

# Crystal structure of poly[[ $(\mu_3$ -hydroxido- $\kappa^3$ O:O:O)- $(\mu_3$ -selenato- $\kappa^3$ O<sup>1</sup>:O<sup>2</sup>:O<sup>3</sup>)tris[ $\mu_3$ -2-(1,2,4-triazol-4-yl)acetato- $\kappa^3$ N<sup>1</sup>:N<sup>2</sup>:O]tricopper(II)] dihydrate]

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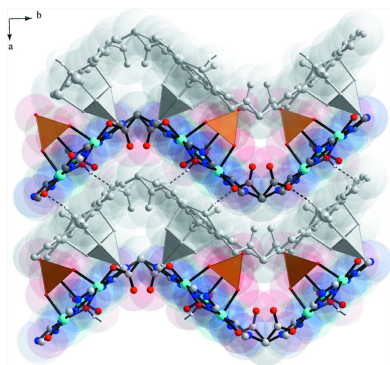
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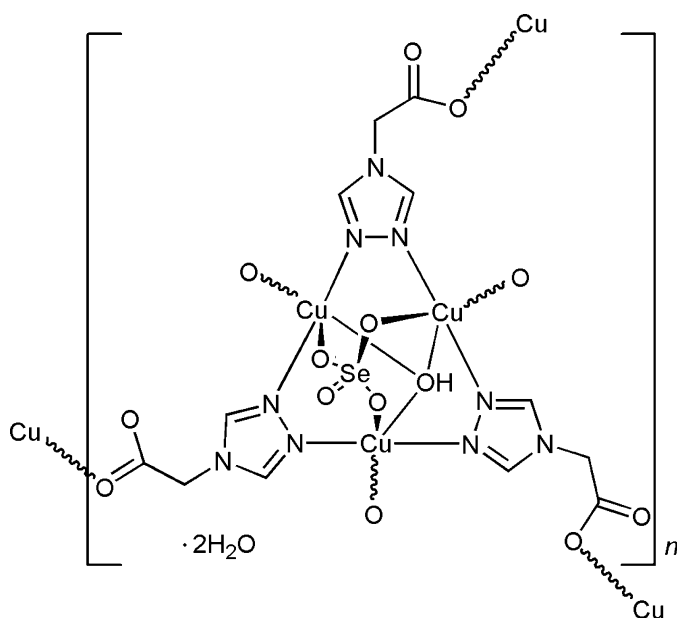
The title coordination polymer,  $\{[\text{Cu}_3(\text{C}_4\text{H}_4\text{N}_3\text{O}_9)_3(\text{SeO}_4)(\text{OH})]\cdot 2\text{H}_2\text{O}\}_n$  or  $[\text{Cu}_3(\mu_3\text{-OH})(\text{trgly})_3(\text{SeO}_4)]\cdot 2\text{H}_2\text{O}$ , crystallizes in the monoclinic space group  $P2_1/c$ . The three independent  $\text{Cu}^{2+}$  cations adopt distorted square-pyramidal geometries with  $\{\text{O}_2\text{N}_2+\text{O}\}$  polyhedra. The three copper centres are bridged by a  $\mu_3$ -OH anion, leading to a triangular  $[\text{Cu}_3(\mu_3\text{-OH})]$  core. 2-(1,2,4-Triazol-4-yl)acetic acid (trgly-H) acts in a deprotonated form as a  $\mu_3$ - $\kappa^3$ N<sup>1</sup>:N<sup>2</sup>:O ligand. The three triazolyl groups bridge three copper centres of the hydroxo-cluster in an N<sup>1</sup>:N<sup>2</sup> mode, thus supporting the triangular geometry. The  $[\text{Cu}_3(\mu_3\text{-OH})(\text{tr})_3]$  clusters serve as secondary building units (SBUs). Each SBU can be regarded as a six-connected node, which is linked to six neighbouring triangles through carboxylate groups, generating a two-dimensional uninodal (3,6) coordination network. The selenate anion is bound in a  $\mu_3$ - $\kappa^3$ O<sup>1</sup>:O<sup>2</sup>:O<sup>3</sup> fashion to the trinuclear copper platform. The  $[\text{Cu}_3(\text{OH})(\text{trgly})_3(\text{SeO}_4)]$  coordination layers and guest water molecules are linked together by numerous O—H...O and C—H...O hydrogen bonds, leading to a three-dimensional structure.

## 1. Chemical context

Extended coordination networks incorporating trinuclear 1,2,4-triazole (tr)-based hydroxo(oxo) clusters  $[\text{Cu}_3(\mu_3\text{-OH/or O})(\text{tr})_3]$  as secondary building units (SBUs) are a subject of high interest in many interdisciplinary fields including gas storage and sorption (Lincke *et al.*, 2012), magnetism (Ouelllette *et al.*, 2006), anion exchange and separation (Wang *et al.*, 2007). In these clusters, the copper(II) cations display either distorted tetragonal-pyramidal (TP) or (and) octahedral coordination geometries, two of the most stable configurations in the OH<sup>−</sup>/tr ligand arrangement. Typically, the basal plane for a five-coordinate  $\text{Cu}^{\text{II}}$  atom (or the equatorial plane for six-coordinate  $\text{Cu}^{\text{II}}$ ) consists of two nitrogen atoms from two *trans*-coordinated tr groups, an oxygen atom from OH<sup>−</sup>/O<sup>2−</sup> and an O (N, or Cl<sup>−</sup>) donor atom (or anion) from an extra ligand, whereas the apical position is occupied by a water molecule or anionic ligand (Lysenko *et al.*, 2006; Naik *et al.*, 2010). The alternative trigonal-bipyramidal (TBP) environment around the copper centres can not be realized in the specific ligand configuration. Addison *et al.* (1984) introduced a useful structural parameter,  $\tau$ , as a criterion for distinguishing between TP and TBP polyhedra. This parameter, which varies from 0 (in TP) to 1 (in TBP), could perhaps be used to predict the anion binding affinity of closely related anions (e.g.  $\text{SO}_4^{2-}$  versus  $\text{SeO}_4^{2-}$ ) toward the  $[\text{Cu}_3(\mu_3\text{-OH/or O})(\text{tr})_3]$  SBUs. The higher binding affinity might be associated



with the lower  $\tau$  parameter. As a matter of fact, the  $[\text{Cu}_3(\mu_3\text{-OH/or O})(\text{tr})_3]$  cationic clusters are perfectly suited for the binding of tetrahedral anions through its three apical sites. In this context, it would be interesting to clarify how the size of the coordinating anions correlates with the  $\tau$  value. In this paper, we report the crystal structure of the title  $\text{Cu}^{2+}$  complex, (I), which was prepared by reacting  $\text{CuSeO}_4$  and  $\text{trgly-H}$  in an aqueous solution under hydrothermal conditions. The compound is isomorphous to the  $[\text{Cu}_3(\mu_3\text{-OH})(\text{trgly})_3(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$  complex (Vasylevs'kyy *et al.*, 2014).



