Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

A copper(II) paddle-wheel structure of tranexamic acid: dichloro-tetrakis[μ-4-(ammoniomethyl)cyclohexane-1-carboxylato-*O*,*O*′]dicopper(II) dichloride hexahydrate

Muhammad Altaf[a]* and Helen Stoeckli-Evans[b]*

[a]Center of Excellence in Nanotechnology, King Fahd University of Petroleum, & Minerals, 31261 Dahran, Saudi Arabia, and [b]Institute of Physics, University of Neuchâtel, rue Emile-Argand 11, CH-2000 Neuchâtel, Switzerland. *Correspondence e-mail: altaf_dr@hotmail.com, helen.stoeckli-evans@unine.ch

Received 28 August 2017
Accepted 31 August 2017

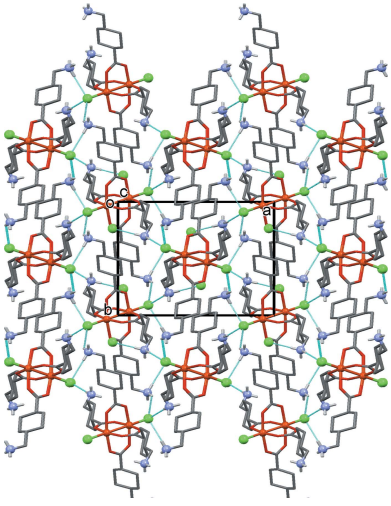
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; tranexamic acid; antifibrinolytic amino acid; fibrinolytic inhibitor; copper(II); paddle-wheel; hydrogen bonding.

CCDC reference: 1571897

Supporting information: this article has supporting information at journals.iucr.org/e

Tranexamic acid [systematic name: *trans*-4-(aminomethyl)cyclohexane-1-carboxylic acid], is an antifibrinolytic amino acid that exists as a zwitterion [*trans*-4-(ammoniomethyl)cyclohexane-1-carboxylate] in the solid state. Its reaction with copper chloride leads to the formation of a compound with a copper(II) paddle-wheel structure that crystallizes as a hexahydrate, $[Cu_2Cl_2(C_8H_{15}NO_2)_4]^{2+}\cdot 2Cl^-\cdot 6H_2O$. The asymmetric unit is composed of a copper(II) cation, two zwitterionic tranexamic acid units, a coordinating Cl^- anion and a free Cl^- anion, together with three water molecules of crystallization. The whole structure is generated by inversion symmetry, with the Cu$\cdots$Cu axle of the paddle-wheel dication being located about a center of symmetry. The cyclohexane rings of the zwitterionic tranexamic acid units have chair conformations. The carboxylate groups that bridge the two copper(II) cations are inclined to one another by 88.4 (8)°. The copper(II) cation is ligated by four carboxylate O atoms in the equatorial plane and by a Cl^- ion in the axial position. Hence, it has a fivefold O_4Cl coordination sphere with a perfect square-pyramidal geometry and a τ_5 index of zero. In the crystal, the paddle-wheel dications are linked by a series of N—H$\cdots$Cl hydrogen bonds, involving the coordinating and free Cl^- ions, forming a three-dimensional network. This network is strengthened by a series of N—H$\cdots O_{water}$, O_{water}—H$\cdots$Cl and O_{water}—H$\cdots$O hydrogen bonds.

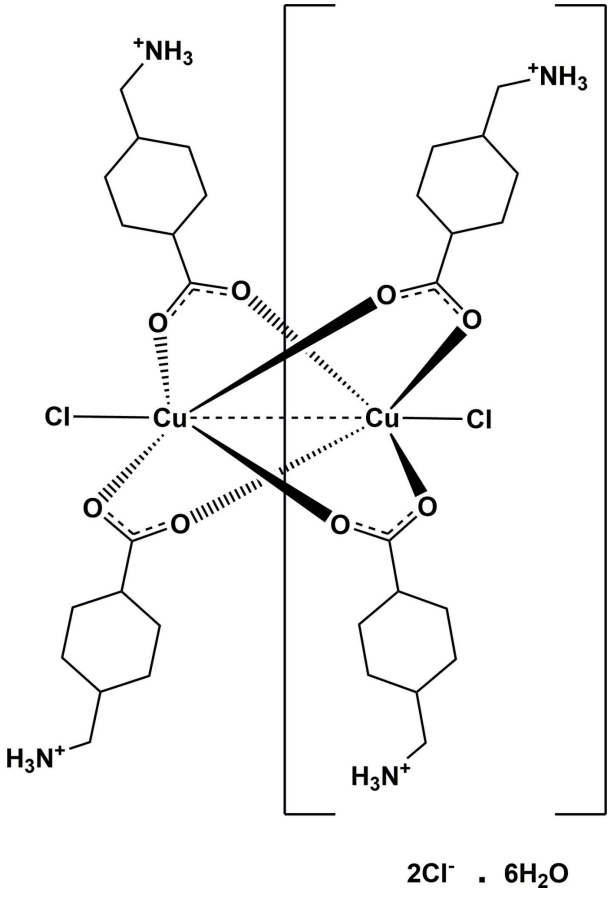


OPEN ACCESS

1. Chemical context

Tranexamic acid (TA) is a derivative of the amino acid lysine. It has important antifibrinolytic activity and is used extensively in both trauma and normal surgery to prevent excessive blood loss (Napolitano *et al.*, 2013; Melvin *et al.*, 2015). It was first synthesized in the early 1960s by the Japanese husband and wife team Shosuke and Utako Okamato (1962). They showed amino-methyl-cyclohexane-carboxylic acid (AMCHA) to be a new inhibitor of fibrinolysis. Almost simultaneously with a Swedish group (Melander *et al.*, 1965), they were able to show that the antifibrinolytic active isomer (Okamoto *et al.*, 1964) has a *trans*-conformation (TA; Fig. 1) with the aminomethyl and carboxylic acid substituents on the cyclohexane ring occupying equatorial positions (Fig. 1). The *cis*-isomer (Fig. 1), in which the carboxylic acid moiety is axial, is almost inactive. The latter was shown to exist as the free acid in the solid state (Yamazaki *et al.*, 1981), in contrast to the *trans*-isomer, which exists as a zwitterion in the solid state (Groth, 1968; Shahzadi *et al.*, 2007). Recently, Tengborn *et al.*

