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Bis(lysine-κ^2N,O)hexa-μ_2-oxido-hexaoxidobis(1,10-phenanthroline-κ^2N,N')dicopper(II)tetravanadium(V) tetrahydrate

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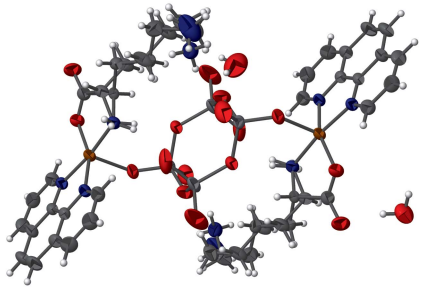
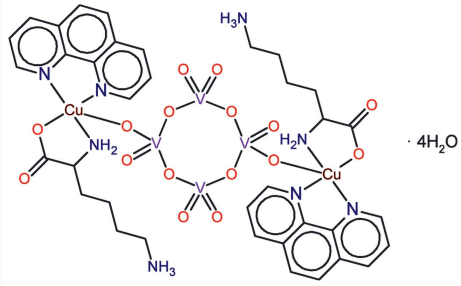
The heterometallic coordination compound $[Cu(Lys)(phen)]_2V_4O_{12}\cdot 4H_2O$ (Lys is the amino acid lysine, $C_6H_{14}N_2O_2$, and phen is 1,10-phenanthroline, $C_{12}H_8N_2$) lies across an inversion centre. Two $[Cu(Lys)(phen)]^{2+}$ units coordinate to the *cyclo*-vanadate fragment and the formula unit is completed by four solvent water molecules. The lysine ligand is in the zwitterionic form and chelates the Cu^{II} atom *via* the α-NH_2 and α-COO^- donor groups, while the ε-NH_3^+ group is involved in intramolecular hydrogen bonds with the central $[V_4O_{12}]^{4-}$ core and with solvent water molecules. In the crystal, N—H···O and O—H···O hydrogen bonds connect the components of the structure to form a three-dimensional network. The crystal structure is further stabilized by π–π interactions involving the phen ligands. The lysine group is disordered over two sets of sites with refined occupancies of 0.534 (11) and 0.466 (11).

3D view



Chemical scheme



Structure description

Vanadate $[VO_4]^{3-}$ is prone to condensation in aqueous solutions and forms oligomeric polyoxovanadate ions, whose formula and structure depend on pH, vanadate concentration, temperature and ionic strength. In basic media, predominant species are dimeric $[V_2O_7]^{4-}$, tetrameric $[V_4O_{12}]^{4-}$ and pentameric $[V_5O_{15}]^{5-}$ anions, while the decameric cluster $[V_{10}O_{28}]^{6-}$ is the most stable species in acidic media (Amado *et al.*, 1993; Aureliano & Crans, 2009). The ring system $[V_4O_{12}]^{4-}$ is of interest in coordination chemistry, given that this anion may behave as a bridging ligand, providing an entry to heterometallic complexes. Hence, the crystal structures of some V/Cu compounds, including

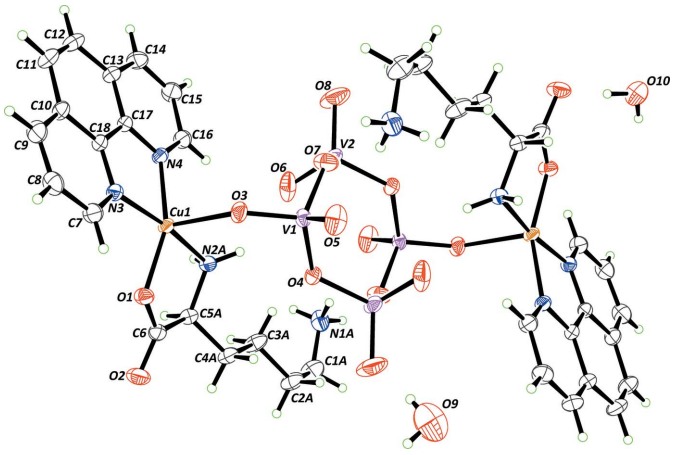


Figure 1
Molecular entities in the crystal structure of the title compound with displacement ellipsoids for non-H atoms at the 30% probability level. Only the major component of disorder for the lysine group is presented and only the symmetry-unique water molecules are shown. Unlabelled atoms are generated by the symmetry operator $(1 - x, 1 - y, -z)$.

$[V_4O_{12}]^{4-}$, have been reported (Yucesan *et al.*, 2006; Joniaková *et al.*, 2006; Wang *et al.*, 2007; Paredes-García *et al.*, 2008). Within the sub-set of heterometallic complexes containing V and Cu as transition metals for which an X-ray characterization is available, the compound reported herein is the first one including an amino acid, namely lysine.

