{I}}$ complexes with polarizable or π-accepting ligands is well illustrated by the adducts of Cu$^{\mathrm{I}}$ and Ag$^{\mathrm{I}}$ perchlorate with substituted pyridine bases, L. With no bulky substituents in the 2-position, derivatives of the form [ML_4]ClO_4 may be obtained.[23] Introduction of a single methyl group in this position decreases the co-ordination number to three, as in the case of tris(2-methylpyridine)copper(I) perchlorate, the structure determination of which shows the cation to adopt a distorted trigonal planar configuration of N atoms about the central metal atom (N–Cu–N = 139, 118, and 113°).[24]

Available chemical and spectroscopic evidence [25] suggests that methyl substitution in both the 2- and 6-positions of pyridine further decreases the co-ordination number to two. The same study indicates that the ligand 2,4-dimethylpyridine (2,4Me$_2$-py), which might be expected to have similar *steric* properties to 2-methylpyridine but similar *electronic* properties to 2,6-dimethylpyridine (2,6Me$_2$-py) gives rise to a two- rather than three-co-ordinate perchlorate complex. The obviously finely balanced relationship between the steric and electronic properties of these ligands and the stereochemical environment of the central metal atom is of considerable chemical interest. As yet, however, no structural data exist for two-co-ordinate complexes of this type; in fact a strictly two-co-ordinate complex of copper(I) with a polarizable, neutral nitrogen-base ligand has yet to be characterized structurally. This paper seeks to improve the situation by reporting single-crystal X-ray structure determinations of [Cu(2,6Me$_2$-py)$_2$]ClO_4 (1), [Cu(2,6Me$_2$-py)$_2$]NO_3 (2), and [Cu(2,4Me$_2$-py)$_2$]ClO_4 (3) together with the silver(I) analogues [Ag(2,6Me$_2$-py)$_2$]ClO_4 (4) and [Ag(2,6Me$_2$-py)$_2$]NO_3 (5).

Experimental

Copper(I) complexes were prepared according to the general methods outlined in the literature for the preparation of nitrogen base–copper(I) complexes,[25] namely by the reaction of the nitrogen base in an oxygen-free acetonitrile solution of Cu$^{\mathrm{I}}$ perchlorate or nitrate respectively, these being prepared by the reduction of the appropriate Cu$^{\mathrm{II}}$ salt by electrolytic copper. {The less stable [Cu(CH_3CN)$_4$]NO_3 was not isolated

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* Part 11 is the preceding paper.[26]

† *Supplementary data available* (No. SUP 56058, 17 pp.): thermal parameters, H-atom co-ordinates, ligand geometries, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

as the solid.} Crystals suitable for structure determination were obtained by slow evaporation of the reaction mixture under a stream of argon gas. These were subject to decomposition and oxidation on exposure to the atmosphere and the crystals used in the structure analysis were encapsulated in dry argon-filled capillaries. [An alternative method of synthesis, involving the reaction of stoicheiometric amounts of copper(I) iodide with the appropriate bis(2,6-dimethylpyridine)silver(I) perchlorate or nitrate, to produce the required complex plus insoluble AgI, also appeared to produce crystalline material suitable for *X*-ray work. Subsequent refinement of the data, however, showed that for these crystals, a significant percentage of the copper sites (~10%) were replaced by silver(I) atoms, and data derivative of them were discarded.]

The silver adducts were prepared by addition of the base to a hot acetonitrile solution of the appropriate silver salt, the reaction mixture being protected from light. Slow cooling produced crystals of the compounds suitable for structure determination.

Crystallography.—General details are given in the preceding paper.[26]

[Cu(2,6Me$_2$-py)$_2$]ClO$_4$ (1). [Cu(C$_7$H$_9$N)$_2$]ClO$_4$ ≡ C$_{14}$H$_{18}$ClCuN$_2$O$_4$, M = 377.3, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), a = 15.175(6), b = 8.151(3), c = 13.227(10) Å, β = 99.26(4)°, U = 1 615(1) Å^3, D_c (Z = 4) = 1.56 g cm^{-3}, $F(000)$ = 776, μ_{Mo} = 14.6 cm^{-1}. Specimen: 0.25 × 0.09 × 0.07 mm; $2\theta_{max.}$ = 50°; N, N_o = 1 476, 724; R, R' = 0.045, 0.047.

[Cu(2,6Me$_2$-py)$_2$]NO$_3$ (2). [Cu(C$_7$H$_9$N)$_2$]NO$_3$ ≡ C$_{14}$H$_{18}$CuN$_3$O$_3$, M = 339.9, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14), a = 12.774(3), b = 14.252(4), c = 8.373(4) Å, β = 93.56(3)°, U = 1 521(1) Å^3, D_c (Z = 4) = 1.48 g cm^{-3}, $F(000)$ = 704, μ_{Mo} = 13.5 cm^{-1}. Specimen: 0.30 × 0.16 × 0.10 mm; $2\theta_{max.}$ = 45°; N, N_o = 1 999, 1 203; R, R' = 0.051, 0.060.

