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A [Cu$_3$(μ_3-O)]–pyrazolate metallacycle with terminal nitrate ligands exhibiting point group symmetry 3

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The trinuclear triangular cuprate anion of the title compound, tris[bis(triphenylphosphoranylidene)ammonium] tris(μ_2-4-chloropyrazolato-$\kappa^2N:N'$)-μ_3-oxido-tris[(nitrato-κ^2O,O')cuprate(II)] nitrate monohydrate, (C$_{36}$H$_{30}$P$_2$N)-[Cu$_3$(C$_3$H$_2$ClN$_2$)$_3$(NO$_3$)$_3$O]NO$_3$·H$_2$O, has point group symmetry 3., with the μ_3-O atom located on the threefold rotation axis. The distorted square-pyramidal coordination sphere of the Cu^{II} atom is completed by two N atoms of *trans*-bridging pyrazolate groups and a chelating nitrate anion. The complex anion is slightly bent, with the nitrate and pyrazolate groups occupying positions above and below the Cu$_3$ plane, respectively. In the crystal, weak O—H···O and C—H···O hydrogen bonds, as well as π–π interactions, are present.

1. Chemical context

Trinuclear copper complexes with a triangular arrangement of the copper(II) cations are of importance in terms of their magnetic and redox properties (Rivera-Carrillo *et al.*, 2008). Moreover, Cu$_3$(μ_3-O/OH) moieties make up the active sites of several multicopper oxidase enzymes (Solomon *et al.*, 2014). Pyrazolate anions as ligands are of bidentate chelating nature and are able to bind to the the Cu^{II} cations in suitable angles to form triangular complexes (Halcrow, 2009; Viciano-Chumillas *et al.*, 2010).
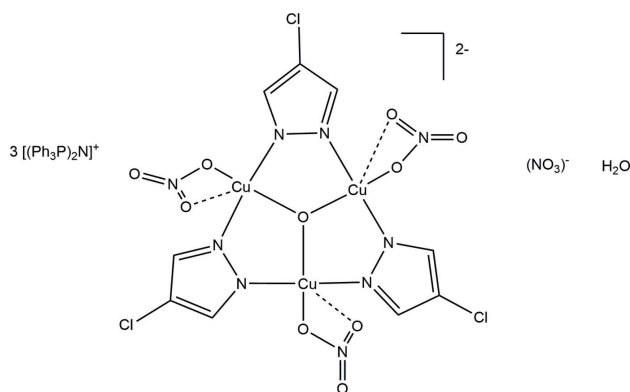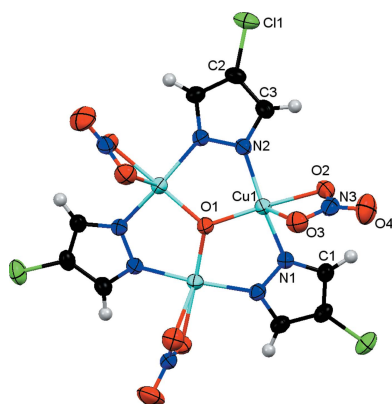
Nitrato and pyrazolato ligands are commonly studied ligands in Cu^{II} coordination chemistry. Simple Cu^{II} nitrate complexes are aplenty in the literature and have been studied in detail with respect to their part in the nitrogen cycle. Triangular trinuclear Cu^{II} complexes with terminal nitrate ligands, however, are scarcer (Alsalme *et al.*, 2014). Nitrates, being good hydrogen-bonding acceptors, are able to form Cu$_3$(μ_3-OH) complexes, with hydrogen bonds to the μ_3-OH group and to ancilliary ligands and water molecules.
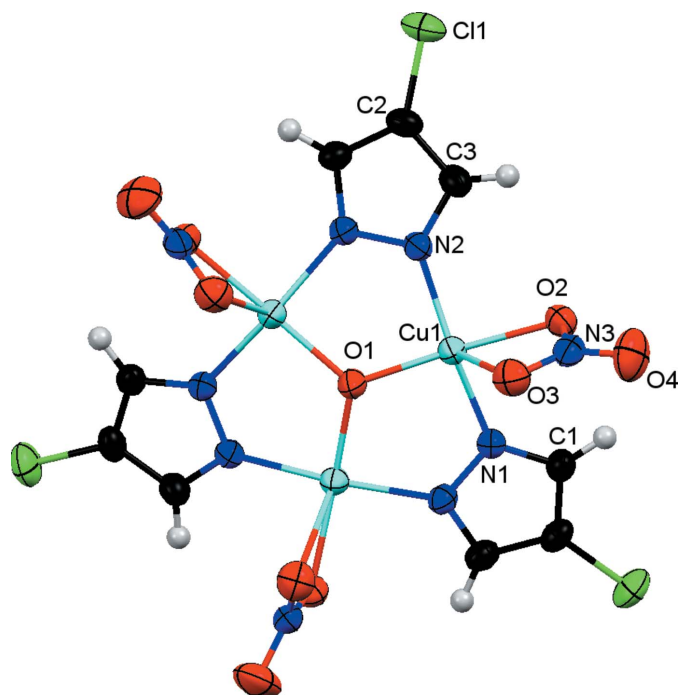
Figure 1
The molecular structure of the trinuclear pyrazolatocuprate anion in the title compound showing the atom-labeling scheme for the symmetry-independent atoms. Non-H atoms are shown as displacement ellipsoids at the 30% probability level.

