METAL-ORGANIC COMPOUNDS

A complex containing Cu^I linearly coordinated by two tetracyclic tetraamines

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Abstract

The preparation and crystal structure of bis(10b,10c-*cis*-3a,5a,8a,10a-tetraazaperhydropyrene)copper(I) hexafluorophosphate, [Cu(C$_{12}$H$_{22}$N$_4$)$_2$]PF$_6$, are described. The Cu^I ion lies on an inversion centre and is linearly coordinated, with one bond to each of two tetracyclic tetraamine ligands [Cu—N = 1.976 (2) Å].

Comment

The tetracyclic condensation products of glyoxal and tetraaza-macrocycles have been known for nearly 20 years (Caulkett *et al.*, 1977; Alcock *et al.*, 1980; Weisman *et al.*, 1980; Kolinski & Riddel, 1981; Möller *et al.*, 1991; Okawara *et al.*, 1995). These interesting molecules are formed when each glyoxal aldehyde functional group reacts with two secondary amines of the macrocycle, producing a tetracyclic pane-like molecule. For both kinetic (Alcock *et al.*, 1980) and thermodynamic reasons (Okawara *et al.*, 1995), the central two-carbon bridge has *cis*-H atoms, causing the tetracycle to be folded. Two non-adjacent N atoms direct their lone pairs into the fold, while the other two non-adjacent N atoms direct their lone pairs out from the convex side. This arrangement has recently been utilized to give the first transition metal complexes of these tetracycles with Pd^{II} (Hubin *et al.*, 1998) and Cu^{II} (Hubin *et al.*, 1999), in which the tetracycle acts as a bidentate ligand bound to the metal ion through its inward-pointing N atoms.

The reaction of copper(I) with 10b,10c-*cis*-3a,5a,-8a,10a-tetraazaperhydropyrene, (2), the glyoxal condensate of cyclam, was examined to broaden the coordination chemistry of these tetracyclic ligands. Though equimolar amounts of the metal ion and the ligand were reacted, the major product isolated corre-

sponds to the bis-ligand complex, (1), of Cu^I. The X-ray crystal structure determination reveals that the metal ion lies on an inversion centre and is bound to one N atom from each of two separate tetracycle ligands, (2). The linear two-coordinate geometry is the most striking feature of this complex; Cu^{II} and Pd^{II} both bind the same tetracyclic ligand in a bidentate manner, although the interaction of the second N atom is much weaker than the first in each case. This binding of two ligands to the Cu^I atom must be thermodynamically favoured since the reaction mixture had a 1:1 stoichiometry.

(1)   ·PF$_6^-$ (2)
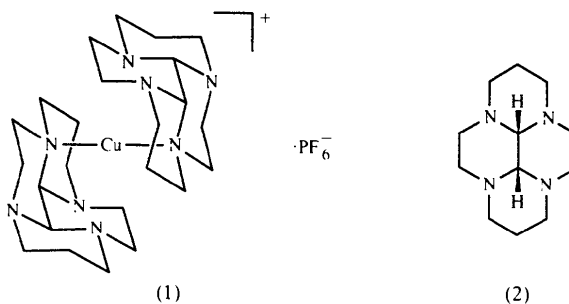
Linear coordination of the Cu^I atom by *N*-donors is not as common as for the other Group 11 metal ions, Ag^I and Au^I. However, it is found, for example, in Cu^I complexes with *N*-methylimidazole (Tan *et al.*, 1990) and with hindered pyridines (Engelhardt *et al.*, 1985). The Cu—N distance [1.976 (2) Å] is similar to that in the Cu^I complex with 2,6-dimethylpyridine [1.936 (5) Å], but significantly longer than in the imidazole complex (1.86 Å). The relatively long
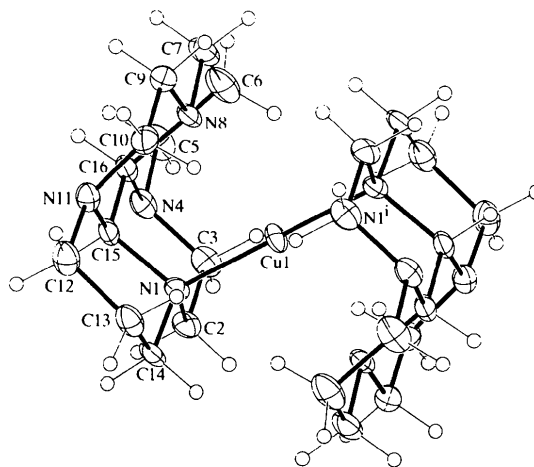

Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) −*x*, −*y*, −*z*.]

distance in (1) suggests significant steric effects, which may dictate the binding mode of the ligand. Although a correctly positioned second donor atom is present in each of the tetracycles, the ligand bulk may prevent two such ligands from binding in tetrahedral or square-planar geometry. The Cu$\cdots$N8 distances [2.828 (2) Å], almost 1 Å longer than the primary bonds, are certainly too long to represent substantial directional bonding, but may well indicate additional weak interactions.