[Cu(2,4Me$_2$-py)$_2$]ClO$_4$ (3). [Cu(C$_7$H$_9$N)$_2$]ClO$_4$ ≡ C$_{14}$H$_{18}$ClCuN$_2$O$_4$, M = 377.3, orthorhombic, space group $Fdd2$ (C_{2v}^{19}, no. 43), a = 29.69(1), b = 10.007(5), c = 11.285(4) Å, U = 3 353(2) Å^3, D_c (Z = 8) = 1.50 g cm^{-3}, $F(000)$ = 1 552, μ_{Mo} = 15.8 cm^{-1}. Specimen: 0.25 × 0.12 × 0.08 mm; $2\theta_{max.}$ = 40°; N, N_o = 422, 291; R, R' = 0.060, 0.068 (both chiralities).

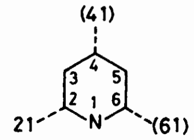
[Ag(2,6Me$_2$-py)$_2$]ClO$_4$ (4). [Ag(C$_7$H$_9$N)$_2$]ClO$_4$ ≡ C$_{14}$H$_{18}$AgClN$_2$O$_4$, M = 421.6, tetragonal, space group $I4_1/acd$ (D_{4h}^{20}, no. 142), a = 15.234(3), c = 14.428(6) Å, U = 3 348.5(6) Å^3, D_c (Z = 8) = 1.67 g cm^{-3}, $F(000)$ = 1 696, μ_{Mo} = 13.5 cm^{-1}. Specimen: cuboid, 0.2 mm; $2\theta_{max.}$ = 50°; N, N_o = 879, 423; R, R' = 0.041, 0.056.

[Ag(2,6Me$_2$-py)$_2$]NO$_3$ (5). [Ag(C$_7$H$_9$N)$_2$]NO$_3$ ≡ C$_{14}$H$_{18}$AgN$_3$O$_3$, M = 384.2, monoclinic, space group $P2_1/n$, a = 13.235(3), b = 14.280(3), c = 8.284(3) Å, β = 94.54(2)°, U = 1 561(1) Å^3, D_c (Z = 4) = 1.63 g cm^{-3}, $F(000)$ = 872, μ_{Mo} = 12.8 cm^{-1}. Specimen: 0.40 × 0.10 × 0.32 mm; $2\theta_{max.}$ = 45°; N, N_o = 2 149, 1 288; R, R' = 0.037, 0.044.

Abnormal features. Perchlorate disorder (or a lower symmetry space group?) in complex (3) was modelled in terms of oxygen atoms with 0.5 populations. Non-metal atom thermal parameters were refined isotropically because of limited data.

For complexes (2) and (5) high thermal motion is observed on the non-co-ordinated oxygen of the nitrate group, and on the methyl substituents of the ligands. Caution should be exercised in the interpretation of geometrical parameters in the vicinity, in the absence of libration correction.

Ligand non-hydrogen atom numbering is as shown below.



Atomic co-ordinates for complexes (1)—(5) are given in Tables 1—5 respectively.

Results and Discussion

Bis(2,6-*dimethylpyridine*)*copper*(I) *Perchlorate* (1).—The structure determination establishes the stoicheiometry of the

Table 1. Non-hydrogen atomic co-ordinates for [Cu(2,6-Me$_2$-py)$_2$]ClO$_4$ (1)

Atom	x	y	z
Cu	0	0	0
Cl	$\frac{1}{2}$	0.356 5(3)	$\frac{3}{4}$
O(1)	0.567 2(4)	0.458 8(8)	0.801 5(4)
O(2)	0.535 6(5)	0.263 3(9)	0.677 7(5)
N(1)	0.091 7(3)	−0.143 2(6)	0.070 2(4)
C(2)	0.177 9(4)	−0.099 5(8)	0.083 7(5)
C(21)	0.200 9(5)	0.065 5(9)	0.046 8(6)
C(3)	0.244 4(4)	−0.198 8(9)	0.132 5(5)
C(4)	0.222 7(5)	−0.346 9(9)	0.170 4(5)
C(5)	0.134 6(5)	−0.393 8(8)	0.157 0(5)
C(6)	0.070 1(4)	−0.289 1(8)	0.106 7(5)
C(61)	−0.027 0(5)	−0.333 5(9)	0.090 8(6)

Table 2. Non-hydrogen atomic co-ordinates for [Cu(2,6Me$_2$-py)$_2$]NO$_3$ (2)