In this communication we describe the accidental synthesis and the structure of a trinuclear Cu–pyrazolato complex, *viz.* $(PPN)_3[Cu_3(\mu_3-O)(\mu-4-Clpz)_3(NO_3)_3](NO_3)\cdot H_2O$, where PPN = bis(triphenylphosphoranylidene)ammonium; 4-Cl-pz =

Table 1
Selected bond lengths (Å).

Cu1—O1	1.8816 (7)	Cu1—O2	2.059 (3)
Cu1—N2	1.952 (4)	Cu1—O3	2.483 (4)
Cu1—N1	1.960 (4)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13$\cdots$O3^i	0.93	2.53	3.410 (11)	157

Symmetry code: (i) $-x + y + \frac{4}{3}, -x + \frac{2}{3}, z - \frac{1}{3}$.

4-chloropyrazolate. A related Cu_3-pyrazolato complex was reported by Angaridis *et al.* (2002).

2. Structural commentary

The nine-membered metallacycle Cu_3N_6 in the cuprate anion (Fig. 1) is strung together by a μ_3-O group located at the center of the triangle (point group symmetry of the complete molecule 3.), forming an almost planar $Cu_3(\mu_3-O)$-core, where the μ_3-O atom O1 is located 0.122 (7) Å above the Cu_3 plane. The distorted square-pyramidal geometry of the Cu^{II} atom is completed by the two N atoms of symmetry-related *trans*-bridging pyrazolato ligands, and a terminal nitrato ligand that is bound to the metal in a chelating fashion (Table 1). The complex is slightly bent with the nitrate and pyrazolato groups occupying positions above and below the Cu_3 plane, respectively. The Cl atom of the pyrazole anion is located approximately 1.28 Å below the Cu_3 plane. The non-coordinating
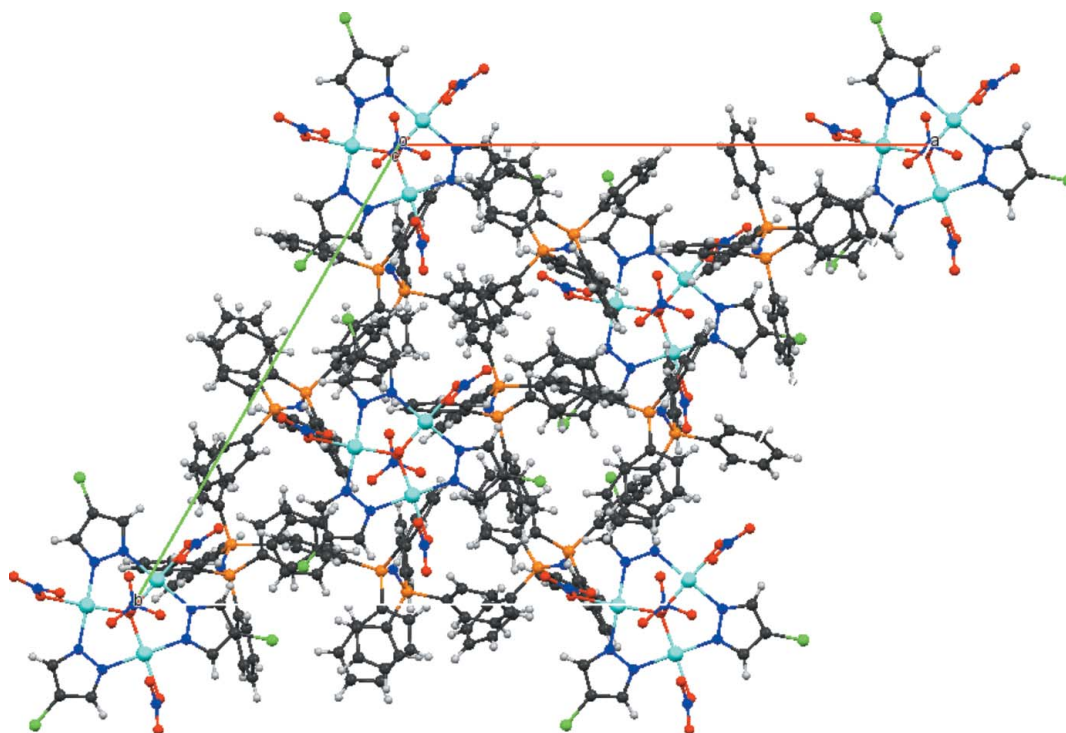

