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Crystal structure of (*N*,*N*′-ethylenebis{3-[2-(3-nitrophenyl)hydrazin-1-ylidene]-4-oxopentan-2-iminato})copper(II)–3-[2-(3-nitrophenyl)hydrazin-1-ylidene]pentane-2,4-dione (1/1)

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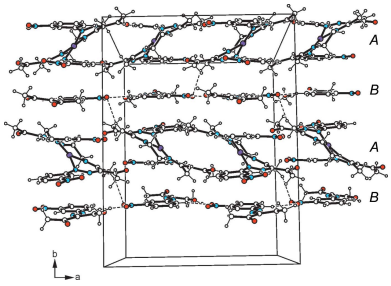
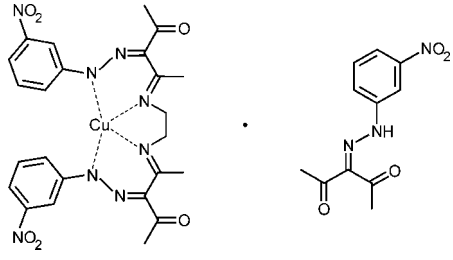
In the title 1:1 co-crystal, $[Cu(C_{24}H_{24}N_8O_6)]\cdot C_{11}H_{11}N_3O_4$, each of the crystal components forms undulating layers which stack alternately along the *b*-axis direction. Molecules of the Cu^{II} complex are connected *via* C—H···O hydrogen bonds involving the nitro and keto oxygen atoms, thus forming supramolecular networks. Molecules of the arylhydrazone component are linked by C—H···O interactions into zigzag strands showing no interstrand association.

1. Chemical context

Hydrazone imines derived from *β*-diketones and aryldiazonium salts using a Japp–Klingemann route (Phillips, 1959) have attracted considerable interest as precursors of potential antidiabetic drugs (Garg & Prakash, 1971; Küçükgüzel *et al.*, 1999) as well as regarding their particular property of hydrogen bonding (Marten *et al.*, 2007; Sethukumar & Arul Prakasam, 2010) and their remarkable behavior in the formation of metal complexes. Transition-metal chelates of the respective hydrazine imines have been described in great numbers (Albert *et al.*, 1997; Mishra *et al.*, 2000; Marten *et al.*, 2005). Preferentially, the chelates with Cu^{II}, Co^{II} and Ni^{II} show a tetrahedrally distorted square N_2O_2 coordination environment. In the presence of a diamine and Ni^{II}, related bis(hydrazonoimine) complexes are formed displaying an unusual behavior of the effective magnetic moment at low temperature (Khudina *et al.*, 2007). A corresponding chelate complex, formed of 3-[2-(3-nitrophenyl)hydrazin-1-ylidene]-pentane-2,4-dione (Marten *et al.*, 2018) and bis(ethylenediamine)copper(II) chloride yielded a co-crystal consisting of *N*,*N*′-ethylenebis{3-[2-(3-nitrophenyl)hydrazine-1-ylidene]-4-oxopentane-2-iminato}copper(II) and 3-[2-(3-nitrophenyl)-hydrazine-1-ylidene]pentane-2,4-dione in a 1:1 stoichiometric composition (the title compound), whose crystal structure is reported on herein.





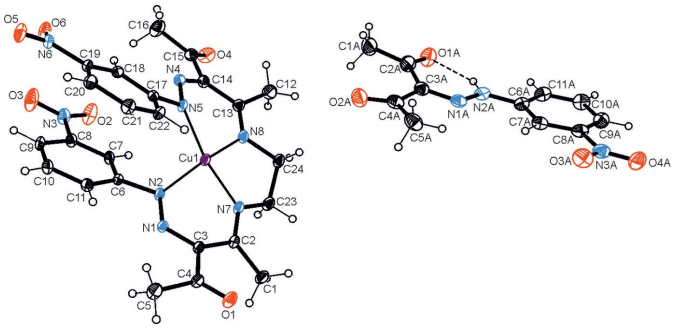


Figure 1
Perspective view of an asymmetric unit of the title co-crystal with atom labeling. Displacement ellipsoids of non-H atoms are shown at the 40% probability level.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11A—H11A···O4A^{i}	0.95	2.43	3.320 (3)	156
N2A—H2A···O1A	0.90 (1)	1.81 (2)	2.531 (3)	135 (3)
C22—H22···O1^{ii}	0.95	2.27	3.207 (3)	169
C16—H16A···O5^{iii}	0.98	2.63	3.532 (3)	154
C12—H12B···O3A^{iv}	0.98	2.53	3.413 (3)	151
C11—H11···O3^{v}	0.95	2.50	3.350 (3)	150
C5—H5C···O3^{v}	0.98	2.65	3.426 (3)	137
C1—H1B···O3A^{vi}	0.98	2.58	3.490 (3)	154
C1—H1B···O1	0.98	2.34	2.842 (3)	111

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+2$; (ii) $-x, -y, -z+1$; (iii) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (v) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (vi) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$.

2. Structural commentary

The title co-crystal possesses orthorhombic symmetry (space group *Pbca*) with one molecule of the Cu^{II} complex and one molecule of the arylhydrazone in the asymmetric unit. A perspective view is shown in Fig. 1. The metal center of the complex adopts a tetrahedrally distorted square coordination environment formed by four nitrogen atoms (N2, N4, N7, N8) of the ligand. As a result of the tetradentate coordination mode and the steric interaction between the terminal aromatic rings of the ligand, the complex molecule adopts a helical geometry with a distance of 3.384 (4) Å between the benzene ring centroids and a dihedral angle of 10.43 (4)° between the benzene ring planes. The Cu—N distances are 1.940 (2), 1.943 (2), 1.953 (2) and 1.957 (2) Å, the bond angles N7—Cu—N8, N7—Cu—N2, N8—Cu—N5 and N2—Cu—N5 are 86.3 (1), 88.4 (1), 89.1 (1) and 100.4 (1)°, respectively. The nitro groups deviate slightly from the planes of the respective benzene rings, with plane N3/O2/O3 being inclined to benzene ring C6–C11 of 3.8 (1)° and plane N6/O5/O6 being inclined to benzene ring C17–C22 by 5.1 (2)° between the nitro groups and the respective benzene rings. The conformation of the arylhydrazone component is nearly identical with that found in the reported structure of this compound (Marten *et al.*, 2018). The molecule features an intramolecular N—H···O=C interaction that yields a six-membered hydrogen-bonded ring. The dihedral angle between the mean plane of this ring and the aromatic ring is 7.8 (2)°. The nitro group is tilted at an angle of 5.8 (2)° with respect to the benzene ring.

