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A redetermination of [*N*,*N*-bis(3,5-dimethyl-1*H*-pyrazol-1-ylmethyl-κN^2)-2-hydroxyethylamine-κN]-(3,5-dimethyl-1*H*-pyrazole-κN^2)nitratocopper(II) nitrate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.010 Å
Disorder in main residue
R factor = 0.087
wR factor = 0.231
Data-to-parameter ratio = 15.5

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

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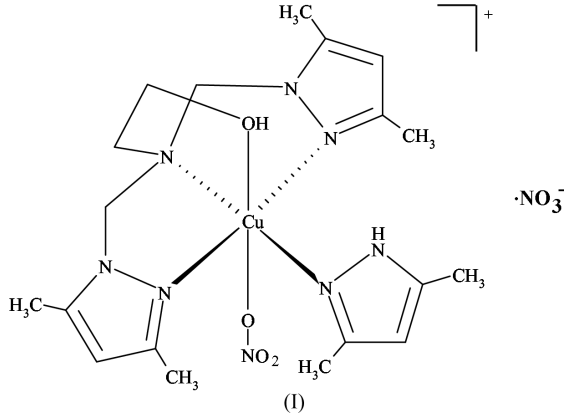
The new crystal structure analysis of the title compound, $[Cu(NO_3)(C_5H_8N_2)(C_{14}H_{23}N_5O)]NO_3$, reveals that the copper(II) ion lies in a distorted octahedral environment, with four N atoms in the equatorial plane and two O atoms at the axial positions. The O atoms of the nitrate group are involved in intra- and intermolecular hydrogen bonding.

Comment

Several papers on copper complexes with the *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane ligand (*L*) have been published to date. They describe the synthesis and X-ray crystal structure of di-1-chloro-bis{[*N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxyethanamine]-copper(II)}dichloride dihydrate (El Kodadi *et al.*, 2004), $[Cu(L)(Lo)(ClO_4)_2]$ (Boyd *et al.*, 1997) and $[Cu(L)(Lo)(NO_3)_2]$ (El Kodadi *et al.*, 2003), where *Lo* is 3,5-dimethylpyrazole. In the chloride compound, the Cu atom displays a distorted octahedral coordination, while in the perchlorate and nitrate compounds, the copper coordination geometry is described as distorted square-pyramidal.



(I)

We have redetermined the crystal structure of the title compound, (I), $[Cu(L)(Lo)(NO_3)_2]$, and found, in contradiction with our former description (El Kodadi *et al.*, 2003), that the Cu atom has a distorted octahedral coordination. The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1.

The equatorial plane of the distorted octahedron contains four N atoms, *viz*. N2, N31, N4 and N6 (Table 1). The axial positions are occupied by atom O11 of the hydroxy group and atom O5 of the nitrate group.

An intramolecular hydrogen bond occurs between atoms N9 and O6, and an intermolecular one between hydroxyl atom O11 and nitrate atom O3^{i} (Fig. 2 and Table 2).

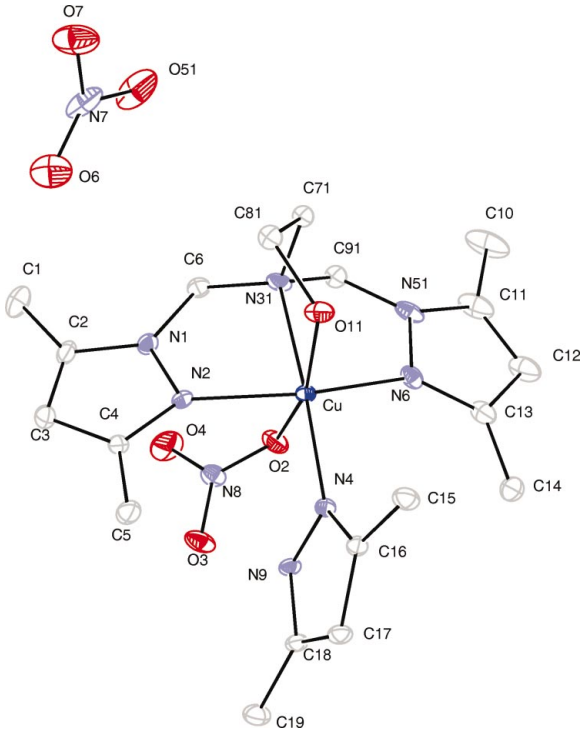


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms and the second disorder component have been omitted.