Figure 2
The crystal packing diagram for the title compound shown down [001].

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Crystal data	
Chemical formula	$(C_{36}H_{30}P_2N)[Cu_3(C_3H_2ClN_2)_3(NO_3)_3O]NO_3 \cdot H_2O$
M_r	2390.85
Crystal system, space group	Trigonal, $R3$
Temperature (K)	296
a, c (Å)	23.038 (2), 18.4214 (17)
V (Å^3)	8466.9 (17)
Z	3
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.79
Crystal size (mm)	$0.23 \times 0.14 \times 0.13$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2005)
T_{min}, T_{max}	0.840, 0.905
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30414, 7675, 6428
R_{int}	0.033
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.088, 1.03
No. of reflections	7675
No. of parameters	468
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.41, −0.29
Absolute structure	Flack x determined using 2750 quotients [$(I^+)-(I^-)$]/[$(I^+)+(I^-)$] (Parsons *et al.*, 2013)
Absolute structure parameter	0.004 (5)

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

nitrate counter-anion is located about a special position with the nitrogen atom on the threefold rotation axis.

The triphenylphosphene groups in the PPN cation are staggered around the central N atom [P—N—P angle 139.5 (2)°] and show bond lengths and angles characteristic for this unit (Beckett *et al.*, 2010).

3. Supramolecular features

The interstitial water O atom is also located on a threefold rotation axis which consequently results in disordered H atoms of this moiety. Although these H atoms could not be located, three O⋯O distances to the chelating nitrate anions of 3.367 (6) Å point to weak O—H⋯O hydrogen bonds in the structure. This nitrate O atom is additionally involved in weak non-classical hydrogen-bonding interactions with one of the C–H groups of the PPN cation (Table 2). The latter shows also π–π interactions [3.902 (7) Å] with one of the pyrazolate rings, leading to an overall three-dimensional network. The packing of the molecular units is shown in Fig. 2.

4. Synthesis and crystallization

4-Cl-pz and the hexanuclear Cu$_6$-pyrazolato complex (PPN)[{Cu$_3$(μ_3-O)(μ-4-Cl-pz)$_3$}$_2$(μ-3,5-Ph$_2$pz)$_3$], were synthesized by published procedures (Maresca *et al.*, 1997; Mezei *et al.*, 2007). (NH$_4$)$_2$Ce(NO$_3$)$_6$ (2 eq.) was dissolved in 5 ml of acetonitrile and was layered over a CH$_2$Cl$_2$ solution of the hexanuclear copper(II) complex (1 eq.). Slow mixing of the reactants and solvent evaporation over a few weeks yielded dark-blue crystals of the title compound.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were placed geometrically, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). The isolated water solvent O atom, O1*W*, was refined isotropically. H atoms bound to the water oxygen atom could not be placed satisfactorily with agreeable occupancy as O1*W* resides on a threefold rotation axis, resulting in crystallographically disordered H atoms. These H atoms were not modelled but are included in the formula of the title compound.