The asymmetric unit for $[Cu(Lys)(phen)]_2V_4O_{12}\cdot 4H_2O$, where Lys is lysine and phen is 1,10-phenanthroline, contains one half complex molecule and two solvent water molecules. The formula unit is completed by an inversion center (Fig. 1). The centrosymmetric $[V_4O_{12}]^{4-}$ anion shows an eight-membered ring structure built up from four corner sharing tetrahedra and displays a chair-like conformation. The V—O bond lengths and V—O—V angles are found in normal ranges,

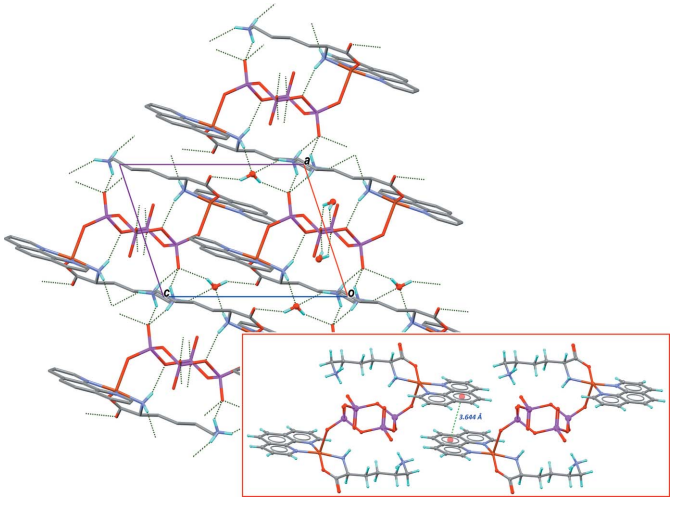


Figure 2
Part of the crystal structure showing the O—H···O and N—H···O hydrogen bonds, which are represented by dotted green lines, and only H atoms involved in hydrogen bonds are shown. The inset displays two molecules interacting through π–π contacts between symmetry-related phenanthroline ligands.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A1···O5^{i}	0.89	2.09	2.794 (7)	136
N1A—H1A2···O10^{ii}	0.89	2.21	2.979 (7)	145
N1A—H1A3···O5^{iii}	0.89	1.89	2.769 (8)	169
N2A—H2AC···O4	0.89	2.25	3.094 (3)	159
N2A—H2AD···O10^{iv}	0.89	2.22	3.077 (3)	163
N2B—H2BC···O4	0.89	2.48	3.094 (3)	127
N2B—H2BC···O7	0.89	2.39	3.127 (4)	141
N2B—H2BD···O10^{iv}	0.89	2.23	3.077 (3)	159
O9—H91···O8	0.84	2.00	2.780 (6)	155
O9—H92···O8^{v}	0.84	2.21	2.861 (6)	135
O10—H101···O5^{vi}	0.84	2.09	2.837 (4)	148
O10—H102···O2	0.84	2.07	2.811 (4)	147

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

in comparison with other structures containing this poly-oxovanadate (*e.g.* Paredes-García *et al.*, 2008).

The $[V_4O_{12}]^{4-}$ anion serves as a bridge between two $[Cu(Lys)(phen)]^{2+}$ moieties, a complex which has been shown to present a photo-induced DNA cleavage activity (Patra *et al.*, 2005). The Cu^{II} atom displays the common distorted square pyramidal geometry: the α-amino N and α-carboxylate O atoms of lysine and the two N donors of phenanthroline are placed in basal positions, while the apical position is occupied by O3 belonging to the $[V_4O_{12}]^{4-}$ anion, with a longer Cu—O bond length of 2.282 (2) Å. The value of the structural parameter τ_5 for Cu is 0.26, reflecting a limited distortion toward the trigonal–bipyramidal geometry (Addison *et al.*, 1984). The Cu atom is displaced by 0.24 Å above the basal mean plane O1/N2A/N3/N4. The zwitterionic lysine is folded in such a way that both the ε-NH_3^+ and the α-NH_2 donor groups interact with the $[V_4O_{12}]^{4-}$ core ring and the water molecule O10, *via* weak N—H···O hydrogen bonds (Table 1).

In the crystal, O—H···O and N—H···O hydrogen bonds involving the water molecules O9, O10 and the N atoms of the lysine molecule as donors connect the components of the structure forming a three-dimensional network (Table 1, Fig. 2). In addition, the crystal structure is further stabilized by π–π parallel-displaced stacking interactions between the phen ligands, characterized by a separation of 3.6446 (2) Å between the centroids of the central rings C10/C11/C12/C13/C17/C18 for two symmetry-related phen ligands (see Fig. 2, inset). The shortest Cu···Cu intermolecular distance is Cu···Cu^{i} = 6.2251 (7) Å [symmetry code: (i) $1 - x, 1 - y, 1 - z$], large enough to avoid any significant magnetic interactions in the crystal.

Synthesis and crystallization

The title compound was prepared by a general synthetic method in which 1.0 mmol of 1,10-phenanthroline hydrochloride was added to an aqueous solution of lysine hydrochloride (0.18 g, 1.0 mmol in 30 ml H_2O) under stirring and slight warming in order to dissolve the heterocyclic base. An amount of $CuCl_2\cdot 2H_2O$ (0.170 g, 1 mmol) was added to this

mixture, and the pH of the resulting solution was adjusted to 9.5 by slow addition of KOH (10%), giving a dark-blue solution. Then, NH_4VO_3 (0.116 g, 1.0 mmol in 15 ml H_2O) was added dropwise to the solution, which was filtered and kept outdoors at room temperature for three days. Blue prismatic crystals were separated from the solution without any other impurity and used for X-ray diffraction. The final pH of the solution at 298 K was 8.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. ADPs for non-H atoms of the lysine ligand evidenced that this molecule is disordered over two positions. The disorder was modelled using independent sites *A* and *B*, and occupancies for each part were refined, which converged to 0.534 (11) and 0.466 (11) for sites *A* and *B*, respectively. Since atoms N2*A* and N2*B*, corresponding to the α-NH_2 group coordinating the metal, were difficult to resolve their sites were constrained to have the same coordinates and displacement parameters (*EXYZ* and *EADP* constrictions in *SHELXL*; Sheldrick, 2015*b*).