Ligand	n = 1			n = 2		
Atom	x	y	z	x	y	z
Cu	0.296 01(6)	0.142 69(6)	0.451 5(1)			
N	0.292 5(5)	0.348 1(4)	0.454 4(8)			
O(1)	0.326 3(5)	0.302 3(5)	0.570 9(7)			
O(2)	0.263 2(5)	0.303 0(5)	0.332 2(7)			
O(3)	0.285 8(9)	0.430 1(5)	0.456 5(13)			
N(n1)	0.443 6(4)	0.126 7(4)	0.403 4(7)	0.150 1(4)	0.124 9(4)	0.503 0(7)
C(n2)	0.521 0(6)	0.125 9(5)	0.518 6(9)	0.122 8(6)	0.123 0(5)	0.654 7(9)
C(n21)	0.490 2(7)	0.128 8(6)	0.689 5(9)	0.210 5(6)	0.122 7(6)	0.782 8(10)
C(n3)	0.624 2(5)	0.122 2(6)	0.483 4(11)	0.018 2(6)	0.121 4(6)	0.692 7(9)
C(n4)	0.650 1(6)	0.121 3(6)	0.328 3(11)	−0.058 1(6)	0.121 1(6)	0.575 5(10)
C(n5)	0.571 7(7)	0.122 9(6)	0.208 7(10)	−0.033 4(5)	0.122 4(6)	0.419 7(10)
C(n6)	0.468 2(5)	0.124 1(5)	0.247 9(9)	0.0718 (6)	0.123 0(5)	0.384 5(9)
C(n61)	0.381 8(6)	0.124 5(7)	0.120 4(10)	0.102 1(6)	0.123 3(6)	0.214 5(10)

complex to be [Cu(2,6Me$_2$-py)$_2$]ClO$_4$ as postulated. The copper atoms are located at crystallographic inversion centres, so that only one of the ligands is independent, and the anions lie on crystallographic two-fold axes (Figure 1). Crystal symmetry requires that the two ligand planes lie parallel and, in fact, they are essentially coplanar, perhaps in consequence of perchlorate contacts (see below).

Completion of this structure permits a comparison of the geometric parameters for isolated cations in the series of salts: [CuL$_2$]ClO$_4$, [CuL$_3$]ClO$_4$, and [CuL$_4$]ClO$_4$. As expected the copper–nitrogen distance decreases from 2.046(4) Å in tetrakis(pyridine)copper(I) perchlorate,[23b] to 1.99 Å (mean) in tris(2-methylpyridine)copper(I) perchlorate,[24] to 1.936(5) Å (Table 6) in complex (1). This latter copper–nitrogen distance is among the longest observed for two-co-ordinate Cu–N systems (Table 7) and may reflect either the lower base strength of the ligand, or, more probably, the degree of steric crowding inherent in its structure [*cf.* Cu–N of 1.86(1) Å for complex (3)]. The co-ordination geometries of the four- and two-co-ordinate complexes (tetrahedral and linear) are as would be expected from simple electron repulsion considerations. The three-co-ordinate complex, however, reflects the asymmetric steric demands of the ligand, and does not adopt the ideally trigonal structure, with one copper–nitrogen bond length *ca.* 0.05 Å longer than the other two and the opposite N–Cu–N angle *enlarged* to 139°. The perchlorate group, as postulated by i.r. spectroscopic studies,[25] is essentially non-co-ordinating [Cu ··· O(1) ($x - \frac{1}{2}$, $y - \frac{1}{2}$, $z - 1$), ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$), 2.984(6) Å; Cu ··· O(2) ($\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$), ($x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$), 3.022(7) Å; these oxygen atoms also contact the ligand methyl hydrogens: O(1) ··· H(61A) ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$), 2.4_4 Å]. The shortest H ··· H estimate between methyl hydrogens on the two different ligands is 2.3 Å [corresponding C ··· C, 3.67(1) Å], *cf.* van der Waals contact estimate of 2.4 Å.

Table 3. Non-hydrogen atomic co-ordinates for [Cu(2,4Me$_2$-py)$_2$]-ClO$_4$ (3)

Atom	*x*	*y*	*z*
Cu	0	0	0
Cl	$\frac{1}{4}$	$\frac{1}{4}$	0.901 8(9)
O(1) *	0.253(2)	0.200(4)	1.013(4)
O(2)	0.261 3(9)	0.365(3)	0.836(3)
O(3)*	0.201(1)	0.279(4)	0.881(4)
N(1)	0.061 2(5)	−0.034(1)	0.015(2)
C(2)	0.094 7(6)	0.047(2)	−0.019(2)
C(21)	0.080 0(9)	0.179(3)	−0.077(2)
C(3)	0.139 9(5)	0.020(2)	−0.003(2)
C(4)	0.151 5(7)	−0.098(2)	0.048(2)
C(41)	0.200 6(8)	−0.135(3)	0.066(3)
C(5)	0.119 5(7)	−0.186(2)	0.082(2)
C(6)	0.075 3(6)	−0.152(2)	0.059(2)

* Population: 0.5.