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supporting information

A [Cu₃(μ₃-O)]–pyrazolate metallacycle with terminal nitrate ligands exhibiting point group symmetry 3

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Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

\ Tris[bis(triphenylphosphoranylidene)ammonium] tris(μ_2-4-chloropyrazolato-κ^2N:N')-μ_3-oxido-\ tris[(nitrato-κ^2O,O')cuprate(II)] nitrate monohydrate

Crystal data

$(C_{36}H_{30}P_2N)[Cu_3(C_3H_2ClN_2)_3(NO_3)_3O]NO_3 \cdot H_2O$	$D_x = 1.407$ Mg m^{-3}
$M_r = 2390.85$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $R3$	Cell parameters from 9882 reflections
$a = 23.038$ (2) Å	$\theta = 2.3$–26.0°
$c = 18.4214$ (17) Å	$\mu = 0.79$ mm^{-1}
$V = 8466.9$ (17) Å^3	$T = 296$ K
$Z = 3$	Polygon, blue
$F(000) = 3687$	0.23 × 0.14 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer	30414 measured reflections
Radiation source: sealed tube	7675 independent reflections
Graphite monochromator	6428 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.033$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$\theta_{max} = 26.4°$, $\theta_{min} = 2.3°$
	$h = -28 \rightarrow 28$
	$k = -28 \rightarrow 28$
$T_{min} = 0.840$, $T_{max} = 0.905$	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.1352P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.41$ e Å^{-3}
7675 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
468 parameters	Absolute structure: Flack x determined using
1 restraint	2750 quotients [(I^+)-(I^-)]/[(I^+)+(I^-)] (Parsons *et al.*, 2013)
Hydrogen site location: inferred from neighbouring sites	Absolute structure parameter: 0.004 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1W	0.0000	1.0000	0.3698 (7)	0.141 (4)*
Cu1	0.57819 (3)	0.31688 (3)	0.88140 (3)	0.04893 (15)
O1	0.6667	0.3333	0.8748 (4)	0.0691 (18)
O2	0.48058 (17)	0.29648 (18)	0.8736 (2)	0.0619 (9)
N1	0.54504 (18)	0.22155 (19)	0.8997 (2)	0.0504 (9)
N2	0.61014 (18)	0.41208 (18)	0.8960 (2)	0.0493 (9)
N3	0.4670 (2)	0.28251 (19)	0.8087 (3)	0.0582 (10)
C1	0.4851 (2)	0.1710 (2)	0.9186 (3)	0.0590 (12)
H1	0.4465	0.1738	0.9249	0.071*
C2	0.4893 (3)	0.1144 (2)	0.9272 (3)	0.0570 (12)
C3	0.5783 (3)	0.4455 (3)	0.9126 (3)	0.0582 (12)
H3	0.5321	0.4274	0.9141	0.070*
Cl1	0.42537 (8)	0.03570 (7)	0.95132 (10)	0.0859 (5)
O3	0.5141 (2)	0.2937 (2)	0.7664 (2)	0.0753 (10)
O4	0.4095 (2)	0.2572 (3)	0.7874 (3)	0.1105 (17)
P1	0.81315 (5)	0.23893 (5)	0.23155 (5)	0.0379 (2)
P2	0.78221 (5)	0.16748 (5)	0.37198 (5)	0.0392 (2)
N4	0.78666 (18)	0.21790 (18)	0.31150 (18)	0.0461 (8)
C4	0.7627 (2)	0.1937 (2)	0.4558 (2)	0.0440 (10)
C5	0.7353 (2)	0.2344 (2)	0.4544 (2)	0.0487 (11)
H5	0.7293	0.2500	0.4101	0.058*
C6	0.7165 (3)	0.2526 (3)	0.5183 (3)	0.0625 (13)
H6	0.6978	0.2803	0.5167	0.075*
C7	0.7254 (3)	0.2299 (3)	0.5829 (3)	0.0754 (17)
H7	0.7129	0.2424	0.6256	0.090*
C8	0.7527 (3)	0.1887 (3)	0.5860 (3)	0.0788 (17)
H8	0.7584	0.1732	0.6305	0.095*
C9	0.7717 (3)	0.1703 (3)	0.5224 (3)	0.0615 (13)
H9	0.7904	0.1427	0.5242	0.074*
C10	0.8593 (2)	0.1669 (2)	0.3837 (2)	0.0463 (10)
C11	0.9135 (2)	0.2251 (3)	0.4090 (3)	0.0610 (12)
H11	0.9081	0.2606	0.4241	0.073*
C12	0.9761 (3)	0.2304 (4)	0.4120 (3)	0.0801 (18)
H12	1.0128	0.2696	0.4289	0.096*
C13	0.9836 (3)	0.1783 (4)	0.3899 (3)	0.0796 (18)
H13	1.0257	0.1819	0.3922	0.095*
C14	0.9302 (3)	0.1205 (4)	0.3645 (4)	0.0833 (18)
H14	0.9363	0.0855	0.3490	0.100*
C15	0.8679 (3)	0.1139 (3)	0.3617 (3)	0.0629 (13)