## 2. Structural commentary

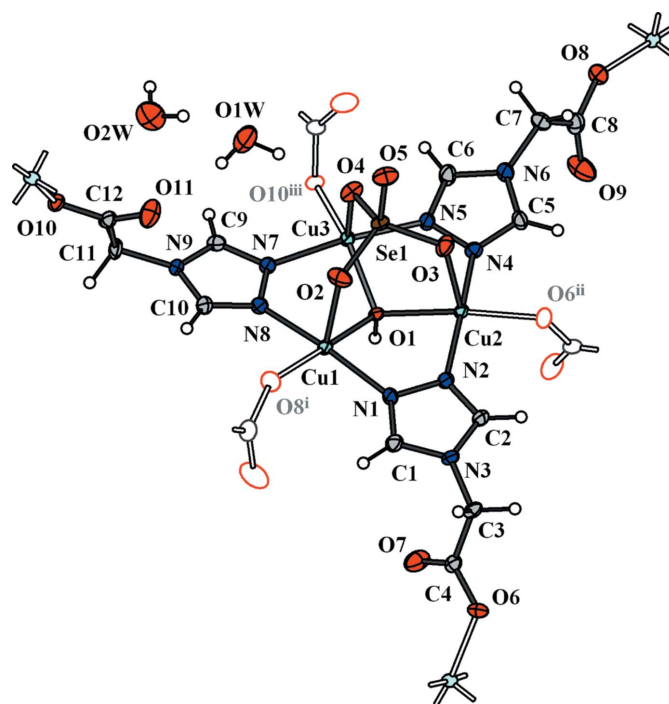
The title compound crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$ . The asymmetric unit consists of three copper(II) cations, one selenate anion, one hydroxide anion, three deprotonated  $\text{trgly}^-$  ligands and two water molecules (Fig. 1 and Table 1). Each copper centre adopts a similar tetragonal–pyramidal coordination environment with the  $\{\text{O}_2\text{N}_2+\text{O}\}$  donor set. The basal plane of Cu1 is completed by atom O1 of the  $\mu_3$ -bridging hydroxide group [Cu1–O1 = 2.022 (2) Å], atom N1 from one bridging tr-group [Cu1–N1 = 1.980 (3) Å], atom N8 from the other bridging tr-group [Cu1–N8, 1.993 (3) Å] and a carboxylate O atom from the  $\text{trgly}$  ligand [Cu1–O8<sup>i</sup> = 1.935 (3) Å; symmetry code: (i)  $x, y, z - 1$ ]. The basal planes of Cu2 and Cu3 cations consist four short bonds as follows: Cu2–N2 = 1.979 (3), Cu2–N4 = 1.986 (3), Cu2–O1 = 2.039 (3) and Cu2–O6<sup>ii</sup> 1.954 (3) Å and Cu3–N5 = 1.974 (3), Cu3–N7 = 1.982 (3), Cu3–O1 = 2.039 (2) and Cu3–O10<sup>iii</sup> 1.990 (3) Å for Cu2 and for Cu3, respectively [symmetry codes: (ii)  $x, -y - \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ]. The basal planes of the three square pyramids share a common corner at the O1 atom of the  $\text{OH}^-$  anion, forming a triangular  $[\text{Cu}_3(\mu_3\text{-OH})]$  core. The trinuclear motif is supported by a facially coordinating tripodal selenate anion [Cu1–O2 2.182 (3), Cu2–O3 = 2.146 (3) and Cu3–O4 = 2.182 (3) Å]. The value of the Addison structural parameter  $\tau$  varies from

**Table 1**  
Selected bond lengths (Å).

Cu1–O8 <sup>i</sup>	1.935 (3)	Cu3–N5	1.974 (3)
Cu1–N1	1.980 (3)	Cu3–N7	1.982 (3)
Cu1–N8	1.993 (3)	Cu3–O10 <sup>iii</sup>	1.990 (3)
Cu1–O1	2.022 (2)	Cu3–O1	2.039 (2)
Cu1–O2	2.182 (3)	Cu3–O4	2.182 (3)
Cu2–O6 <sup>ii</sup>	1.954 (3)	Se1–O5	1.632 (3)
Cu2–N2	1.979 (3)	Se1–O2	1.637 (3)
Cu2–N4	1.986 (3)	Se1–O3	1.645 (3)
Cu2–O1	2.039 (3)	Se1–O4	1.649 (3)
Cu2–O3	2.146 (3)		

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

0.025 for Cu2 through 0.070 for Cu1 to 0.189 for Cu3, indicating the preference of a TP configuration (*versus* TBP) around the copper centres. A comparison of the  $\tau$  values for (I) with the corresponding values for the isomorphous sulfate complex  $[\text{Cu}_3(\mu_3\text{-OH})(\text{trgly})_3(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$  ( $\tau = 0.021, 0.103, 0.211$ ; Vasylevs'kyy *et al.*, 2014) indicates a lower degree of TBP distortion for the selenate compound. This tendency is also observed for the other two isomorphous MOFs  $[\text{Cu}_3(\mu_3\text{-OH})(X)]_4\{\text{Cu}_2(\text{H}_2\text{O})_2\}_3(\text{trz-ia})_{12}$  [ $X = \text{SO}_4^{2-}$  and  $\text{SeO}_4^{2-}$ ,  $\text{trz-ia}$  is the 5-(4*H*-1,2,4-triazol-4-yl)isophthalate anion], where the  $\tau$  parameter values are 0.096 and 0.083 for the sulfate and selenate complexes, respectively (Lincke *et al.*, 2012). Unlike  $[\text{Cu}_3(\mu_3\text{-OH})(\text{trgly})_3(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ , in which the highest  $\tau$  value corresponds with the longest Cu–O axial bond, the  $\tau$  parameter values for the title compound do not correlate with the Cu–O axial bond lengths. Atoms Cu1 and Cu3 with the lowest and highest  $\tau$  values, respectively, have the same Cu–



**Figure 1**  
A portion of the structure of (I), showing the atom-labelling scheme and the copper coordination environments. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $x, -y - \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ].