Bis(2,6-*dimethylpyridine*)*copper*(I) *Nitrate*, (2).—[The structure is isomorphous with that of (5), depicted in Figure 3.] Again the structure determination confirms the stoicheiometry of the complex to be as postulated, namely [Cu(2,6Me$_2$-py)$_2$]-NO$_3$. The structure is generally of lower symmetry than that of the perchlorate with one formula unit comprising the asymmetric unit, in spite of the presence of pseudo-symmetry in both cation and anion, and in their interaction. Thermal motion in the structure is very anisotropic, and particularly so in the ligands. The complex cation comprises a copper atom co-ordinated pseudo-linearly by a pair of 2,6-dimethylpyridine ligands, the planes of which lie normal to *b*. Unlike the perchlorate, the co-ordination of the copper atom is not constrained by symmetry to be exactly linear, and we find that in complex (2) the N–Cu–N angle is appreciably reduced from 180 to 165.9(2)°, while Cu–N are correspondingly enlarged from 1.936(5) [in (1)] to 1.966(5), 1.956(5) Å. The apparent cause of this distortion from linearity is interaction with the nitrate species, the two nitrogen atoms about the copper being bent away from the approach of the nitrate. The mode of interaction of the nitrate is symmetrical bidentate; the oxygen atoms are equidistant from the copper at 2.506(7), 2.518(7) Å, with angles subtended at the 'chelating' oxygen atoms of 97.3(4), 96.2(4)°.

Interaction with the copper is reflected in the geometry of the nitrate; N–O(1,2) are very appreciably longer than N–O(3) [1.230(9) and 1.246(9) compared to 1.173(9) Å], while O(1)–N–O(2) is correspondingly diminished below 120° [116.8(7)°].

Table 4. Non-hydrogen atomic co-ordinates for [Ag(2,6Me$_2$-py)$_2$]-ClO$_4$ (4)

Atom	*x*	*y*	*z*
Ag	0	$\frac{1}{4}$	$\frac{1}{8}$
Cl	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$
O	0.4558(4)	0.1885(3)	0.1828(4)
N(1)	0.100 6(3)	0.149 4(3) *	$\frac{1}{8}$
C(2)	0.186 3(4)	0.171 4(5)	0.126 9(6)
C(21)	0.206 9(5)	0.267 8(5)	0.129 0(6)
C(3)	0.251 6(4)	0.108 8(6)	0.127 0(6)
C(4)	0.229 0(6)	0.021 0(6) *	$\frac{1}{8}$

* Constraint imposed by *x*.

Table 5. Non-hydrogen atomic co-ordinates for [Ag(2,6Me$_2$-py)$_2$]NO$_3$ (5)

Ligand		$n = 1$			$n = 2$	
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ag	0.295 37(5)	0.136 14(4)	0.436 33(8)			
N	0.289 0(6)	0.353 6(5)	0.435 7(12)			
O(1)	0.329 3(6)	0.311 1(5)	0.556 9(9)			
O(2)	0.259 7(6)	0.307 0(5)	0.316 4(9)			
O(3)	0.278 9(7)	0.436 3(6)	0.435 6(12)			
N(*n*1)	0.453 6(5)	0.122 7(4)	0.379 2(7)	0.138 4(4)	0.121 2(4)	0.495 7(7)
C(*n*2)	0.528 8(6)	0.122 7(5)	0.498 7(8)	0.114 7(7)	0.122 5(6)	0.652 0(8)
C(*n*21)	0.498 3(6)	0.126 2(6)	0.669 3(9)	0.2033 (7)	0.122 3(7)	0.779 6(10)
C(*n*3)	0.628 3(7)	0.121 6(6)	0.466 9(10)	0.0166 (7)	0.123 3(6)	0.690 9(10)
C(*n*4)	0.651 8(7)	0.120 0(6)	0.307 8(12)	−0.0615 (7)	0.123 7(7)	0.570 4(13)
C(*n*5)	0.574 3(8)	0.120 4(6)	0.185 9(10)	−0.037 1(7)	0.121 8(6)	0.411 1(10)
C(*n*6)	0.475 7(6)	0 121 7(5)	0.223 4(8)	0.062 9(6)	0.122 6(5)	0.377 6(9)
C(*n*61)	0.389 6(7)	0.121 1(7)	0.096 0(9)	0.091 0(6)	0.121 0(6)	0.206 6(9)