H15	0.8315	0.0743	0.3451	0.075*
C16	0.7162 (2)	0.0829 (2)	0.3546 (2)	0.0467 (10)
C17	0.6790 (2)	0.0681 (3)	0.2917 (3)	0.0569 (12)
H17	0.6875	0.1021	0.2589	0.068*
C18	0.6291 (3)	0.0032 (3)	0.2771 (3)	0.0732 (15)
H18	0.6053	−0.0064	0.2338	0.088*
C19	0.6146 (3)	−0.0466 (3)	0.3259 (4)	0.0771 (17)
H19	0.5810	−0.0902	0.3158	0.093*
C20	0.6493 (3)	−0.0327 (3)	0.3896 (4)	0.0807 (18)
H20	0.6381	−0.0665	0.4236	0.097*
C21	0.7012 (3)	0.0315 (3)	0.4039 (3)	0.0737 (16)
H21	0.7260	0.0403	0.4465	0.088*
C22	0.8529 (2)	0.1956 (2)	0.1928 (2)	0.0414 (9)
C23	0.8160 (2)	0.1331 (2)	0.1628 (3)	0.0532 (11)
H23	0.7698	0.1141	0.1578	0.064*
C24	0.8467 (3)	0.0979 (3)	0.1398 (3)	0.0678 (14)
H24	0.8214	0.0559	0.1185	0.081*
C25	0.9149 (3)	0.1251 (3)	0.1483 (3)	0.0666 (14)
H25	0.9355	0.1010	0.1339	0.080*
C26	0.9520 (3)	0.1870 (3)	0.1778 (3)	0.0630 (13)
H26	0.9980	0.2055	0.1828	0.076*
C27	0.9219 (2)	0.2228 (2)	0.2003 (3)	0.0505 (10)
H27	0.9477	0.2652	0.2204	0.061*
C28	0.7444 (2)	0.2268 (2)	0.1749 (2)	0.0415 (9)
C29	0.6909 (2)	0.2287 (2)	0.2075 (3)	0.0526 (11)
H29	0.6902	0.2334	0.2575	0.063*
C30	0.6394 (2)	0.2237 (3)	0.1659 (3)	0.0674 (14)
H30	0.6037	0.2250	0.1880	0.081*
C31	0.6397 (3)	0.2167 (3)	0.0916 (3)	0.0738 (16)
H31	0.6048	0.2140	0.0636	0.089*
C32	0.6910 (3)	0.2138 (3)	0.0599 (3)	0.0698 (15)
H32	0.6906	0.2081	0.0098	0.084*
C33	0.7439 (3)	0.2192 (3)	0.1000 (2)	0.0578 (12)
H33	0.7791	0.2176	0.0772	0.069*
C34	0.8736 (2)	0.3267 (2)	0.2287 (3)	0.0468 (10)
C35	0.8897 (3)	0.3652 (3)	0.2894 (4)	0.0845 (19)
H35	0.8686	0.3462	0.3331	0.101*
C36	0.9372 (5)	0.4322 (3)	0.2866 (5)	0.123 (3)
H36	0.9495	0.4580	0.3287	0.147*
C37	0.9664 (4)	0.4611 (3)	0.2211 (5)	0.106 (3)
H37	0.9980	0.5065	0.2190	0.127*
C38	0.9497 (3)	0.4245 (3)	0.1612 (4)	0.0813 (18)
H38	0.9697	0.4445	0.1173	0.098*
C39	0.9028 (3)	0.3568 (2)	0.1633 (3)	0.0632 (13)
H39	0.8908	0.3316	0.1208	0.076*
N5	0.6667	0.3333	0.3566 (5)	0.069 (2)
O5	0.6275 (3)	0.2721 (2)	0.3545 (3)	0.1083 (16)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0436 (3)	0.0458 (3)	0.0582 (3)	0.0230 (3)	0.0029 (3)	0.0017 (3)
O1	0.044 (2)	0.044 (2)	0.119 (6)	0.0220 (10)	0.000	0.000
O2	0.058 (2)	0.069 (2)	0.065 (2)	0.0356 (18)	0.0048 (17)	−0.0040 (18)
N1	0.044 (2)	0.046 (2)	0.060 (2)	0.0217 (18)	0.0012 (17)	−0.0010 (17)
N2	0.049 (2)	0.048 (2)	0.054 (2)	0.0268 (19)	0.0061 (17)	0.0045 (17)
N3	0.054 (3)	0.048 (2)	0.073 (3)	0.025 (2)	−0.011 (2)	0.007 (2)
C1	0.047 (3)	0.053 (3)	0.069 (3)	0.019 (2)	0.005 (2)	−0.002 (2)
