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Tetrakis(1-ethyl-1H-1,2,4-triazole-κN^4)bis(nitrato-κO)copper(II) and bis(nitrato-κO)tetrakis(1-propyl-1H-1,2,4-triazole-κN^4)copper(II)

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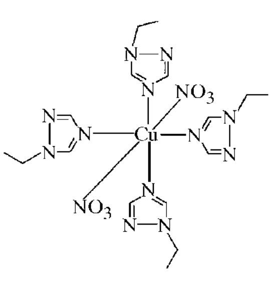
The copper(II) environments for tetrakis(1-ethyl-1,2,4-triazole)dinitratocopper(II), [Cu(NO$_3$)$_2$(C$_4$H$_7$N$_3$)$_4$], and tetrakis(1-propyl-1,2,4-triazole)dinitratocopper(II), [Cu(NO$_3$)$_2$(C$_5$H$_9$N$_3$)$_4$], are distorted square bipyramidal. Both structures are centrosymmetric, with the copper(II) ions located at inversion centers coordinated by four N atoms of four triazole molecules and by two O atoms of two nitrate ions in an elongated octahedral geometry. This elongation is a result of the Jahn–Teller effect. The largest distortion is that of the N—Cu—O angles, which differ from 90° by 5.68 (10)° in the ethyl and 5.59 (8)° in the propyl derivative.

Comment

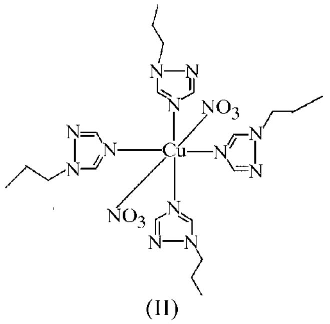
The complexing behavior of 1-alkyl-1,2,4-triazoles has been investigated in aqueous solution by means of pH-metric and spectrophotometric methods (Gabryszewski, 1992). It has been concluded that the bulk of the alkyl group does not influence significantly the stability of complexes of 1-alkyl-1,2,4-triazoles. The stability of such complexes is approximately equal to that of unsubstituted 1,2,4-triazole (Gabryszewski, 1992). This fact suggested coordination of ligands through the N atom in the 4-position, since it is the N atom furthest from the alkyl group and thus the least sterically affected.

The coordination complexes tetrakis(1-ethyl-1,2,4-triazole)dinitratocopper(II), (I), and tetrakis(1-propyl-1,2,4-triazole)dinitratocopper(II), (II), were prepared in the solid state and initially characterized using IR, far-IR and visible spectroscopy, and magnetic susceptibility data (Gabryszewski & Wieczorek, 2000). These methods indicated that the ligands are monodentate and form complexes with distorted octahedral environments. However, in order to determine the donor N atoms of the ligands, the X-ray single-crystal diffraction method was used.

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. Selected geometric parameters are listed in Tables 1 and 3. Both complexes possess a distorted octahedral geometry, with the copper(II) ions located on centers of inversion coordinated by four N atoms of four triazole rings and two O atoms from two nitrate ions. The N atoms form a rectangular plane containing the copper ion at the center. The two nitrate ligands are positioned *trans* to one another, above and below the CuN$_4$ plane, thus completing the tetragonally distorted octahedral coordination of the copper ion. This elongation is a result of the Jahn–Teller effect for Cu^{2+}. Similar elongated octahedral coordination of Cu^{II} atoms is found in other molecules with CuN$_4$O$_2$ environments, *e.g.* bis(2-aminomethylpyridine-κ^2N,N')bis(nitrato-κO)copper(II) (Kooijman *et al.*, 1997), bis(benzene-1,2-diamine)dinitratocopper(II) (Supriya & Das, 2003) and bis(di-2-pyridylamine)dinitratocopper(II) (Muñoz *et al.*, 1993). The Cu—N bond lengths in those compounds are between 1.998 (1) and 2.019 (1) Å, very close to those found in (I) and (II). The Cu—O bond lengths lie between 2.477 (2) (Muñoz *et al.*, 1993) and 2.543 (1) Å (Kooijman *et al.*, 1997), and are significantly longer than those found in (I) and (II).