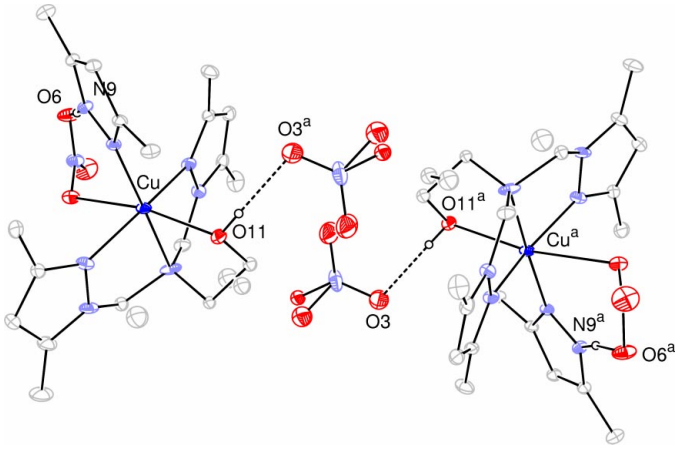


Figure 2
Intra- and intermolecular hydrogen bonds (dashed lines) established in the crystal structure of (I) [symmetry code: (*a*) $1-x, -y, -z$]. The majority of H atoms have been omitted for clarity.

Experimental

The title copper(II) complex, (I), was prepared by the addition of a solution of the tridentate ligand *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane (0.277 g, 1 mmol) in ethanol (3 ml) to a solution of copper(II) dinitrate [$Cu(NO_3)_2{\cdot}3H_2O$; 0.2415 g, 1 mmol] in ethanol (3 ml). The resulting solution was filtered and allowed to stand at 298 K. Blue crystals of (I) formed after a few days, and these were filtered off and washed with small amounts of cold ethanol, and then dried in air.

Crystal data

$[Cu(NO_3)(C_5H_8N_2)(C_{14}H_{23}N_5O)]$-$NO_3$	$Z = 2$
$M_r = 561.07$	$D_x = 1.516$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 8.351$ (1) Å	Cell parameters from 17 830 reflections
$b = 11.220$ (1) Å	$\theta = 3.3$–$26.5°$
$c = 13.566$ (1) Å	$\mu = 0.95$ mm^{-1}
$\alpha = 89.40$ (1)°	$T = 173$ (2) K
$\beta = 75.91$ (1)°	Parallelepiped, blue
$\gamma = 85.68$ (1)°	0.29 × 0.15 × 0.10 mm
$V = 1229.3$ (2) Å^3	

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	$R_{int} = 0.130$
ω scans	$\theta_{max} = 26.6°$
17 830 measured reflections	$h = -10 \rightarrow 10$
5106 independent reflections	$k = -14 \rightarrow 14$
4170 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0861P)^2 + 7.0572P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.087$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.231$	$\Delta\rho_{max} = 1.25$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.74$ e Å^{-3}
5106 reflections	
329 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu—N4	1.973 (4)	Cu—N31	2.074 (5)
Cu—N6	1.991 (5)	Cu—O5	2.747 (5)
Cu—N2	1.995 (5)	Cu—O11	2.273 (5)
N4—Cu—N6	98.1 (2)	N6—Cu—O5	77.25 (17)
N4—Cu—N2	95.46 (18)	N2—Cu—O5	81.82 (18)
N6—Cu—N2	155.7 (2)	N31—Cu—O5	81.46 (18)
N4—Cu—N31	174.67 (19)	N4—Cu—O11	103.30 (17)
N6—Cu—N31	82.9 (2)	N6—Cu—O11	102.54 (19)
N2—Cu—N31	81.79 (19)	N2—Cu—O11	93.82 (19)
N4—Cu—O5	93.66 (17)	N31—Cu—O11	81.48 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
N9—H9···O6	0.86	1.91	2.756 (7)	169
O11—H11*O*···O3^{i}	0.82	1.92	2.708 (8)	162

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

Part of the cation of (I) is disordered, with three C atoms occupying split positions [C71/C72, C81/C82 and C91/C92, each in the ratio 0.59 (1):0.41 (1)]. It was not possible to refine these atoms with anisotropic displacement parameters. Their bond lengths were restrained to values observed in similar molecules (El Kodadi *et al.*, 2004). The nitrate group close to this disordered branch is consequently affected by some disorder and one O atom was split over two positions (O21/O22, in the same ratio). All H atoms were placed in geometrically idealized positions, with an N—H distance of 0.86 Å and C—H distances in the range 0.93–0.97 Å and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ (1.5 for H atoms of methyl and hydroxy groups). Since it was not possible, even from several preparations, to obtain single crystals of very good quality, the

data were collected at low temperature (173 K) to minimize the problem of disorder. Attempts to solve and refine the structure in the non-centrosymmetric space group *P*1 did not allow us to overcome the disorder problems.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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