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

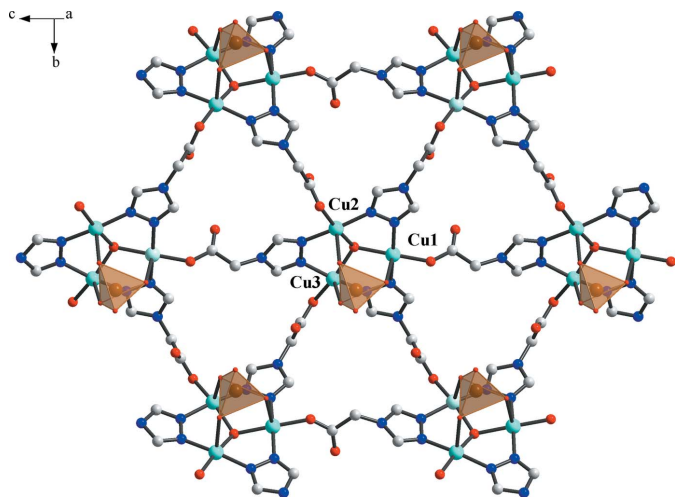
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O $\cdots$ O10 <sup>iv</sup>	0.85	2.01	2.811 (4)	156
O1W—H1W $\cdots$ O11	0.85	2.11	2.940 (5)	166
O1W—H2W $\cdots$ O4	0.85	1.93	2.767 (4)	168
O2W—H3W $\cdots$ O9 <sup>v</sup>	0.85	1.95	2.798 (5)	178
O2W—H4W $\cdots$ O1W	0.85	2.00	2.812 (6)	159
C1—H1 $\cdots$ O5 <sup>vi</sup>	0.94	2.58	3.346 (5)	139
C2—H2 $\cdots$ O5 <sup>vii</sup>	0.94	2.28	2.955 (5)	128
C5—H5 $\cdots$ O3 <sup>viii</sup>	0.94	2.39	2.941 (5)	117
C6—H6 $\cdots$ O2W <sup>iii</sup>	0.94	2.30	3.176 (6)	154
C7—H7A $\cdots$ O3 <sup>viii</sup>	0.98	2.25	3.094 (6)	144
C7—H7B $\cdots$ O1W <sup>iii</sup>	0.98	2.38	3.338 (5)	164
C9—H9 $\cdots$ O7 <sup>ix</sup>	0.94	2.25	3.067 (6)	144

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

O axial bond lengths. For compound (I), the hydroxide oxygen atom O1 is displaced by 0.532 Å from the centroid of the Cu1–Cu2–Cu3 triangular fragment, whereas for  $[\text{Cu}_3(\mu_3\text{-OH})(\text{tr-gly})_3(\text{SO}_4)]\cdot 2\text{H}_2\text{O}$ , the O–centroid distance is 0.570 Å. Thus, the larger anion–anion repulsion ( $\text{OH}^-/\text{SO}_4^{2-}$  versus  $\text{OH}^-/\text{SeO}_4^{2-}$ ) in the sulfate complex also confirms the higher TBP distortion. The trinuclear clusters function as SBUs (six-connected nodes), which self-assemble into a two-dimensional coordination network (Fig. 2) with all of the selenate anions on the same side of the coordination layer. The resultant 2D network topology can be rationalized as a (3,6) type. Interestingly, the selenate anions of two neighbouring layers point in opposite directions (Fig. 3).

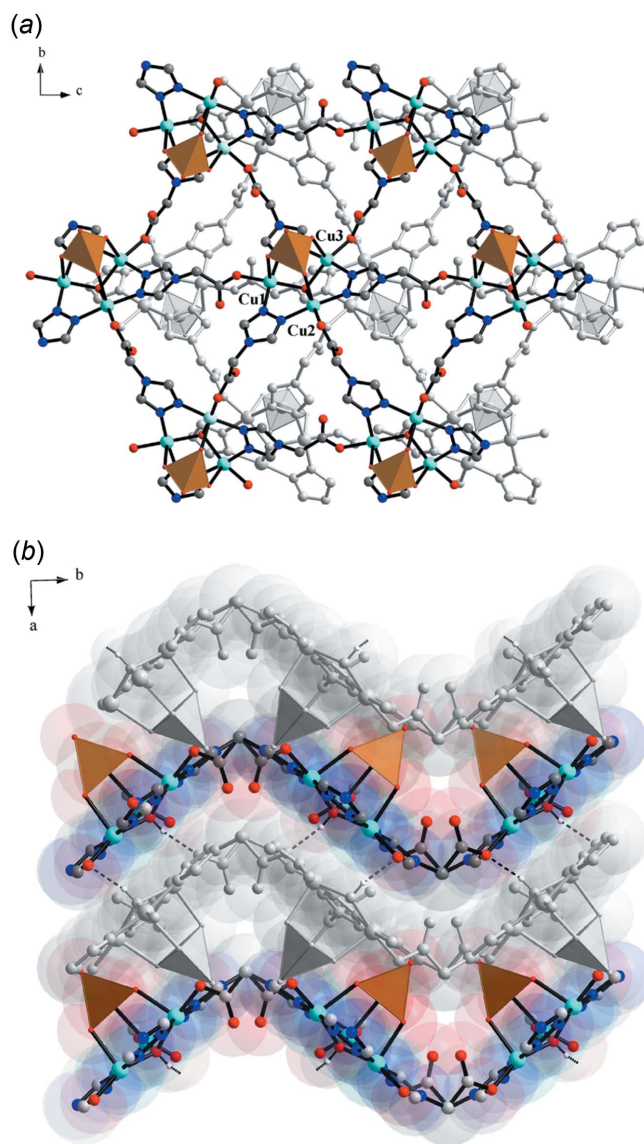
### 3. Supramolecular features

The trinuclear  $[\text{Cu}_3(\mu_3\text{-OH})(\text{tr})_3]$  clusters are involved in inter- and intramolecular hydrogen-bonding interactions. Adjacent layers are linked together by hydrogen bonding between the hydroxide oxygen atoms (O1 as H-atom donor) and carboxylate group oxygen atoms (O10 as H-atom



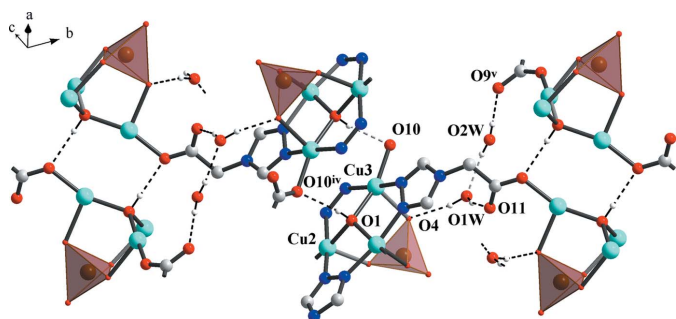
**Figure 2**  
 A single layer of the structure has the (3,6) topological type (view along the  $[401]$  direction, selenates shown as tetrahedra).