(I)



(II)

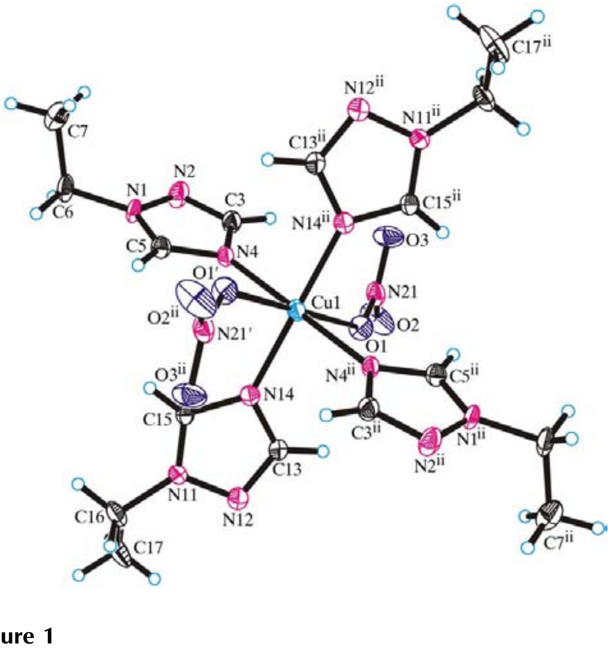


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (ii) $1 - x, 1 - y, 1 - z$.]

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The N—Cu—N angles in (I) and (II) are all close to the ideal in a regular octahedron. The *trans* angles are 180°, as required by symmetry, while the *cis* angles differ only slightly from 90°. For (II), the difference is 0.18 (7)°, whereas for (I), it is 1.21 (11)°. The largest angular distortions of the octahedron occur in the N—Cu—O angles. They differ from 90° by 3.74 (11) and by 5.68 (10)° in (I), and by 0.02 (8) and 5.59 (8)° in (II).

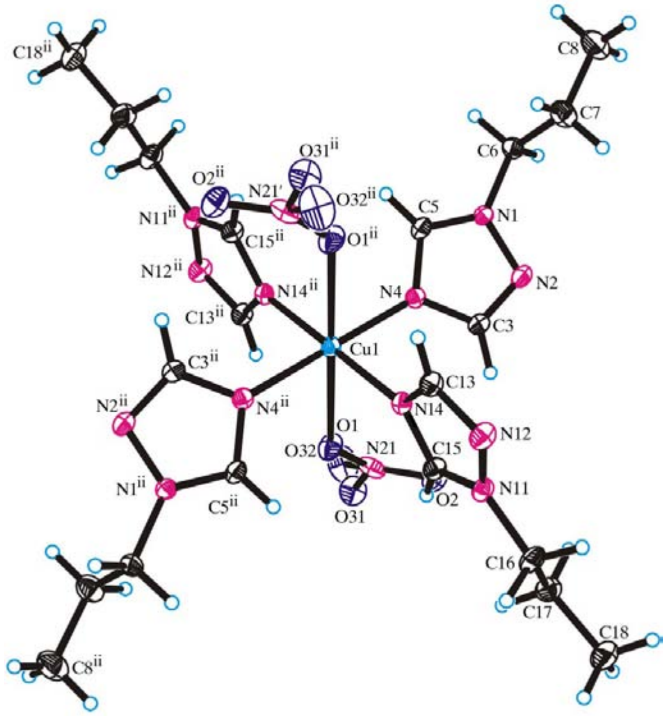

Figure 2
The molecular structure of (II). Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (ii) $1 - x, 1 - y, 1 - z$.]

Examples of complexes containing four 1,2,4-triazole ligands, coordinating through atoms N4, are tetrakis[3,3-dimethyl-1-(1 *H*-1,2,4-triazolyl)-2-butanone]copper(II) diperchlorate (Jiansheng *et al.*, 1997), which shows square-planar coordination of copper(II), and tetrakis[1-(3-chloropropyl)-1,2,4-triazole]bis(tetrafluoroborato)copper(II) (Mills *et al.*, 2002), which has a distorted octahedral coordination. In those structures, the N—Cu bond lengths are similar to those found in (I) and (II). The *cis* N—Cu—N angles again do not differ from 90° by more than 1.5°, while the *trans* N—Cu—N angles differ from 180° by not more than 3.5°.

The N1/N2/C3/N4/C5 plane of the triazole ring is tilted by 47.06 (1)° in (I) and 68.64 (14)° in (II) with respect to the CuN_4 coordination plane, whereas the N11/N12/C13/N14/C15 plane is tilted with respect to the CuN_4 plane by 85.43 (8)° for (I) and 74.25 (14)° for (II).