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_{12}H_8N_2)(C_6H_{14}N_2O_2)]_2$-$[V_4O_{12}]\cdot 4H_2O$
M_r	1247.69
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	295
a, b, c (Å)	9.2807 (4), 11.2960 (4), 12.7697 (5)
α, β, γ (°)	72.259 (3), 69.999 (3), 81.523 (3)
V (Å^3)	1196.75 (9)
Z	1
Radiation type	Ag $K\alpha$, λ = 0.56083 Å
μ (mm^{-1})	0.89
Crystal size (mm)	0.30 × 0.20 × 0.20
Data collection	
Diffractometer	Stoe Stadivari
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46672, 7667, 5850
R_{int}	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.728
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.119, 1.04
No. of reflections	7667
No. of parameters	371
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.05, −1.04

Computer programs: *X-AREA* (Stoe & Cie, 2015), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *XP* in *SHELXTL-Plus* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

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full crystallographic data

IUCrData (2017). **2**, x171050 [https://doi.org/10.1107/S2414314617010501]

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Crystal data

$[Cu(C_{12}H_8N_2)(C_6H_{14}N_2O_2)]_2[V_4O_{12}]\cdot 4H_2O$
M_r = 1247.69
Triclinic, $P\overline{1}$
a = 9.2807 (4) Å
b = 11.2960 (4) Å
c = 12.7697 (5) Å
α = 72.259 (3)°
β = 69.999 (3)°
γ = 81.523 (3)°
V = 1196.75 (9) Å^3
Z = 1
$F(000)$ = 634
D_x = 1.731 Mg m^{-3}
Ag $K\alpha$ radiation, λ = 0.56083 Å
Cell parameters from 29693 reflections
θ = 2.3–28.7°
μ = 0.89 mm^{-1}
T = 295 K
Prism, blue
0.30 × 0.20 × 0.20 mm

Data collection

Stoe Stadivari diffractometer
Radiation source: Sealed X-ray tube, Axo Microfocus source
Mirror monochromator
Detector resolution: 5.81 pixels mm^{-1}
ω scans
46672 measured reflections
7667 independent reflections
5850 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 24.1°, θ_{min} = 2.3°
h = −13→13
k = −16→16
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.119
S = 1.04
7667 reflections
371 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 1.8611P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −1.04 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.

Refinement. The H atoms for water molecules O9 and O10 were located from a difference Fourier map, and then included with idealized O—H bond lengths of 0.84 Å. All other H atoms were placed in calculated positions and refined in the riding-motion approximation.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.28666 (4)	0.37528 (3)	0.42645 (3)	0.03113 (9)	
V1	0.60736 (5)	0.45877 (4)	0.16289 (4)	0.03081 (11)	
V2	0.48289 (8)	0.31044 (5)	0.03247 (4)	0.04600 (15)	
O1	0.2405 (3)	0.52471 (18)	0.47897 (18)	0.0385 (4)	
O2	0.0915 (3)	0.6963 (2)	0.4704 (2)	0.0553 (6)	
O3	0.5310 (3)	0.4070 (2)	0.30298 (17)	0.0411 (5)	
O4	0.4868 (3)	0.58607 (19)	0.11187 (16)	0.0383 (4)	
O5	0.7830 (3)	0.4986 (3)	0.1340 (2)	0.0632 (7)	
O6	0.6154 (3)	0.3387 (2)	0.0954 (2)	0.0565 (7)	
O7	0.3068 (4)	0.3382 (3)	0.1098 (2)	0.0769 (9)	
O8	0.5116 (6)	0.1674 (2)	0.0252 (3)	0.0980 (14)	
N3	0.3584 (3)	0.2840 (2)	0.56278 (19)	0.0325 (5)	
N4	0.2610 (3)	0.2000 (2)	0.42780 (19)	0.0321 (5)	
N1A	−0.0245 (7)	0.6630 (7)	−0.0520 (5)	0.0511 (17)	0.534 (11)
H1A1	0.068783	0.628719	−0.053834	0.077*	0.534 (11)
H1A2	−0.036718	0.675570	−0.120727	0.077*	0.534 (11)
H1A3	−0.094914	0.612355	0.002064	0.077*	0.534 (11)
N2A	0.1937 (3)	0.4754 (2)	0.3046 (2)	0.0324 (5)	0.534 (11)
H2AC	0.267423	0.500729	0.237479	0.039*	0.534 (11)
H2AD	0.132401	0.428641	0.295082	0.039*	0.534 (11)
C1A	−0.0422 (15)	0.7850 (10)	−0.0239 (11)	0.065 (3)	0.534 (11)
H1AA	−0.151129	0.802817	0.009100	0.078*	0.534 (11)
H1AB	−0.006459	0.848649	−0.096551	0.078*	0.534 (11)
C2A	0.0364 (14)	0.8003 (7)	0.0564 (8)	0.052 (2)	0.534 (11)
H2AA	0.140387	0.824892	0.011591	0.062*	0.534 (11)
H2AB	−0.017196	0.866728	0.090425	0.062*	0.534 (11)
C3A	0.042 (3)	0.683 (3)	0.153 (2)	0.052 (5)	0.534 (11)
H3AA	0.106097	0.619819	0.118836	0.062*	0.534 (11)
H3AB	−0.060707	0.652883	0.191254	0.062*	0.534 (11)
C4A	0.1031 (13)	0.7010 (7)	0.2422 (8)	0.0430 (18)	0.534 (11)
H4AA	0.206876	0.729162	0.204135	0.052*	0.534 (11)
H4AB	0.040617	0.765710	0.274879	0.052*	0.534 (11)
C5A	0.1047 (10)	0.5842 (6)	0.3398 (7)	0.0349 (14)	0.534 (11)
H5AA	−0.002022	0.560109	0.377435	0.042*	0.534 (11)
N1B	−0.0843 (17)	0.7332 (13)	−0.0599 (9)	0.092 (4)	0.466 (11)
H1B1	−0.056330	0.653128	−0.053176	0.138*	0.466 (11)