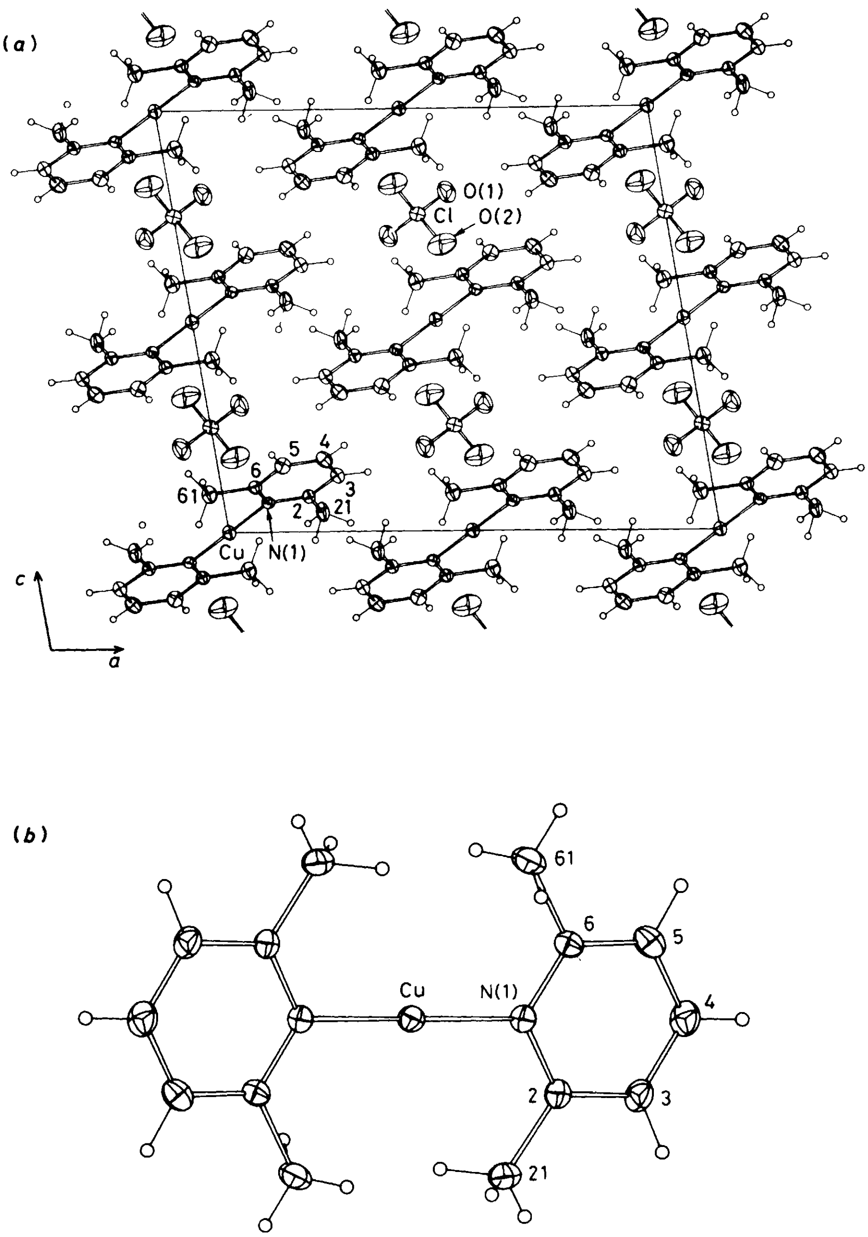


Figure 1. (*a*) Unit-cell contents of (1) projected down *b*. 20% Thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å. (*b*) The cation of (1)

The results for this complex can be compared to the similar phosphine complex, $[Cu(PPh_3)_2(NO_3)]$.[27] Here, interaction of the $[CuL_2]^+$ moiety with the nitrate group is significantly greater: Cu–O = 2.223(10) Å; O–Cu–O = 57.5(3); P–Cu–P = 131.2(1)°; and N–O = 1.16(2), 1.25(1) Å. An interesting comparison can also be made with parameters recorded for the three-co-ordinate complex, iodobis(2,6-dimethylpyridine)copper(I) [28] (both phases) where the N–Cu–N angle is reduced to 149.6(2) (α) and 143.5(2)° (β) and the Cu–N bond length increases to 1.98 Å.