3. Supramolecular features

In the crystal, the Cu^{II} complexes as well as the arylhydrazone molecules form undulating layers extending parallel to the *ac* plane and arranged in an alternating order along the *b*-axis direction (Fig. 2). Within a layer of complexes, one carbonyl oxygen and one nitro group per molecule interact *via* C$_{arene}$—H···O hydrogen bonding (Desiraju & Steiner, 1999), thus generating a supramolecular network (Table 1, Fig. 3). The arylhydrazone molecules are connected by means of C$_{aryl}$—H···O$_{nitro}$ interactions to form zigzag-like strands that run along the *a*-axis direction (Table 1, Fig. 4). No directed non-covalent bonds are observed between the supramolecular strands. In the stacking direction, the molecules are linked by C—H···O interactions involving a nitro oxygen atom of the

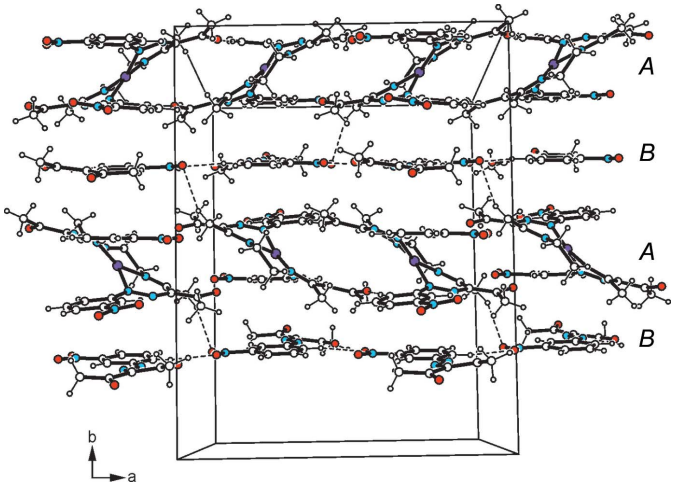


Figure 2
Packing structure of the of the title co-crystal viewed down the crystallographic *c* axis. Dashed lines represent hydrogen bonds.

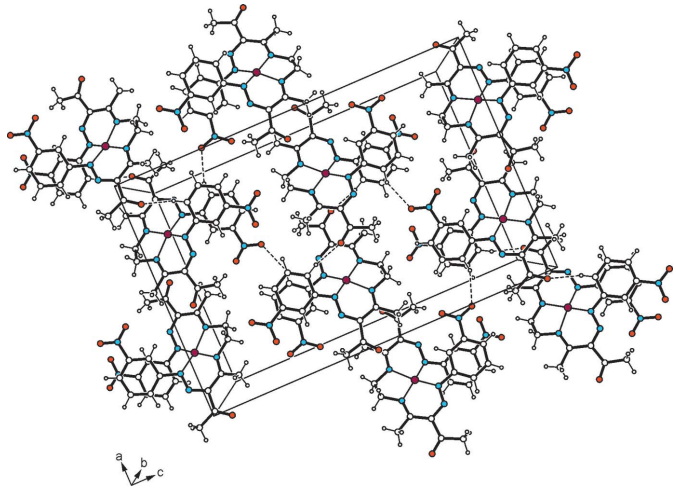


Figure 3
Structure of the Cu^{II} complex layer viewed along the *b* axis. The C—H···O interactions (Table 1) are shown as dashed lines.

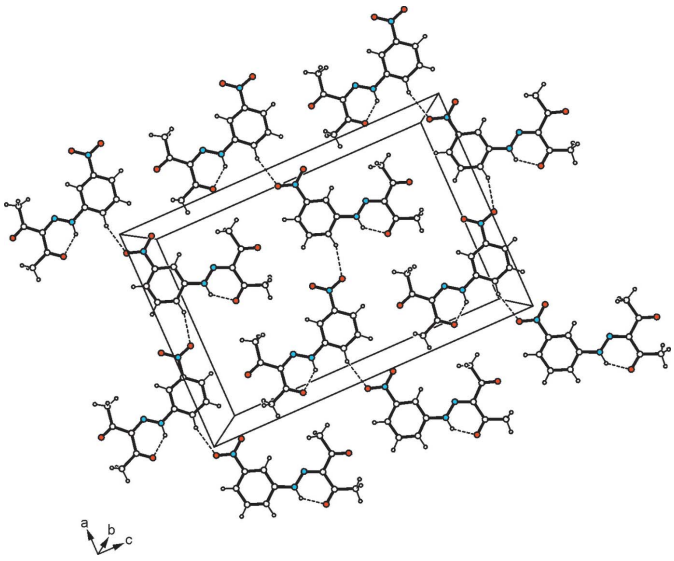


Figure 4
Layer structure of the arylhydrazone viewed along the *b* axis. Dashed lines represent the C—H···O interactions (Table 1).

arylhydrazone molecule and a methyl hydrogen of the coordinated ligand.

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.38, update February 2017; Groom *et al.*, 2016) revealed one hit for a crystal structure of a transition-metal complex containing a structurally related ligand species. The complex *N*,*N*′-ethylene-bis[3-(4-methylphenyl)hydrazono-4-oxo-5,5,6,6,7,7,8,8-octafluorooctane-2-iminato]nickel(II) (JIXQAJ; Khudina *et al.*, 2007) adopts a helical geometry that resembles that of the title complex. As a result of the presence of two extended fluoroalkyl moieties, the pattern of intermolecular non-covalent bonding is dominated by C—H···F and F···F interactions (Reichenbächer *et al.*, 2005), creating a three-dimensional supramolecular architecture. Unlike the title structure, in the reported crystal structure of 3-[2-(3-nitrophenyl)hydrazine-1-ylidene]pentane-2,4-dione (Marten *et al.*, 2018) the molecules are connected *via* C_{arene}—H···O_{nitro} and C_{arene}—H···O_{keto} interactions giving rise to supramolecular sheets.

