METAL-ORGANIC COMPOUNDS

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trans-Diaquabis(2-thienyl 2-pyridyl ketone-*O*,*N*)copper(II) Tetrafluoroborate

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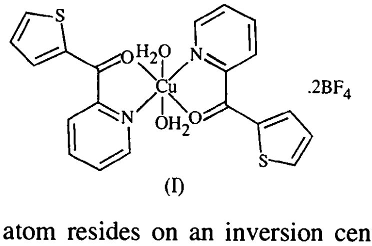
Abstract

The title complex, $[Cu(C_{10}H_7NOS)_2(H_2O)_2](BF_4)_2$, contains tetragonally elongated octahedral diaquabis(2-thienyl 2-pyridyl ketone)copper(II) cations counterbalanced with BF_4^- anions. The Cu atom resides on an inversion center and is bonded to the ligand through the pyridine N and the carbonyl O atoms [1.986 (2) Å], with a bite angle of 81.39 (10)°. The thiophene is not involved in coordination. The coordinated water molecules are hydrogen bridged to adjacent BF_4^- anions, linking the cation and anion in an extended chain.

Comment

The interaction of transition metals with sulfur-containing heterocycles is of fundamental importance in catalysis, particularly in the hydrodesulfurization process. Herein, we report the structure of a Cu^{II} complex, (I), which is the first example containing the ligand 2-thienyl 2-pyridyl ketone (tpk), a chelate which presents hard donors (*i.e.* O and N) together with a thiophene S atom.



(I)

The Cu^{II} atom resides on an inversion center in the midst of a tetragonally elongated octahedral coordination sphere. The two tpk ligands coordinate through the pyridine N and the carbonyl O atoms, forming the equatorial square plane with water molecules occupying the two axial positions. The bond distances in the equatorial plane are typical of Cu—N and Cu—O, and are unremarkable. However, those to the axial waters are significantly longer (by ~0.4 Å) at 2.409 (3) Å. Tetragonal elongation in Cu^{II} complexes is well characterized (Procter, Hathaway & Nicholls, 1968; van Koningsbruggen *et al.*, 1995) and the distances observed are within the range expected of a Jahn–Teller distortion.

The thiophene moiety is not involved in coordination, exhibiting behavior similar to that observed for the sulfur-containing ligand *N*-(2-pyridylmethylidene)-2-thienylmethylamine (Atria *et al.*, 1994), where coordination occurred solely through the pyridine and imine N atoms, with no sulfur–metal interaction. The thiophene is twisted out of the square plane defined by the tpk heteroatoms and the Cu atom by 16.7 (2)°, and is planar [maximum deviation from the mean plane of 0.001 (2) Å]. Although disorder in thiophene rings is relatively common, no evidence of this was observed in the present structure when interconverting the S and the C atoms related by an approximate twofold rotation about the C6—C7 bond (Gallucci, Mathur & Shechter, 1995; Chaloner, Gunatunga & Hitchcock, 1994).

The BF_4^- ion has large displacement parameters, indicating that some disorder is present. The largest residual electron density on the difference map is located near the B atom at the expected bonding distance of an F atom. However, no chemically reasonable model of the disorder was found that would contribute to a real understanding of the structure. The bond lengths and angles describe an almost regular tetrahedron, with mean B—F distances of 1.353 Å and angles of 109.5°;

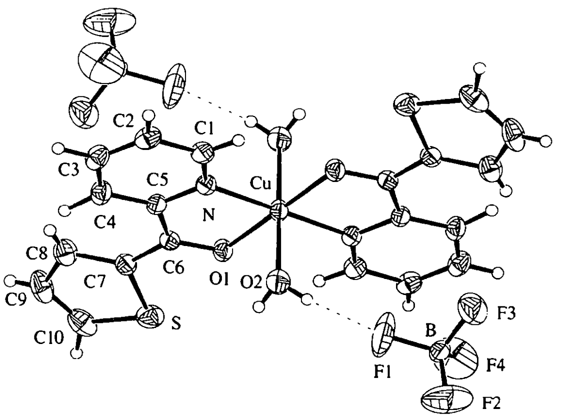


Fig. 1. Displacement ellipsoid plot (40% probability level) of the title complex. H atoms are shown as spheres of arbitrary radii. The shortest hydrogen bond to the BF_4^- anion of the asymmetric unit is shown as a dashed line.

