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Structure of (2,2′-Bipyridine)bis(difluorophosphinato)copper(II), (bpy)Cu(PF_2O_2)$_2$

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Abstract. [Cu($C_{10}H_8N_2$)(PF_2O_2)$_2$], $M_r = 421·7$, monoclinic, $C2/c$, $a = 17·706\,(4)$, $b = 10·465\,(3)$, $c = 7·632\,(2)$ Å, $\beta = 90·99\,(2)°$, $V = 1414$ Å^3, $Z = 4$, $D_x = 1·981$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 18·6$ cm^{-1}, $F(000) = 836$, $T = 213$ K, $R = 0·030$ for 858 observed data with $I > 3\sigma(I)$. Crystals of (bpy)Cu(PF_2O_2)$_2$ (bpy = 2,2′-bipyridine) form in the decomposition of [Cu$_2$(bpy)$_2$(phenylacetylene)][PF_6]$_2$ in wet 2-butanone–hexane solution. The arrangement of ligands about the Cu atom is that of a tetragonally distorted octahedron. There are two short Cu—O bonds in the plane of the bipyridine ligand and two long bonds to the Cu atom from O atoms in $PF_2O_2^-$ ligands in planar units above and below the plane containing the first Cu atom.

Introduction. In an attempt to grow crystallographic-quality crystals of the yellow copper(I) alkyne complex [Cu$_2$(bpy)$_2$(phenylacetylene)][PF_6]$_2$ (Reger & Huff, 1991) (bpy = 2,2′-bipyridine) by the vapor diffusion method, colorless crystals formed that appeared to be different from the starting material. We report here crystallographic characterization of these crystals as (bpy)Cu(PF_2O_2)$_2$, a molecule that has an interesting polymeric structure in the solid state.

Experimental. All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. All solvents were dried, degassed, and distilled prior to use.

Colorless crystals of (bpy)Cu(PF_2O_2)$_2$ are reproducibly obtained as follows. [Cu$_2$(bpy)$_2$(phenylacetylene)][PF_6]$_2$ (Reger & Huff, 1990) in 2-butanone is placed in one side of a U-tube and hexane in the other. One drop of water from a microsyringe is added to the butanone side and the tube is sealed under vacuum after degassing by three freeze-pump-thaw sequences. After two or three days at 298 K, three types of crystals, colorless, orange and blue, form that can be separated by hand.

A transparent, prismatic crystal with dimensions 0·3 × 0·2 × 0·1 mm was mounted in a thin-walled capillary tube on a CAD-4 diffractometer with a graphite monochromator at 213 K. The unit cell was determined and refined from 25 general reflections ($8 < \theta < 12$) using the ω-scan technique. There were 1142 reflections measured in the 2θ range 4–46° ($0 \leq h \leq 19$, $0 \leq k \leq 11$, $-8 \leq l \leq 8$) with a crystal decay of less than 0·1% for 3 standard reflections. Absorption correction was by the method of Walker & Stuart (1983) with relative transmission factors: max. 1·378, min. 0·696, average 0·983. The structure was solved by the heavy-atom method and refined with use of *SDP-Plus* (Frenz, 1983). H atoms were placed in calculated positions and not refined. Full-matrix least-squares refinements (on F) were carried out with weights $w = [\sigma^2(F) + 0·0004F^2]^{-1}$ for reflections with $I > 3\sigma(I)$. At the final stage: 109 variables, $R = 0·030$, $wR = 0·040$, $S = 1·87$, $(\Delta/\sigma)_{\max} = 0·04$, max. and min. peak heights in the final difference Fourier synthesis 0·39 and $-0·21$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1† shows atomic parameters for (bpy)Cu(PF_2O_2)$_2$.

Discussion. Crystals of (bpy)Cu(PF_2O_2)$_2$ (see below) are obtained from the solution decomposition of [Cu$_2$bpy$_2$(phenylacetylene)][PF_6]$_2$ in wet butanone.

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53729 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters for* (bpy)$Cu(PF_2O_2)_2$ *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Cu	0·000	0·16185 (5)	0·250	2·72 (1)
P(1)	0·09532 (5)	0·09293 (9)	−0·1387 (1)	2·50 (2)
F(1)	0·1265 (1)	0·1682 (2)	−0·2963 (3)	4·13 (5)
F(2)	0·1702 (1)	−0·0858 (3)	0·4675 (3)	4·81 (6)
O(3)	0·0407 (2)	0·1709 (2)	−0·0476 (3)	3·49 (5)
O(4)	0·0794 (2)	0·0359 (2)	0·3003 (4)	3·97 (6)
N(1)	0·0710 (2)	0·3080 (3)	0·2953 (4)	2·47 (5)
C(2)	0·0406 (2)	0·4242 (3)	0·2781 (4)	2·61 (7)
C(3)	0·0807 (2)	0·5340 (4)	0·3097 (6)	4·04 (9)
C(4)	0·1567 (2)	0·5241 (4)	0·3601 (6)	4·39 (9)
C(5)	0·1882 (2)	0·4043 (4)	0·3735 (6)	4·00 (8)
C(6)	0·1442 (2)	0·2984 (4)	0·3413 (5)	3·40 (8)

