metal-organic papers

# Di-μ-fluoro-bis[(acetonitrile){*N*,*N*′-bis[(dimethylamino)(morpholino)methylene]propane-1,3-diamine}copper(II)] bis(hexafluorophosphate): the first di-μ-fluoro-bridged dicopper bisguanidine compound

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The title compound, $[Cu_2(C_{15}H_{31}N_6O_2)F_2(CH_3CN)_2](PF_6)_2$, has an $N_2Cu(\mu\text{-}F)_2CuN_2$ core as the central element. The Cu_2F_2 ring is planar due to crystallographic inversion symmetry. The N atom from the enclosed acetonitrile solvent molecule serves as the fifth coordinating atom to the Cu centre. The crystal packing exhibits intermolecular hydrogen bonds.

Comment

Guanidines are a potentially useful ligand class due to their versatile coordination chemistry (Coles, 2006). The development of polyfunctional nitrogen donor ligands which are able to stabilise unusually high metal oxidation states is a very important objective in coordination and bio-inorganic chemistry. Therefore, we have extended our interests towards guanidyl-type systems (Pohl *et al.*, 2000) and developed a library of bisguanidine ligands (Herres-Pawlis *et al.*, 2005). For synthetic reasons, up to now, the guanidine units had to be symmetrical. With the synthesis of bis[N^1,N^1-(morpholino)-N^3,N^3-dimethylmethylene]propane-1,3-diamine (MorphDMG$_2$p) and its derivatives, we have been able to design a guanidine system which provides on the one hand steric hindrance and on the other hand good access to the copper site for precatalytic coordination (Herres-Pawlis, 2005; Herres-Pawlis *et al.*, 2006). The reaction of the MorphDMG$_2$p-containing precursor complex $[Cu_2(MorphDMG_2p)_2](PF_6)_2$ with dioxygen and subsequent steps (see *Experimental* and scheme) afforded the di-μ-fluoro-dicopper(II) title complex, (I).
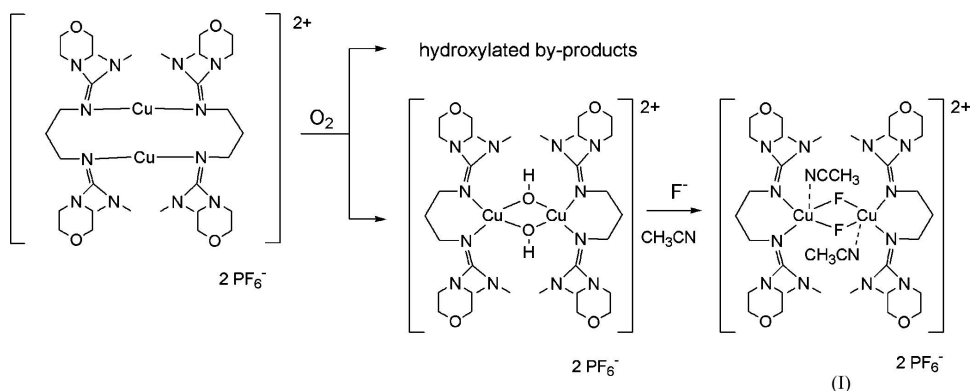
To date, (I) (Fig. 1) is the first crystallographically determined structure with fourfold coordinated Cu centres in an $N_2Cu(\mu\text{-}F)_2CuN_2$ core. The geometric centre of the cation lies on a crystallographic inversion centre, thus the Cu_2F_2 ring is planar with slightly different Cu–F bond lengths. The devia-
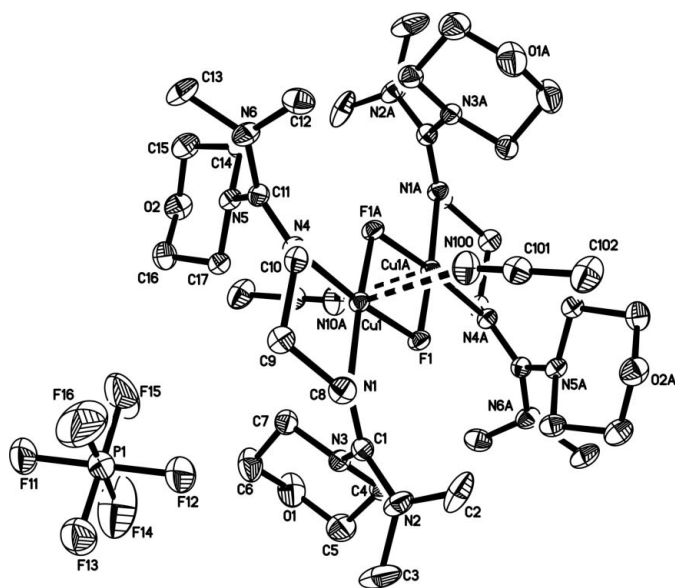
Figure 1
The molecular structure with H atoms omitted. Displacement ellipsoids are drawn at the 50% probability level. Only one PF_6^- anion is shown, the second one is symmetry-related. The symmetry operator for atoms with suffix A is $(-x, -y, 1-z)$.
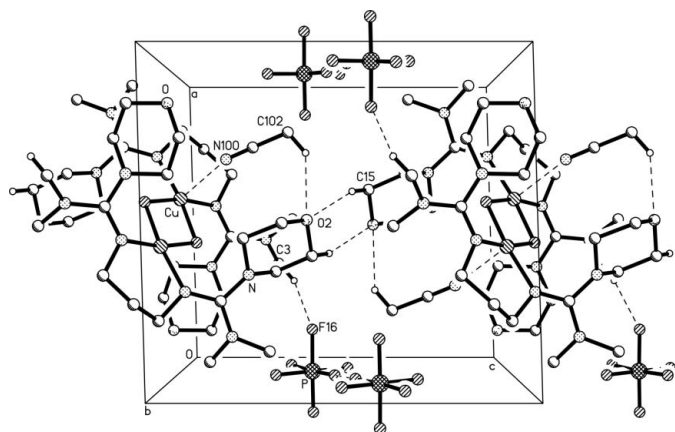