5. Synthesis and crystallization

A solution containing 3-[2-(3-nitrophenyl)hydrazine-1-ylidene]pentane-2,4-dione and bis(ethylenediamine)copper(II) chloride in *n*-butanol was heated for several hours. After cooling and storing the reaction solution, blue-colored crystals could be isolated which turned out to consist of the title compound.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_{24}H_{24}N_8O_6)]\cdot C_{11}H_{11}N_3O_4$
M_r	833.28
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	153
a, *b*, *c* (Å)	15.5820 (5), 20.0517 (7), 23.3082 (8)
V (Å^3)	7282.5 (4)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.68
Crystal size (mm)	0.54 × 0.44 × 0.07
Data collection	
Diffractometer	Bruker SMART APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.712, 0.954
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	86372, 9862, 6112
R_{int}	0.106
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.130, 0.96
No. of reflections	9862
No. of parameters	524
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.01, −0.68

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* (Farrugia, 2012).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH H atom of 3-[2-(3-nitrophenyl)-hydrazine-1-ylidene]pentane-2,4-dione was located in a difference-Fourier map and freely refined. The C-bound and N-bound H atoms were included in the model in calculated positions and refined as riding atoms: C—H = 0.95–0.99 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl and U_{iso}(H) = 1.2U_{eq}(C) for other H atoms.

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supporting information

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Crystal structure of (*N*,*N*′-ethylenebis{3-[2-(3-nitrophenyl)hydrazin-1-ylidene]-4-oxopentan-2-iminato})copper(II)–3-[2-(3-nitrophenyl)hydrazin-1-ylidene]pentane-2,4-dione (1/1)

Jan Marten, Wilhelm Seichter and Edwin Weber

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(*N*,*N*′-Ethylenebis{3-[2-(3-nitrophenyl)hydrazin-1-ylidene]-4-oxopentan-2-iminato})copper(II)–3-[2-(3-nitrophenyl)hydrazine-1-ylidene]pentane-2,4-dione (1/1)

Crystal data

$[Cu(C_{24}H_{24}N_8O_6)]\cdot C_{11}H_{11}N_3O_4$
M_r = 833.28
Orthorhombic, *Pbca*
a = 15.5820 (5) Å
b = 20.0517 (7) Å
c = 23.3082 (8) Å
V = 7282.5 (4) Å^3
Z = 8
$F(000)$ = 3448
D_x = 1.520 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8051 reflections
θ = 2.2–28.2°
μ = 0.68 mm^{-1}
T = 153 K
Plate, blue
0.54 × 0.44 × 0.07 mm

Data collection

Bruker SMART APEXII diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.712, T_{max} = 0.954
86372 measured reflections
9862 independent reflections
6112 reflections with $I > 2\sigma(I)$
R_{int} = 0.106
θ_{max} = 29.3°, θ_{min} = 2.2°
h = −20→21
k = −27→25
l = −31→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.130
S = 0.96
9862 reflections
524 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 0.2354P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.00$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.23540 (2)	0.01555 (2)	0.46535 (2)	0.01874 (9)
O1	−0.07371 (10)	−0.09037 (9)	0.50519 (7)	0.0288 (4)
O2	0.46419 (12)	−0.03799 (13)	0.31472 (9)	0.0542 (6)
O3	0.43989 (13)	−0.02538 (13)	0.22515 (9)	0.0543 (6)
O4	0.56630 (10)	0.08866 (10)	0.47203 (8)	0.0357 (4)
O5	0.23463 (12)	0.16123 (9)	0.16939 (7)	0.0348 (4)
O6	0.35277 (12)	0.13307 (11)	0.21053 (8)	0.0419 (5)
N1	0.10026 (11)	−0.06399 (9)	0.41500 (7)	0.0171 (4)
N2	0.17823 (11)	−0.04081 (9)	0.40872 (7)	0.0181 (4)
N3	0.41581 (13)	−0.03341 (11)	0.27448 (9)	0.0293 (5)
N4	0.36211 (11)	0.10044 (9)	0.41302 (8)	0.0197 (4)
N5	0.27979 (11)	0.08627 (9)	0.41566 (7)	0.0180 (4)
N6	0.27544 (13)	0.14372 (10)	0.21161 (8)	0.0244 (4)
N7	0.18147 (11)	−0.03715 (10)	0.52509 (7)	0.0200 (4)
N8	0.31978 (12)	0.04022 (10)	0.52296 (8)	0.0208 (4)
C1	0.07728 (15)	−0.11055 (13)	0.57134 (10)	0.0282 (5)
H1A	0.1254	−0.1339	0.5895	0.042*
H1B	0.0352	−0.1432	0.5576	0.042*
H1C	0.0500	−0.0809	0.5994	0.042*
C2	0.10993 (14)	−0.06983 (11)	0.52124 (9)	0.0188 (4)
C3	0.06458 (13)	−0.07253 (11)	0.46652 (9)	0.0176 (4)
C4	−0.02728 (13)	−0.09027 (11)	0.46301 (10)	0.0203 (5)
C5	−0.06491 (15)	−0.10480 (14)	0.40497 (10)	0.0315 (6)
H5A	−0.1214	−0.1256	0.4096	0.047*
H5B	−0.0269	−0.1352	0.3840	0.047*
H5C	−0.0710	−0.0631	0.3834	0.047*
C6	0.20627 (13)	−0.04200 (11)	0.35057 (9)	0.0175 (4)
C7	0.29434 (13)	−0.04252 (11)	0.34078 (9)	0.0191 (4)
H7	0.3338	−0.0463	0.3717	0.023*
C8	0.32268 (14)	−0.03731 (12)	0.28491 (10)	0.0214 (5)
C9	0.26778 (15)	−0.03286 (11)	0.23830 (10)	0.0224 (5)
H9	0.2895	−0.0283	0.2004	0.027*
C10	0.18059 (15)	−0.03522 (11)	0.24867 (10)	0.0227 (5)
H10	0.1415	−0.0339	0.2174	0.027*
C11	0.14957 (14)	−0.03950 (11)	0.30421 (9)	0.0204 (5)
H11	0.0894	−0.0407	0.3108	0.025*