acceptor) and are shifted with respect to each other, forming a H-bonded double layer (Fig. 3a, Table 2). The guest water molecules are trapped between neighboring double-layers, forming a set of hydrogen bonds to selenate oxygen atoms [ $\text{O1W}\cdots\text{O4} = 2.767 (4) \text{ \AA}$ ,  $\text{O1W}-\text{H2W}\cdots\text{O4} = 168^\circ$ ], carboxylate oxygen atoms [ $\text{O1W}\cdots\text{O11} = 2.940 (5) \text{ \AA}$ ,  $\text{O1W}-\text{H1W}\cdots\text{O11} = 166^\circ$ , and  $\text{O2W}\cdots\text{O9}^v = 2.798 (5) \text{ \AA}$ ,  $\text{O2W}-\text{H3W}\cdots\text{O9}^v = 178^\circ$ , symmetry code: (v)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ] and to one another [ $\text{O2W}\cdots\text{O1W} = 2.812 (6) \text{ \AA}$ ,  $\text{O2W}-\text{H4W}\cdots\text{O1W} = 159^\circ$ , Fig. 4]. Apparently, the presence of the hydrogen bond between the O1W water molecule and the selenate oxygen atom O4 leads to an increase in the trigonal-bipyramidal distortion of the square-pyramidal coordination



**Figure 3**  
 Crystal packing of compound (I) (a) along the  $a$  axis, and (b) along the  $c$  axis. In (a), neighboring layers are shifted relative to one another while in (b) they are held together by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between hydroxide oxygen atoms and carboxylate group oxygen atoms [ $\text{O1}\cdots\text{O10}^{iv} = 2.811 (4) \text{ \AA}$ ,  $\text{O1}-\text{H1O}\cdots\text{O10}^{iv} = 156^\circ$ ; symmetry code: (iv)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ].



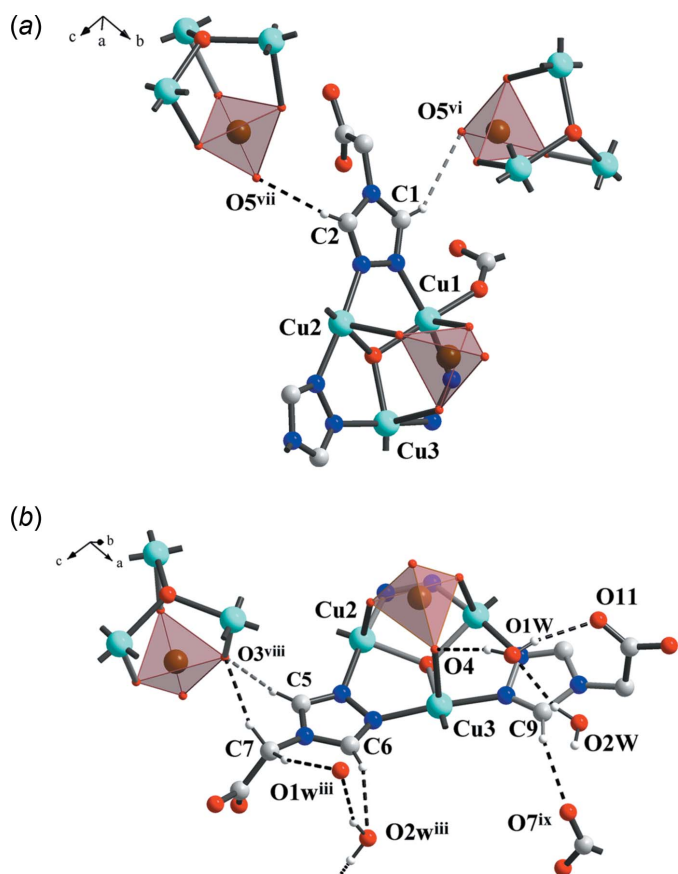


**Figure 4**  
Crystal packing pattern in (I) showing the O—H...O hydrogen-bonding interactions between neighboring layers.

polyhedra of Cu3 ( $\tau = 0.189$  for Cu3, markedly higher than the values of 0.070 and 0.025 for Cu1 and for Cu2, respectively) in the trinuclear  $[\text{Cu}_3(\mu_3\text{-OH})(\text{tr})_3]$  core.

The coordination polymeric network is reinforced by weak C—H...O hydrogen-bonding interactions (Desiraju & Steiner, 1999, Fig. 5, Table 2). These C—H hydrogen bonds with one acceptor oxygen atom [C...O distances ranging from 2.955 (5) to 3.440 (5) Å] help to stabilize the resulting three-dimensional hydrogen-bonded network.

Thus, the hydrothermal reaction of  $\text{CuSeO}_4$  and  $\text{trgly-H}$  leads to a two-dimensional coordination network  $[\text{Cu}_3(\mu_3\text{-OH})(\text{trgly})_3(\text{SeO}_4)]$  based on the trinuclear coordination



**Figure 5**  
Crystal packing patterns in (I) showing the presence of C—H...O hydrogen bonds.

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}_3(\text{C}_4\text{H}_4\text{N}_3\text{O}_9)_3(\text{SeO}_4)(\text{OH})] \cdot 2\text{H}_2\text{O}$
$M_r$	764.92
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	213
$a, b, c$ (Å)	10.9403 (8), 17.5393 (15), 12.1289 (9)
$\beta$ (°)	108.965 (8)
$V$ (Å <sup>3</sup> )	2201.0 (3)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	4.62
Crystal size (mm)	0.20 × 0.16 × 0.14
Data collection	
Diffractometer	Stoe Image plate diffraction system
Absorption correction	Numerical [ $X\text{-RED}$ (Stoe & Cie, 2001) and $X\text{-SHAPE}$ (Stoe & Cie, 1999)]
$T_{\text{min}}, T_{\text{max}}$	0.405, 0.569
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	16928, 4681, 3306
$R_{\text{int}}$	0.057
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.634
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.072, 0.88
No. of reflections	4681
No. of parameters	343
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.99, -0.64

Computer programs: *IPDS Software* (Stoe & Cie, 2000), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

clusters  $[\text{Cu}_3(\mu_3\text{-OH})]$ . The five-coordinate copper(II) centres in the  $[\text{Cu}_3(\mu_3\text{-OH})(\text{tr})_3]$  SBU display less-distorted square-pyramidal arrangements in comparison to those of the isomorphous complex  $[\text{Cu}_3(\mu_3\text{-OH})(\text{trgly})_3(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ .

### 3.1. Database survey

Among the known  $[\text{Cu}_3(\mu_3\text{-OH/or O})(\text{tr})_3]$  complexes (CSD version 5.39, update of May 2018; Groom *et al.*, 2016), the highest possible value of  $\tau$  (0.313) in the five-coordinate copper(II) cation was once observed for the copper(II)-polyoxomolybdate complex with 4-amino-1,2,4-triazole  $[\text{Cu}_3(4\text{-atrz})_3(\text{Mo}_8\text{O}_{27})(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$  (Wang *et al.*, 2015). However, the authors described the trinuclear cationic core as  $[\text{Cu}_3(\mu_3\text{-H}_2\text{O})(4\text{-atrz})_3]$ . They also interpreted the five-coordinate copper geometry as trigonal-bipyramidal, although the  $\tau$  parameter is closer to 0 than to 1.

