Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0.28216 (3)	0.03943 (3)	0.31612 (3)	0.0212 (1)
Cl(1)	0.43823 (7)	0.12910 (8)	0.38924 (7)	0.0386 (3)
Cl(2)	0.26654 (6)	0.47159 (7)	0.22988 (7)	0.0334 (2)
Cl(3)	−0.02847 (7)	0.20454 (8)	0.10086 (7)	0.0369 (2)
C(1)	0.2486 (3)	−0.1447 (3)	0.1530 (3)	0.0385 (11)
C(2)	0.1396 (3)	−0.0915 (3)	0.1589 (3)	0.0405 (12)
C(3)	0.0691 (3)	0.0035 (3)	0.3113 (3)	0.0323 (10)
C(4)	0.0931 (3)	0.0835 (3)	0.4097 (3)	0.0395 (12)
C(5)	0.3956 (3)	−0.0031 (4)	0.1401 (3)	0.0452 (14)
C(6)	0.3216 (3)	0.0956 (4)	0.0939 (3)	0.0476 (15)
C(7)	0.4122 (3)	−0.1529 (3)	0.2943 (3)	0.0388 (11)
C(8)	0.3545 (5)	−0.1875 (3)	0.3902 (3)	0.0376 (12)
N(1)	0.3390 (2)	−0.0734 (2)	0.2179 (2)	0.0290 (8)
N(2)	0.1475 (2)	−0.0223 (2)	0.2613 (2)	0.0246 (7)
N(3)	0.1995 (2)	0.1382 (2)	0.4063 (2)	0.0331 (9)
N(4)	0.2734 (2)	0.1480 (2)	0.1882 (2)	0.0324 (9)
N(5)	0.3108 (2)	−0.0793 (2)	0.4364 (2)	0.0294 (8)
O(1)	0.3235 (2)	0.4060 (2)	0.1538 (2)	0.0497 (10)
O(2)	0.1896 (3)	0.5447 (3)	0.1646 (3)	0.0720 (13)
O(3)	0.2140 (3)	0.3923 (3)	0.2948 (3)	0.0723 (14)
O(4)	0.3387 (3)	0.5424 (3)	0.3033 (3)	0.0897 (14)
O(5)	−0.0937 (2)	0.2930 (2)	0.0432 (2)	0.0485 (9)
O(6)	0.0597 (2)	0.1806 (3)	0.0407 (3)	0.0584 (11)
O(7)	0.0141 (3)	0.2425 (3)	0.2125 (2)	0.0701 (12)
O(8)	−0.0894 (3)	0.1004 (3)	0.1045 (3)	0.0675 (12)

Table 2. *Selected geometric parameters* (Å, °)