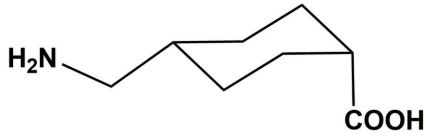
(2015) published an excellent review article, entitled 'Tranexamic acid – an old drug still going strong and making a revival', in which they recount the history of the development of TA and its mechanism of action, pharmokinetics and other details, including clinical uses. Herein, we report on the first crystal structure of a metal complex of tranexamic acid. The reaction of TA with copper(II) chloride leads to the formation of the title compound with a copper(II) paddle-wheel structure, that crystallizes as a hexahydrate. The reaction of TA with copper(II) bromide leads to the formation of an isotypical compound; however, the crystals were twinned and the subsequent X-ray analysis was of insufficient quality to be submitted or deposited.



2. Structural commentary

The molecular structure of the dication of the title compound is illustrated in Fig. 2. The asymmetric unit is composed of a copper(II) cation coordinated by the carboxylate O atoms (O1–O4) of two zwitterionic tranexamic acid units and a Cl^- anion, Cl1, together with a free Cl^- anion, Cl2, and three water molecules of crystallization. The whole structure is generated by inversion symmetry, with the Cu1···Cu1^i axle [2.6649 (11) Å; symmetry code (i): $-x+1, -y+1, -z+1$] of the paddle-wheel being located about a center of symmetry. Selected bond lengths and angles in the paddle-wheel dication are given in Table 1. Atom Cu1 is coordinated by four carboxylate O atoms (O1–O4) in the equatorial plane and a

***trans*-4-(aminomethyl)cyclohexane-1-carboxylic acid (TA)**



***cis*-4-(aminomethyl)cyclohexane-1-carboxylic acid**

Figure 1
The *trans*- and *cis*-isomers of 4-(aminomethyl)cyclohexane-1-carboxylic acid.

Cl^- ion, Cl1, in the axial position. The Cu—O distances vary from 1.950 (4) to 1.991 (3) Å, with a longer Cu1—Cl1 axial distance of 2.499 (1) Å (Table 1). The copper(II) cation, Cu1 (Cu1^i), has a perfect square-pyramidal coordination sphere with a τ_5 index of 0.0 (τ_5 = 0 for an ideal square-pyramidal coordination sphere, and = 1 for an ideal trigonal–pyramidal coordination sphere; Addison *et al.*, 1984).

The conformations of the two zwitterionic tranexamic acid units differ slightly. The cyclohexane rings (C2–C7 and C10–C15) have chair conformations; puckering parameters for ring C2–C7 are Q = 0.569 (7) Å, θ = 176.3 (6)°, φ = 358 (13)°, and

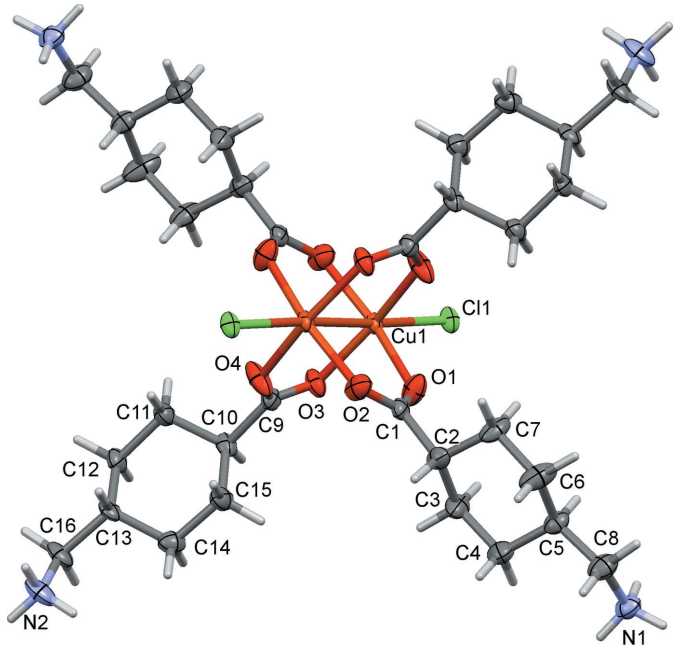


Figure 2
A view of the molecular structure of the title dication, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to the labelled atoms by inversion symmetry (symmetry operation: $-x+1, -y+1, -z+1$).

Table 1
Selected geometric parameters (Å, °).

Cu1—Cu1^{i}	2.6649 (11)	Cu1—O4^{i}	1.965 (4)
Cu1—O1	1.950 (4)	Cu1—O3	1.991 (3)
Cu1—O2^{i}	1.955 (4)	Cu1—Cl1	2.4990 (12)
O1—Cu1—O2^{i}	167.02 (15)	O4^{i}—Cu1—Cl1	92.57 (11)
O1—Cu1—O4^{i}	89.3 (2)	O3—Cu1—Cl1	100.08 (10)
O2^{i}—Cu1—O4^{i}	89.9 (2)	O1—Cu1—Cu1^{i}	83.04 (11)
O1—Cu1—O3	88.33 (18)	O2^{i}—Cu1—Cu1^{i}	84.05 (11)
O2^{i}—Cu1—O3	89.60 (18)	O4^{i}—Cu1—Cu1^{i}	80.24 (11)
O4^{i}—Cu1—O3	167.27 (15)	O3—Cu1—Cu1^{i}	87.06 (10)
O1—Cu1—Cl1	94.31 (11)	Cl1—Cu1—Cu1^{i}	172.34 (4)
O2^{i}—Cu1—Cl1	98.68 (11)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

