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Aquatetrakis(2-methylpyrazine-*κN*)(nitrato-*κO*)-copper(II) nitrate

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The copper(II) ion in the title compound, $[Cu(NO_3)(mepyz)_4(H_2O)]NO_3$, where mepyz is 2-methylpyrazine ($C_5H_6N_2$), has a distorted octahedral geometry with four N atoms of the methylpyrazine ligands in the equatorial positions and two O atoms from water and semi-coordinated nitrate moieties in the axial sites.

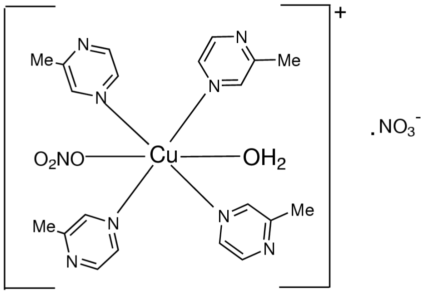
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.049
wR factor = 0.129
Data-to-parameter ratio = 12.3

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

Comment

The preparation of coordination complexes may be influenced by several factors, including metal-to-ligand mole ratio, leading to the formation of multiple structural types from a single set of components. For example, the reaction of copper(II) nitrate and 1,2-diazine (pyridazine, pdz) in various mole ratios produces four distinct products: the trimetallic complex, $[Cu(pdz)_3(NO_3)_3]_2Cu$, and the monometallic complexes $Cu(pdz)_3(NO_3)_2$, $Cu(pdz)_4(NO_3)_2$ and $[Cu(pdz)_4(NO_3)](NO_3)$ (Otieno *et al.*, 1995). In the case of the 1,4-diazine (pyrazine, pyz) analogue, three different coordination polymers, having compositions of $Cu(pyz)(NO_3)_2$, $Cu(pyz)_2(NO_3)_2$ and $Cu(pyz)_3(NO_3)_2$, are obtained (Otieno *et al.*, 2002). This work extends our investigations of the structural effects of copper(II)-nitrate-to-diazine-ligand mole ratio to include 2-methylpyrazine (mepyz).



(I)

The reaction of an aqueous solution of $Cu(NO_3)_2{\cdot}xH_2O$ and 2-methylpyrazine in a 1:1 molar ratio produces a coordination polymer with the stoichiometry $Cu(mepyz)(NO_3)_2$ (Amaral *et al.*, 2001). A 1:12 molar ratio of the same reagents in water produces a monometallic species of composition $[Cu(mepyz)_4(H_2O)(NO_3)]NO_3$, (I), whose structure is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The compound consists of the $[Cu(mepyz)_4(H_2O)(NO_3)]^+$ cation and NO_3^- counter-ion. The copper(II) ion has a distorted octahedral geometry with the four mepyz ligands in the equatorial positions and the semi-coordinated nitrate ion and water molecule in the axial sites. The mepyz ligands are

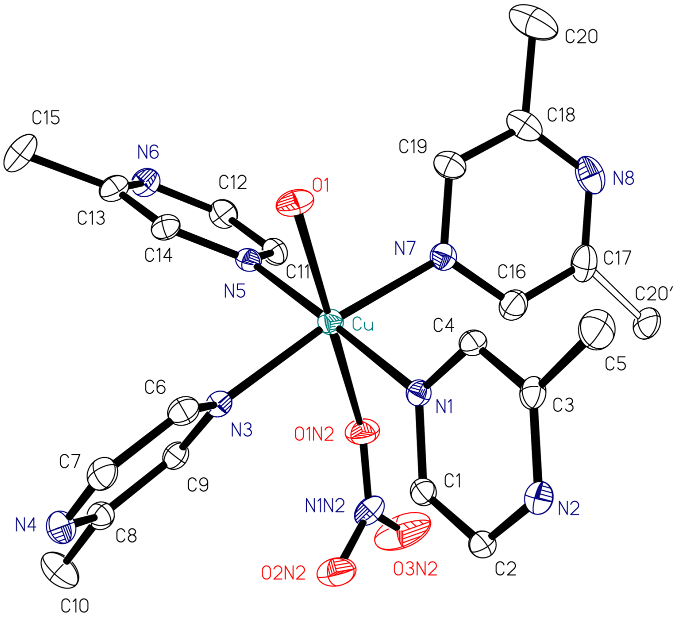


Figure 1
Atom-numbering scheme for the cation in the title compound, shown with 30% probability ellipsoids. The nitrate counter-ion has been omitted for clarity.