H1B2	−0.103320	0.767266	−0.126794	0.138*	0.466 (11)
H1B3	−0.168642	0.740242	−0.001552	0.138*	0.466 (11)
N2B	0.1937 (3)	0.4754 (2)	0.3046 (2)	0.0324 (5)	0.466 (11)
H2BC	0.254448	0.469107	0.235269	0.039*	0.466 (11)
H2BD	0.103074	0.446448	0.317935	0.039*	0.466 (11)
C1B	0.0327 (15)	0.7939 (11)	−0.0569 (9)	0.055 (3)	0.466 (11)
H1BA	0.036663	0.880480	−0.101643	0.066*	0.466 (11)
H1BB	0.132517	0.751270	−0.078464	0.066*	0.466 (11)
C2B	−0.0450 (15)	0.7745 (13)	0.0883 (10)	0.062 (3)	0.466 (11)
H2BA	−0.060180	0.853549	0.106720	0.074*	0.466 (11)
H2BB	−0.142491	0.735132	0.118419	0.074*	0.466 (11)
C3B	0.073 (3)	0.692 (3)	0.136 (2)	0.040 (4)	0.466 (11)
H3BA	0.173286	0.725887	0.093264	0.048*	0.466 (11)
H3BB	0.076685	0.610213	0.124312	0.048*	0.466 (11)
C4B	0.0414 (11)	0.6762 (9)	0.2659 (8)	0.0365 (17)	0.466 (11)
H4BA	0.025226	0.757614	0.279834	0.044*	0.466 (11)
H4BB	−0.051585	0.631427	0.310312	0.044*	0.466 (11)
C5B	0.1740 (10)	0.6059 (6)	0.3064 (6)	0.0255 (13)	0.466 (11)
H5BA	0.268464	0.646941	0.254025	0.031*	0.466 (11)
C6	0.1564 (4)	0.6087 (3)	0.4323 (2)	0.0364 (6)	
C7	0.4109 (4)	0.3304 (3)	0.6255 (3)	0.0407 (6)	
H7A	0.419788	0.415905	0.606119	0.049*	
C8	0.4533 (4)	0.2536 (3)	0.7205 (3)	0.0480 (8)	
H8A	0.491515	0.288232	0.762469	0.058*	
C9	0.4389 (4)	0.1284 (3)	0.7515 (3)	0.0498 (8)	
H9A	0.465751	0.077469	0.815119	0.060*	
C10	0.3828 (4)	0.0767 (3)	0.6865 (2)	0.0408 (6)	
C11	0.3672 (5)	−0.0537 (3)	0.7089 (3)	0.0535 (9)	
H11A	0.392773	−0.109731	0.771058	0.064*	
C12	0.3157 (5)	−0.0964 (3)	0.6404 (3)	0.0552 (9)	
H12A	0.304755	−0.181337	0.657416	0.066*	
C13	0.2778 (4)	−0.0142 (3)	0.5428 (3)	0.0412 (6)	
C14	0.2262 (4)	−0.0526 (3)	0.4671 (3)	0.0511 (8)	
H14A	0.213642	−0.136481	0.479431	0.061*	
C15	0.1949 (4)	0.0339 (3)	0.3756 (3)	0.0487 (8)	
H15A	0.161247	0.009298	0.325069	0.058*	
C16	0.2137 (4)	0.1603 (3)	0.3580 (3)	0.0404 (6)	
H16A	0.192236	0.218353	0.295089	0.048*	
C17	0.2930 (3)	0.1139 (2)	0.5187 (2)	0.0310 (5)	
C18	0.3457 (3)	0.1596 (2)	0.5914 (2)	0.0312 (5)	
O9	0.2826 (5)	0.0017 (5)	0.0903 (4)	0.1215 (16)	
H91	0.332940	0.065801	0.060048	0.182*	
H92	0.308060	−0.029729	0.034468	0.182*	
O10	0.0727 (3)	0.6510 (3)	0.7036 (2)	0.0613 (7)	
H101	0.130220	0.593952	0.729652	0.092*	
H102	0.115531	0.669602	0.631782	0.092*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0444 (2)	0.02394 (14)	0.02671 (15)	−0.00129 (12)	−0.01526 (14)	−0.00487 (11)
V1	0.0309 (2)	0.0383 (2)	0.0236 (2)	0.00036 (17)	−0.01121 (17)	−0.00697 (16)
V2	0.0816 (4)	0.0301 (2)	0.0266 (2)	−0.0047 (2)	−0.0206 (3)	−0.00322 (18)
O1	0.0528 (12)	0.0331 (9)	0.0374 (10)	0.0036 (8)	−0.0229 (9)	−0.0134 (8)
O2	0.0801 (18)	0.0393 (12)	0.0570 (15)	0.0152 (11)	−0.0316 (13)	−0.0251 (11)