The packing diagrams of structures (I) and (II) are presented in Figs. 3 and 4. The copper(II) centers of the complexes are well separated, the closest distance being 8.386 (1) Å in (I) and 8.027 (1) Å in (II).

In both structures, there are only weak C—H···O hydrogen bonds, the closest C···O distances being between 3.010 (4) and 3.382 (5) Å in (I), and 3.139 (3) and 3.420 (3) Å in (II) (Tables 2 and 4). The nitrate group in (II) is disordered. We first determined the structures of both (I) and (II) at room temperature. Since the displacement ellipsoid of atom O3 for (II) was very large, we decided to determine both structures at 100 K. We found that the distortion of atom O3 is also present at 100 K, and therefore it was split into two positions, each with an occupancy of 50%, denoted O31 and O32. The disorder apparently arises from the fact that there is a possibility of forming hydrogen bonds at both positions, *viz*. C5–H5*A*···O31^{i} and C13–H13*A*···O32^{ii} [symmetry codes: (i) $x - 1, y, z$; (ii) $x - 1, 1 + y, z$].

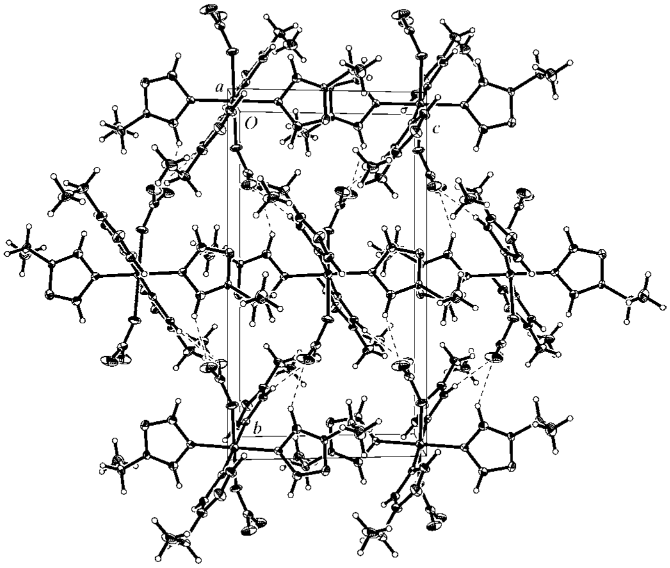

Figure 3
A packing diagram of (I). Displacement ellipsoids are shown at the 50% probability level. Dashed lines indicate C—H···O hydrogen bonds.

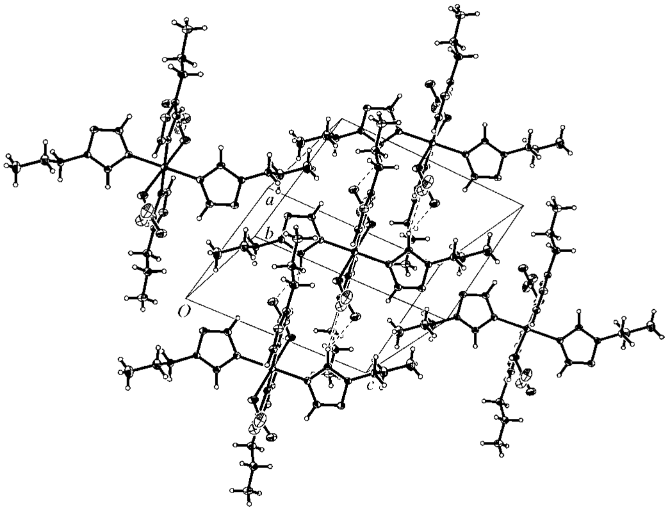

Figure 4
A packing diagram of (II). Displacement ellipsoids are shown at the 50% probability level. Dashed lines indicate C—H···O hydrogen bonds.

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Experimental

1-Ethyl-1,2,4-triazole (m.p. 451 K) and 1-propyl-1,2,4-triazole (m.p. 462–463 K) were synthesized in the Walocha–Nowak Chemical Laboratory in Cracow (Poland). Other chemicals were procured from POCh–Gliwice (Poland). The complexes were formed during the reaction of ethanol solutions of the ligands with $Cu(NO_3)_2$. A solution of $Cu(NO_3)_2$ (5 mmol) in anhydrous ethanol (30 ml) with ethyl orthoformate (2 ml) was added to a solution of the ligand (35 mmol) in anhydrous ethanol (60 ml) with stirring. Blue complexes of Cu^{II} were formed. The products were each digested on a water bath for 1 h, washed repeatedly with anhydrous ethanol and ethyl ether, and dried in a vacuum desiccator.

