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Aqua(diethylenetriamine)(isonicotinato)-copper(II) Hexafluorophosphate

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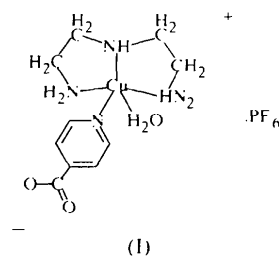
Abstract

The Cu atom in the title complex, [*N*-(2-aminoethyl)-*N*]-1,2-ethylenediamine-*N,N'*]aqua(4-pyridinecarboxylato-*N*)copper(II) hexafluorophosphate, [Cu(C₆H₄NO₂)(C₄H₁₃N₃)(H₂O)]PF₆, is coordinated in a square-pyramidal arrangement by three N atoms

of *N*-(2-aminoethyl)-1,2-ethylenediamine (diethylenetriamine) and one N atom from the pyridine ring of isonicotinate in equatorial positions, and by one water molecule in an axial position.

Comment

Isonicotinate is a ligand with two types of binding site. It can coordinate with transition metal ions *via* one or two O atoms from the carboxylate group or the N atom from the pyridine ring. Only a few structures containing copper(II) and isonicotinate have been reported (Okabe *et al.*, 1993). In the course of our systematic study of the coordination mode of isonicotinate with copper(II) in mixed-ligand systems, we isolated the complex [Cu(dien)(iso)(H₂O)]PF₆ (I), where dien is diethylenetriamine and iso is isonicotinate. We report here its preparation and structure.



The crystal structure of (I) comprises discrete [Cu(dien)(iso)(H₂O)]⁺ cations and hexafluorophosphate anions (Fig. 1). The coordination polyhedron of the Cu atom is a square pyramid whose base is formed by three N atoms from the amine ligand and one pyridine N atom from isonicotinate. A coordinated water molecule occupies the apex of the pyramid with a Cu—O distance of 2.316(2) Å. The Cu atom lies 0.199(1) Å above the mean plane defined by the four basal N atoms. This is in good agreement with the situation found in most square-pyramidal structures where the Cu atom is lifted *ca* 0.2 Å towards the apex of the pyramid (Hathaway & Billing, 1970). The Cu—N bond lengths to dien fall in the range 2.005(2)–2.017(2) Å. Among these, that from the Cu atom to the secondary N atom of the amine ligand is the shortest, as was found by Sato *et al.* (1986) and Hu *et al.* (1997). The Cu to pyridine N (Cu—N₁) bond length is 2.016(2) Å. This is comparable to the Cu—N_{iso} bond length found in the square-planar coordinated Cu^{II} complex [Cu(iso)₂(H₂O)₂].2H₂O (2.004 Å; Okabe *et al.*, 1993). The dihedral angle between the pyridine ring plane and the basal plane of the square pyramid is 61.49(7)°. The hexafluorophosphate anion is below the square pyramid and F1 is close to the Cu atom at a distance of 2.969(2) Å. An extensive hydrogen-bonding network is present in the crystal, with hydro-

gen bonds formed by each of the amine and water H atoms to either the carboxylate O atoms or the hexafluorophosphate F atoms.

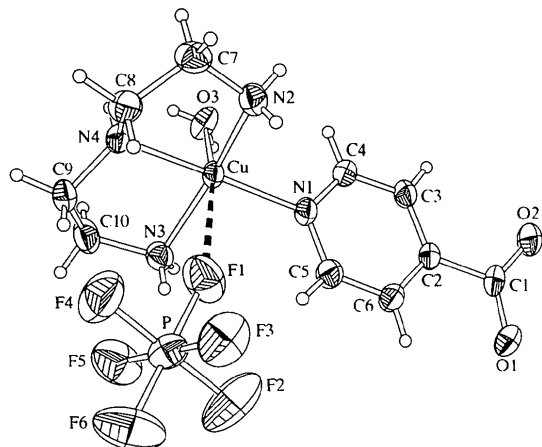


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids for non-H atoms.

Experimental

A methanol solution (10 ml) of sodium isonicotinate (62 mg, 0.5 mmol) was added to a methanol solution (10 ml) of Cu(ClO₄)₂·6H₂O (186 mg, 0.5 mmol) forming a sky-blue precipitate. A methanol solution (10 ml) of diethylenetriamine (52 mg, 0.5 mmol) was then added whilst stirring. After 30 min, a methanol (5 ml) solution of NH₄PF₆ (82 mg, 0.5 mmol) was added to the above solution. Violet-blue crystals suitable for X-ray structure determination were obtained after one week at room temperature. Analysis found: C 26.54, H 4.04, N 12.12%; calculated for C₁₀H₁₉CuN₄O₃PF₆: C 26.59, H 4.24, N 12.40%.