C2	0.059 (3)	0.045 (3)	0.051 (3)	0.014 (2)	−0.001 (2)	0.005 (2)
C3	0.060 (3)	0.061 (3)	0.062 (3)	0.037 (3)	0.011 (2)	0.014 (2)
Cl1	0.0748 (10)	0.0513 (8)	0.0996 (11)	0.0075 (7)	0.0071 (8)	0.0112 (7)
O3	0.084 (3)	0.078 (3)	0.064 (2)	0.040 (2)	0.008 (2)	0.0030 (19)
O4	0.068 (3)	0.129 (4)	0.118 (4)	0.037 (3)	−0.030 (3)	0.004 (3)
P1	0.0386 (6)	0.0401 (6)	0.0386 (5)	0.0224 (5)	0.0019 (4)	0.0017 (4)
P2	0.0378 (5)	0.0423 (6)	0.0376 (5)	0.0200 (5)	−0.0016 (4)	0.0010 (4)
N4	0.053 (2)	0.055 (2)	0.0393 (18)	0.0341 (19)	0.0026 (16)	0.0058 (16)
C4	0.038 (2)	0.044 (2)	0.040 (2)	0.0136 (19)	−0.0028 (17)	−0.0008 (18)
C5	0.046 (2)	0.050 (3)	0.046 (3)	0.021 (2)	0.0003 (19)	−0.0051 (19)
C6	0.055 (3)	0.063 (3)	0.064 (3)	0.025 (3)	0.010 (2)	−0.008 (3)
C7	0.068 (4)	0.094 (4)	0.054 (3)	0.033 (3)	0.009 (3)	−0.020 (3)
C8	0.083 (4)	0.100 (5)	0.036 (3)	0.033 (4)	0.001 (2)	0.007 (3)
C9	0.071 (3)	0.076 (3)	0.043 (3)	0.041 (3)	−0.003 (2)	0.003 (2)
C10	0.041 (2)	0.057 (3)	0.044 (2)	0.027 (2)	0.0013 (18)	0.008 (2)
C11	0.048 (3)	0.065 (3)	0.066 (3)	0.026 (3)	−0.007 (2)	−0.005 (3)
C12	0.042 (3)	0.103 (5)	0.078 (4)	0.023 (3)	−0.008 (3)	0.005 (3)
C13	0.057 (4)	0.120 (6)	0.077 (4)	0.056 (4)	0.006 (3)	0.027 (4)
C14	0.081 (4)	0.098 (5)	0.099 (5)	0.066 (4)	0.006 (4)	0.009 (4)
C15	0.059 (3)	0.061 (3)	0.080 (3)	0.038 (3)	0.004 (3)	0.008 (3)
C16	0.040 (2)	0.046 (2)	0.054 (3)	0.022 (2)	0.0006 (19)	0.000 (2)
C17	0.048 (3)	0.059 (3)	0.056 (3)	0.022 (2)	−0.009 (2)	−0.003 (2)
C18	0.055 (3)	0.079 (4)	0.071 (3)	0.023 (3)	−0.013 (3)	−0.020 (3)
C19	0.051 (3)	0.055 (3)	0.105 (5)	0.011 (3)	−0.001 (3)	−0.022 (3)
C20	0.073 (4)	0.048 (3)	0.103 (5)	0.017 (3)	−0.004 (3)	0.009 (3)
C21	0.069 (3)	0.055 (3)	0.077 (4)	0.016 (3)	−0.015 (3)	0.011 (3)
C22	0.041 (2)	0.046 (2)	0.042 (2)	0.026 (2)	0.0018 (17)	0.0011 (18)
C23	0.044 (2)	0.046 (3)	0.067 (3)	0.021 (2)	0.002 (2)	−0.006 (2)
C24	0.067 (3)	0.050 (3)	0.090 (4)	0.032 (3)	0.005 (3)	−0.016 (3)
C25	0.069 (4)	0.063 (3)	0.087 (4)	0.047 (3)	0.020 (3)	0.005 (3)
C26	0.045 (3)	0.068 (3)	0.085 (4)	0.035 (3)	0.012 (2)	0.008 (3)
C27	0.042 (2)	0.047 (3)	0.065 (3)	0.025 (2)	0.002 (2)	−0.001 (2)
C28	0.044 (2)	0.042 (2)	0.043 (2)	0.0243 (19)	0.0007 (17)	0.0019 (17)
C29	0.053 (3)	0.062 (3)	0.052 (3)	0.036 (2)	0.002 (2)	0.000 (2)
C30	0.049 (3)	0.077 (4)	0.086 (4)	0.038 (3)	−0.006 (3)	−0.004 (3)
C31	0.069 (4)	0.079 (4)	0.082 (4)	0.044 (3)	−0.026 (3)	−0.001 (3)
C32	0.080 (4)	0.088 (4)	0.049 (3)	0.047 (3)	−0.013 (3)	0.004 (3)
C33	0.064 (3)	0.076 (3)	0.045 (3)	0.043 (3)	0.001 (2)	0.006 (2)