Co—Cl(1)	2.2725 (9)	N(3)—C(4)	1.486 (5)
Co—N(1)	1.954 (3)	C(5)—C(6)	1.512 (6)
Co—N(2)	1.863 (2)	N(4)—C(6)	1.488 (5)
Co—N(3)	1.968 (3)	C(7)—C(8)	1.505 (6)
Co—N(4)	1.962 (3)	N(5)—C(8)	1.493 (4)
Co—N(5)	1.971 (3)	Cl(2)—O(1)	1.452 (3)
N(1)—C(1)	1.516 (4)	Cl(2)—O(2)	1.421 (3)
N(1)—C(5)	1.492 (5)	Cl(2)—O(3)	1.422 (4)
N(1)—C(7)	1.502 (4)	Cl(2)—O(4)	1.418 (4)
C(1)—C(2)	1.515 (5)	Cl(3)—O(5)	1.414 (3)
N(2)—C(2)	1.450 (5)	Cl(3)—O(6)	1.441 (3)
N(2)—C(3)	1.268 (5)	Cl(3)—O(7)	1.431 (3)
C(3)—C(4)	1.486 (5)	Cl(3)—O(8)	1.419 (3)
Cl(1)—Co—N(1)	98.8 (1)	Co—N(2)—C(3)	118.7 (2)
Cl(1)—Co—N(2)	174.6 (1)	C(2)—N(2)—C(3)	124.7 (3)
Cl(1)—Co—N(3)	91.8 (1)	N(2)—C(3)—C(4)	116.0 (3)
Cl(1)—Co—N(4)	87.7 (1)	C(3)—C(4)—N(3)	108.2 (3)
Cl(1)—Co—N(5)	88.6 (1)	Co—N(3)—C(4)	109.3 (2)
N(1)—Co—N(2)	86.4 (1)	N(1)—C(5)—C(6)	107.6 (3)
N(1)—Co—N(3)	169.4 (1)	C(5)—C(6)—N(4)	108.8 (3)
N(1)—Co—N(4)	85.8 (1)	Co—N(4)—C(6)	111.1 (2)
N(1)—Co—N(5)	86.9 (1)	N(1)—C(7)—C(8)	107.5 (3)
N(2)—Co—N(3)	83.1 (1)	C(7)—C(8)—N(5)	108.4 (3)
N(2)—Co—N(4)	91.3 (1)	Co—N(5)—C(8)	109.5 (2)
N(2)—Co—N(5)	93.1 (1)	O(1)—Cl(2)—O(2)	108.5 (2)
N(3)—Co—N(4)	95.6 (1)	O(1)—Cl(2)—O(3)	109.5 (2)
N(3)—Co—N(5)	92.6 (1)	O(1)—Cl(2)—O(4)	110.5 (2)
N(4)—Co—N(5)	171.1 (1)	O(2)—Cl(2)—O(3)	109.8 (2)
Co—N(1)—C(1)	110.2 (2)	O(2)—Cl(2)—O(4)	109.1 (2)
Co—N(1)—C(5)	106.1 (2)	O(3)—Cl(2)—O(4)	109.4 (2)
Co—N(1)—C(7)	106.2 (2)	O(5)—Cl(3)—O(6)	109.1 (2)
C(1)—N(1)—C(5)	111.2 (3)	O(5)—Cl(3)—O(7)	110.4 (2)
C(1)—N(1)—C(7)	109.4 (3)	O(5)—Cl(3)—O(8)	109.6 (2)
C(5)—N(1)—C(7)	113.5 (3)	O(6)—Cl(3)—O(7)	108.5 (2)
N(1)—C(1)—C(2)	112.2 (3)	O(6)—Cl(3)—O(8)	108.6 (2)
C(1)—C(2)—N(2)	108.2 (3)	O(7)—Cl(3)—O(8)	110.6 (2)
Co—N(2)—C(2)	116.5 (2)		

Intensity data were processed as described previously (Fallon & Gatehouse, 1980). The atomic scattering factors for neutral atoms were corrected for anomalous dispersion by using values from Ibers & Hamilton (1984). All calculations were performed on a VAX 11/780 computer. The program used for least-squares refinement was *SHELX*76 (Sheldrick, 1976). The structure was solved by direct methods. Refinement was by full-matrix least-squares employing anisotropic displacement parameters for all non-H atoms and a single isotropic displacement parameter for H atoms positioned in geometrically idealized positions, which refined to 0.043 (2) Å^2 (C—H 0.96, N—H 0.90 Å).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: OH1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro[(1-methyl-2-imidazolyl-κN³-methyl)-bis(2-pyridyl-κN-methyl)amine-κN]copper(II) Hexafluorophosphate, [CuCl(C₁₇H₁₉N₅)]PF₆

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Abstract

The coordination polyhedron of the Cu^{II} ion in the title compound is best described as a distorted trigo-

nal bipyramid with an imidazole and two pyridine N atoms bonded in the equatorial plane, and a Cl⁻ ion and an amine N atom bonded along the axial direction. The Cu—N(amine) bond length is 2.087 (4) Å, while the Cu—N(imidazole) and Cu—N(pyridine) bond lengths are 1.979 (3), 2.044 (3) and 2.153 (3) Å, respectively. The Cu—Cl distance is 2.232 (1) Å. A fairly satisfactory model was found for the disordered PF_6^- counterion.