O3	0.0470 (12)	0.0459 (11)	0.0264 (9)	−0.0012 (9)	−0.0135 (9)	−0.0024 (8)
O4	0.0475 (12)	0.0371 (10)	0.0266 (9)	0.0023 (8)	−0.0133 (8)	−0.0038 (7)
O5	0.0394 (13)	0.091 (2)	0.0561 (15)	−0.0165 (13)	−0.0183 (12)	−0.0059 (14)
O6	0.089 (2)	0.0452 (12)	0.0485 (13)	0.0218 (12)	−0.0407 (14)	−0.0220 (10)
O7	0.087 (2)	0.102 (2)	0.0321 (13)	−0.0295 (19)	−0.0035 (13)	−0.0103 (14)
O8	0.196 (4)	0.0305 (12)	0.081 (2)	−0.0135 (18)	−0.063 (3)	−0.0098 (13)
N3	0.0394 (12)	0.0306 (10)	0.0282 (10)	0.0005 (9)	−0.0132 (9)	−0.0071 (8)
N4	0.0412 (12)	0.0265 (10)	0.0281 (10)	−0.0033 (9)	−0.0118 (9)	−0.0049 (8)
N1A	0.045 (3)	0.067 (4)	0.041 (3)	0.010 (3)	−0.021 (2)	−0.012 (3)
N2A	0.0391 (12)	0.0295 (10)	0.0329 (11)	−0.0004 (9)	−0.0170 (10)	−0.0089 (8)
C1A	0.071 (7)	0.060 (5)	0.066 (7)	0.001 (6)	−0.044 (6)	0.001 (5)
C2A	0.075 (6)	0.034 (3)	0.056 (5)	−0.002 (4)	−0.043 (5)	−0.002 (3)
C3A	0.067 (12)	0.036 (4)	0.064 (13)	−0.007 (8)	−0.046 (10)	0.001 (7)
C4A	0.058 (5)	0.028 (3)	0.047 (5)	−0.003 (3)	−0.027 (4)	−0.004 (3)
C5A	0.036 (4)	0.028 (3)	0.041 (3)	−0.001 (2)	−0.015 (3)	−0.007 (2)
N1B	0.121 (10)	0.091 (9)	0.078 (6)	−0.045 (8)	−0.055 (7)	0.004 (6)
N2B	0.0391 (12)	0.0295 (10)	0.0329 (11)	−0.0004 (9)	−0.0170 (10)	−0.0089 (8)
C1B	0.059 (6)	0.064 (5)	0.042 (5)	−0.002 (5)	−0.028 (5)	−0.002 (4)
C2B	0.063 (7)	0.075 (7)	0.056 (6)	0.023 (5)	−0.032 (5)	−0.027 (5)
C3B	0.043 (7)	0.044 (10)	0.031 (4)	0.006 (6)	−0.012 (4)	−0.011 (5)
C4B	0.038 (5)	0.035 (4)	0.033 (4)	0.005 (3)	−0.010 (3)	−0.010 (3)
C5B	0.026 (3)	0.026 (3)	0.023 (3)	−0.005 (2)	−0.006 (2)	−0.004 (2)
C6	0.0450 (16)	0.0310 (12)	0.0350 (13)	−0.0041 (11)	−0.0129 (12)	−0.0103 (10)
C7	0.0483 (17)	0.0404 (14)	0.0386 (15)	−0.0012 (12)	−0.0190 (13)	−0.0125 (12)
C8	0.0525 (19)	0.062 (2)	0.0389 (16)	0.0045 (15)	−0.0232 (14)	−0.0202 (14)
C9	0.056 (2)	0.0589 (19)	0.0358 (15)	0.0147 (16)	−0.0249 (15)	−0.0103 (14)
C10	0.0463 (16)	0.0387 (14)	0.0300 (13)	0.0054 (12)	−0.0138 (12)	−0.0007 (11)
C11	0.069 (2)	0.0369 (15)	0.0435 (17)	0.0038 (15)	−0.0216 (17)	0.0069 (13)
C12	0.076 (3)	0.0269 (13)	0.0524 (19)	−0.0041 (14)	−0.0192 (18)	0.0036 (13)
C13	0.0493 (17)	0.0271 (12)	0.0393 (15)	−0.0041 (11)	−0.0077 (13)	−0.0040 (11)
C14	0.061 (2)	0.0315 (14)	0.059 (2)	−0.0095 (14)	−0.0126 (17)	−0.0143 (14)
C15	0.061 (2)	0.0450 (16)	0.0485 (18)	−0.0100 (15)	−0.0185 (16)	−0.0198 (14)
C16	0.0506 (17)	0.0389 (14)	0.0357 (14)	−0.0042 (12)	−0.0167 (13)	−0.0115 (11)
C17	0.0329 (13)	0.0271 (11)	0.0277 (11)	−0.0024 (9)	−0.0057 (10)	−0.0041 (9)
C18	0.0344 (13)	0.0298 (11)	0.0261 (11)	0.0014 (10)	−0.0090 (10)	−0.0048 (9)
O9	0.079 (3)	0.172 (5)	0.126 (4)	0.014 (3)	−0.040 (3)	−0.060 (3)
O10	0.0671 (17)	0.0685 (17)	0.0555 (15)	−0.0091 (13)	−0.0349 (14)	−0.0068 (13)