## 4. Synthesis and crystallization

1,2,4-Triazol-4-yl-acetic acid, (trgly-H) was prepared in a yield of 30% by reacting glycine and *N,N*-dimethylformamide azine in boiling toluene under acidic conditions (Vasylev'skyy *et al.*, 2014). Copper(II) selenate pentahydrate was prepared by treating basic copper carbonate with selenic acid followed by crystallization. A solution of  $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$  (59.2 mg, 0.20 mmol) in 4 mL of water was added to a solution of trgly-

H (27.2 mg, 0.20 mmol) in water (2 mL). The resulting solution was placed in a 20 mL Teflon-lined steel autoclave and heated at 393 K for 24 h. Cooling from to rt over 48 h afforded green–blue crystals of the product (yield 52%). Analysis calculated for  $C_{12}H_{17}Cu_3N_9O_{13}Se$  (%): C, 18.84; H, 2.24; N, 16.48. Found: C, 18.79; H, 2.28; N, 16.40. Elemental analysis was carried out with a Vario EL-Heraeus microanalyzer.

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All C-bound H atoms were placed at calculated positions [C–H = 0.94 Å (aromatic), C–H = 0.98 Å (aliphatic)] and refined using a riding model with  $U_{iso}(H) = 1.2U_{eq}(CH)$ . All O-bound H atoms were located in a difference-Fourier map and then fixed at O–H = 0.85 Å and with  $U_{iso}(H) = 1.5U_{eq}(O)$ .

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## supporting information

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## Crystal structure of poly[[ $(\mu_3$ -hydroxido- $\kappa^3$ O:O:O)( $\mu_3$ -selenato- $\kappa^3$ O<sup>1</sup>:O<sup>2</sup>:O<sup>3</sup>)tris- $[\mu_3$ -2-(1,2,4-triazol-4-yl)acetato- $\kappa^3$ N<sup>1</sup>:N<sup>2</sup>:O]tricopper(II)] dihydrate]

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### Computing details

Data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software* (Stoe & Cie, 2000); data reduction: *IPDS Software* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Poly[[ $(\mu_3$ -hydroxido- $\kappa^3$ O:O:O)( $\mu_3$ -selenato- $\kappa^3$ O<sup>1</sup>:O<sup>2</sup>:O<sup>3</sup>)tris $[\mu_3$ -2-(1,2,4-triazol-4-yl)acetato- $\kappa^3$ N<sup>1</sup>:N<sup>2</sup>:O]tricopper(II)] dihydrate]

### Crystal data

$[\text{Cu}_3(\text{C}_4\text{H}_4\text{N}_3\text{O}_9)_3(\text{SeO}_4)(\text{OH})] \cdot 2\text{H}_2\text{O}$

$M_r = 764.92$

Monoclinic,  $P2_1/c$

$a = 10.9403$  (8) Å

$b = 17.5393$  (15) Å

$c = 12.1289$  (9) Å

$\beta = 108.965$  (8)°

$V = 2201.0$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 1508$

$D_x = 2.308$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8000 reflections

$\theta = 2.0$ – $26.8$ °

$\mu = 4.62$  mm<sup>-1</sup>

$T = 213$  K

Prism, blue

$0.20 \times 0.16 \times 0.14$  mm

### Data collection

Stoe Image plate diffraction system  
diffractometer

Radiation source: fine-focus sealed tube

$\varphi$  oscillation scans

Absorption correction: numerical

[X-RED (Stoe & Cie, 2001) and X-SHAPE  
(Stoe & Cie, 1999)]

$T_{\min} = 0.405$ ,  $T_{\max} = 0.569$

16928 measured reflections

4681 independent reflections

3306 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\max} = 26.8$ °,  $\theta_{\min} = 2.0$ °

$h = -13 \rightarrow 13$

$k = -22 \rightarrow 22$

$l = -15 \rightarrow 15$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.072$

$S = 0.88$

4681 reflections

343 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.99 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.64 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.27623 (5)	0.00328 (2)	0.16661 (4)	0.01311 (11)
Cu2	0.17026 (5)	-0.07181 (2)	0.37617 (4)	0.01200 (11)
Cu3	0.39077 (5)	0.07288 (3)	0.44294 (4)	0.01223 (11)
Se1	0.08793 (4)	0.10530 (2)	0.27442 (3)	0.01415 (10)
O1	0.3177 (3)	-0.01857 (14)	0.3386 (2)	0.0113 (5)
H1O	0.378780	-0.050942	0.354877	0.017*
O2	0.1203 (3)	0.08350 (16)	0.1556 (2)	0.0237 (7)
O3	0.0502 (3)	0.02779 (15)	0.3325 (3)	0.0228 (7)
O4	0.2182 (3)	0.14261 (15)	0.3694 (3)	0.0218 (7)
O5	-0.0323 (3)	0.16534 (15)	0.2454 (3)	0.0231 (7)
O6	0.0419 (3)	-0.36472 (15)	-0.0871 (2)	0.0174 (6)
O7	0.2019 (3)	-0.28370 (17)	-0.0029 (3)	0.0301 (8)
O8	0.2547 (3)	0.02330 (16)	1.0045 (2)	0.0253 (7)
O9	0.3408 (4)	-0.0683 (2)	0.9233 (3)	0.0375 (9)
O10	0.5155 (3)	0.36051 (14)	0.0589 (2)	0.0160 (6)
O11	0.3676 (3)	0.28549 (17)	0.0946 (3)	0.0307 (8)
N1	0.1686 (4)	-0.09003 (18)	0.1341 (3)	0.0148 (7)
N2	0.1237 (4)	-0.11875 (18)	0.2195 (3)	0.0165 (7)
N3	0.0471 (3)	-0.18786 (17)	0.0647 (3)	0.0139 (7)
N4	0.2432 (3)	-0.03365 (18)	0.5386 (3)	0.0142 (7)
N5	0.3327 (3)	0.02449 (18)	0.5642 (3)	0.0152 (7)
N6	0.2564 (4)	0.01245 (19)	0.7085 (3)	0.0177 (8)
N7	0.4666 (3)	0.10867 (18)	0.3243 (3)	0.0135 (7)
N8	0.4102 (4)	0.08493 (17)	0.2103 (3)	0.0143 (7)
N9	0.5346 (3)	0.18128 (17)	0.2111 (3)	0.0146 (7)
C1	0.1208 (4)	-0.1327 (2)	0.0416 (4)	0.0174 (9)
H1	0.135662	-0.125898	-0.029885	0.021*
C2	0.0507 (4)	-0.1772 (2)	0.1748 (4)	0.0180 (9)
H2	0.007193	-0.207386	0.214252	0.022*
C3	-0.0143 (4)	-0.2514 (2)	-0.0127 (3)	0.0151 (8)
H3A	-0.070577	-0.231321	-0.087360	0.018*
H3B	-0.067585	-0.281162	0.022723	0.018*
C4	0.0885 (4)	-0.3024 (2)	-0.0333 (3)	0.0153 (8)
C5	0.1996 (4)	-0.0399 (2)	0.6262 (3)	0.0173 (9)
H5	0.137619	-0.075582	0.631377	0.021*
C6	0.3394 (5)	0.0504 (2)	0.6674 (4)	0.0209 (9)