for ring C10–C15 are $Q = 0.568$ (6) Å, $\theta = 6.0$ (6)°, $\varphi = 137$ (6)°. The carboxylate groups (C1/O1/O2 and C9/O3/O4) are inclined to the mean planes of the four planar atoms of the respective cyclohexane rings (C3/C4/C6/C7 and C11/C12/C14/C15) by 67.5 (6) and 85.8 (7)°, while they are inclined to one another by 88.4 (8)°. The ammoniomethyl units, C5/C8/N1 and C13/C16/N2, are inclined to the mean planes of the four planar atoms of the respective cyclohexane rings (C3/C4/C6/C7 and C11/C12/C14/C15) by 34.9 (6) and 47.5 (6)°.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1^{ii}	0.91	2.63	3.316 (5)	133
N1—H1C···Cl1^{iii}	0.91	2.52	3.394 (5)	160
N2—H2B···Cl1^{iv}	0.91	2.25	3.123 (5)	160
N2—H2C···Cl2^{v}	0.91	2.24	3.151 (6)	179
N1—H1B···O1W^{vi}	0.91	1.90	2.760 (7)	156
N2—H2A···O2W^{vii}	0.91	2.06	2.789 (9)	137
O1W—H1WA···Cl2^{v}	0.89 (2)	2.57 (8)	3.218 (6)	130 (8)
O2W—H2WA···Cl2^{viii}	0.90 (2)	2.46 (7)	3.176 (6)	137 (9)
O2W—H2WB···O3^{i}	0.90 (2)	2.22 (8)	2.820 (6)	124 (8)
O3W—H3WA···Cl1^{ix}	0.88 (2)	2.66 (6)	3.258 (5)	127 (6)
O3W—H3WB···Cl2^{x}	0.88 (2)	2.35 (3)	3.182 (5)	158 (7)

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

3. Supramolecular features

In the crystal, the NH_3^+ groups of the zwitterionic tranexamic acid units and the coordinating and free Cl^- ions are linked by a series of N—H···Cl hydrogen bonds forming a three-dimensional framework (Table 2 and Fig. 3). This framework is strengthened by a series of N—H···O$_{water}$, O$_{water}$—H···Cl

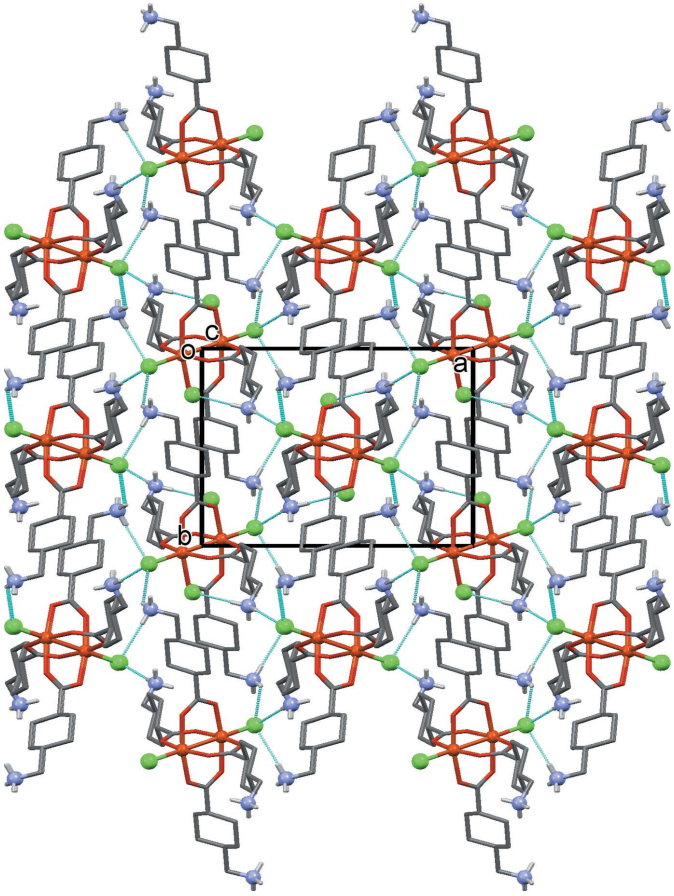


Figure 3
A view along the *c* axis of the crystal structure of the title compound with the water solvent molecules omitted. The N—H···Cl hydrogen bonds are shown as dashed lines (see Table 2), and the C-bound H atoms have been omitted for clarity.