Bis(2,4-*dimethylpyridine*)*copper*(I) *Perchlorate* (3).—In spite of the restricted precision available from a limited data set, the structure determination confirms the above stoicheiometry and displays several features of interest (Figure 2). Within the high-symmetry space group, both cation and anion lie with the heavy atom superimposed on a crystallographic symmetry element, so that, in the cation, only one ligand is crystallographically independent (the other being generated by the intra cation two-fold symmetry axis) while the anion is disordered, or, alternatively, an artefact of a lower symmetry space group unresolvable with the present data. The cation–anion disposition more closely resembles that of complex (2) rather than (1). The N–Cu–N angle departs appreciably from linearity [170(1)°] and the cation interacts substantially with O(1) of the perchlorate, indicated by Cu···O(1) ($\frac{1}{4} - x$, $\frac{1}{4} + y$, $1\frac{1}{4} + z$) [2.72(4) Å]. [The distance of O(1) to its two-fold rotor image is 1.01(6) Å.] In complex (3), as in tris(2-methylpyridine)copper(I) perchlorate, and unlike the remaining complexes reported in this paper, there is a substantial dihedral angle between the ligand planes (50.7°). This observation, coupled with the remarkably short (although admittedly imprecise) Cu–N distance of 1.86(1) Å in (3), suggests that, in the other complexes reported herein, the ligand disposition, with confronting methyl groups, may not be that adopted by the cation in isolation but may rather be a compromise consequent upon interaction of the metal atom with the anion as well, even in (1), with a consequent resultant weakening of the copper–nitrogen bonds. Presumably also, in the present complex, the change in base strength of the ligand, coupled with the observed cation–anion interactions, results in the occurrence of the bis(ligand) complex rather than the tris(ligand) complex, as occurs with 2-methylpyridine. Here it is relevant to note that in iodobis(2,6-dimethylpyridine)copper(I), where the two ligands adopt the conformation with confronting methyl groups as found in complexes (1), (2), (4), and (5), the closure of the N–Cu–N angle consequent upon increase in co-ordination number is compensated for by an increased copper–nitrogen distance. $CH_3 \cdots CH_3$ in [CuI(2,6Me$_2$-py)$_2$] are 3.54(1) (α-phase) and 3.62(2) Å (β-phase).[28]

Table 6. Metal atom environments in complexes (1)—(5); θ/° is the interplanar dihedral angle between the ligands. Also given is the interligand $CH_3 \cdots CH_3$ C–C distance

Compound	M–N,N′/Å	N–M–N′/°	θ/°	$CH_3 \cdots CH_3$/Å
M = Cu				
(1)	1.936(5)	180.0(—)	0.0	3.67(1)
(2)	1.966(5) 1.956(5)	165.9(2)	2.3	3.47(1)
(3)	1.86(1)	170(1)	50.7	>4
M = Ag				
(4)	2.166(4)	180.0(—)	2.7	3.77(1)
(5)	2.192(6) 2.182(6)	169.3(2)	0.3	>4 >4

Relevant to all three copper complexes is the recently determined structure of the bis(mesityl)cuprate(1−) anion.[29] Cu–C is 1.915(9) Å, midway between the two shorter Cu–N distances reported here [1.86(1) and 1.936(5) Å]; the interplanar dihedral angle between the pair of aryl ligands is 26.3°. The anion lies disposed on a crystallographic 2 axis with a C–Cu–C angle of 180.0(7)°.

Bis(2,6-*dimethylpyridine*)*silver*(I) *Perchlorate*, (4).—The structure determined confirms the above stoicheiometry, [Ag(2,6Me$_2$-py)$_2$]ClO$_4$; it is of very high symmetry with the silver atom of the cation at Wyckoff sites *b* (origin at $\bar{1}$) with 222 symmetry, and the anionic chlorine at Wyckoff *a* sites of $\bar{4}$ symmetry. Although the cation ligands are not required crystallographically to be co-planar, they are nearly so, and the cation symmetry is a good approximation to *mmm*. Ag $\cdots$ O contacts are found at 3.004(6) Å ($\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$) (*etc.*) and 3.081(7) Å ($x - \frac{1}{2}, y, \frac{1}{2} - z$) (*etc.*). Each of the contacts is pairwise from perchlorate ions in the columnar array of metal and perchlorate species up crystallographic *c*; the resulting co-ordination number of the silver might be taken as six, with four long contacts and two short.

The silver–nitrogen bond length of 2.166(4) Å is similar to values reported for two-co-ordinate and pseudo two-co-ordinate complexes of silver(I) with σ-bonding ligands

Table 7. Geometrical parameters of two-co-ordinate CuN$_2$ and AgN$_2$ systems

Compound	M–N/Å	N–M–N/°	M $\cdots$ X $\leqslant$ 3.0 Å	Ref.
[{Cu^I(NMe–N=NMe)}$_4$]	1.87(3) (mean)	172.5 (mean)		12
[{Cu^I(NPh–N=NPh)}$_2$]	1.898(18)—1.939(18)	172		11
[Cu$^I_2$(L^1)][ClO$_4$]$_2$[a]	1.869(4)—1.876(4)	170.9	2.774(4)	14
[Cu^I(L^2)]$^+$ [b]	1.918(4)	168.5	2.867(2)	15
[Cu$^I_{10}$Cu$^{II}_2$(C$_4$H$_5$N$_2$S)$_{12}$(MeCN)$_4$][BPh$_4$]$_2$·4MeCN	1.867(8)—1.885(8)	179.2	2.92(2)	13
(1) [Cu(2,6Me$_2$-py)]ClO$_4$	1.936(5)	180.0	2.984(6)	This work
(2) [Cu(2,6Me$_2$-py)$_2$]NO$_3$	1.956(5)—1.966(5)	165.9	2.51 (mean)	This work
(3) [Cu(2,4Me$_2$-py)$_2$]ClO$_4$	1.86(1)	170	2.74(4)	This work
[Ag(im)$_2$]NO$_3$[c]	2.120(8)—2.132(8)	172.0	—	16
[{Ag(en)}$_n$][ClO$_4$]$_n$[d]	2.17(1)	175.8(3)	—	18
[{Ag(pyz)}$_n$][NO$_3$]$_n$[e]	2.21(1)	159.2(9)	2.72(2)	17
(4) [Ag(2,6Me$_2$-py)$_2$]ClO$_4$	2.166(4)	179.9	3.04 (mean)	This work
(5) [Ag(2,6Me$_2$-py)$_2$]NO$_3$	2.182(6)—2.192(6)	169.3(2)	2.69 (mean)	This work