Crystal data

[Cu(C₆H₄NO₂)(C₄H₁₃N₃)(H₂O)]PF₆
M_r = 451.80
 Monoclinic
*P*2₁/*n*
a = 13.1568 (6) Å
b = 7.9676 (4) Å
c = 16.1884 (10) Å
 β = 96.246 (5)°
V = 1686.92 (15) Å³
Z = 4
D_x = 1.779 Mg m⁻³
D_m not measured

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.732, *T_{max}* = 0.863

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 11.64–13.83°
 μ = 1.471 mm⁻¹
T = 293 (2) K
 Rectangular
 0.29 × 0.25 × 0.15 mm
 Dark violet-blue

3171 reflections with *I* > 2 σ (*I*)
R_{int} = 0.013
 θ_{\max} = 26.97°
h = -16 → 16
k = 0 → 10
l = -20 → 0

3793 measured reflections
 3665 independent reflections

3 standard reflections
 frequency: 60 min
 intensity decay: 0.3%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.031
wR(*F*²) = 0.076
S = 1.12
 3665 reflections
 303 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 1.4171P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max}$ = 0.30 e Å⁻³
 $\Delta\rho_{\min}$ = -0.29 e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997a)
 Extinction coefficient: 0.0035 (4)
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—N4	2.0049 (18)	N3—C10	1.483 (3)
Cu—N2	2.013 (2)	N4—C8	1.468 (3)
Cu—N1	2.0156 (18)	N4—C9	1.480 (3)
Cu—N3	2.017 (2)	C1—C2	1.522 (3)
Cu—O3	2.3160 (19)	C2—C3	1.382 (3)
O1—C1	1.247 (3)	C2—C6	1.384 (3)
O2—C1	1.250 (3)	C3—C4	1.376 (3)
N1—C5	1.336 (3)	C5—C6	1.379 (3)
N1—C4	1.343 (3)	C7—C8	1.506 (4)
N2—C7	1.488 (3)	C9—C10	1.509 (4)
N4—Cu—N2	83.85 (9)	N4—Cu—O3	94.78 (8)
N4—Cu—N1	174.77 (8)	N2—Cu—O3	106.13 (10)
N2—Cu—N1	93.61 (8)	N1—Cu—O3	90.32 (8)
N4—Cu—N3	84.48 (8)	N3—Cu—O3	92.20 (9)
N2—Cu—N3	158.99 (10)	O3—Cu—F1	166.14 (7)
N1—Cu—N3	96.53 (8)	Cu—F1—P	154.75 (11)

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H19...O2 ⁱ	0.70 (3)	2.17 (4)	2.870 (3)	172 (4)
O3—H18...O1 ⁱⁱ	0.73 (3)	2.07 (4)	2.790 (3)	171 (4)
N2—H13...O2 ⁱⁱⁱ	0.83 (3)	2.22 (3)	2.957 (3)	148 (3)
N2—H14...F2 ⁱⁱⁱ	0.79 (3)	2.29 (3)	3.082 (3)	177 (3)
N3—H15...O2 ⁱⁱⁱ	0.81 (3)	2.28 (3)	3.081 (3)	170 (3)
N3—H16...F1	0.83 (3)	2.54 (3)	3.094 (3)	125 (2)
N3—H16...F5	0.83 (3)	2.46 (3)	3.201 (3)	149 (2)
N4—H17...O1 ⁱ	0.81 (3)	2.06 (3)	2.869 (3)	170 (3)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

All H atoms were located by difference Fourier synthesis and refined isotropically. The refined C—H, N—H and O—H bond lengths fall in the ranges 0.88 (3)–0.93 (3), 0.79 (3)–0.83 (3) and 0.70 (3)–0.73 (3) Å, respectively, with the H-atom *U* values in the range 0.031 (7)–0.05 (1) Å².

Data collection: CAD-4 Argus Software (Nonius BV, 1996). Cell refinement: CAD-4 Argus Software. Data reduction: MolEN (Enraf-Nonius, 1990). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a). Molecular graphics: SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1389). Services for accessing these data are described at the back of the journal.

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