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consequently the BF_4^- ion was refined as an ordered model.

Two hydrogen bonds are observed: the first occurs between the *HW*1 atom of the coordinated water and the BF_4^- ion located within the asymmetric unit, and the second occurs between the *HW*2 atom and a symmetry-related BF_4^- ion (Table 2). These two intermolecular interactions link monomeric units together into a loose extended structure.

Experimental

The title compound was prepared as follows: copper(II) tetrafluoroborate was combined with 2-thienyl 2-pyridyl ketone in a 2:1 stoichiometric ratio in acetonitrile. The resulting solution was filtered and allowed to evaporate slowly. Green crystals suitable for X-ray diffraction studies were isolated.

Crystal data

$[Cu(C_{10}H_7NOS)_2(H_2O)_2]-(BF_4)_2$
$M_r = 651.64$
Monoclinic
$P2_1/n$
$a = 7.0367(2)$ Å
$b = 12.2343(4)$ Å
$c = 15.1467(5)$ Å
$\beta = 103.202(1)°$
$V = 1269.50(7)$ Å^3
$Z = 2$
$D_x = 1.705$ Mg m^{-3}
$D_m = 1.67(1)$ Mg m^{-3}
D_m measured by flotation in hexane/1,2-dibromopropane

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 2–28°$
$\mu = 1.11$ mm^{-1}
$T = 173$ K
Block
0.32 × 0.26 × 0.13 mm
Green

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Sheldrick, 1994)
$T_{min} = 0.719$, $T_{max} = 0.869$
5899 measured reflections
2790 independent reflections

2537 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 28.18°$
$h = -8 \rightarrow 4$
$k = -9 \rightarrow 15$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R(F) = 0.057$
$wR(F^2) = 0.146$
$S = 1.060$
2789 reflections
205 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 2.8678P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—N	1.965 (3)	C5—C6	1.499 (4)
Cu—O1	1.986 (2)	C6—C7	1.441 (5)
Cu—O2	2.409 (3)	C7—C8	1.411 (5)
S—C10	1.688 (5)	C8—C9	1.417 (6)
S—C7	1.731 (4)	C9—C10	1.358 (7)
O1—C6	1.253 (4)		
N—Cu—O1	81.39 (10)	O1—C6—C5	116.7 (3)
N—Cu—O1^i	98.61 (10)	C7—C6—C5	124.9 (3)
N—Cu—O2	85.67 (11)	C8—C7—S	111.4 (3)
O1—Cu—O2	93.84 (11)	C6—C7—S	116.3 (3)
N—Cu—O2^i	94.33 (11)	C7—C8—C9	110.3 (4)
O1—Cu—O2^i	86.16 (11)	C10—C9—C8	113.6 (4)
C10—S—C7	91.6 (2)	C9—C10—S	113.1 (3)
N—C5—C6	112.0 (3)		

Symmetry code: (i) $-x, -y, -z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—*HW*1···F1	0.79 (7)	1.95 (7)	2.726 (4)	170 (6)
O2—*HW*2···F2^i	0.77 (7)	2.09 (7)	2.828 (5)	159 (6)

Symmetry code: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$.

The first 50 frames were remeasured at the end of data collection; the intensity decay was < 1%. H atoms were located from a difference synthesis and refined. Displacement parameters were fixed at $1.2U_{iso}$ of the bound C or $1.5U_{iso}$ of the bound O atom. The C—H bond lengths range from 0.73 (5) to 1.01 (5) Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SHELXTL* (Siemens, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*5 (McArdle, 1995). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1082). Services for accessing these data are described at the back of the journal.

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