C12	0.44975 (16)	0.08755 (14)	0.56354 (11)	0.0351 (6)
H12A	0.4146	0.1030	0.5958	0.053*
H12B	0.4891	0.1232	0.5518	0.053*
H12C	0.4829	0.0483	0.5753	0.053*
C13	0.39251 (14)	0.06942 (11)	0.51413 (10)	0.0213 (5)
C14	0.41621 (13)	0.08968 (11)	0.45596 (9)	0.0204 (5)
C15	0.50662 (15)	0.10235 (12)	0.43992 (11)	0.0257 (5)
C16	0.52487 (15)	0.12956 (15)	0.38115 (11)	0.0377 (7)
H16A	0.5842	0.1457	0.3795	0.057*
H16B	0.4856	0.1665	0.3730	0.057*
H16C	0.5168	0.0943	0.3526	0.057*
C17	0.23544 (13)	0.10738 (10)	0.36559 (9)	0.0172 (4)
C18	0.27775 (13)	0.11919 (11)	0.31372 (9)	0.0191 (4)
H18	0.3385	0.1164	0.3114	0.023*
C19	0.22975 (14)	0.13491 (11)	0.26627 (9)	0.0200 (5)
C20	0.14114 (14)	0.14071 (11)	0.26706 (10)	0.0228 (5)
H20	0.1098	0.1516	0.2334	0.027*
C21	0.10001 (14)	0.12994 (11)	0.31900 (10)	0.0238 (5)
H21	0.0393	0.1339	0.3212	0.029*
C22	0.14640 (13)	0.11353 (11)	0.36762 (9)	0.0204 (5)
H22	0.1172	0.1064	0.4029	0.025*
C23	0.23529 (15)	−0.04049 (13)	0.57677 (10)	0.0249 (5)
H23A	0.2720	−0.0808	0.5752	0.030*
H23B	0.1984	−0.0437	0.6112	0.030*
C24	0.29118 (15)	0.02124 (13)	0.58082 (10)	0.0260 (5)
H24A	0.2582	0.0583	0.5982	0.031*
H24B	0.3416	0.0120	0.6055	0.031*
O1A	0.46165 (13)	0.22072 (15)	0.78627 (10)	0.0664 (7)
O2A	0.28475 (13)	0.17207 (10)	0.66034 (9)	0.0457 (5)
O3A	0.04080 (11)	0.24229 (10)	0.94118 (10)	0.0469 (5)
O4A	0.06525 (13)	0.25224 (11)	1.03186 (10)	0.0499 (6)
N1A	0.28478 (13)	0.20901 (10)	0.80646 (10)	0.0296 (5)
N2A	0.33228 (13)	0.21815 (11)	0.85192 (10)	0.0332 (5)
H2A	0.3888 (7)	0.2245 (15)	0.8469 (13)	0.051 (9)*
N3A	0.08951 (14)	0.24565 (11)	0.98228 (12)	0.0370 (6)
C1A	0.45036 (19)	0.21587 (17)	0.68630 (13)	0.0501 (8)
H1A1	0.5084	0.2346	0.6880	0.075*
H1A2	0.4142	0.2441	0.6619	0.075*
H1A3	0.4527	0.1707	0.6703	0.075*
C2A	0.41369 (17)	0.21322 (14)	0.74488 (13)	0.0386 (7)
C3A	0.32060 (16)	0.20372 (12)	0.75493 (11)	0.0295 (6)
C4A	0.25922 (17)	0.18854 (13)	0.70795 (13)	0.0341 (6)
C5A	0.16462 (17)	0.19307 (15)	0.71948 (13)	0.0423 (7)
H5A1	0.1413	0.2328	0.7006	0.063*
H5A2	0.1548	0.1962	0.7609	0.063*
H5A3	0.1360	0.1532	0.7045	0.063*
C6A	0.29704 (16)	0.22805 (12)	0.90680 (11)	0.0277 (5)
C7A	0.20906 (16)	0.22976 (12)	0.91655 (12)	0.0291 (6)

