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Bis(μ-di-2-pyridylaminato 1-oxide)-bis[(trifluoroacetato)copper(II)] acetonitrile disolvate

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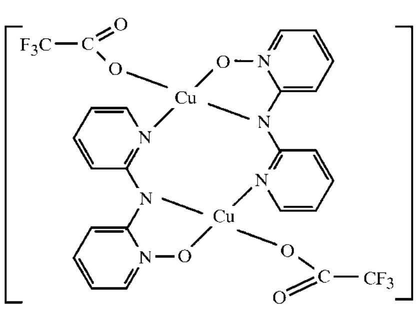
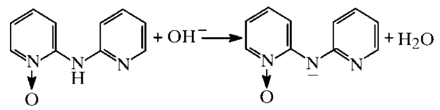
The crystal structure of the title compound, $[Cu_2(C_2F_3O_2)_2(C_{10}H_8N_3O)_2]\cdot 2CH_3CN$, contains discrete $[Cu_2(CF_3COO)_2(O\text{-}dpa)_2]$ molecules (O-dpaH is di-2-pyridylamine 1-oxide) which have imposed crystallographic twofold symmetry and an acetonitrile molecule of solvation. The O-dpa$^-$ ligand is both bidentate and bridging, linking two Cu atoms with a separation of 3.4270 (11) Å. Each Cu atom is surrounded by four coordinated atoms that are almost coplanar, with dimensions Cu—N = 1.940 (2) and 1.984 (3) Å, and Cu—O = 1.912 (2) and 1.945 (2) Å.

Comment

In attempts to develop polynuclear compounds of transition metals using multidentate N-donor groups as ligands (Shieh *et al.*, 1997; Wang *et al.*, 1998; Chang *et al.*, 1999; Peng *et al.*, 2000), we have noticed the behavior of the polypyridylamine *N*-oxides, because *N*-oxides offer functional group manipulation and structural modification possibilities that are not usually accessible by other methods (Cope & Ciganek, 1963). In our research system, di-2-pyridylamine 1-oxide (O-dpaH; O-dpa$^-$ is the di-2-pyridylaminate 1-oxide anion) is the simplest polypyridylamine oxide. The O-dpaH frame is stable in air but, to the best of our knowledge, no transition metal complexes of O-dpaH have been reported. We report here the synthesis and structure of the title dinuclear Cu^{II} complex, (I).



(I)



$$4Cu^{I} + 2H_2O + O_2 \rightarrow 4Cu^{II} + 4OH^-$$

As shown in Fig. 1, complex (I) has crystallographically imposed twofold symmetry and the O-dpa$^-$ ligand is both bidentate and bridging, linking two Cu atoms with a separation of 3.4270 (11) Å. The O-dpa$^-$ ligand takes the *syn* form, with each Cu atom coordinated to four atoms, *viz*. an amide N atom, an *N*-oxide O atom of one O-dpa$^-$ anion, with a bite angle O1—Cu1—N2 of 83.09 (10)°, a pyridine N atom of another O-dpa$^-$ anion, and an O atom of a trifluoroacetate group. Atom Cu1 is 0.1648 (10) Å from the best plane of the CuN_2O_2 moiety. Although this compound can be considered as basically four-coordinate, atoms N2^{i} and O3 (see Fig. 1) occupy possible fifth and sixth coordination sites, with Cu1···N2^{i} = 2.904 (3) Å [symmetry code: (i) $-x, y, \frac{1}{2} - z$] and Cu1···O3 = 3.103 (3) Å. This type of coordination is perhaps best described as intermediate between square-planar four-coordination and distorted octahedral geometry. The eight-membered Cu1—N3^{i}—C6^{i}—N2^{i}—Cu1^{i}—N3—C6—N2 chelate ring (Fig. 1) adopts a boat conformation. The individual pyridyl rings are essentially planar [the maximum deviation from their planes is 0.008 (2) Å for atom C5], with the pyridyl-ring planes forming a dihedral angle of 55.11 (12)°. There is no H atom on amide atom N2; the original amide H atom is eliminated rather than being transferred to the N atom of a pyridine ring. The N2—C6 bond length [1.404 (4) Å] is almost