H6	0.394363	0.089864	0.707040	0.025*
C7	0.2191 (5)	0.0356 (2)	0.8093 (3)	0.0196 (9)
H7A	0.124993	0.030830	0.788261	0.024*
H7B	0.240617	0.089592	0.824842	0.024*
C8	0.2803 (4)	-0.0084 (2)	0.9205 (4)	0.0202 (9)
C9	0.5423 (4)	0.1668 (2)	0.3220 (4)	0.0156 (8)
H9	0.593603	0.193848	0.387670	0.019*
C10	0.4526 (4)	0.1297 (2)	0.1453 (4)	0.0174 (9)
H10	0.429103	0.126325	0.063676	0.021*
C11	0.5883 (4)	0.2477 (2)	0.1676 (4)	0.0182 (9)
H11A	0.635122	0.230577	0.115612	0.022*
H11B	0.649085	0.275010	0.233175	0.022*
C12	0.4785 (4)	0.3008 (2)	0.1017 (3)	0.0159 (9)
O1W	0.3015 (4)	0.28114 (19)	0.3110 (4)	0.0441 (10)
H1W	0.309086	0.277778	0.243576	0.066*
H2W	0.264986	0.240868	0.323686	0.066*
O2W	0.5427 (4)	0.3544 (2)	0.3669 (3)	0.0408 (9)
H3W	0.576259	0.378437	0.430505	0.061*
H4W	0.471669	0.335127	0.367685	0.061*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0193 (3)	0.0112 (2)	0.0091 (2)	-0.00358 (19)	0.0050 (2)	-0.00138 (17)
Cu2	0.0176 (3)	0.0096 (2)	0.0093 (2)	-0.00239 (19)	0.0050 (2)	-0.00079 (17)
Cu3	0.0169 (3)	0.0109 (2)	0.0091 (2)	-0.00224 (19)	0.0045 (2)	-0.00038 (17)
Se1	0.0155 (2)	0.01058 (17)	0.01497 (19)	0.00218 (16)	0.00297 (17)	0.00008 (15)
O1	0.0139 (16)	0.0091 (12)	0.0104 (12)	-0.0007 (10)	0.0033 (12)	-0.0019 (10)
O2	0.0289 (19)	0.0285 (16)	0.0131 (14)	0.0102 (13)	0.0061 (14)	0.0027 (12)
O3	0.0225 (18)	0.0143 (13)	0.0333 (17)	0.0021 (12)	0.0114 (15)	0.0066 (12)
O4	0.0208 (18)	0.0158 (14)	0.0243 (15)	-0.0005 (12)	0.0013 (14)	-0.0001 (12)
O5	0.0201 (18)	0.0172 (14)	0.0275 (16)	0.0101 (12)	0.0014 (15)	0.0007 (12)
O6	0.0208 (17)	0.0165 (13)	0.0147 (14)	0.0032 (12)	0.0056 (13)	-0.0039 (11)
O7	0.021 (2)	0.0212 (15)	0.046 (2)	0.0001 (14)	0.0079 (17)	-0.0058 (15)
O8	0.045 (2)	0.0250 (15)	0.0092 (13)	-0.0068 (14)	0.0130 (15)	-0.0017 (12)
O9	0.046 (2)	0.045 (2)	0.0257 (17)	0.0226 (18)	0.0176 (18)	0.0120 (16)
O10	0.0215 (17)	0.0116 (13)	0.0151 (14)	0.0002 (11)	0.0063 (13)	0.0023 (10)
O11	0.023 (2)	0.0256 (17)	0.041 (2)	-0.0006 (14)	0.0068 (17)	0.0117 (15)
N1	0.020 (2)	0.0161 (16)	0.0088 (15)	-0.0036 (13)	0.0059 (15)	-0.0001 (12)
N2	0.026 (2)	0.0129 (16)	0.0124 (16)	-0.0029 (14)	0.0086 (16)	-0.0006 (12)
N3	0.018 (2)	0.0099 (15)	0.0123 (16)	-0.0009 (13)	0.0032 (15)	-0.0016 (12)
N4	0.014 (2)	0.0145 (15)	0.0123 (16)	-0.0019 (13)	0.0023 (15)	-0.0024 (13)
N5	0.020 (2)	0.0157 (16)	0.0104 (16)	-0.0047 (14)	0.0050 (15)	-0.0008 (12)
N6	0.023 (2)	0.0201 (17)	0.0100 (16)	-0.0050 (14)	0.0057 (16)	-0.0009 (13)
N7	0.0153 (19)	0.0140 (15)	0.0102 (15)	-0.0015 (14)	0.0028 (15)	0.0001 (12)
N8	0.0177 (19)	0.0147 (16)	0.0096 (15)	-0.0005 (13)	0.0034 (15)	0.0002 (12)
N9	0.019 (2)	0.0107 (15)	0.0165 (17)	-0.0012 (13)	0.0089 (16)	0.0008 (12)
C1	0.023 (3)	0.0138 (18)	0.0154 (19)	-0.0007 (16)	0.0069 (19)	0.0008 (15)



C2	0.026 (3)	0.0131 (18)	0.017 (2)	-0.0056 (16)	0.010 (2)	-0.0036 (15)
C3	0.017 (2)	0.0120 (17)	0.0123 (19)	-0.0029 (15)	0.0001 (18)	-0.0027 (14)
C4	0.021 (3)	0.0128 (18)	0.0108 (18)	-0.0008 (16)	0.0037 (18)	0.0023 (14)
C5	0.020 (3)	0.021 (2)	0.0123 (19)	-0.0051 (17)	0.0077 (19)	-0.0011 (15)
C6	0.027 (3)	0.022 (2)	0.0140 (19)	-0.0078 (18)	0.007 (2)	0.0000 (16)
C7	0.025 (3)	0.022 (2)	0.0127 (19)	-0.0013 (18)	0.0076 (19)	-0.0029 (16)
C8	0.019 (2)	0.023 (2)	0.018 (2)	-0.0069 (18)	0.004 (2)	-0.0012 (17)
C9	0.018 (2)	0.0141 (18)	0.0146 (19)	0.0023 (16)	0.0048 (18)	-0.0006 (15)
C10	0.023 (3)	0.0156 (18)	0.016 (2)	-0.0018 (16)	0.009 (2)	0.0009 (15)
C11	0.021 (3)	0.0146 (19)	0.021 (2)	-0.0025 (17)	0.010 (2)	0.0057 (16)
C12	0.023 (3)	0.0129 (17)	0.0122 (19)	-0.0027 (16)	0.0061 (19)	0.0006 (14)
O1W	0.053 (3)	0.0231 (17)	0.064 (3)	-0.0041 (17)	0.029 (2)	0.0046 (17)
O2W	0.037 (2)	0.054 (2)	0.0280 (19)	-0.0025 (18)	0.0055 (18)	-0.0045 (17)