Geometric parameters (Å, º)

Cu1—O1	1.940 (2)	N1B—H1B2	0.8900
Cu1—N2B	2.001 (2)	N1B—H1B3	0.8900
Cu1—N2A	2.001 (2)	N2B—C5B	1.464 (6)
Cu1—N3	2.008 (2)	N2B—H2BC	0.8900
Cu1—N4	2.023 (2)	N2B—H2BD	0.8900
Cu1—O3	2.282 (2)	C1B—C2B	1.700 (17)
V1—O3	1.631 (2)	C1B—H1BA	0.9700
V1—O5	1.643 (2)	C1B—H1BB	0.9700
V1—O4	1.788 (2)	C2B—C3B	1.50 (4)
V1—O6	1.796 (2)	C2B—H2BA	0.9700
V2—O8	1.624 (3)	C2B—H2BB	0.9700
V2—O7	1.636 (3)	C3B—C4B	1.54 (3)
V2—O6	1.792 (3)	C3B—H3BA	0.9700
V2—O4^{i}	1.8090 (19)	C3B—H3BB	0.9700
O1—C6	1.272 (3)	C4B—C5B	1.520 (12)
O2—C6	1.224 (4)	C4B—H4BA	0.9700
N3—C7	1.323 (4)	C4B—H4BB	0.9700
N3—C18	1.353 (3)	C5B—C6	1.570 (6)
N4—C16	1.325 (4)	C5B—H5BA	0.9800
N4—C17	1.358 (3)	C7—C8	1.402 (4)
N1A—C1A	1.499 (15)	C7—H7A	0.9300
N1A—H1A1	0.8900	C8—C9	1.361 (5)
N1A—H1A2	0.8900	C8—H8A	0.9300
N1A—H1A3	0.8900	C9—C10	1.408 (5)
N2A—C5A	1.476 (7)	C9—H9A	0.9300
N2A—H2AC	0.8900	C10—C18	1.402 (4)
N2A—H2AD	0.8900	C10—C11	1.433 (5)
C1A—C2A	1.506 (14)	C11—C12	1.355 (6)
C1A—H1AA	0.9700	C11—H11A	0.9300
C1A—H1AB	0.9700	C12—C13	1.428 (5)
C2A—C3A	1.52 (3)	C12—H12A	0.9300
C2A—H2AA	0.9700	C13—C17	1.403 (4)
C2A—H2AB	0.9700	C13—C14	1.409 (5)
C3A—C4A	1.51 (3)	C14—C15	1.362 (5)
C3A—H3AA	0.9700	C14—H14A	0.9300
C3A—H3AB	0.9700	C15—C16	1.404 (4)
C4A—C5A	1.516 (11)	C15—H15A	0.9300
C4A—H4AA	0.9700	C16—H16A	0.9300
C4A—H4AB	0.9700	C17—C18	1.430 (4)
C5A—C6	1.526 (7)	O9—H91	0.8356
C5A—H5AA	0.9800	O9—H92	0.8396
N1B—C1B	1.383 (16)	O10—H101	0.8369
N1B—H1B1	0.8900	O10—H102	0.8367
O1—Cu1—N2B	83.94 (9)	H1B1—N1B—H1B3	109.5
O1—Cu1—N2A	83.94 (9)	H1B2—N1B—H1B3	109.5