Comment

Copper(II) complexes of tetradentate N_4 tripodal ligands have been found with both trigonal-bipyramidal and square-pyramidal geometries, depending on the steric restriction imposed by the ligand. In addition, it has been shown that ligand strain effects are not only influenced by the size of the chelate ring, but also by the strength of the metal–pendant bond (Oberhausen, O'Brien, Richardson & Buchanan, 1990). As part of our continuing studies involving copper(II) complexes of N_4 tetradentate tripod ligands, and our general interest in copper–imidazole chemistry, we report herein the crystal stucture of a copper(II) complex, chloro[(1-methyl-2-imidazolyl-κN^3-methyl)bis(2-pyridyl-κN-methyl)amine-κN]copper(II) hexafluorophosphate, (I), containing a mixed pyridine/imidazole tripod ligand. This compound was prepared following a previously published procedure (Oberhausen, O'Brien, Richardson & Buchanan, 1990).
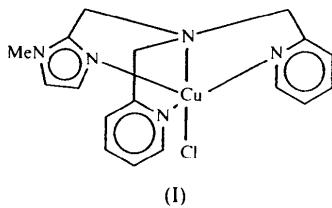
(I)

An ORTEP (Johnson, 1965) plot of the [Cu(bpia)-Cl]⁺ ion is shown in Fig. 1, where bpia is (1-methyl-2-imidazolylmethyl)bis(2-pyridylmethyl)amine. The cation has distorted trigonal bipyramidal geometry similar to that reported previously for the structurally similar copper tripod complex [Cu(bipa)Cl]PF₆, where bipa is bis(1-methyl-2-imidazolylmethyl)(2-pyridylmethyl)amine (Oberhausen, O'Brien, Richardson & Buchanan, 1990). The Cu atom is bonded to two pyridine N atoms [Cu—N(4) = 2.044 (3) and Cu—N(5) = 2.153 (3) Å] and an imidazole N atom [Cu—N(2) = 1.979 (3) Å], which occupy positions within the equatorial plane of the trigonal bipyramid. The Cu–pyridine bonds are significantly longer than the Cu–imidazole bonds, reflecting the greater π-bonding ability of the 1-methylimidazole pendant. The structurally similar complex ion [Cu(tpa)Cl]⁺,

where tpa is tris(2-pyridylmethyl)amine (Karlin, Hayes, Juen, Hutchinson & Zubieta, 1982), has a nearly ideal trigonal bipyramidal structure with N_{eq}—Cu—N_{eq} bond angles close to 120°. In contrast, [Cu(bpia)Cl]⁺ displays N_{eq}—Cu—N_{eq} bond angles that reflect a greater distortion of the coordination environment of the metal. This distortion is probably due to the presence of mixed-ligand pendants associated with the tripod ligand. The amine N atom of the bpia ligand and the Cl atom occupy apical positions in the trigonal bipyramid, with a Cl—Cu—N(amine) bond angle of 179.6 (1)°. The Cu—Cl bond distance is 2.232 (1) Å and is within the range of values observed for other [Cu(L)Cl]⁺ complexes, where L represents the tetradentate tripod ligand (Oberhausen, O'Brien, Richardson & Buchanan, 1990). The Cu—N(amine) bond length on the other hand is 2.087 (4) Å, shorter than bond lengths reported for [Cu(tmima)Cl]⁺, where tmima is tris(1-methyl-2-imidazolylmethyl)amine, and [Cu(bipa)Cl]⁺ [2.167 (3) and 2.121 (3) Å, respectively], but closer to the Cu—N(amine) bond length reported for [Cu(tpa)Cl]⁺ [2.050 (6) Å].