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *for* (bpy)$Cu(PF_2O_2)_2$ *with e.s.d.'s in parentheses*

Cu—O(3)	2·396 (2)*	N(1)—C(2)	1·335 (3)
Cu—O(4)	1·960 (3)	N(1)—C(6)	1·340 (4)
Cu—N(1)	2·007 (2)	C(2)—C(2)	1·495 (5)
P(1)—F(1)	1·548 (2)	C(2)—C(3)	1·369 (4)
P(1)—F(2)	1·544 (2)	C(3)—C(4)	1·398 (5)
P(1)—O(3)	1·453 (2)	C(4)—C(5)	1·375 (5)
P(1)—O(4)	1·452 (3)	C(5)—C(6)	1·374 (5)

O(3)—Cu—O(3)	175·46 (9)*	F(2)—P(1)—O(3)	110·4 (1)
O(3)—Cu—O(4)	89·19 (9)*	F(2)—P(1)—O(4)	106·5 (1)
O(3)—Cu—O(4)	93·86 (8)*	O(3)—P(1)—O(4)	123·2 (1)
O(3)—Cu—N(1)	86·30 (8)*	C(2)—N(1)—C(6)	118·6 (2)
O(3)—Cu—N(1)	90·25 (7)*	N(1)—C(2)—C(2)	114·3 (1)
O(4)—Cu—O(4)	95·5 (1)	N(1)—C(2)—C(3)	122·7 (3)
O(4)—Cu—N(1)	91·94 (9)	C(2)—C(2)—C(3)	122·9 (2)
O(4)—Cu—N(1)	172·57 (9)	C(2)—C(3)—C(4)	118·7 (3)
N(1)—Cu—N(1)	80·6 (1)	C(3)—C(4)—C(5)	118·4 (3)
F(1)—P(1)—F(2)	96·8 (2)	C(4)—C(5)—C(6)	119·7 (3)
F(1)—P(1)—O(3)	109·6 (2)	N(1)—C(6)—C(5)	121·9 (3)
F(1)—P(1)—O(4)	107·0 (1)		

* The Cu—O(3) bond distances and angles represent interactions between different square-planar units

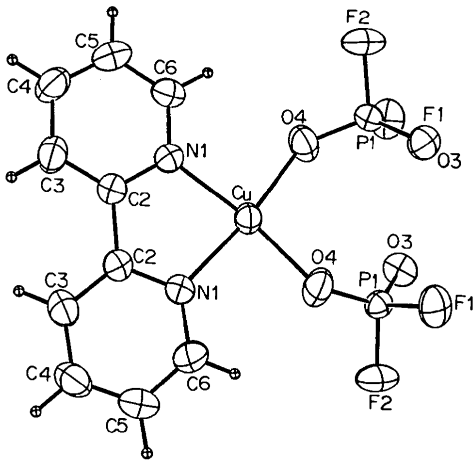

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the square-planar portion of (bpy)$Cu(PF_2O_2)_2$.

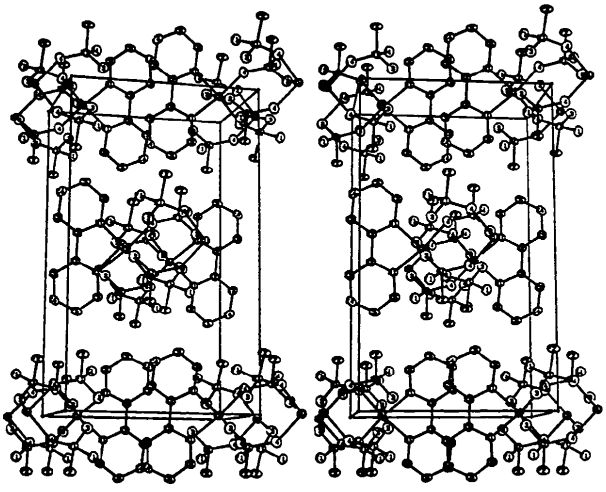

Fig. 2. Stereoview of the unit cell of (bpy)$Cu(PF_2O_2)_2$.

These crystals did not form from analogous solutions in which the solvent had been rigorously dried. The formation of $PF_2O_2^-$ from hydrolysis of PF_6^- in the presence of transition metal complexes has been reported previously (White, Thompson & Maitlis, 1977; Bruce, Cifuentes, Grundy, Liddell, Snow & Tiekink, 1988; Clark & Jones, 1970, 1971).