[a] L^1 = *NNN′N′*-Tetrakis(benzimidazol-2-ylmethyl)ethylenediamine. [b] L^2 = 1,7-Bis(benzimidazol-2′-yl)-2,6-dithiaheptane. [c] im = Imidazole. [d] en = Ethylenediamine. [e] pyz = Pyrazine.

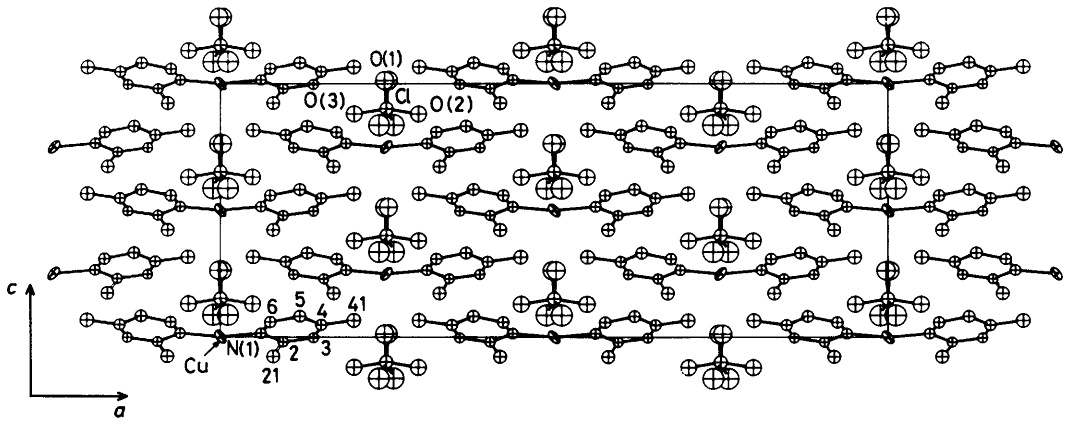


Figure 2. Unit-cell contents of (3), projected down *b*. All thermal motion envelopes except Cu are isotropic at the 20% level. The perchlorate is disordered