Experimental

To 10b,10c-*cis*-3a,5a,8a,10a-tetraazaperhydropyrene [(2); 0.222 g, 0.001 mol] (obtained according to literature procedures; Weisman *et al.*, 1980) dissolved in MeCN (5 ml) was added [Cu(MeCN)$_4$]PF$_6$ (0.373 g, 0.001 mol) in MeCN (5 ml) under an inert atmosphere. The reaction was stirred at room temperature for 12 h, filtered, and the solvent evaporated. Recrystallization of the resulting white solid from acetonitrile under nitrogen yielded two types of colourless crystals, namely plates and blocks. Only the colourless plates gave diffraction data.

Crystal data

[Cu(C$_{12}$H$_{22}$N$_4$)$_2$]PF$_6$
M_r = 653.18
Triclinic
$P\bar{1}$
a = 8.0589 (6) Å
b = 9.2783 (7) Å
c = 10.0365 (8) Å
α = 81.755 (5)°
β = 87.512 (5)°
γ = 67.632 (5)°
V = 686.77 (9) Å^3
Z = 1
D_x = 1.579 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 2942 reflections
θ = 2.0–28.4°
μ = 0.926 mm^{-1}
T = 180 (2) K
Plate
0.30 × 0.30 × 0.08 mm
Colourless

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction:
  ψ scan (*SADABS*; Sheldrick, 1996)
  T_{min} = 0.60, T_{max} = 0.95
4075 measured reflections
2972 independent reflections

2351 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 28.47°
h = −10 → 10
k = −8 → 12
l = −12 → 13

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.092
S = 0.916
2972 reflections
184 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.579 e Å^{-3}
$\Delta\rho_{min}$ = −0.575 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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}
Cu1	0	0	0	0.02002 (14)
N1	−0.0296 (2)	−0.1807 (2)	−0.06386 (18)	0.0174 (4)
C2	−0.1740 (3)	−0.2181 (3)	0.0127 (2)	0.0231 (5)
C3	−0.1261 (3)	−0.2633 (3)	0.1609 (2)	0.0254 (5)
N4	0.0413 (3)	−0.4012 (2)	0.18072 (19)	0.0228 (4)
C5	0.0926 (4)	−0.4543 (3)	0.3239 (2)	0.0320 (6)
C6	0.1591 (4)	−0.3427 (3)	0.3832 (2)	0.0347 (7)
C7	0.3088 (4)	−0.3190 (3)	0.2971 (2)	0.0302 (6)
N8	0.2533 (3)	−0.2664 (2)	0.15372 (19)	0.0199 (4)
C9	0.4109 (3)	−0.2629 (3)	0.0756 (2)	0.0252 (5)
C10	0.3668 (3)	−0.2139 (3)	−0.0737 (2)	0.0253 (5)
N11	0.2885 (3)	−0.3164 (2)	−0.12226 (19)	0.0217 (4)
C12	0.2431 (4)	−0.2777 (3)	−0.2670 (2)	0.0292 (6)
C13	0.0724 (4)	−0.1311 (3)	−0.2978 (2)	0.0272 (6)
C14	−0.0802 (3)	−0.1468 (3)	−0.2110 (2)	0.0241 (5)
C15	0.1395 (3)	−0.3299 (3)	−0.0449 (2)	0.0198 (5)
C16	0.1897 (3)	−0.3794 (3)	0.1043 (2)	0.0196 (5)
P1	−1/2	0	−1/2	0.0367 (3)
F1	−0.6947 (3)	−0.0021 (3)	−0.50881 (19)	0.0707 (7)
F2	−0.4806 (3)	0.0014 (3)	−0.65910 (18)	0.0738 (7)
F3	−0.5777 (3)	0.1853 (3)	−0.5228 (3)	0.0934 (8)

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model (including free rotation about C—C bonds for methyl groups). They were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the carrier atom.

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *SHELXTL* (Siemens, 1994b). Software used to prepare material for publication: *SHELXTL*.

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