X-ray analysis of these colorless crystals shows them to be (bpy)$Cu(PF_2O_2)_2$. Fig. 1 shows an *ORTEP* (Johnson, 1965) view of the square-planar portion of the compound and Table 2 shows bond distances and angles.

The Cu atom is located on the twofold crystallographic symmetry axis. It is bonded to the bipyridine ligand and one O atom [O(4)] of each $PF_2O_2^-$ ligand. As shown in the stereoview (Fig. 2), there is also a weak interaction above and below the (bpy)-Cu[O(4)]$_2$ plane with the other O atom [O(3)] of the $PF_2O_2^-$ ligand from a *different* square-planar unit [the Cu—O(3) bond distances and angles given in Table 2 represent interaction between different square-planar units]. Within each planar unit, one O(3) O atom bonds to a Cu atom above the plane while this second planar unit through one of its O(3) O atoms bonds back to the first Cu atom. These interactions form eight-membered $Cu_2F_2O_2P_2$ rings. In addition, the second O(3) O atom of the initial (bpy)Cu[O(4)]$_2$ planar unit bonds to a Cu atom below the plane forming a spiral polymeric structure made up of repeating Cu—O(4)—P—O(3) units. The bipyridine rings are stacked parallel on two sides of the polymeric spiral. Thus, the overall geometry about the Cu atom is a tetragonally distorted octahedron, a structure frequently observed for copper(II) (Cotton & Wilkinson, 1988; Toofan, Boushehri & Haque, 1976; Stephens, 1969).

The copper–bipyridine bonding is similar to known examples with the N—Cu—N angle restricted to 80·6 (1)° by the bite angle of the chelate ligand (Toofan, Boushehri & Haque, 1976; Stephens, 1969) instead of the 90° angle of a square plane. This restriction causes the opposite O(4)—Cu—O(4) angle to open to 95·5 (1)°. The other bond angles are close to those expected for a distorted octahedron.

The structure of the $PF_2O_2^-$ anion is best described as a distorted tetrahedron. The four F—P—O bond angles are within 3° of the 109·5° tetrahedral angle. The angle formed by the two O atoms, O(4)—P—O(3), is significantly enlarged to 123·2 (1)° and the opposite F(1)—P—F(2) angle correspondingly contracted at 96·8 (2)°. These bond distances and angles are all very close to those reported for $PF_2O_2^-$ when not coordinated to a transition metal (Wells, 1984; Harrison & Trotter, 1969; Granier, Durand, Cot & Galigne, 1975).

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Crystal Phases of Dodecyl Sulfates Obtained from Aqueous Solutions: Structure of the Hexaaquamagnesium Salt

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Abstract. Hexaaquamagnesium dodecyl sulfate, $[Mg(H_2O)_6][C_{12}H_{25}O_4S]_2$, $M_r = 663{\cdot}2$, monoclinic, $A2$, $a = 6{\cdot}2860$ (4), $b = 7{\cdot}0234$ (6), $c = 42{\cdot}086$ (3) Å, $\beta = 92{\cdot}915$ (5)°, $V = 1855{\cdot}7$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}19$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 18·9 cm^{-1}, $F(000) = 724$, room temperature, $R = 0{\cdot}074$ for 1614 independent reflections with $I \geq 1{\cdot}5\sigma(I)$. The crystal packing is characterized by a lamellar structure where polar and apolar regions alternate. In the polar region each magnesium ion is hydrated by six water molecules octahedrally coordinated and each water molecule forms two hydrogen bonds with different O atoms of the adjacent polar heads. Therefore, the Coulombic interactions in the polar region are partially shielded by the water molecules surrounding the cation. In contrast with previously determined crystal packings of Na and Rb dodecyl sulfates, in the apolar region the hydrocarbon chains of opposite bilayer halves interdigitate completely and form a common matrix. The intermolecular contacts among the C atoms of the adjacent hydrocarbon chains show, however, that weak van der Waals interactions contribute to the packing in this region.

Introduction. The current models of micellar aggregates in aqueous solutions do not account satisfactorily for the available data and often give rise to contradictions (Dill, Koppel, Cantor, Dill, Bendedouch & Chen, 1984; Menger & Doll, 1984). In order to obtain models of micellar aggregates formed from sodium dodecyl sulfate (SDS) and to verify them with various techniques in the study of micellar solutions, we are following a strategy successfully applied in the structural elucidation of deoxycholate micelles (Campanelli, Candeloro De Sanctis, Giglio & Petriconi, 1984; Conte, Di Blasi, Giglio, Parretta & Pavel, 1984; Esposito, Zanobi, Giglio, Pavel & Campbell, 1987; Esposito, Giglio, Pavel & Zanobi, 1987; Giglio, Loreti & Pavel, 1988). Therefore, crystal phases of sodium dodecyl sulfate,

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