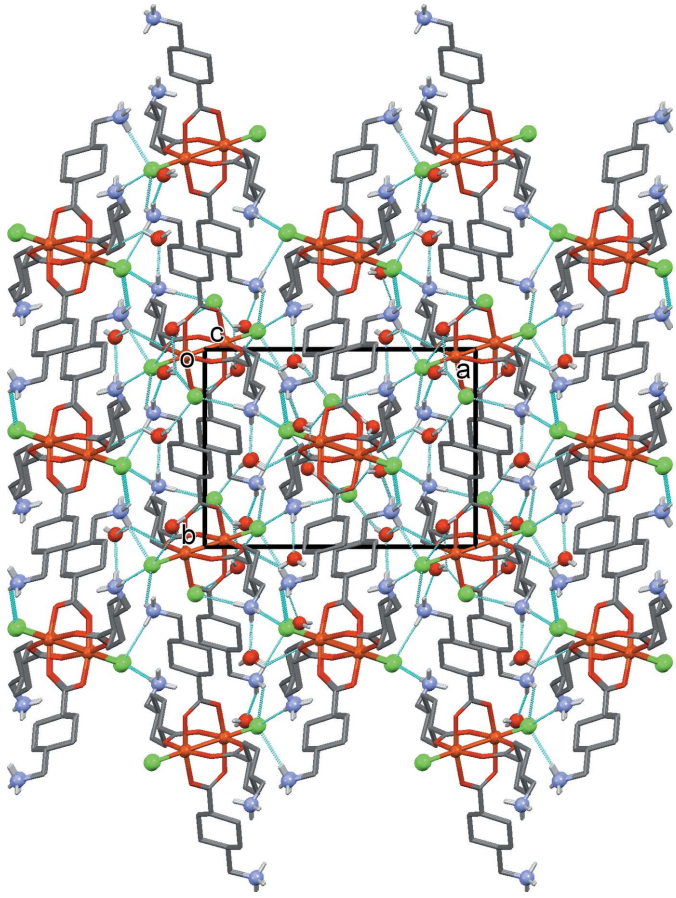


Figure 4
A view along the *c* axis of the crystal structure of the title compound, with the hydrogen bonds shown as dashed lines (see Table 2). The C-bound H atoms have been omitted for clarity.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu_2Cl_2(C_8H_{15}NO_2)_4](Cl_2)\cdot 6H_2O$
M_r	1005.81
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	153
a, b, c (Å)	14.7100 (11), 10.7163 (6), 14.9312 (12)
β (°)	91.828 (10)
V (Å^3)	2352.5 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.19
Crystal size (mm)	0.34 × 0.30 × 0.20
Data collection	
Diffractometer	STOE *IPDS* 1
Absorption correction	Multi-scan (*MULABS*; Spek, 2009)
T_{min}, T_{max}	0.712, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18018, 4545, 3172
R_{int}	0.091
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.196, 1.02
No. of reflections	4545
No. of parameters	273
No. of restraints	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.80, −0.93

Computer programs: *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004), *SHELXS2016/6* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL2016/6* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

and O_{water}—H···O hydrogen bonds (Table 2 and Fig. 4). The packing index, or percentage of filled space, is 67.1 (Kitajgorodskij, 1973) and the unit cell contains no residual solvent-accessible voids.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.38, update May 2017; Groom *et al.*, 2016) for the skeleton of amino-methyl-cyclohexane-carboxylic acid gave 13 hits, of which six structures concern the *cis*- and *trans*-isomers. The crystal structures of the hydrobromide of the *trans*-isomer (CSD refcode: CHCAHB) and the hydrochloride of the *cis*-isomer (CHCAHC) were reported in 1966 (Kadoya *et al.*, 1966). The crystal structure of the hydrobromide of the *cis*-isomer has also been reported (AMHCAC; Groth & Hassel, 1965), and that of the free *cis*-isomer (AMCHCA; Yamazaki *et al.*, 1981), which does not exist as a zwitterion in the solid state. The room temperature analysis of the *trans*-isomer (TA), *viz*. tranexamic acid (AMMCHC10; Groth, 1968), and a low-temperature analysis at 173 K (AMMCHC11; Shahzadi *et al.*, 2007) showed that it crystallizes in the chiral orthorhombic space group $P2_12_12_1$ and exists as a zwitterion in the solid state. Interestingly, in the low-temperature structure it can be seen that the carboxylate group (COO^-) is inclined to the mean plane of the four planar atoms of the cyclohexane ring by 48.9 (2)°, compared to 67.5 (6) and 85.8 (7)° in the title compound. The plane of the ammoniomethyl unit (C_{ar}—C—N) is inclined to the same mean plane of the four planar atoms of the cyclohexane ring by 37.4 (2)°, compared to 34.9 (6) and 47.5 (6)° in the title compound. Hence, on complexation the cyclohexane rings are rotated about the $C_{carboxylate}$—$C_{cyclohexane}$ bonds (C1—C2 and C9—C10), most probably to minimize steric hindrance.

In the CSD over 1500 copper(II) paddle-wheel structures have been deposited. There are only 13 compounds in which the axial position is occupied by a Cl^- anion (see *Supporting information*). The Cu···Cu distances vary from *ca* 2.63 to 2.84 Å, with the carboxylate groups being inclined to one another by *ca* 84.65–90°, and the Cu—Cl distances varying from *ca* 2.41 to 2.49 Å. The values observed for the title compound fall within these limits (see Section 2, *Structural commentary*). In all 13 compounds the copper atoms have perfect square-pyramidal geometry, with $\tau_5 = 0.0$.

5. Synthesis and crystallization

Tranexamic acid (0.785 g, 0.5 mmol) dissolved in 10 ml of deionized water was added dropwise to a transparent blue solution of $CuCl_2\cdot 2H_2O$ (0.426 g, 0.25 mmol) in 20 ml of acetonitrile at ambient temperature and the mixture was stirred for 30 min. The green solution obtained was filtered and the filtrate kept undisturbed at room temperature for slow evaporation. After five days green plate-like crystals of the title compound were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms of the water molecules were located in difference-Fourier maps and refined with distance restraints: O—H = 0.88 (2) Å with U_{iso}(H) = 1.5U_{eq}(O). The ammonium H atoms and the C-bound H atoms were included in calculated positions and treated as riding: N—H = 0.91 Å, C-H = 0.99–1.00 Å with U_{iso}(H) = 1.5U_{eq}(N-ammonium) and 1.2U_{eq}(C) for other H atoms. In the final difference-Fourier map the residual density peaks [$\Delta\rho_{max}$, $\Delta\rho_{min}$ 1.80, −0.93 e Å^{-3}] are located at a distance of 1.2 and 0.9 Å, respectively, from the copper atoms.