O1—Cu1—N3	90.65 (9)	C5B—N2B—Cu1	109.4 (3)
N2B—Cu1—N3	172.79 (10)	C5B—N2B—H2BC	109.8
N2A—Cu1—N3	172.79 (10)	Cu1—N2B—H2BC	109.8
O1—Cu1—N4	157.13 (10)	C5B—N2B—H2BD	109.8
N2B—Cu1—N4	101.14 (9)	Cu1—N2B—H2BD	109.8
N2A—Cu1—N4	101.14 (9)	H2BC—N2B—H2BD	108.3
N3—Cu1—N4	82.07 (9)	N1B—C1B—C2B	92.3 (11)
O1—Cu1—O3	101.31 (9)	N1B—C1B—H1BA	113.2
N2B—Cu1—O3	92.76 (9)	C2B—C1B—H1BA	113.2
N2A—Cu1—O3	92.76 (9)	N1B—C1B—H1BB	113.2
N3—Cu1—O3	92.97 (9)	C2B—C1B—H1BB	113.2
N4—Cu1—O3	100.70 (9)	H1BA—C1B—H1BB	110.6
O3—V1—O5	108.89 (13)	C3B—C2B—C1B	103.3 (12)
O3—V1—O4	107.83 (10)	C3B—C2B—H2BA	111.1
O5—V1—O4	112.78 (13)	C1B—C2B—H2BA	111.1
O3—V1—O6	109.91 (12)	C3B—C2B—H2BB	111.1
O5—V1—O6	108.72 (15)	C1B—C2B—H2BB	111.1
O4—V1—O6	108.68 (10)	H2BA—C2B—H2BB	109.1
O8—V2—O7	111.8 (2)	C2B—C3B—C4B	113.4 (17)
O8—V2—O6	108.32 (17)	C2B—C3B—H3BA	108.9
O7—V2—O6	109.89 (14)	C4B—C3B—H3BA	108.9
O8—V2—O4^{i}	109.20 (14)	C2B—C3B—H3BB	108.9
O7—V2—O4^{i}	107.28 (13)	C4B—C3B—H3BB	108.9
O6—V2—O4^{i}	110.39 (12)	H3BA—C3B—H3BB	107.7
C6—O1—Cu1	115.86 (18)	C5B—C4B—C3B	111.3 (13)
V1—O3—Cu1	134.84 (12)	C5B—C4B—H4BA	109.4
V1—O4—V2^{i}	129.04 (12)	C3B—C4B—H4BA	109.4
V2—O6—V1	129.23 (14)	C5B—C4B—H4BB	109.4
C7—N3—C18	119.0 (2)	C3B—C4B—H4BB	109.4
C7—N3—Cu1	128.5 (2)	H4BA—C4B—H4BB	108.0
C18—N3—Cu1	112.50 (17)	N2B—C5B—C4B	113.6 (7)
C16—N4—C17	118.0 (2)	N2B—C5B—C6	107.7 (4)
C16—N4—Cu1	130.04 (19)	C4B—C5B—C6	112.0 (6)
C17—N4—Cu1	111.87 (18)	N2B—C5B—H5BA	107.8
C1A—N1A—H1A1	109.5	C4B—C5B—H5BA	107.8
C1A—N1A—H1A2	109.5	C6—C5B—H5BA	107.8
H1A1—N1A—H1A2	109.5	O2—C6—O1	124.2 (3)
C1A—N1A—H1A3	109.5	O2—C6—C5A	116.7 (3)
H1A1—N1A—H1A3	109.5	O1—C6—C5A	117.7 (3)
H1A2—N1A—H1A3	109.5	O2—C6—C5B	122.0 (3)
C5A—N2A—Cu1	109.5 (3)	O1—C6—C5B	112.5 (3)
C5A—N2A—H2AC	109.8	N3—C7—C8	121.5 (3)
Cu1—N2A—H2AC	109.8	N3—C7—H7A	119.3
C5A—N2A—H2AD	109.8	C8—C7—H7A	119.3
Cu1—N2A—H2AD	109.8	C9—C8—C7	120.2 (3)
H2AC—N2A—H2AD	108.2	C9—C8—H8A	119.9
N1A—C1A—C2A	119.4 (8)	C7—C8—H8A	119.9
N1A—C1A—H1AA	107.5	C8—C9—C10	119.4 (3)

C2A—C1A—H1AA	107.5	C8—C9—H9A	120.3
N1A—C1A—H1AB	107.5	C10—C9—H9A	120.3
C2A—C1A—H1AB	107.5	C18—C10—C9	116.9 (3)
H1AA—C1A—H1AB	107.0	C18—C10—C11	118.8 (3)
C3A—C2A—C1A	113.4 (13)	C9—C10—C11	124.3 (3)
C3A—C2A—H2AA	108.9	C12—C11—C10	120.7 (3)
C1A—C2A—H2AA	108.9	C12—C11—H11A	119.7
C3A—C2A—H2AB	108.9	C10—C11—H11A	119.7
C1A—C2A—H2AB	108.9	C11—C12—C13	121.7 (3)
H2AA—C2A—H2AB	107.7	C11—C12—H12A	119.2
C2A—C3A—C4A	114.1 (19)	C13—C12—H12A	119.2
C2A—C3A—H3AA	108.7	C17—C13—C14	116.8 (3)
C4A—C3A—H3AA	108.7	C17—C13—C12	118.7 (3)
C2A—C3A—H3AB	108.7	C14—C13—C12	124.5 (3)
C4A—C3A—H3AB	108.7	C15—C14—C13	119.6 (3)
H3AA—C3A—H3AB	107.6	C15—C14—H14A	120.2
C5A—C4A—C3A	113.7 (13)	C13—C14—H14A	120.2
C5A—C4A—H4AA	108.8	C14—C15—C16	119.8 (3)
C3A—C4A—H4AA	108.8	C14—C15—H15A	120.1
C5A—C4A—H4AB	108.8	C16—C15—H15A	120.1
C3A—C4A—H4AB	108.8	N4—C16—C15	122.4 (3)
H4AA—C4A—H4AB	107.7	N4—C16—H16A	118.8
N2A—C5A—C4A	115.8 (7)	C15—C16—H16A	118.8
N2A—C5A—C6	109.4 (4)	N4—C17—C13	123.5 (3)
C4A—C5A—C6	111.9 (6)	N4—C17—C18	116.6 (2)
N2A—C5A—H5AA	106.4	C13—C17—C18	119.9 (2)
C4A—C5A—H5AA	106.4	N3—C18—C10	123.0 (3)
C6—C5A—H5AA	106.4	N3—C18—C17	116.7 (2)
C1B—N1B—H1B1	109.5	C10—C18—C17	120.3 (2)
C1B—N1B—H1B2	109.5	H91—O9—H92	100.7
H1B1—N1B—H1B2	109.5	H101—O10—H102	104.1
C1B—N1B—H1B3	109.5		

