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Second crystal form of dinitrito(1,10-phenanthroline)-copper(II)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.037
wR factor = 0.109
Data-to-parameter ratio = 9.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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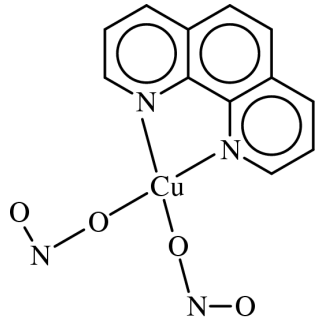
The crystal structure of a second form of green $[Cu(NO_2)_2(phen)]$, where phen is 1,10-phenanthroline ($C_{12}H_8N_2$), containing six-coordinate copper(II) with a distorted tetragonal $[Cu^{II}N_2O_4]$ core is reported. The first form had a crystal symmetry of *C*2/*c* [Breneman *et al.* (1999). *Acta Cryst.* C**55**, IUC9900158], while the form reported here is *Pbcn*. The nitrito ligands are bonded to the central copper through both O atoms, with short Cu—O bond distances of 1.987 (3) Å and longer Cu—O bond distances of 2.410 (4) Å. Both nitrito groups are significantly displaced from the plane defined by the 1,10-phenanthroline and the square-planar arrangement of the ligands around the Cu^{II} atom.

Comment

The title molecule, (I), in this second form (Fig. 1) is very similar to that in the first form except this second form possesses twofold crystallographic symmetry.



(I)

Each nitrito group is bonded to the copper(II) by an oxygen, with a short and long distance of 1.999 (3) and 2.056 (2) Å, respectively, in the first form and 1.987 (3) Å for both bonds in the second form. Each remaining O atom of the nitrito groups appears to interact with the copper at longer distances of 2.470 (3) and 2.396 (3) Å in the first form, and 2.410 (4) Å for both bonds in the second form. These two O atoms complete what could be described as a distorted tetragonal coordination around the central copper(II) in both forms. These observed Cu—O distances of 2.470 (3) and 2.396 (3) Å in the first form, and 2.410 (4) Å in the second form are all shorter than the normal non-bonded distance of *ca* 2.9 Å for Cu^{II}. The Cu—N(phen) distances of 1.995 (3) and 2.021 (2) Å in the first form are close to the Cu—N1 bond distance of 1.997 (2) Å in the second form. The planes of the nitrito groups are significantly displaced from the planar

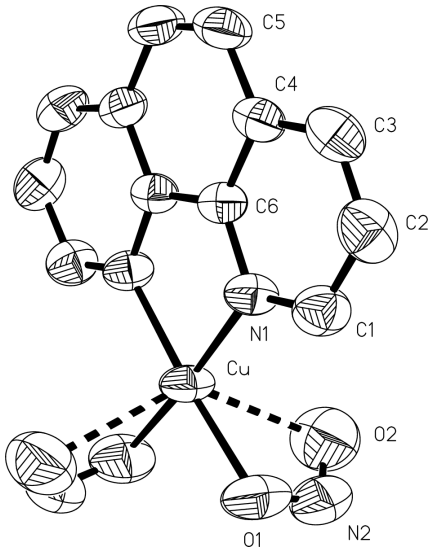


Figure 1
Displacement ellipsoid (50% probablility) plot of $[Cu(NO_2)_2(phen)]$ showing the atom-numbering scheme. H atoms have been omitted.

arrangement of the Cu and the two N atoms of the 1,10-phenanthroline including the planar ring structure. The two forms differ in their crystal packing with regard to how the phenanthroline rings on adjacent molecules overlap.

Experimental

$[Cu(NO_2)_2(phen)]$ was prepared by the slow addition of a 25 ml solution of 1,10-phenanthroline monohydrate (1.01 g, 5.0 mmol) in ethanol to a 20 ml solution of $Cu(NO_3)_2.3H_2O$ (1.20 g, 5.0 mmol) dissolved in water. To the resulting pale green solution, 30 ml of an aqueous solution of $NaNO_2$ (0.69 g, 10.0 mmol) was slowly added with continuous stirring. The product was a green solution from which a single crop of dark-green crystals was produced by evaporation of the solvent. Both prisms and plates were present with prisms being the first form (*C*2/*c* symmetry) and the plates being the second form (*Pbcn* symmetry).

Crystal data

$[Cu(NO_2)_2(C_{12}H_8N_2)]$
$M_r = 335.76$
Orthorhombic, *Pbcn*
$a = 9.773\ (1)$ Å
$b = 17.404\ (2)$ Å
$c = 7.440\ (1)$ Å
$V = 1265.4\ (3)$ Å^3
$Z = 4$
$D_x = 1.763$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
$\theta = 20.2$–$22.9°$
$\mu = 1.75$ mm^{-1}
$T = 295$ K
Plate, green
0.50 × 0.50 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{min} = 0.445$, $T_{max} = 0.875$
1054 measured reflections
875 independent reflections
813 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 23.0°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 8$
1 standard reflection
frequency: 167 min
intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.109$
$S = 1.15$
875 reflections
96 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2 + 0.6552]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.987 (3)	O1—N2	1.231 (5)
Cu—N1	1.997 (2)	O2—N2	1.184 (5)
Cu—O2	2.410 (4)		
O1—Cu—N1	93.91 (12)	N2—O2—Cu	84.3 (3)
O1—Cu—O2	54.79 (15)	C1—N1—Cu	129.4 (2)
N1—Cu—O2	94.32 (12)	C6—N1—Cu	112.53 (19)
N2—O1—Cu	104.0 (2)		

H atoms were set to ride on respective C atoms. C—H bond lengths were constrained to 0.96 Å and H-atom U_{iso} values to 0.08 Å^2

Data collection: *CAD*-4 *Software* (Schagen *et al.*, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXTL*/*PC* (Siemens, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXL*97.

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