Funding information

Funding was provided by the Swiss National Science Foundation and the University of Neuchâtel.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Groth, P., Hassel, O., Klaeboe, P. & Enari, T.-M. (1965). *Acta Chem. Scand.* **19**, 1709–1714.
Groth, P., Rasmussen, S. E., Taylor, D. B., Haug, A., Enzell, C. & Francis, G. (1968). *Acta Chem. Scand.* **22**, 143–158.

Kadoya, S., Hanazaki, F. & Iitaka, Y. (1966). *Acta Cryst.* **21**, 38–49.
Kitajgorodskij, A. I. (1973). Molecular Crystals and Molecules. New York: Academic Press, USA.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Melander, B., Gliniecki, G., Granstrand, B. & Hanshoff, G. (1965). *Acta Pharmacol. Toxicol.* **22**, 340–352.
Melvin, J. S., Stryker, L. S. & Sierra, R. J. (2015). *J. Am. Acad. Orthop. Surg.* **23**, 732–740.
Napolitano, L. M., Cohen, M. J., Cotton, B. A., Schreiber, M. A. & Moore, E. E. (2013). *J. Trauma Acute Care Surg.* **74**, 1575–1786.
Okamoto, S. & Okamoto, U. (1962). *Keio j. Med.* **11**, 105–115.
Okamoto, S., Sato, S., Takada, Y. & Okamoto, U. (1964). *Keio J. Med.* **13**, 177–185.
Shahzadi, S., Ali, S. M., Parvez, M., Badshah, A., Ahmed, E. & Malik, A. (2007). *Russ. J. Inorg. Chem.* **52**, 386–393.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stoe & Cie (2004). *IPDS*I Bedienungshandbuch. Stoe & Cie GmbH, Darmstadt, Germany.
Tengborn, L., Blombäck, M. & Berntorp, E. (2015). *Thromb. Res.* **135**, 231–242.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yamazaki, K., Watanabe, A., Moroi, R. & Sano, M. (1981). *Acta Cryst.* B**37**, 1447–1449.

supporting information

Acta Cryst. (2017). E**73**, 1421-1425 [https://doi.org/10.1107/S2056989017012543]

A copper(II) paddle-wheel structure of tranexamic acid: dichloro-tetrakis-[μ-4-(ammoniomethyl)cyclohexane-1-carboxylato-*O*,*O*′]dicopper(II) dichloride hexahydrate

Muhammad Altaf and Helen Stoeckli-Evans

Computing details

Data collection: *EXPOSE* in *IPDS-I* (Stoe & Cie, 2004); cell refinement: *CELL* in *IPDS-I* (Stoe & Cie, 2004); data reduction: *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS2016/6* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2016/6* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Dichloro-tetrakis[μ-4-(ammoniomethyl)cyclohexane-1-carboxylato-*O*,*O*′]dicopper(II) dichloride hexahydrate

Crystal data

$[Cu_2Cl_2(C_8H_{15}NO_2)_4](Cl_2)\cdot 6H_2O$
M_r = 1005.81
Monoclinic, $P2_1/n$
a = 14.7100 (11) Å
b = 10.7163 (6) Å
c = 14.9312 (12) Å
β = 91.828 (10)°
V = 2352.5 (3) Å^3
Z = 2
$F(000)$ = 1060
D_x = 1.420 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8000 reflections
θ = 2.3–25.9°
μ = 1.19 mm^{-1}
T = 153 K
Plate, green
0.34 × 0.30 × 0.20 mm

Data collection

STOE IPDS 1 diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
φ rotation scans
Absorption correction: multi-scan (MULABS; Spek, 2009)
T_{min} = 0.712, T_{max} = 1.000
18018 measured reflections
4545 independent reflections
3172 reflections with $I > 2\sigma(I)$
R_{int} = 0.091
θ_{max} = 25.9°, θ_{min} = 2.3°
h = −18→18
k = −13→13
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.196
S = 1.02
4545 reflections
273 parameters
9 restraints
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

$w = 1/[\sigma^2(F_o^2) + (0.1331P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.80$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ 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	0.57200 (3)	0.53341 (6)	0.55087 (4)	0.0195 (2)
Cl1	0.69386 (7)	0.59126 (13)	0.66374 (7)	0.0253 (3)
O1	0.5727 (3)	0.3572 (4)	0.5833 (3)	0.0384 (10)
O2	0.4505 (3)	0.3014 (4)	0.5009 (3)	0.0369 (10)
O3	0.6477 (2)	0.4905 (4)	0.4471 (2)	0.0297 (9)
O4	0.5250 (2)	0.4381 (5)	0.3640 (3)	0.0445 (12)
N1	0.6876 (3)	−0.1791 (5)	0.8123 (3)	0.0339 (11)
H1A	0.715646	−0.207468	0.762784	0.051*
H1B	0.688742	−0.239545	0.855069	0.051*
H1C	0.717108	−0.110116	0.833690	0.051*
N2	0.6727 (3)	0.1961 (6)	−0.0237 (3)	0.0451 (14)
H2A	0.674668	0.130093	0.014673	0.068*
H2B	0.702133	0.175997	−0.074399	0.068*
H2C	0.613684	0.215079	−0.038025	0.068*
C1	0.5154 (3)	0.2771 (5)	0.5551 (3)	0.0244 (11)
C2	0.5225 (4)	0.1471 (5)	0.5916 (4)	0.0299 (12)
H2	0.490146	0.089283	0.548741	0.036*
C3	0.6224 (4)	0.1033 (6)	0.6034 (4)	0.0377 (14)
H3A	0.650187	0.098871	0.543974	0.045*
H3B	0.657016	0.165255	0.640008	0.045*
C4	0.6295 (4)	−0.0230 (6)	0.6482 (4)	0.0388 (14)
H4A	0.694444	−0.045681	0.657197	0.047*
H4B	0.600371	−0.086743	0.608849	0.047*
C5	0.5841 (3)	−0.0227 (5)	0.7379 (4)	0.0288 (12)
H5	0.614942	0.042295	0.776158	0.035*
C6	0.4837 (4)	0.0149 (6)	0.7258 (6)	0.0472 (18)
H6A	0.451049	−0.048267	0.688621	0.057*
H6B	0.455311	0.017746	0.784995	0.057*
C7	0.4754 (3)	0.1418 (6)	0.6811 (4)	0.0372 (14)
H7A	0.502404	0.205796	0.721666	0.045*
H7B	0.410239	0.162109	0.671203	0.045*
C8	0.5915 (4)	−0.1465 (6)	0.7881 (4)	0.0397 (14)
H8A	0.556328	−0.141231	0.843406	0.048*
H8B	0.564509	−0.213527	0.750187	0.048*