C34	0.046 (2)	0.038 (2)	0.059 (3)	0.023 (2)	0.004 (2)	−0.0018 (19)
C35	0.089 (4)	0.055 (3)	0.077 (4)	0.011 (3)	0.013 (3)	−0.009 (3)
C36	0.157 (8)	0.054 (4)	0.106 (6)	0.015 (4)	0.015 (5)	−0.025 (4)
C37	0.084 (5)	0.045 (3)	0.166 (8)	0.015 (3)	0.029 (5)	0.000 (4)
C38	0.074 (4)	0.055 (3)	0.118 (5)	0.035 (3)	0.035 (4)	0.021 (4)
C39	0.064 (3)	0.049 (3)	0.074 (3)	0.026 (3)	0.017 (3)	0.009 (2)
N5	0.065 (3)	0.065 (3)	0.077 (5)	0.0327 (16)	0.000	0.000
O5	0.090 (3)	0.074 (3)	0.150 (5)	0.032 (3)	0.020 (3)	0.000 (3)

Geometric parameters (Å, º)

Cu1—O1	1.8816 (7)	C10—C15	1.393 (7)
Cu1—N2	1.952 (4)	C11—C12	1.385 (8)
Cu1—N1	1.960 (4)	C12—C13	1.360 (9)
Cu1—O2	2.059 (3)	C13—C14	1.366 (9)
Cu1—O3	2.483 (4)	C14—C15	1.367 (8)
O1—Cu1^{i}	1.8816 (7)	C16—C17	1.379 (6)
O1—Cu1^{ii}	1.8816 (7)	C16—C21	1.391 (7)
O2—N3	1.237 (5)	C17—C18	1.382 (7)
N1—C1	1.334 (6)	C18—C19	1.362 (9)
N1—N2^{i}	1.345 (5)	C19—C20	1.365 (9)
N2—C3	1.337 (6)	C20—C21	1.386 (8)
N2—N1^{ii}	1.345 (5)	C22—C23	1.371 (6)
N3—O4	1.215 (6)	C22—C27	1.393 (6)
N3—O3	1.253 (6)	C23—C24	1.382 (7)
C1—C2	1.364 (7)	C24—C25	1.379 (8)
C2—C3^{i}	1.368 (7)	C25—C26	1.356 (8)
C2—Cl1	1.727 (5)	C26—C27	1.381 (6)
C3—C2^{ii}	1.368 (7)	C28—C33	1.389 (6)
P1—N4	1.575 (4)	C28—C29	1.391 (6)
P1—C34	1.794 (4)	C29—C30	1.368 (7)
P1—C28	1.799 (4)	C30—C31	1.379 (8)
P1—C22	1.805 (4)	C31—C32	1.350 (8)
P2—N4	1.576 (4)	C32—C33	1.378 (7)
P2—C10	1.795 (4)	C34—C35	1.358 (7)
P2—C4	1.795 (4)	C34—C39	1.386 (7)
P2—C16	1.802 (4)	C35—C36	1.376 (9)
C4—C5	1.366 (6)	C36—C37	1.379 (11)
C4—C9	1.397 (6)	C37—C38	1.323 (10)
C5—C6	1.391 (7)	C38—C39	1.384 (8)
C6—C7	1.356 (8)	N5—O5^{i}	1.238 (5)
C7—C8	1.379 (9)	N5—O5	1.238 (5)
C8—C9	1.388 (8)	N5—O5^{ii}	1.238 (5)
C10—C11	1.378 (7)		
O1—Cu1—N2	91.18 (12)	C8—C9—C4	119.5 (5)
O1—Cu1—N1	90.73 (12)	C11—C10—C15	119.6 (4)
N2—Cu1—N1	162.20 (16)	C11—C10—P2	117.0 (4)