O5—V1—O3—Cu1	162.47 (18)	C18—N3—C7—C8	0.0 (5)
O4—V1—O3—Cu1	39.8 (2)	Cu1—N3—C7—C8	178.5 (2)
O6—V1—O3—Cu1	−78.53 (19)	N3—C7—C8—C9	−1.1 (5)
O3—V1—O4—V2^{i}	174.60 (15)	C7—C8—C9—C10	0.8 (5)
O5—V1—O4—V2^{i}	54.3 (2)	C8—C9—C10—C18	0.4 (5)
O6—V1—O4—V2^{i}	−66.30 (19)	C8—C9—C10—C11	178.0 (3)
O8—V2—O6—V1	−160.5 (2)	C18—C10—C11—C12	−0.8 (5)
O7—V2—O6—V1	−38.2 (2)	C9—C10—C11—C12	−178.4 (4)
O4^{i}—V2—O6—V1	80.0 (2)	C10—C11—C12—C13	1.1 (6)
O3—V1—O6—V2	95.4 (2)	C11—C12—C13—C17	−0.8 (6)
O5—V1—O6—V2	−145.5 (2)	C11—C12—C13—C14	178.9 (4)
O4—V1—O6—V2	−22.4 (2)	C17—C13—C14—C15	0.4 (5)
N1A—C1A—C2A—C3A	−35 (2)	C12—C13—C14—C15	−179.2 (4)
C1A—C2A—C3A—C4A	−173.0 (13)	C13—C14—C15—C16	−0.3 (6)
C2A—C3A—C4A—C5A	178.6 (12)	C17—N4—C16—C15	0.5 (5)

Cu1—N2A—C5A—C4A	146.8 (6)	Cu1—N4—C16—C15	−176.5 (2)
Cu1—N2A—C5A—C6	19.2 (6)	C14—C15—C16—N4	−0.2 (5)
C3A—C4A—C5A—N2A	57.7 (16)	C16—N4—C17—C13	−0.4 (4)
C3A—C4A—C5A—C6	−176.0 (11)	Cu1—N4—C17—C13	177.1 (2)
N1B—C1B—C2B—C3B	115.6 (18)	C16—N4—C17—C18	179.2 (3)
C1B—C2B—C3B—C4B	171.0 (15)	Cu1—N4—C17—C18	−3.3 (3)
C2B—C3B—C4B—C5B	−172.6 (14)	C14—C13—C17—N4	−0.1 (5)
Cu1—N2B—C5B—C4B	−151.4 (6)	C12—C13—C17—N4	179.6 (3)
Cu1—N2B—C5B—C6	−26.8 (6)	C14—C13—C17—C18	−179.6 (3)
C3B—C4B—C5B—N2B	−67.3 (16)	C12—C13—C17—C18	0.1 (4)
C3B—C4B—C5B—C6	170.4 (13)	C7—N3—C18—C10	1.3 (4)
Cu1—O1—C6—O2	164.7 (3)	Cu1—N3—C18—C10	−177.4 (2)
Cu1—O1—C6—C5A	−1.3 (5)	C7—N3—C18—C17	−178.1 (3)
Cu1—O1—C6—C5B	−28.3 (4)	Cu1—N3—C18—C17	3.2 (3)
N2A—C5A—C6—O2	−179.6 (4)	C9—C10—C18—N3	−1.5 (4)
C4A—C5A—C6—O2	50.7 (10)	C11—C10—C18—N3	−179.3 (3)
N2A—C5A—C6—O1	−12.5 (8)	C9—C10—C18—C17	177.9 (3)
C4A—C5A—C6—O1	−142.2 (7)	C11—C10—C18—C17	0.2 (4)
N2B—C5B—C6—O2	−156.2 (4)	N4—C17—C18—N3	0.1 (4)
C4B—C5B—C6—O2	−30.6 (9)	C13—C17—C18—N3	179.7 (3)
N2B—C5B—C6—O1	36.5 (6)	N4—C17—C18—C10	−179.3 (3)
C4B—C5B—C6—O1	162.1 (6)	C13—C17—C18—C10	0.2 (4)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*1···O5^{i}	0.89	2.09	2.794 (7)	136
N1*A*—H1*A*2···O7^{ii}	0.89	2.49	2.958 (7)	114
N1*A*—H1*A*2···O10^{iii}	0.89	2.21	2.979 (7)	145
N1*A*—H1*A*3···O5^{iv}	0.89	1.89	2.769 (8)	169
N2*A*—H2*AC*···O4	0.89	2.25	3.094 (3)	159
N2*A*—H2*AD*···O10^{v}	0.89	2.22	3.077 (3)	163
C1*A*—H1*AA*···O9^{ii}	0.97	2.56	3.157 (11)	120
C5*A*—H5*AA*···O1^{v}	0.98	2.44	3.390 (10)	163
N1*B*—H1*B*1···O5^{iv}	0.89	2.60	3.090 (10)	115
N2*B*—H2*BC*···O4	0.89	2.48	3.094 (3)	127
N2*B*—H2*BC*···O7	0.89	2.39	3.127 (4)	141
N2*B*—H2*BD*···O10^{v}	0.89	2.23	3.077 (3)	159
C1*B*—H1*BB*···O6^{i}	0.97	2.37	3.326 (13)	167
C5*B*—H5*BA*···O4	0.98	2.39	3.140 (8)	133
C8—H8*A*···O4^{vi}	0.93	2.51	3.412 (4)	162
C16—H16*A*···O7	0.93	2.31	3.097 (4)	143
O9—H91···O8	0.84	2.00	2.780 (6)	155
O9—H92···O8^{vii}	0.84	2.21	2.861 (6)	135

O10—H101···O5^{vi}	0.84	2.09	2.837 (4)	148
O10—H102···O2	0.84	2.07	2.811 (4)	147

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