Figure 2
The crystal packing, viewed along [010], with the hydrogen-bonding pattern and Cu$\cdots$acetonitrile coordination indicated by dashed lines. H atoms not involved have been omitted.

tion of the Cu atom from the N_2F_2 plane is 0.059 (1) Å. The axis of the acetonitrile solvent molecule is perpendicular to this plane with a Cu$\cdots$N100 distance of 2.571 (3) Å, so Cu would then reach square pyramidal coordination. The Cu$\cdots$Cu distance of 3.0377 (6) Å is slightly shortened compared with that of the related di-μ-hydroxo-bis-$\{[(N,N'$-bis(dipiperidinomethylene)propane-1,3-diamine-N,N']-copper(II)$\}$ bis(hexafluorophosphate) complex [3.0740 (6) Å; Herres *et al.*, 2004]. The chelate heterocycle in (I) adopts a chair conformation. The bite angle N1—Cu—N4 and all the other geometric parameters (Table 1) are comparable with those of the above-mentioned di-μ-hydroxo-dicopper(II) complex. The crystal packing shows a number of intermolecular C—H$\cdots$O and C—H$\cdots$F bridges shorter than

2.5 Å (Table 2) which link each two morpholino rings of a cation with another one and each two methylamino groups to PF_6^- anions. Additionally, there is a hydrogen bridge from the acetonitrile solvent to one morpholine O atom.

Experimental

The ligand MorphDMG$_2$p and the precursor complex [Cu$_2$(MorphDMG$_2$p)$_2$](PF$_6$)$_2$ were prepared according to literature procedures (Herres-Pawlis, 2005; Herres-Pawlis *et al.*, 2006). A solution of 563 mg (0.5 mmol) of [Cu$_2$(MorphDMG$_2$p)$_2$](PF$_6$)$_2$ in 20 ml of MeCN was treated at room temperature with dioxygen. The reaction leads *via* a di-μ-oxo-dicopper(III) complex to presumably two products, a di-μ-alkoxo- and a di-μ-hydroxo-dicopper(II) complex (Herres *et al.*, 2005). The latter complex then reacts in the following step with the hexafluorophosphate ions present, giving [Cu$_2$(MorphDMG$_2$p)$_2$(μ-F)$_2$](PF$_6$)$_2$. Copper(II) complexes are known to be able to abstract fluorine from hexafluorophosphate (Lee & Holm, 1993). Dark-blue crystals suitable for X-ray diffraction were grown by slow diffusion of diisopropyl ether into MeCN (yield 48%, 278 mg).

Crystal data

[Cu$_2$(C$_{15}$H$_{31}$N$_6$O$_2$)F$_2$-(C$_2$H$_3$N)$_2$](PF$_6$)$_2$	$V = 2632.8$ (4) Å^3
$M_r = 1246.13$	$Z = 2$
Monoclinic, $P2_1/n$	$D_x = 1.572$ Mg m^{-3}
$a = 11.1872$ (11) Å	Mo $K\alpha$ radiation
$b = 19.1481$ (19) Å	$\mu = 0.97$ mm^{-1}
$c = 12.2954$ (12) Å	$T = 120$ (2) K
$\beta = 91.595$ (2)$^\circ$	Block, blue
	$0.40 \times 0.32 \times 0.23$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	22595 measured reflections
φ and ω scans	6619 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	3786 reflections with $I > 2\sigma(I)$
$T_{min} = 0.697$, $T_{max} = 0.807$	$R_{int} = 0.060$
	$\theta_{max} = 28.5^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2]$
$wR(F^2) = 0.104$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.86$	$(\Delta/\sigma)_{max} = 0.001$
6619 reflections	$\Delta\rho_{max} = 0.86$ e Å^{-3}
339 parameters	$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, $^\circ$).

Cu1—F1^i	1.9339 (16)	N2—C1	1.372 (4)
Cu1—F1	1.9484 (16)	N3—C1	1.354 (4)
Cu1—N1	1.952 (2)	N4—C11	1.307 (3)
Cu1—N4	1.968 (2)	N5—C11	1.365 (4)
N1—C1	1.308 (4)	N6—C11	1.348 (4)
F1^i—Cu1—F1	77.03 (7)	N3—C1—N2	115.7 (3)
N1—Cu1—N4	96.47 (10)	N4—C11—N6	124.0 (3)
Cu1^i—F1—Cu1	102.97 (7)	N4—C11—N5	120.7 (3)
N1—C1—N3	121.4 (3)	N6—C11—N5	115.3 (3)
N1—C1—N2	122.8 (3)		

Symmetry code: (i) $-x, -y, -z + 1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$C\cdots$F16[ii]	0.98	2.47	3.396 (5)	157
C15—H15$B\cdots$O2[iii]	0.99	2.49	3.428 (4)	159
C102—H10$A\cdots$O2[i]	0.98	2.47	3.286 (4)	140

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

H atoms were found in Fourier difference maps and refined at idealized positions, riding on their attached C atoms, with isotropic displacement parameters $U_{iso}(H) = 1.2 U_{eq}(C)$ and $1.5 U_{eq}$(methyl C). All CH$_3$ groups were allowed to rotate but not to tip. F atoms of the PF$_6$ anion show rather larger anisotropic displacement parameters, indicating some amount of anion disorder which, however, could not be resolved any further.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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