H7A	0.1691	0.2227	0.8864	0.035*
C8A	0.18222 (15)	0.24215 (12)	0.97171 (12)	0.0310 (6)
C9A	0.23753 (18)	0.25281 (14)	1.01735 (14)	0.0367 (6)
H9A	0.2164	0.2613	1.0549	0.044*
C10A	0.32440 (17)	0.25058 (13)	1.00628 (13)	0.0369 (6)
H10A	0.3642	0.2577	1.0366	0.044*
C11A	0.35401 (16)	0.23805 (13)	0.95142 (12)	0.0330 (6)
H11A	0.4140	0.2363	0.9443	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01805 (14)	0.02554 (15)	0.01264 (15)	−0.00435 (10)	−0.00054 (11)	0.00152 (11)
O1	0.0193 (8)	0.0433 (10)	0.0237 (10)	−0.0008 (7)	0.0055 (7)	0.0031 (8)
O2	0.0194 (10)	0.1091 (19)	0.0342 (12)	0.0037 (10)	−0.0026 (9)	0.0060 (12)
O3	0.0299 (11)	0.1047 (19)	0.0285 (12)	−0.0084 (11)	0.0138 (9)	−0.0071 (11)
O4	0.0180 (8)	0.0470 (11)	0.0420 (12)	−0.0009 (7)	−0.0038 (8)	0.0096 (9)
O5	0.0451 (11)	0.0437 (11)	0.0155 (9)	0.0029 (8)	−0.0008 (8)	0.0026 (8)
O6	0.0291 (10)	0.0713 (14)	0.0254 (11)	0.0017 (9)	0.0110 (8)	0.0074 (9)
N1	0.0152 (9)	0.0209 (9)	0.0152 (10)	−0.0009 (7)	0.0019 (7)	0.0002 (7)
N2	0.0149 (9)	0.0263 (10)	0.0132 (10)	−0.0015 (7)	0.0019 (7)	−0.0010 (7)
N3	0.0193 (10)	0.0425 (13)	0.0261 (12)	0.0009 (8)	0.0057 (9)	−0.0055 (9)
N4	0.0166 (9)	0.0229 (10)	0.0197 (10)	−0.0026 (7)	0.0023 (7)	−0.0014 (7)
N5	0.0160 (9)	0.0259 (10)	0.0122 (9)	−0.0009 (7)	0.0000 (7)	−0.0001 (7)
N6	0.0328 (12)	0.0263 (10)	0.0140 (11)	−0.0034 (8)	0.0029 (9)	−0.0022 (8)
N7	0.0187 (9)	0.0287 (10)	0.0125 (10)	−0.0021 (7)	−0.0001 (7)	0.0017 (7)
N8	0.0201 (9)	0.0283 (10)	0.0139 (10)	−0.0030 (8)	−0.0017 (7)	0.0000 (8)
C1	0.0287 (13)	0.0370 (14)	0.0189 (13)	−0.0090 (10)	0.0002 (10)	0.0064 (10)
C2	0.0189 (11)	0.0234 (11)	0.0142 (11)	0.0018 (8)	0.0021 (8)	0.0008 (8)
C3	0.0165 (10)	0.0212 (11)	0.0151 (11)	−0.0001 (8)	0.0018 (9)	0.0005 (9)
C4	0.0176 (11)	0.0249 (12)	0.0184 (12)	−0.0002 (8)	0.0006 (9)	0.0036 (9)
C5	0.0186 (12)	0.0507 (16)	0.0251 (14)	−0.0082 (11)	−0.0044 (10)	0.0038 (11)
C6	0.0196 (10)	0.0191 (10)	0.0138 (11)	−0.0022 (8)	0.0021 (9)	−0.0005 (8)
C7	0.0177 (10)	0.0251 (11)	0.0144 (11)	0.0009 (9)	−0.0019 (9)	−0.0019 (9)
C8	0.0162 (10)	0.0283 (12)	0.0196 (12)	−0.0002 (9)	0.0032 (9)	−0.0038 (9)
C9	0.0269 (12)	0.0280 (12)	0.0124 (11)	−0.0011 (9)	0.0047 (9)	−0.0022 (9)
C10	0.0253 (12)	0.0276 (12)	0.0150 (12)	0.0004 (9)	−0.0023 (9)	−0.0012 (9)
C11	0.0170 (11)	0.0245 (11)	0.0197 (12)	−0.0009 (8)	−0.0009 (9)	−0.0009 (9)
C12	0.0307 (14)	0.0470 (16)	0.0275 (15)	−0.0145 (12)	−0.0082 (11)	0.0006 (12)
C13	0.0202 (11)	0.0237 (12)	0.0200 (12)	−0.0013 (8)	−0.0007 (9)	0.0009 (9)
C14	0.0166 (10)	0.0246 (12)	0.0201 (13)	−0.0016 (8)	−0.0011 (9)	−0.0011 (9)
C15	0.0211 (12)	0.0276 (13)	0.0284 (14)	−0.0041 (9)	0.0002 (10)	−0.0010 (10)
C16	0.0212 (12)	0.0599 (19)	0.0320 (16)	−0.0085 (12)	0.0048 (11)	0.0052 (13)
C17	0.0181 (10)	0.0183 (10)	0.0152 (11)	−0.0027 (8)	−0.0004 (9)	−0.0016 (8)
C18	0.0179 (11)	0.0203 (11)	0.0191 (12)	−0.0031 (8)	0.0020 (9)	−0.0006 (9)
C19	0.0273 (12)	0.0196 (11)	0.0132 (11)	−0.0037 (9)	0.0043 (9)	0.0001 (8)
C20	0.0242 (12)	0.0240 (11)	0.0202 (13)	0.0011 (9)	−0.0042 (9)	0.0025 (9)
C21	0.0189 (11)	0.0285 (13)	0.0240 (13)	0.0024 (9)	0.0014 (9)	0.0015 (10)

C22	0.0200 (11)	0.0245 (11)	0.0168 (12)	−0.0001 (8)	0.0051 (9)	0.0020 (9)
C23	0.0241 (11)	0.0348 (13)	0.0157 (12)	−0.0046 (10)	−0.0034 (10)	0.0058 (10)
C24	0.0232 (11)	0.0399 (14)	0.0148 (12)	−0.0082 (10)	−0.0012 (10)	−0.0009 (10)
O1A	0.0253 (11)	0.125 (2)	0.0487 (15)	−0.0036 (13)	0.0007 (10)	−0.0065 (14)
O2A	0.0480 (12)	0.0499 (13)	0.0391 (13)	−0.0020 (9)	−0.0019 (10)	−0.0082 (10)
O3A	0.0217 (10)	0.0523 (13)	0.0666 (16)	0.0003 (8)	−0.0052 (10)	−0.0050 (11)
O4A	0.0394 (12)	0.0507 (13)	0.0598 (16)	−0.0008 (9)	0.0198 (11)	−0.0019 (10)
N1A	0.0268 (11)	0.0212 (10)	0.0408 (14)	0.0010 (8)	−0.0017 (10)	0.0022 (9)
N2A	0.0194 (11)	0.0390 (13)	0.0413 (15)	0.0025 (9)	−0.0025 (10)	0.0045 (10)
N3A	0.0273 (12)	0.0277 (12)	0.0561 (17)	−0.0010 (9)	0.0066 (12)	−0.0004 (11)
C1A	0.0426 (17)	0.058 (2)	0.050 (2)	−0.0103 (14)	0.0105 (15)	−0.0140 (15)
C2A	0.0309 (15)	0.0421 (16)	0.0430 (18)	0.0001 (12)	0.0060 (13)	−0.0037 (13)
C3A	0.0293 (13)	0.0230 (12)	0.0363 (16)	0.0030 (9)	0.0015 (11)	−0.0006 (10)
C4A	0.0338 (15)	0.0234 (13)	0.0451 (18)	0.0008 (10)	−0.0033 (13)	0.0007 (11)
C5A	0.0324 (15)	0.0404 (16)	0.054 (2)	−0.0016 (11)	−0.0050 (13)	−0.0117 (14)
C6A	0.0250 (12)	0.0260 (13)	0.0321 (15)	0.0032 (9)	0.0007 (11)	0.0049 (10)
C7A	0.0235 (12)	0.0246 (12)	0.0392 (16)	0.0001 (9)	−0.0047 (11)	0.0025 (10)
C8A	0.0193 (12)	0.0253 (13)	0.0483 (18)	0.0015 (9)	0.0018 (12)	0.0050 (11)
C9A	0.0367 (15)	0.0365 (15)	0.0369 (16)	0.0031 (11)	0.0011 (12)	0.0034 (12)
C10A	0.0309 (14)	0.0410 (15)	0.0388 (17)	0.0013 (11)	−0.0111 (13)	0.0055 (12)
C11A	0.0218 (12)	0.0347 (14)	0.0426 (18)	0.0023 (10)	−0.0012 (11)	0.0072 (11)