O1—Cu1—O2	172.2 (2)	C15—C10—P2	123.2 (4)
N2—Cu1—O2	91.22 (15)	C10—C11—C12	119.8 (5)
N1—Cu1—O2	89.25 (14)	C13—C12—C11	119.8 (6)
Cu1—O1—Cu1^i	119.59 (5)	C12—C13—C14	120.8 (5)
Cu1—O1—Cu1^{ii}	119.59 (5)	C13—C14—C15	120.4 (6)
Cu1^i—O1—Cu1^{ii}	119.59 (5)	C14—C15—C10	119.6 (6)
N3—O2—Cu1	103.4 (3)	C17—C16—C21	118.6 (4)
C1—N1—N2^i	108.1 (4)	C17—C16—P2	120.0 (4)
C1—N1—Cu1	132.6 (3)	C21—C16—P2	121.4 (4)
N2^i—N1—Cu1	119.3 (3)	C16—C17—C18	120.6 (5)
C3—N2—N1^{ii}	108.3 (4)	C19—C18—C17	120.3 (5)
C3—N2—Cu1	132.1 (3)	C18—C19—C20	120.1 (5)
N1^{ii}—N2—Cu1	118.9 (3)	C19—C20—C21	120.4 (6)
O4—N3—O2	120.7 (5)	C20—C21—C16	119.9 (5)
O4—N3—O3	121.5 (5)	C23—C22—C27	118.8 (4)
O2—N3—O3	117.9 (4)	C23—C22—P1	121.4 (3)
N1—C1—C2	109.1 (4)	C27—C22—P1	119.4 (3)
C1—C2—C3^i	105.8 (4)	C22—C23—C24	120.6 (4)
C1—C2—Cl1	127.0 (4)	C25—C24—C23	120.0 (5)
C3^i—C2—Cl1	127.2 (4)	C26—C25—C24	119.9 (5)
N2—C3—C2^{ii}	108.6 (4)	C25—C26—C27	120.6 (5)
N4—P1—C34	109.7 (2)	C26—C27—C22	120.1 (5)
N4—P1—C28	108.61 (19)	C33—C28—C29	118.8 (4)
C34—P1—C28	106.6 (2)	C33—C28—P1	123.1 (3)
N4—P1—C22	115.14 (19)	C29—C28—P1	118.1 (3)
C34—P1—C22	106.8 (2)	C30—C29—C28	120.1 (5)
C28—P1—C22	109.62 (19)	C29—C30—C31	120.6 (5)
N4—P2—C10	113.0 (2)	C32—C31—C30	119.5 (5)
N4—P2—C4	107.2 (2)	C31—C32—C33	121.3 (5)
C10—P2—C4	108.3 (2)	C32—C33—C28	119.7 (5)
N4—P2—C16	112.4 (2)	C35—C34—C39	118.9 (5)
C10—P2—C16	108.4 (2)	C35—C34—P1	121.2 (4)
C4—P2—C16	107.4 (2)	C39—C34—P1	119.9 (4)
P1—N4—P2	139.5 (2)	C34—C35—C36	120.4 (6)
C5—C4—C9	119.3 (4)	C35—C36—C37	119.7 (7)
C5—C4—P2	119.6 (3)	C38—C37—C36	120.5 (6)
C9—C4—P2	121.0 (4)	C37—C38—C39	120.6 (6)
C4—C5—C6	120.8 (5)	C38—C39—C34	119.8 (5)
C7—C6—C5	119.7 (5)	O5^i—N5—O5	119.91 (5)
C6—C7—C8	120.7 (5)	O5^i—N5—O5^{ii}	119.90 (6)
C7—C8—C9	119.8 (5)	O5—N5—O5^{ii}	119.91 (5)

Symmetry codes: (i) −*y*+1, *x*−*y*, *z*; (ii) −*x*+*y*+1, −*x*+1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C13—H13···O3[iii]	0.93	2.53	3.410 (11)	157

Symmetry code: (iii) $-x+y+4/3$, $-x+2/3$, $z-1/3$.