The hexafluorophosphate counter ion was found to be disordered. The nature of the disordering involved rotation about the F(1)—P—F(6) axis. The model consists of a set of four equatorial F atoms of occupancy 0.7 and a number of fractional equatorial F atoms (such that the total is four atoms). Devia-
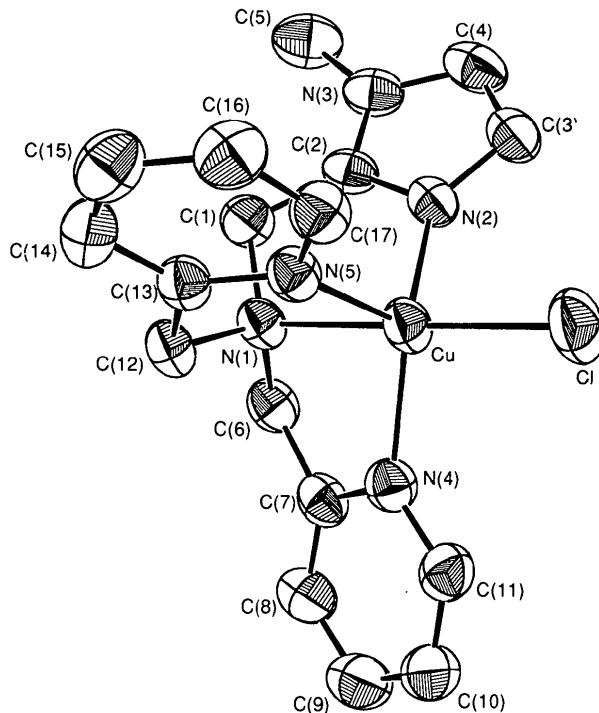

Fig. 1. ORTEP (Johnson, 1965) plot of the [Cu(bpia)Cl]⁺ cation with numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

tions from octahedral symmetry (see supplementary data, Table S3) show the model to be incomplete.

Experimental

Crystal data
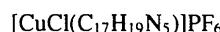
[CuCl(C₁₇H₁₉N₅)]PF₆	Mo $K\alpha$ radiation
$M_r = 537.33$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 14.235\ (3)$ Å	$\theta = 12–16°$
$b = 11.368\ (3)$ Å	$\mu = 1.297$ mm^{-1}
$c = 13.860\ (3)$ Å	$T = 296$ K
$\beta = 108.84\ (2)°$	Block
$V = 2122.6$ Å^3	$0.50 \times 0.32 \times 0.32$ mm
$Z = 4$	Pale blue
$D_x = 1.68$ Mg m^{-3}	Crystal source: recrystallization from CH₃CN/H₂O