Geometric parameters (Å, º)

Cu1—N7	1.9395 (18)	C15—C16	1.502 (3)
Cu1—N8	1.9434 (18)	C16—H16A	0.9800
Cu1—N2	1.9527 (18)	C16—H16B	0.9800
Cu1—N5	1.9573 (18)	C16—H16C	0.9800
O1—C4	1.221 (3)	C17—C22	1.394 (3)
O2—N3	1.207 (3)	C17—C18	1.397 (3)
O3—N3	1.220 (3)	C18—C19	1.372 (3)
O4—C15	1.225 (3)	C18—H18	0.9500
O5—N6	1.223 (2)	C19—C20	1.386 (3)
O6—N6	1.224 (3)	C20—C21	1.387 (3)
N1—N2	1.309 (2)	C20—H20	0.9500
N1—C3	1.334 (3)	C21—C22	1.384 (3)
N2—C6	1.424 (3)	C21—H21	0.9500
N3—C8	1.473 (3)	C22—H22	0.9500
N4—N5	1.315 (2)	C23—C24	1.516 (3)
N4—C14	1.326 (3)	C23—H23A	0.9900
N5—C17	1.421 (3)	C23—H23B	0.9900
N6—C19	1.470 (3)	C24—H24A	0.9900
N7—C2	1.296 (3)	C24—H24B	0.9900
N7—C23	1.469 (3)	O1A—C2A	1.230 (3)
N8—C13	1.292 (3)	O2A—C4A	1.224 (3)
N8—C24	1.471 (3)	O3A—N3A	1.224 (3)
C1—C2	1.513 (3)	O4A—N3A	1.223 (3)
C1—H1A	0.9800	N1A—N2A	1.305 (3)

C1—H1B	0.9800	N1A—C3A	1.329 (3)
C1—H1C	0.9800	N2A—C6A	1.406 (3)
C2—C3	1.459 (3)	N2A—H2A	0.898 (10)
C3—C4	1.477 (3)	N3A—C8A	1.467 (3)
C4—C5	1.503 (3)	C1A—C2A	1.481 (4)
C5—H5A	0.9800	C1A—H1A1	0.9800
C5—H5B	0.9800	C1A—H1A2	0.9800
C5—H5C	0.9800	C1A—H1A3	0.9800
C6—C7	1.391 (3)	C2A—C3A	1.482 (4)
C6—C11	1.397 (3)	C3A—C4A	1.485 (4)
C7—C8	1.379 (3)	C4A—C5A	1.501 (4)
C7—H7	0.9500	C5A—H5A1	0.9800
C8—C9	1.386 (3)	C5A—H5A2	0.9800
C9—C10	1.381 (3)	C5A—H5A3	0.9800
C9—H9	0.9500	C6A—C11A	1.382 (4)
C10—C11	1.385 (3)	C6A—C7A	1.390 (4)
C10—H10	0.9500	C7A—C8A	1.375 (4)
C11—H11	0.9500	C7A—H7A	0.9500
C12—C13	1.501 (3)	C8A—C9A	1.386 (4)
C12—H12A	0.9800	C9A—C10A	1.379 (4)
C12—H12B	0.9800	C9A—H9A	0.9500
C12—H12C	0.9800	C10A—C11A	1.382 (4)
C13—C14	1.463 (3)	C10A—H10A	0.9500
C14—C15	1.479 (3)	C11A—H11A	0.9500

N7—Cu1—N8	86.32 (8)	C15—C16—H16B	109.5
N7—Cu1—N2	88.42 (8)	H16A—C16—H16B	109.5
N8—Cu1—N2	157.38 (8)	C15—C16—H16C	109.5
N7—Cu1—N5	166.59 (8)	H16A—C16—H16C	109.5
N8—Cu1—N5	89.16 (7)	H16B—C16—H16C	109.5
N2—Cu1—N5	100.40 (7)	C22—C17—C18	119.0 (2)
N2—N1—C3	122.21 (18)	C22—C17—N5	118.85 (18)
N1—N2—C6	112.66 (17)	C18—C17—N5	122.12 (18)
N1—N2—Cu1	123.59 (14)	C19—C18—C17	118.63 (19)
C6—N2—Cu1	120.87 (13)	C19—C18—H18	120.7
O2—N3—O3	123.4 (2)	C17—C18—H18	120.7
O2—N3—C8	118.9 (2)	C18—C19—C20	123.5 (2)
O3—N3—C8	117.7 (2)	C18—C19—N6	117.53 (19)
N5—N4—C14	123.34 (18)	C20—C19—N6	118.9 (2)
N4—N5—C17	111.82 (17)	C19—C20—C21	117.3 (2)
N4—N5—Cu1	121.92 (14)	C19—C20—H20	121.3
C17—N5—Cu1	122.01 (13)	C21—C20—H20	121.3
O5—N6—O6	123.0 (2)	C22—C21—C20	120.7 (2)
O5—N6—C19	118.68 (19)	C22—C21—H21	119.6
O6—N6—C19	118.27 (19)	C20—C21—H21	119.6
C2—N7—C23	121.64 (18)	C21—C22—C17	120.9 (2)
C2—N7—Cu1	126.75 (15)	C21—C22—H22	119.6
C23—N7—Cu1	111.48 (13)	C17—C22—H22	119.6