C9	0.6099 (3)	0.4514 (5)	0.3760 (3)	0.0244 (11)
C10	0.6679 (3)	0.4182 (5)	0.2966 (3)	0.0244 (11)
H10	0.733515	0.427604	0.315003	0.029*
C11	0.6461 (4)	0.5081 (6)	0.2187 (4)	0.0288 (12)
H11A	0.579838	0.507245	0.204844	0.035*
H11B	0.663545	0.593965	0.236560	0.035*
C12	0.6970 (4)	0.4710 (6)	0.1351 (3)	0.0299 (12)
H12A	0.681611	0.530032	0.085930	0.036*
H12B	0.763338	0.475985	0.147985	0.036*
C13	0.6722 (3)	0.3405 (5)	0.1063 (3)	0.0262 (12)
H13	0.604822	0.337427	0.095228	0.031*
C14	0.6965 (4)	0.2495 (6)	0.1830 (4)	0.0332 (13)
H14A	0.677871	0.164112	0.164965	0.040*
H14B	0.763281	0.249287	0.193720	0.040*
C15	0.6507 (4)	0.2838 (6)	0.2693 (4)	0.0319 (12)
H15A	0.584401	0.270120	0.261501	0.038*
H15B	0.673527	0.227990	0.317868	0.038*
C16	0.7174 (4)	0.3051 (6)	0.0196 (4)	0.0347 (14)
H16A	0.714618	0.376924	−0.022083	0.042*
H16B	0.782239	0.285487	0.032601	0.042*
Cl2	0.53120 (11)	0.73439 (19)	0.07190 (12)	0.0537 (5)
O1W	0.3515 (3)	0.3850 (6)	0.0849 (3)	0.0600 (14)
H1WA	0.385 (4)	0.405 (9)	0.038 (3)	0.090*
H1WB	0.393 (4)	0.383 (9)	0.130 (3)	0.090*
O2W	0.1694 (4)	0.5612 (6)	0.5040 (4)	0.0651 (15)
H2WA	0.134 (5)	0.589 (9)	0.548 (5)	0.098*
H2WB	0.222 (3)	0.602 (8)	0.514 (6)	0.098*
O3W	0.1194 (3)	0.1039 (6)	0.3118 (3)	0.0619 (15)
H3WA	0.104 (5)	0.075 (8)	0.259 (3)	0.093*
H3WB	0.073 (4)	0.148 (8)	0.329 (5)	0.093*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0152 (3)	0.0291 (4)	0.0144 (3)	0.0005 (2)	0.0036 (2)	0.0010 (2)
Cl1	0.0213 (6)	0.0352 (8)	0.0193 (6)	−0.0045 (5)	0.0001 (4)	0.0005 (5)
O1	0.035 (2)	0.039 (3)	0.041 (2)	−0.0092 (18)	−0.0129 (17)	0.0117 (19)
O2	0.035 (2)	0.033 (2)	0.041 (2)	0.0018 (17)	−0.0158 (17)	−0.0035 (19)
O3	0.0195 (16)	0.050 (3)	0.0195 (17)	−0.0029 (16)	0.0022 (13)	−0.0049 (17)
O4	0.0187 (18)	0.088 (4)	0.027 (2)	−0.0061 (19)	0.0057 (14)	−0.018 (2)
N1	0.031 (2)	0.032 (3)	0.038 (3)	0.007 (2)	−0.0064 (19)	0.001 (2)
N2	0.041 (3)	0.056 (4)	0.039 (3)	0.001 (3)	0.018 (2)	−0.019 (3)
C1	0.024 (2)	0.031 (3)	0.018 (2)	0.004 (2)	0.0067 (19)	0.004 (2)
C2	0.032 (3)	0.025 (3)	0.032 (3)	0.001 (2)	−0.008 (2)	−0.003 (2)
C3	0.032 (3)	0.048 (4)	0.034 (3)	0.015 (3)	0.016 (2)	0.011 (3)
C4	0.039 (3)	0.040 (4)	0.038 (3)	0.015 (3)	−0.001 (2)	0.003 (3)
C5	0.020 (2)	0.029 (3)	0.037 (3)	0.001 (2)	−0.002 (2)	0.004 (2)
C6	0.022 (3)	0.036 (4)	0.084 (5)	0.002 (2)	0.010 (3)	0.022 (4)