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.012$
$\theta/2\theta$ scans	$\theta_{max} = 25°$
Absorption correction: empirical	$h = -10 \rightarrow 10$
	$k = 0 \rightarrow 8$
$T_{min} = 0.84$, $T_{max} = 1.00$	$l = -10 \rightarrow 0$
4115 measured reflections	3 standard reflections
3946 independent reflections	frequency: 60 min
3114 observed reflections	intensity variation: 1.9%
$[I > 3.0\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.06$
$R = 0.045$	$\Delta\rho_{max} = 0.68\ (7)$ e Å^{-3}
$wR = 0.048$	$\Delta\rho_{min} = -0.71\ (7)$ e Å^{-3}
$S = 1.06$	Extinction correction: none
3114 reflections	Atomic scattering factors
288 parameters	from Enraf–Nonius
H-atom parameters not refined	MolEN Software (Fair, 1990)
$w = 1/[\sigma^2(F) + 0.01F^2 + 1.0]$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	B_{eq}
Cu	1.0	0.75237 (4)	0.41042 (4)	0.34607 (3)	3.41 (1)
Cl	1.0	0.80912 (9)	0.3374 (1)	0.22598 (8)	5.37 (3)
N(1)	1.0	0.6986 (2)	0.4779 (3)	0.4582 (2)	3.18 (7)
N(2)	1.0	0.7255 (2)	0.2591 (3)	0.4028 (2)	3.39 (7)
N(3)	1.0	0.6567 (3)	0.1622 (3)	0.4989 (3)	3.91 (8)
N(4)	1.0	0.8554 (2)	0.5391 (3)	0.4043 (2)	3.46 (7)
N(5)	1.0	0.6127 (2)	0.4837 (3)	0.2540 (2)	3.20 (7)
C(1)	1.0	0.6434 (3)	0.3855 (4)	0.4934 (3)	3.79 (9)
C(2)	1.0	0.6762 (3)	0.2684 (4)	0.4686 (3)	3.28 (8)
C(3)	1.0	0.7378 (3)	0.1403 (4)	0.3906 (3)	4.1 (1)
C(4)	1.0	0.6957 (4)	0.0796 (4)	0.4483 (4)	4.5 (1)
C(5)	1.0	0.6025 (4)	0.1367 (5)	0.5687 (4)	5.4 (1)
C(6)	1.0	0.7881 (3)	0.5158 (4)	0.5418 (3)	3.68 (9)
C(7)	1.0	0.8591 (3)	0.5753 (4)	0.4979 (3)	3.59 (9)
C(8)	1.0	0.9274 (3)	0.6580 (4)	0.5523 (4)	4.5 (1)
C(9)	1.0	0.9928 (4)	0.7045 (4)	0.5089 (4)	5.1 (1)
C(10)	1.0	0.9884 (3)	0.6693 (4)	0.4125 (4)	4.7 (1)
C(11)	1.0	0.9194 (3)	0.5864 (4)	0.3620 (3)	4.02 (9)
C(12)	1.0	0.6342 (3)	0.5801 (4)	0.4131 (3)	3.51 (8)
C(13)	1.0	0.5687 (3)	0.5489 (4)	0.3075 (3)	3.24 (8)
C(14)	1.0	0.4709 (3)	0.5859 (4)	0.2660 (3)	4.21 (9)
C(15)	1.0	0.4179 (3)	0.5531 (5)	0.1686 (4)	4.8 (1)
C(16)	1.0	0.4630 (3)	0.4866 (5)	0.1137 (3)	4.5 (1)
C(17)	1.0	0.5603 (3)	0.4534 (4)	0.1590 (3)	3.81 (9)
P	1.0	0.65225 (9)	-0.2215 (1)	0.69170 (9)	4.35 (3)
F(1)	1.0	0.6641 (2)	-0.2638 (3)	0.8029 (2)	7.11 (9)
F(2A)	0.7	0.7608 (3)	-0.2698 (4)	0.6998 (3)	5.51 (8)
F(3A)	0.7	0.5944 (4)	-0.3283 (6)	0.6357 (4)	9.4 (2)
F(4A)	0.7	0.5570 (4)	-0.1468 (6)	0.6825 (4)	9.3 (1)
F(5A)	0.7	0.7038 (3)	-0.0991 (4)	0.7352 (4)	7.0 (1)
F(2B)	0.15	0.721 (2)	-0.331 (2)	0.699 (2)	6.8 (5)
F(3B)	0.15	0.633 (1)	-0.094 (2)	0.726 (1)	4.9 (4)
F(4B)	0.15	0.532 (1)	-0.267 (2)	0.683 (1)	5.3 (4)
F(5B)	0.15	0.744 (1)	-0.135 (1)	0.758 (1)	4.3 (3)
F(2C)	0.10	0.765 (2)	-0.208 (2)	0.722 (2)	4.5 (5)
F(4C)	0.2	0.5368 (7)	-0.2077 (9)	0.6744 (7)	3.0 (2)
F(5C)	0.30	0.6332 (6)	-0.3637 (7)	0.6547 (6)	4.3 (2)
F(6)	1.0	0.6445 (3)	-0.1763 (4)	0.5815 (2)	9.0 (1)

Table 2. *Selected geometric parameters (Å, °)*

Cu—Cl	2.232 (1)	Cu—N(4)	2.044 (3)
Cu—N(1)	2.087 (4)	Cu—N(5)	2.153 (3)
Cu—N(2)	1.979 (3)		
Cl—Cu—N(1)	179.6 (1)	N(1)—Cu—N(4)	80.3 (1)
Cl—Cu—N(2)	97.8 (1)	N(1)—Cu—N(5)	78.9 (1)
Cl—Cu—N(4)	100.0 (1)	N(2)—Cu—N(4)	132.1 (1)
Cl—Cu—N(5)	100.9 (1)	N(2)—Cu—N(5)	108.1 (1)
N(1)—Cu—N(2)	81.9 (1)	N(4)—Cu—N(5)	111.4 (1)

*MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and *MolEN* (Fair, 1990) were used for crystallographic computations.

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