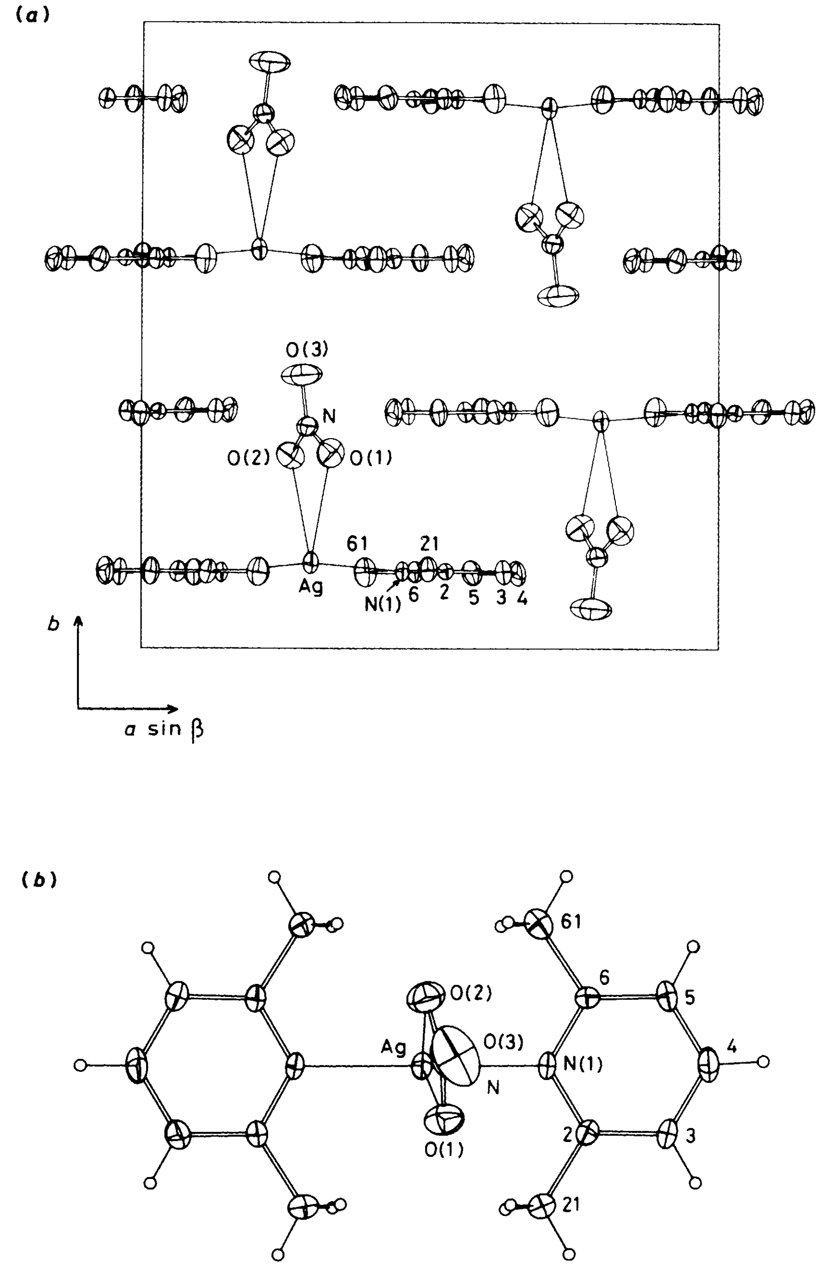


Figure 3. (*a*) Unit-cell contents of (5), projected down *c*. (*b*) The cation of (5), together with the anion, showing the 'chelate' interaction of the latter

(Table 7). The decrease (Δ) in Ag–N distance in passing from the four-co-ordinate pyridine complex ^{23b} to (4) [Ag–N(py), 2.322(3) Å; Δ, 0.156 Å] is considerably greater than the corresponding change for the analogous copper complexes [complex (1) 2.046(4), 1.936(5); Δ, 0.110 Å], and it may be that the parameters of the two-co-ordinate copper complex (1) are influenced as much by repulsive interactions between the ligands as by the strength of the metal–nitrogen bond. The difference in the copper–nitrogen distance in passing from the pyridine complex to the 2,4-dimethylpyridine complex (3), 0.18 Å, highlights the influence of the ligand as well as co-ordination number on these molecular parameters.

Bis(2,6-*dimethylpyridine*)*silver*(II) *Nitrate*, (5).—This compound is isomorphous with (2), with similar structural features (Figure 3). As with (2), the nitrate behaves as a weakly chelating ligand, Ag · · · O being 2.715(8), 2.663(7) Å; the angles subtended at the 'chelating' oxygen atoms are 95.9(5), 99.2(5)°, while N–O(1,2,3) are similarly disposed [1.26(1), 1.23(1), and 1.19(1) Å] as are O(3)–N–O(1,2) [121.4(9), 120.6(9)°], *cf.* O(1)–N–O(2), 118.0(7)°. Ag–N(1) in compound (5) [2.192(6), 2.182(6) Å] are also some 0.03 Å longer than in the perchlorate (4) [as with Cu–N(1) in (1) and (2)] in spite of the dissimilar lattices of (1) compared to (4).

Ligand Geometries.—Overall, the ligand geometries are, within experimental error, consistent with results from previous studies. However, irrespective of ligand disposition in the present series, we note that there is a consistent angular asymmetry at *all* 2-methyl substituents: N(1)–C(2,6)–C(21,61) are all *less* than 120°, while C(3)–C(2,6)–C(21,61) are all greater than 120°, suggesting that irrespective of any interligand steric interactions between those implied above, the substituent disposition is more greatly affected by the hydrogen substituent at the 3(5) position.

Conclusions

The data recorded for structures (1)—(5) add to the small number of MN_2 complexes with primarily a linear geometry, only a small subset of which have no significant interactions with a third ligand (Table 7).* It is of interest to note that the available data do not suggest that significant differences in metal–nitrogen bond length occur between polarizable and non-polarizable ligands, any differences observed being generally ascribable to steric effects.

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* *Note added in proof.* The problem of obtaining two-co-ordinate complexes of copper(I) with unidentate nitrogen bases has been addressed independently in a paper [30] which has become available since the acceptance of the present one, but which utilizes predominantly five-membered ring bases (imidazole and pyrazole) variously substituted with methyl groups. Structure determinations are reported for $[CuL_2]BF_4$ (L = 1-methylpyrazole or 1,3,5-trimethylpyrazole). The Cu–N distances are in the range 1.863(4)—1.879(3) Å, comparable with the shortest distance reported in the present study; both cations are substantially planar, although relative to compound (1) of the present study methyl ··· methyl interactions are reduced because of the change in ring size. In ref. 30, the synthesis of a complex with L = 2,6-dimethylpyridine is also reported.

We also note a recent report [31] of a solution study of the interaction of silver(I) with 2,6-dimethylpyridine (L) to give $[AgL_2]^+$ species.

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Received 10*th January* 1984; *Paper* 4/048