C13—N8—C24	121.95 (19)	N7—C23—C24	109.98 (19)
C13—N8—Cu1	126.78 (16)	N7—C23—H23A	109.7
C24—N8—Cu1	111.27 (13)	C24—C23—H23A	109.7
C2—C1—H1A	109.5	N7—C23—H23B	109.7
C2—C1—H1B	109.5	C24—C23—H23B	109.7
H1A—C1—H1B	109.5	H23A—C23—H23B	108.2
C2—C1—H1C	109.5	N8—C24—C23	109.15 (18)
H1A—C1—H1C	109.5	N8—C24—H24A	109.8
H1B—C1—H1C	109.5	C23—C24—H24A	109.8
N7—C2—C3	119.72 (19)	N8—C24—H24B	109.8
N7—C2—C1	120.57 (19)	C23—C24—H24B	109.8
C3—C2—C1	119.46 (19)	H24A—C24—H24B	108.3
N1—C3—C2	125.46 (19)	N2A—N1A—C3A	120.5 (2)
N1—C3—C4	112.64 (18)	N1A—N2A—C6A	122.5 (2)
C2—C3—C4	121.77 (19)	N1A—N2A—H2A	118 (2)
O1—C4—C3	122.0 (2)	C6A—N2A—H2A	119 (2)
O1—C4—C5	119.6 (2)	O4A—N3A—O3A	123.6 (2)
C3—C4—C5	118.32 (19)	O4A—N3A—C8A	117.9 (2)
C4—C5—H5A	109.5	O3A—N3A—C8A	118.5 (2)
C4—C5—H5B	109.5	C2A—C1A—H1A1	109.5
H5A—C5—H5B	109.5	C2A—C1A—H1A2	109.5
C4—C5—H5C	109.5	H1A1—C1A—H1A2	109.5
H5A—C5—H5C	109.5	C2A—C1A—H1A3	109.5
H5B—C5—H5C	109.5	H1A1—C1A—H1A3	109.5
C7—C6—C11	119.83 (19)	H1A2—C1A—H1A3	109.5
C7—C6—N2	117.31 (18)	O1A—C2A—C1A	119.0 (3)
C11—C6—N2	122.79 (19)	O1A—C2A—C3A	119.1 (3)
C8—C7—C6	118.0 (2)	C1A—C2A—C3A	121.9 (3)
C8—C7—H7	121.0	N1A—C3A—C2A	122.9 (2)
C6—C7—H7	121.0	N1A—C3A—C4A	114.4 (2)
C7—C8—C9	123.2 (2)	C2A—C3A—C4A	122.7 (2)
C7—C8—N3	118.4 (2)	O2A—C4A—C3A	121.0 (2)
C9—C8—N3	118.4 (2)	O2A—C4A—C5A	119.8 (2)
C10—C9—C8	117.9 (2)	C3A—C4A—C5A	119.2 (2)
C10—C9—H9	121.0	C4A—C5A—H5A1	109.5
C8—C9—H9	121.0	C4A—C5A—H5A2	109.5
C9—C10—C11	120.6 (2)	H5A1—C5A—H5A2	109.5
C9—C10—H10	119.7	C4A—C5A—H5A3	109.5
C11—C10—H10	119.7	H5A1—C5A—H5A3	109.5
C10—C11—C6	120.3 (2)	H5A2—C5A—H5A3	109.5
C10—C11—H11	119.8	C11A—C6A—C7A	120.5 (2)
C6—C11—H11	119.8	C11A—C6A—N2A	117.0 (2)
C13—C12—H12A	109.5	C7A—C6A—N2A	122.5 (2)
C13—C12—H12B	109.5	C8A—C7A—C6A	117.2 (2)
H12A—C12—H12B	109.5	C8A—C7A—H7A	121.4
C13—C12—H12C	109.5	C6A—C7A—H7A	121.4
H12A—C12—H12C	109.5	C7A—C8A—C9A	123.8 (2)
H12B—C12—H12C	109.5	C7A—C8A—N3A	117.7 (2)