C7	0.019 (2)	0.037 (4)	0.056 (4)	0.007 (2)	0.010 (2)	0.019 (3)
C8	0.028 (3)	0.040 (4)	0.051 (4)	0.005 (3)	0.004 (2)	0.009 (3)
C9	0.022 (2)	0.030 (3)	0.022 (2)	0.001 (2)	0.0045 (19)	0.004 (2)
C10	0.014 (2)	0.039 (3)	0.021 (2)	0.001 (2)	0.0046 (17)	0.000 (2)
C11	0.034 (3)	0.029 (3)	0.024 (3)	0.002 (2)	0.008 (2)	−0.001 (2)
C12	0.032 (3)	0.037 (4)	0.021 (3)	0.004 (2)	0.010 (2)	0.004 (2)
C13	0.020 (2)	0.035 (3)	0.024 (2)	0.004 (2)	0.0101 (18)	−0.006 (2)
C14	0.031 (3)	0.030 (3)	0.039 (3)	0.002 (2)	0.011 (2)	0.000 (3)
C15	0.036 (3)	0.031 (3)	0.030 (3)	0.003 (2)	0.011 (2)	0.002 (2)
C16	0.029 (3)	0.047 (4)	0.028 (3)	0.003 (2)	0.013 (2)	−0.012 (3)
Cl2	0.0453 (9)	0.0647 (13)	0.0518 (10)	−0.0012 (8)	0.0122 (7)	0.0128 (9)
O1W	0.062 (3)	0.068 (4)	0.051 (3)	0.008 (3)	0.014 (2)	0.021 (3)
O2W	0.048 (3)	0.075 (4)	0.071 (4)	0.012 (3)	−0.008 (3)	−0.019 (3)
O3W	0.052 (3)	0.081 (4)	0.053 (3)	0.018 (3)	0.000 (2)	−0.034 (3)

Geometric parameters (Å, º)

Cu1—Cu1^{i}	2.6649 (11)	C6—H6A	0.9900
Cu1—O1	1.950 (4)	C6—H6B	0.9900
Cu1—O2^{i}	1.955 (4)	C7—H7A	0.9900
Cu1—O4^{i}	1.965 (4)	C7—H7B	0.9900
Cu1—O3	1.991 (3)	C8—H8A	0.9900
Cu1—Cl1	2.4990 (12)	C8—H8B	0.9900
O1—C1	1.265 (7)	C9—C10	1.526 (6)
O2—C1	1.258 (6)	C10—C15	1.516 (8)
O3—C9	1.255 (6)	C10—C11	1.536 (7)
O4—C9	1.264 (6)	C10—H10	1.0000
N1—C8	1.489 (7)	C11—C12	1.527 (7)
N1—H1A	0.9100	C11—H11A	0.9900
N1—H1B	0.9100	C11—H11B	0.9900
N1—H1C	0.9100	C12—C13	1.505 (8)
N2—C16	1.479 (8)	C12—H12A	0.9900
N2—H2A	0.9100	C12—H12B	0.9900
N2—H2B	0.9100	C13—C16	1.522 (7)
N2—H2C	0.9100	C13—C14	1.538 (8)
C1—C2	1.499 (8)	C13—H13	1.0000
C2—C7	1.526 (8)	C14—C15	1.518 (7)
C2—C3	1.547 (7)	C14—H14A	0.9900
C2—H2	1.0000	C14—H14B	0.9900
C3—C4	1.512 (9)	C15—H15A	0.9900
C3—H3A	0.9900	C15—H15B	0.9900
C3—H3B	0.9900	C16—H16A	0.9900
C4—C5	1.515 (8)	C16—H16B	0.9900
C4—H4A	0.9900	O1W—H1WA	0.89 (2)
C4—H4B	0.9900	O1W—H1WB	0.90 (2)
C5—C8	1.526 (8)	O2W—H2WA	0.90 (2)
C5—C6	1.536 (7)	O2W—H2WB	0.90 (2)
C5—H5	1.0000	O3W—H3WA	0.88 (2)

C6—C7	1.518 (9)	O3W—H3WB	0.88 (2)
O1—Cu1—O2^{i}	167.02 (15)	C5—C6—H6B	109.6
O1—Cu1—O4^{i}	89.3 (2)	H6A—C6—H6B	108.1
O2^{i}—Cu1—O4^{i}	89.9 (2)	C6—C7—C2	112.7 (5)
O1—Cu1—O3	88.33 (18)	C6—C7—H7A	109.0
O2^{i}—Cu1—O3	89.60 (18)	C2—C7—H7A	109.0
O4^{i}—Cu1—O3	167.27 (15)	C6—C7—H7B	109.0
O1—Cu1—Cl1	94.31 (11)	C2—C7—H7B	109.0
O2^{i}—Cu1—Cl1	98.68 (11)	H7A—C7—H7B	107.8
O4^{i}—Cu1—Cl1	92.57 (11)	N1—C8—C5	112.0 (5)
O3—Cu1—Cl1	100.08 (10)	N1—C8—H8A	109.2
O1—Cu1—Cu1^{i}	83.04 (11)	C5—C8—H8A	109.2
O2^{i}—Cu1—Cu1^{i}	84.05 (11)	N1—C8—H8B	109.2
O4^{i}—Cu1—Cu1^{i}	80.24 (11)	C5—C8—H8B	109.2
O3—Cu1—Cu1^{i}	87.06 (10)	H8A—C8—H8B	107.9
Cl1—Cu1—Cu1^{i}	172.34 (4)	O3—C9—O4	124.6 (5)
C1—O1—Cu1	125.2 (3)	O3—C9—C10	119.4 (4)
C1—O2—Cu1^{i}	123.8 (4)	O4—C9—C10	116.0 (4)
C9—O3—Cu1	119.4 (3)	C15—C10—C9	109.8 (4)
C9—O4—Cu1^{i}	128.7 (3)	C15—C10—C11	111.3 (4)
C8—N1—H1A	109.5	C9—C10—C11	109.5 (4)
C8—N1—H1B	109.5	C15—C10—H10	108.7
H1A—N1—H1B	109.5	C9—C10—H10	108.7
C8—N1—H1C	109.5	C11—C10—H10	108.7
H1A—N1—H1C	109.5	C12—C11—C10	111.1 (4)
H1B—N1—H1C	109.5	C12—C11—H11A	109.4
C16—N2—H2A	109.5	C10—C11—H11A	109.4
C16—N2—H2B	109.5	C12—C11—H11B	109.4
H2A—N2—H2B	109.5	C10—C11—H11B	109.4
C16—N2—H2C	109.5	H11A—C11—H11B	108.0
H2A—N2—H2C	109.5	C13—C12—C11	110.8 (4)
H2B—N2—H2C	109.5	C13—C12—H12A	109.5
O2—C1—O1	123.9 (5)	C11—C12—H12A	109.5
O2—C1—C2	118.0 (5)	C13—C12—H12B	109.5
O1—C1—C2	118.1 (4)	C11—C12—H12B	109.5
C1—C2—C7	108.9 (5)	H12A—C12—H12B	108.1
C1—C2—C3	112.2 (5)	C12—C13—C16	111.5 (5)
C7—C2—C3	110.2 (4)	C12—C13—C14	109.2 (4)
C1—C2—H2	108.5	C16—C13—C14	112.2 (5)
C7—C2—H2	108.5	C12—C13—H13	107.9
C3—C2—H2	108.5	C16—C13—H13	107.9
C4—C3—C2	112.0 (5)	C14—C13—H13	107.9
C4—C3—H3A	109.2	C15—C14—C13	112.3 (5)
C2—C3—H3A	109.2	C15—C14—H14A	109.1
C4—C3—H3B	109.2	C13—C14—H14A	109.1
C2—C3—H3B	109.2	C15—C14—H14B	109.1
H3A—C3—H3B	107.9	C13—C14—H14B	109.1