*Geometric parameters (Å, °)*

Cu1—O8 <sup>i</sup>	1.935 (3)	N4—C5	1.303 (5)
Cu1—N1	1.980 (3)	N4—N5	1.377 (4)
Cu1—N8	1.993 (3)	N5—C6	1.311 (5)
Cu1—O1	2.022 (2)	N6—C6	1.346 (5)
Cu1—O2	2.182 (3)	N6—C5	1.349 (5)
Cu2—O6 <sup>ii</sup>	1.954 (3)	N6—C7	1.466 (5)
Cu2—N2	1.979 (3)	N7—C9	1.320 (5)
Cu2—N4	1.986 (3)	N7—N8	1.382 (4)
Cu2—O1	2.039 (3)	N8—C10	1.301 (5)
Cu2—O3	2.146 (3)	N9—C10	1.339 (5)
Cu3—N5	1.974 (3)	N9—C9	1.345 (5)
Cu3—N7	1.982 (3)	N9—C11	1.478 (5)
Cu3—O10 <sup>iii</sup>	1.990 (3)	C1—H1	0.9400
Cu3—O1	2.039 (2)	C2—H2	0.9400
Cu3—O4	2.182 (3)	C3—C4	1.520 (6)
Se1—O5	1.632 (3)	C3—H3A	0.9800
Se1—O2	1.637 (3)	C3—H3B	0.9800
Se1—O3	1.645 (3)	C5—H5	0.9400
Se1—O4	1.649 (3)	C6—H6	0.9400
O1—H1O	0.8500	C7—C8	1.509 (6)
O6—C4	1.289 (5)	C7—H7A	0.9800
O7—C4	1.219 (5)	C7—H7B	0.9800
O8—C8	1.270 (5)	C9—H9	0.9400
O9—C8	1.235 (5)	C10—H10	0.9400
O10—C12	1.291 (4)	C11—C12	1.525 (6)
O11—C12	1.218 (5)	C11—H11A	0.9800
N1—C1	1.308 (5)	C11—H11B	0.9800
N1—N2	1.379 (4)	O1W—H1W	0.8500
N2—C2	1.304 (5)	O1W—H2W	0.8500
N3—C2	1.337 (5)	O2W—H3W	0.8500
N3—C1	1.346 (5)	O2W—H4W	0.8500
N3—C3	1.471 (5)		

O8 <sup>i</sup> —Cu1—N1	94.55 (13)	C6—N5—Cu3	129.1 (3)
O8 <sup>i</sup> —Cu1—N8	88.65 (13)	N4—N5—Cu3	121.9 (2)
N1—Cu1—N8	170.10 (14)	C6—N6—C5	105.5 (3)
O8 <sup>i</sup> —Cu1—O1	174.35 (13)	C6—N6—C7	125.2 (3)
N1—Cu1—O1	88.18 (11)	C5—N6—C7	128.2 (3)
N8—Cu1—O1	87.86 (12)	C9—N7—N8	107.0 (3)
O8 <sup>i</sup> —Cu1—O2	89.20 (12)	C9—N7—Cu3	132.3 (3)
N1—Cu1—O2	96.79 (13)	N8—N7—Cu3	118.3 (2)
N8—Cu1—O2	92.62 (13)	C10—N8—N7	107.0 (3)
O1—Cu1—O2	95.40 (10)	C10—N8—Cu1	130.4 (3)
O6 <sup>ii</sup> —Cu2—N2	90.12 (12)	N7—N8—Cu1	122.2 (2)
O6 <sup>ii</sup> —Cu2—N4	93.00 (12)	C10—N9—C9	106.3 (3)
N2—Cu2—N4	170.93 (15)	C10—N9—C11	125.9 (3)
O6 <sup>ii</sup> —Cu2—O1	172.41 (11)	C9—N9—C11	127.1 (3)
N2—Cu2—O1	87.23 (12)	N1—C1—N3	109.4 (3)
N4—Cu2—O1	88.59 (12)	N1—C1—H1	125.3
O6 <sup>ii</sup> —Cu2—O3	95.29 (11)	N3—C1—H1	125.3
N2—Cu2—O3	98.97 (13)	N2—C2—N3	109.9 (3)
N4—Cu2—O3	89.24 (13)	N2—C2—H2	125.0
O1—Cu2—O3	92.15 (11)	N3—C2—H2	125.0
N5—Cu3—N7	171.64 (14)	N3—C3—C4	110.0 (3)
N5—Cu3—O10 <sup>iii</sup>	92.21 (12)	N3—C3—H3A	109.7
N7—Cu3—O10 <sup>iii</sup>	88.56 (12)	C4—C3—H3A	109.7
N5—Cu3—O1	88.15 (12)	N3—C3—H3B	109.7
N7—Cu3—O1	88.32 (12)	C4—C3—H3B	109.7
O10 <sup>iii</sup> —Cu3—O1	160.30 (11)	H3A—C3—H3B	108.2
N5—Cu3—O4	95.76 (13)	O7—C4—O6	125.3 (4)
N7—Cu3—O4	92.07 (13)	O7—C4—C3	121.7 (3)
O10 <sup>iii</sup> —Cu3—O4	105.28 (11)	O6—C4—C3	112.9 (4)
O1—Cu3—O4	94.27 (11)	N4—C5—N6	110.1 (4)
O5—Se1—O2	110.53 (15)	N4—C5—H5	125.0
O5—Se1—O3	109.17 (15)	N6—C5—H5	125.0
O2—Se1—O3	109.91 (15)	N5—C6—N6	110.3 (4)
O5—Se1—O4	110.35 (15)	N5—C6—H6	124.9
O2—Se1—O4	108.82 (16)	N6—C6—H6	124.9
O3—Se1—O4	108.01 (15)	N6—C7—C8	116.2 (4)
Cu1—O1—Cu3	113.72 (11)	N6—C7—H7A	108.2
Cu1—O1—Cu2	112.88 (13)	C8—C7—H7A	108.2
Cu3—O1—Cu2	113.63 (11)	N6—C7—H7B	108.2
Cu1—O1—H1O	105.2	C8—C7—H7B	108.2
Cu3—O1—H1O	105.1	H7A—C7—H7B	107.4
Cu2—O1—H1O	105.2	O9—C8—O8	127.3 (4)
Se1—O2—Cu1	119.02 (15)	O9—C8—C7	122.5 (4)
Se1—O3—Cu2	124.02 (16)	O8—C8—C7	110.1 (4)
Se1—O4—Cu3	119.98 (15)	N7—C9—N9	109.3 (4)
C4—O6—Cu2 <sup>iv</sup>	113.7 (3)	N7—C9—H9	125.3
C8—O8—Cu1 <sup>v</sup>	138.6 (3)	N9—C9—H9	125.3