Compound (I)

Crystal data

$[Cu(NO_3)_2(C_4H_7N_3)_4]$
$M_r = 576.06$
Monoclinic, $P2_1/c$
$a = 9.703\ (2)$ Å
$b = 15.288\ (3)$ Å
$c = 8.386\ (2)$ Å
$\beta = 99.97\ (1)°$
$V = 1225.2\ (5)$ Å^3
$Z = 2$
$D_x = 1.561$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7990 reflections
$\theta = 3.3$–$26.0°$
$\mu = 0.96$ mm^{-1}
$T = 100.0\ (1)$ K
Plate, blue
0.2 × 0.2 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
7990 measured reflections
2384 independent reflections
1339 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.085$
$\theta_{\max} = 26.0°$
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 18$
$l = -8 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.089$
$S = 0.83$
2386 reflections
215 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.023P)^2]$
where $P = (F_o^2 + 2F_o^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N14	1.990 (3)	N21—O2	1.239 (4)
Cu1—N4	2.020 (3)	N21—O3	1.248 (4)
Cu1—O1	2.394 (3)	N21—O1	1.266 (4)
N14—Cu1—N4	91.21 (11)	O2—N21—O1	119.1 (3)
N14—Cu1—O1	86.26 (11)	O3—N21—O1	120.0 (3)
N4—Cu1—O1	95.68 (10)	N21—O1—Cu1	135.2 (2)
O2—N21—O3	120.9 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O3	0.93	2.54	3.382 (5)	151
C5—H5A···O2$^{\rm i}$	0.93	2.36	3.178 (5)	146
C5—H5A···O1$^{\rm ii}$	0.93	2.56	3.010 (4)	111
C15—H15A···O3$^{\rm i}$	0.93	2.40	3.237 (4)	149
C17—H17A···O2$^{\rm iii}$	0.96	2.60	3.180 (5)	120

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

Compound (II)

Crystal data

$[Cu(NO_3)_2(C_5H_9N_3)_4]$
$M_r = 632.18$
Triclinic, $P\overline{1}$
$a = 8.027\ (6)$ Å
$b = 8.523\ (5)$ Å
$c = 11.672\ (5)$ Å
$\alpha = 89.67\ (4)°$
$\beta = 73.50\ (5)°$
$\gamma = 70.19\ (6)°$
$V = 716.7\ (8)$ Å^3
$Z = 1$
$D_x = 1.465$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4840 reflections
$\theta = 3.1$–$26.0°$
$\mu = 0.82$ mm^{-1}
$T = 100.0\ (1)$ K
Needle, blue
0.2 × 0.1 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
4840 measured reflections
2766 independent reflections
2358 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 26.0°$
$h = -6 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.061$
$S = 0.98$
2766 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—N4	2.007 (2)	N21—O31	1.226 (2)
Cu1—N14	2.018 (2)	N21—O2	1.255 (2)
Cu1—O1	2.416 (2)	N21—O32	1.296 (2)
O1—N21	1.259 (2)		
N4—Cu1—N14$^{\rm ii}$	90.18 (7)	O31—N21—O1	124.75 (16)
N4—Cu1—O1	95.59 (8)	O2—N21—O1	120.47 (15)
N14—Cu1—O1	90.02 (8)	O2—N21—O32	127.05 (15)
N21—O1—Cu1	134.70 (11)	O1—N21—O32	111.38 (16)
O31—N21—O2	113.35 (16)		

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

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O2	0.93	2.43	3.158 (3)	135
C15—H15···O1	0.93	2.60	3.139 (3)	118
C15—H15···O2	0.93	2.39	3.147 (4)	139
C5—H5A···O2$^{\rm iv}$	0.93	2.49	3.202 (3)	133
C5—H5A···O31$^{\rm iv}$	0.93	2.55	3.420 (3)	157
C13—H13···O32$^{\rm v}$	0.93	2.55	3.234 (4)	131

Symmetry codes: (iv) $x-1, y, z$; (v) $x-1, y+1, z$.

H atoms were treated as riding atoms [C—H = 0.93 (CH), 0.97 (CH_2) and 0.96 Å (CH_3), and $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$ (methyl) or $1.2U_{\rm eq}(C)$ (other H atoms)].

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); publication software: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1194). Services for accessing these data are described at the back of the journal.

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