C3—C4—C5	111.3 (5)	H14A—C14—H14B	107.9
C3—C4—H4A	109.4	C10—C15—C14	112.5 (5)
C5—C4—H4A	109.4	C10—C15—H15A	109.1
C3—C4—H4B	109.4	C14—C15—H15A	109.1
C5—C4—H4B	109.4	C10—C15—H15B	109.1
H4A—C4—H4B	108.0	C14—C15—H15B	109.1
C4—C5—C8	113.9 (5)	H15A—C15—H15B	107.8
C4—C5—C6	110.2 (5)	N2—C16—C13	111.6 (5)
C8—C5—C6	109.8 (5)	N2—C16—H16A	109.3
C4—C5—H5	107.5	C13—C16—H16A	109.3
C8—C5—H5	107.5	N2—C16—H16B	109.3
C6—C5—H5	107.5	C13—C16—H16B	109.3
C7—C6—C5	110.5 (5)	H16A—C16—H16B	108.0
C7—C6—H6A	109.6	H1WA—O1W—H1WB	102 (3)
C5—C6—H6A	109.6	H2WA—O2W—H2WB	103 (3)
C7—C6—H6B	109.6	H3WA—O3W—H3WB	106 (3)

Cu1^{i}—O2—C1—O1	1.1 (7)	Cu1—O3—C9—O4	1.0 (8)
Cu1^{i}—O2—C1—C2	178.1 (4)	Cu1—O3—C9—C10	−179.8 (4)
Cu1—O1—C1—O2	0.9 (7)	Cu1^{i}—O4—C9—O3	−2.3 (9)
Cu1—O1—C1—C2	−176.1 (4)	Cu1^{i}—O4—C9—C10	178.5 (4)
O2—C1—C2—C7	−94.2 (6)	O3—C9—C10—C15	122.8 (5)
O1—C1—C2—C7	82.9 (6)	O4—C9—C10—C15	−57.9 (6)
O2—C1—C2—C3	143.5 (5)	O3—C9—C10—C11	−114.7 (5)
O1—C1—C2—C3	−39.4 (7)	O4—C9—C10—C11	64.5 (6)
C1—C2—C3—C4	174.7 (5)	C15—C10—C11—C12	−53.7 (6)
C7—C2—C3—C4	53.1 (7)	C9—C10—C11—C12	−175.2 (4)
C2—C3—C4—C5	−56.3 (7)	C10—C11—C12—C13	58.9 (6)
C3—C4—C5—C8	−178.1 (5)	C11—C12—C13—C16	176.2 (4)
C3—C4—C5—C6	57.9 (7)	C11—C12—C13—C14	−59.3 (5)
C4—C5—C6—C7	−57.2 (8)	C12—C13—C14—C15	56.5 (6)
C8—C5—C6—C7	176.5 (6)	C16—C13—C14—C15	−179.4 (5)
C5—C6—C7—C2	55.9 (8)	C9—C10—C15—C14	172.3 (4)
C1—C2—C7—C6	−176.8 (5)	C11—C10—C15—C14	50.9 (6)
C3—C2—C7—C6	−53.3 (7)	C13—C14—C15—C10	−52.9 (6)
C4—C5—C8—N1	63.3 (7)	C12—C13—C16—N2	−162.4 (5)
C6—C5—C8—N1	−172.5 (5)	C14—C13—C16—N2	74.9 (6)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1^{ii}	0.91	2.63	3.316 (5)	133
N1—H1*C*···Cl1^{iii}	0.91	2.52	3.394 (5)	160
N2—H2*B*···Cl1^{iv}	0.91	2.25	3.123 (5)	160
N2—H2*C*···Cl2^{v}	0.91	2.24	3.151 (6)	179
N1—H1*B*···O1*W*^{vi}	0.91	1.90	2.760 (7)	156

N2—H2*A*···O2*W*^{vii}	0.91	2.06	2.789 (9)	137
O1*W*—H1*WA*···Cl2^{v}	0.89 (2)	2.57 (8)	3.218 (6)	130 (8)
O2*W*—H2*WA*···Cl2^{viii}	0.90 (2)	2.46 (7)	3.176 (6)	137 (9)
O2*W*—H2*WB*···O3^{i}	0.90 (2)	2.22 (8)	2.820 (6)	124 (8)
O3*W*—H3*WA*···Cl1^{ix}	0.88 (2)	2.66 (6)	3.258 (5)	127 (6)
O3*W*—H3*WB*···Cl2^{x}	0.88 (2)	2.35 (3)	3.182 (5)	158 (7)

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