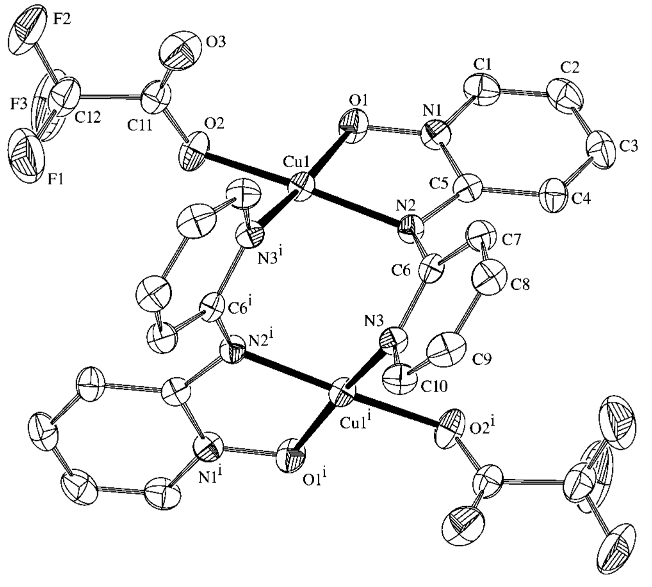


Figure 1
The complex molecule of (I). Displacement ellipsoids are drawn at the 30% probability level and, for clarity, the acetonitrile molecule of solvation and the H atoms have been omitted. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

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equal to that in the free ligand [1.395 (2) Å], while the N2—C5 bond length is apparently shortened from 1.367 (2) Å in the free ligand to 1.347 (4) Å in the complex (Thellend *et al.*, 1997; Bergstad & Backvall, 1998; Jiao & Yu, 2001). The suggested mechanism is illustrated in the reaction scheme above (Wu *et al.*, 1990). The dehydrogenation in (I) only occurs as a consequence of the oxidation of Cu^I to Cu^{II} in the presence of air and traces of water.

Experimental

O-dpaH (0.1 g, 0.535 mmol) was dissolved in acetonitrile (20 ml) and copper(I) trifluoroacetate ($CuCF_3COO$; 0.1 g, 0.568 mmol) was added. The resulting solution was stirred for 10 h in air at room temperature. The mixture was filtered and the filtrate was crystallized by diffusion of ether at room temperature. After several days, green single crystals of (I) were obtained. IR (cm^{-1}): 3441.92, 3092.32, 1695.85, 1508.49, 1477.03, 1384.88, 1189.8, 1139.58, 753.28.

Crystal data

$[Cu_2(C_2F_3O_2)_2(C_{10}H_8N_3O)_2]\cdot 2C_2H_3N$
$M_r = 807.62$
Monoclinic, *C*2/*c*
$a = 21.203\ (4)$ Å
$b = 7.468\ (2)$ Å
$c = 22.123\ (5)$ Å
$\beta = 108.947\ (15)^\circ$
$V = 3313.2\ (13)$ Å^3
$Z = 4$
$D_x = 1.619$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 2991 reflections
$\theta = 2.0$–25.0°
$\mu = 1.37$ mm^{-1}
$T = 293\ (2)$ K
Prism, green
0.38 × 0.25 × 0.22 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.675$, $T_{\max} = 0.738$
2991 measured reflections
2905 independent reflections
2106 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 25.0^\circ$
$h = -25 \rightarrow 0$
$k = -8 \rightarrow 0$
$l = -24 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.095$
$S = 1.02$
2905 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 4.4467P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

In the refinement, H atoms were allowed for as riding atoms, with C—H distances of 0.93 and 0.96 Å.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.912 (2)	O1—N1	1.356 (3)
Cu1—N2	1.940 (2)	N1—C1	1.345 (4)
Cu1—O2	1.945 (2)	N1—C5	1.367 (4)
Cu1—N3$^{\rm i}$	1.984 (3)	N2—C5	1.347 (4)
Cu1—N2$^{\rm i}$	2.904 (3)	N2—C6	1.404 (4)
Cu1—O3	3.103 (3)		
O1—Cu1—N2	83.09 (10)	O1—N1—C5	118.2 (2)
O1—Cu1—O2	90.97 (10)	C5—N2—C6	120.9 (3)
N2—Cu1—N3$^{\rm i}$	97.73 (10)	C5—N2—Cu1	112.6 (2)
O2—Cu1—N3$^{\rm i}$	89.44 (11)	C6—N2—Cu1	120.59 (19)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1219). Services for accessing these data are described at the back of the journal.

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