N8—C13—C14	119.7 (2)	C9A—C8A—N3A	118.4 (2)
N8—C13—C12	120.6 (2)	C10A—C9A—C8A	117.5 (3)
C14—C13—C12	119.6 (2)	C10A—C9A—H9A	121.2
N4—C14—C13	125.75 (19)	C8A—C9A—H9A	121.2
N4—C14—C15	112.74 (19)	C9A—C10A—C11A	120.4 (3)
C13—C14—C15	121.5 (2)	C9A—C10A—H10A	119.8
O4—C15—C14	122.0 (2)	C11A—C10A—H10A	119.8
O4—C15—C16	119.7 (2)	C6A—C11A—C10A	120.5 (2)
C14—C15—C16	118.2 (2)	C6A—C11A—H11A	119.7
C15—C16—H16A	109.5	C10A—C11A—H11A	119.7
C3—N1—N2—C6	174.16 (18)	N4—N5—C17—C22	−162.16 (19)
C3—N1—N2—Cu1	−25.0 (3)	Cu1—N5—C17—C22	40.6 (3)
C14—N4—N5—C17	175.52 (19)	N4—N5—C17—C18	20.8 (3)
C14—N4—N5—Cu1	−27.2 (3)	Cu1—N5—C17—C18	−136.36 (17)
C23—N7—C2—C3	−171.5 (2)	C22—C17—C18—C19	−1.5 (3)
Cu1—N7—C2—C3	4.0 (3)	N5—C17—C18—C19	175.48 (19)
C23—N7—C2—C1	2.7 (3)	C17—C18—C19—C20	1.0 (3)
Cu1—N7—C2—C1	178.17 (17)	C17—C18—C19—N6	−176.94 (18)
N2—N1—C3—C2	−12.0 (3)	O5—N6—C19—C18	−176.2 (2)
N2—N1—C3—C4	172.09 (19)	O6—N6—C19—C18	3.9 (3)
N7—C2—C3—N1	23.5 (3)	O5—N6—C19—C20	5.9 (3)
C1—C2—C3—N1	−150.7 (2)	O6—N6—C19—C20	−174.1 (2)
N7—C2—C3—C4	−161.0 (2)	C18—C19—C20—C21	0.1 (3)
C1—C2—C3—C4	24.8 (3)	N6—C19—C20—C21	177.9 (2)
N1—C3—C4—O1	−168.9 (2)	C19—C20—C21—C22	−0.5 (3)
C2—C3—C4—O1	15.1 (3)	C20—C21—C22—C17	0.0 (3)
N1—C3—C4—C5	7.6 (3)	C18—C17—C22—C21	1.1 (3)
C2—C3—C4—C5	−168.4 (2)	N5—C17—C22—C21	−176.0 (2)
N1—N2—C6—C7	−156.94 (19)	C2—N7—C23—C24	−156.1 (2)
Cu1—N2—C6—C7	41.6 (2)	Cu1—N7—C23—C24	27.8 (2)
N1—N2—C6—C11	26.1 (3)	C13—N8—C24—C23	−149.4 (2)
Cu1—N2—C6—C11	−135.30 (18)	Cu1—N8—C24—C23	30.5 (2)
C11—C6—C7—C8	3.0 (3)	N7—C23—C24—N8	−37.7 (3)
N2—C6—C7—C8	−173.99 (19)	C3A—N1A—N2A—C6A	176.1 (2)
C6—C7—C8—C9	−1.2 (3)	N2A—N1A—C3A—C2A	−5.2 (4)
C6—C7—C8—N3	176.08 (19)	N2A—N1A—C3A—C4A	175.8 (2)
O2—N3—C8—C7	3.4 (3)	O1A—C2A—C3A—N1A	6.4 (4)
O3—N3—C8—C7	−176.3 (2)	C1A—C2A—C3A—N1A	−171.8 (2)
O2—N3—C8—C9	−179.2 (2)	O1A—C2A—C3A—C4A	−174.6 (3)
O3—N3—C8—C9	1.1 (3)	C1A—C2A—C3A—C4A	7.2 (4)
C7—C8—C9—C10	−1.4 (3)	N1A—C3A—C4A—O2A	−168.4 (2)
N3—C8—C9—C10	−178.7 (2)	C2A—C3A—C4A—O2A	12.5 (4)
C8—C9—C10—C11	2.3 (3)	N1A—C3A—C4A—C5A	11.1 (3)
C9—C10—C11—C6	−0.5 (3)	C2A—C3A—C4A—C5A	−167.9 (2)
C7—C6—C11—C10	−2.2 (3)	N1A—N2A—C6A—C11A	−179.2 (2)
N2—C6—C11—C10	174.6 (2)	N1A—N2A—C6A—C7A	−0.9 (4)
C24—N8—C13—C14	−177.5 (2)	C11A—C6A—C7A—C8A	0.5 (3)

Cu1—N8—C13—C14	2.6 (3)	N2A—C6A—C7A—C8A	−177.7 (2)
C24—N8—C13—C12	−2.3 (3)	C6A—C7A—C8A—C9A	0.0 (4)
Cu1—N8—C13—C12	177.78 (18)	C6A—C7A—C8A—N3A	178.6 (2)
N5—N4—C14—C13	−8.6 (3)	O4A—N3A—C8A—C7A	175.2 (2)
N5—N4—C14—C15	173.19 (19)	O3A—N3A—C8A—C7A	−5.2 (3)
N8—C13—C14—N4	22.3 (4)	O4A—N3A—C8A—C9A	−6.1 (3)
C12—C13—C14—N4	−153.0 (2)	O3A—N3A—C8A—C9A	173.5 (2)
N8—C13—C14—C15	−159.6 (2)	C7A—C8A—C9A—C10A	−0.2 (4)
C12—C13—C14—C15	25.1 (3)	N3A—C8A—C9A—C10A	−178.8 (2)
N4—C14—C15—O4	−172.4 (2)	C8A—C9A—C10A—C11A	−0.1 (4)
C13—C14—C15—O4	9.2 (4)	C7A—C6A—C11A—C10A	−0.7 (4)
N4—C14—C15—C16	4.4 (3)	N2A—C6A—C11A—C10A	177.6 (2)
C13—C14—C15—C16	−174.0 (2)	C9A—C10A—C11A—C6A	0.5 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11*A*—H11*A*···O4*A*^{i}	0.95	2.43	3.320 (3)	156
N2*A*—H2*A*···O1*A*	0.90 (1)	1.81 (2)	2.531 (3)	135 (3)
C22—H22···O1^{ii}	0.95	2.27	3.207 (3)	169
C16—H16*A*···O5^{iii}	0.98	2.63	3.532 (3)	154
C12—H12*B*···O3*A*^{iv}	0.98	2.53	3.413 (3)	151
C11—H11···O3^{v}	0.95	2.50	3.350 (3)	150
C5—H5*C*···O3^{v}	0.98	2.65	3.426 (3)	137
C1—H1*B*···O3*A*^{vi}	0.98	2.58	3.490 (3)	154
C1—H1*B*···O1	0.98	2.34	2.842 (3)	111

Symmetry codes: (i) *x*+1/2, −*y*+1/2, −*z*+2; (ii) −*x*, −*y*, −*z*+1; (iii) *x*+1/2, *y*, −*z*+1/2; (iv) *x*+1/2, *y*, −*z*+3/2; (v) *x*−1/2, *y*, −*z*+1/2; (vi) −*x*, *y*−1/2, −*z*+3/2.