coordinated through the N atom distal to the methyl substituent and the pyrazine rings are twisted out of the CuN_4 plane [average = 54.37 (15)°, range = 45.29 (14)–57.79 (13)°], such that the Cu(mepyz)$_4$ fragment assumes a propeller structure. One O atom of each nitrate ion forms $O—H\cdots O$ hydrogen bonds in which the coordinated water molecule acts as the H-atom donor (Table 2). The title compound is isostructural with its perchlorate analogue, $[Cu(mepyz)_4(H_2O)(ClO_4)]ClO_4$ (Navas *et al.*, 1993). The copper–ligand bond lengths in the latter compound are: average $Cu—N = 2.033$ (3) Å, $Cu—OH_2 = 2.310$ (3) Å and $Cu—OClO_3 = 2.721$ (4) Å.

Experimental

Dark-blue crystals of (I) were obtained by slow evaporation of a mixture of a 3 ml aqueous solution of $Cu(NO_3)_2\cdot 2.5H_2O$ (1.00 g, 4.30 mmol) and 2-methylpyrazine (4.70 ml, 4.84 g, 51.4 mmol). Analysis found: C 40.79, H 4.37, N 23.79; $C_{20}H_{26}CuN_{10}O_7$ requires: C 41.27, H 4.50, N 24.06%. IR (cm^{-1}): 1676 (*wbr*), 1602 (*m*), 1524 (*m*), 1478 (*m*), 1396 (*s*), 1373 (*s*), 1316 (*s*), 1298 (*s*), 1253 (*s*), 1081 (*s*), 1040 (*s*), 1028 (*s*), 827 (*s*), 743 (*m*), 497 (*s*), 425 (*s*). Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. Infrared spectra were recorded from hexachloro-1,3-butadiene mulls sandwiched between KRS-5 plates (International Crystal Laboratories) on a Bio–Rad Model FTS3000 FT–IR spectrometer.

Crystal data

$[Cu(NO_3)(C_5H_6N_2)_4(H_2O)]NO_3$
$M_r = 582.05$
Triclinic, $P\overline{1}$
$a = 8.448$ (1) Å
$b = 12.309$ (1) Å
$c = 12.841$ (1) Å
$\alpha = 88.562$ (10)°
$\beta = 72.938$ (10)°
$\gamma = 86.242$ (10)°
$V = 1273.8$ (2) Å^3

$Z = 2$
$D_x = 1.518$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33129 reflections
$\theta = 1.0$–27.5°
$\mu = 0.92$ mm^{-1}
$T = 173$ (2) K
Irregular slab, blue
0.30 × 0.28 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
ω scans at fixed $\chi = 55°$
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.770$, $T_{max} = 0.898$
4496 measured reflections

4496 independent reflections
4037 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.129$
$S = 1.06$
4496 reflections
366 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 1.3703P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 1.25$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0070 (17)

Table 1
Selected geometric parameters (Å, °).

Cu—N3	2.021 (3)	Cu—N5	2.035 (3)
Cu—N7	2.033 (3)	Cu—O1	2.271 (2)
Cu—N1	2.034 (3)	Cu—O1N2	2.613 (3)
N3—Cu—N7	172.61 (11)	N1—Cu—O1	91.42 (10)
N3—Cu—N1	89.75 (10)	N5—Cu—O1	89.96 (10)
N7—Cu—N1	88.95 (10)	N3—Cu—O1N2	90.10 (10)
N3—Cu—N5	89.30 (10)	N7—Cu—O1N2	82.76 (10)
N7—Cu—N5	91.82 (11)	N1—Cu—O1N2	94.63 (10)
N1—Cu—N5	178.36 (10)	N5—Cu—O1N2	84.03 (10)
N3—Cu—O1	92.44 (10)	O1—Cu—O1N2	173.45 (9)
N7—Cu—O1	94.86 (11)		

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O1—H1O\cdots O2N2^{i}$	0.82	1.94	2.746 (5)	164
$O1—H2O\cdots O3N1$	0.86	1.88	2.719 (5)	167

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

H atoms were found in difference Fourier maps and refined using a riding model. Disorder of one of the rings (N7), which causes it to occupy two positions related by a 180° rotation, was identified in a difference map. It was modelled so that both components would maintain similar geometry, but was otherwise freely refined.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97 and local procedures.

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