C12—O10—Cu3 <sup>vi</sup>	121.8 (3)	N8—C10—N9	110.4 (4)
C1—N1—N2	107.1 (3)	N8—C10—H10	124.8
C1—N1—Cu1	133.6 (3)	N9—C10—H10	124.8
N2—N1—Cu1	119.1 (2)	N9—C11—C12	109.4 (3)
C2—N2—N1	107.1 (3)	N9—C11—H11A	109.8
C2—N2—Cu2	131.1 (3)	C12—C11—H11A	109.8
N1—N2—Cu2	121.7 (2)	N9—C11—H11B	109.8
C2—N3—C1	106.4 (3)	C12—C11—H11B	109.8
C2—N3—C3	127.1 (3)	H11A—C11—H11B	108.2
C1—N3—C3	126.3 (3)	O11—C12—O10	125.9 (4)
C5—N4—N5	107.5 (3)	O11—C12—C11	120.0 (3)
C5—N4—Cu2	130.2 (3)	O10—C12—C11	114.1 (4)
N5—N4—Cu2	120.0 (2)	H1W—O1W—H2W	108.4
C6—N5—N4	106.7 (3)	H3W—O2W—H4W	108.4
O5—Se1—O2—Cu1	-179.53 (17)	Cu2 <sup>iv</sup> —O6—C4—C3	176.2 (2)
O3—Se1—O2—Cu1	-59.0 (2)	N3—C3—C4—O7	-10.4 (5)
O4—Se1—O2—Cu1	59.1 (2)	N3—C3—C4—O6	170.9 (3)
O5—Se1—O3—Cu2	175.78 (18)	N5—N4—C5—N6	0.4 (5)
O2—Se1—O3—Cu2	54.4 (2)	Cu2—N4—C5—N6	-161.7 (3)
O4—Se1—O3—Cu2	-64.2 (2)	C6—N6—C5—N4	-1.1 (5)
O5—Se1—O4—Cu3	172.90 (16)	C7—N6—C5—N4	167.1 (4)
O2—Se1—O4—Cu3	-65.7 (2)	N4—N5—C6—N6	-1.2 (5)
O3—Se1—O4—Cu3	53.6 (2)	Cu3—N5—C6—N6	161.3 (3)
C1—N1—N2—C2	-0.1 (5)	C5—N6—C6—N5	1.4 (5)
Cu1—N1—N2—C2	176.8 (3)	C7—N6—C6—N5	-167.2 (4)
C1—N1—N2—Cu2	-179.7 (3)	C6—N6—C7—C8	-103.6 (5)
Cu1—N1—N2—Cu2	-2.8 (4)	C5—N6—C7—C8	90.4 (5)
C5—N4—N5—C6	0.4 (5)	Cu1 <sup>v</sup> —O8—C8—O9	-4.3 (8)
Cu2—N4—N5—C6	164.7 (3)	Cu1 <sup>v</sup> —O8—C8—C7	172.5 (3)
C5—N4—N5—Cu3	-163.6 (3)	N6—C7—C8—O9	-11.9 (6)
Cu2—N4—N5—Cu3	0.7 (4)	N6—C7—C8—O8	171.1 (4)
C9—N7—N8—C10	-0.7 (4)	N8—N7—C9—N9	0.8 (4)
Cu3—N7—N8—C10	163.8 (3)	Cu3—N7—C9—N9	-160.7 (3)
C9—N7—N8—Cu1	-175.1 (3)	C10—N9—C9—N7	-0.6 (5)
Cu3—N7—N8—Cu1	-10.5 (4)	C11—N9—C9—N7	170.5 (4)
N2—N1—C1—N3	-0.1 (5)	N7—N8—C10—N9	0.4 (5)
Cu1—N1—C1—N3	-176.4 (3)	Cu1—N8—C10—N9	174.1 (3)
C2—N3—C1—N1	0.4 (5)	C9—N9—C10—N8	0.1 (5)
C3—N3—C1—N1	-174.2 (4)	C11—N9—C10—N8	-171.1 (4)
N1—N2—C2—N3	0.4 (5)	C10—N9—C11—C12	62.3 (5)
Cu2—N2—C2—N3	179.8 (3)	C9—N9—C11—C12	-107.2 (4)
C1—N3—C2—N2	-0.4 (5)	Cu3 <sup>vi</sup> —O10—C12—O11	-13.8 (6)
C3—N3—C2—N2	174.0 (4)	Cu3 <sup>vi</sup> —O10—C12—C11	167.2 (2)
C2—N3—C3—C4	-110.0 (5)	N9—C11—C12—O11	1.7 (5)

C1—N3—C3—C4	63.4 (5)	N9—C11—C12—O10	-179.2 (3)
Cu2 <sup>iv</sup> —O6—C4—O7	-2.5 (5)		

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

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O $\cdots$ O10 <sup>vii</sup>	0.85	2.01	2.811 (4)	156
O1W—H1W $\cdots$ O11	0.85	2.11	2.940 (5)	166
O1W—H2W $\cdots$ O4	0.85	1.93	2.767 (4)	168
O2W—H3W $\cdots$ O9 <sup>viii</sup>	0.85	1.95	2.798 (5)	178
O2W—H4W $\cdots$ O1W	0.85	2.00	2.812 (6)	159
C1—H1 $\cdots$ O5 <sup>ix</sup>	0.94	2.58	3.346 (5)	139
C2—H2 $\cdots$ O5 <sup>x</sup>	0.94	2.28	2.955 (5)	128
C5—H5 $\cdots$ O3 <sup>xi</sup>	0.94	2.39	2.941 (5)	117
C6—H6 $\cdots$ O2W <sup>xii</sup>	0.94	2.30	3.176 (6)	154
C7—H7A $\cdots$ O3 <sup>xi</sup>	0.98	2.25	3.094 (6)	144
C7—H7B $\cdots$ O1W <sup>xii</sup>	0.98	2.38	3.338 (5)	164
C9—H9 $\cdots$ O7 <sup>xii</sup>	0.94	2.25	3.067 (6)	144

Symmetry codes: (iii)  $x, -y+1/2, z+1/2$ ; (vii)  $-x+1, y-1/2, -z+1/2$ ; (viii)  $-x+1, y+1/2, -z+3/2$ ; (ix)  $-x, -y, -z$ ; (x)  $-x, y-1/2, -z+1/2$ ; (xi)  $-x, -y, -z+1$ ; (xii)  $-x+1, y+1/2, -z+1/2$ .