Crystal structure of 1,10-phenanthrolinium violurate violuric acid pentahydrate

Rüdiger W. Seidel[a]* and Tsonko M. Kolev[b]

[a]Institut für Pharmazie, Martin-Luther-Universität Halle-Wittenberg, Wolfgang-Langenbeck-Str. 4, 06120 Halle (Saale), Germany, and [b]Institute of Molecular Biology "Roumen Tsanev", Bulgarian Academy of Sciences, Acad. G. Bonchev-Str. Bl. 21, Sofia 1113, Bulgaria. *Correspondence e-mail: ruediger.seidel@pharmazie.uni-halle.de

The title compound [systematic name: 1,10-phenanthrolinium 6-hydroxy-5-(oxidoimino)-1,3-diazinane-2,4-dione–6-hydroxy-5-(hydroxyimino)-1,3-diazinane-2,4-dione–water (1/1/5)], $C_{12}H_9N_2^+ \cdot C_4H_2N_3O_4^- \cdot C_4H_3N_3O_4 \cdot 5H_2O$, is a co-crystal salt hydrate comprising 1,10-phenanthrolinium cations, violurate anions, free violuric acid as co-former and five water molecules of crystallization per formula unit. The violurate and the violuric acid residues each form distinct N—H···O hydrogen-bonded tapes with a common $R_2^2(8)$ hydrogen-bond motif extending parallel to (10$\bar{3}$). Solvent water molecules connect the tapes to form a tri-periodic hydrogen-bonded network with channels extending parallel to the a-axis direction, which accommodate the N—H···O$_{water}$ hydrogen-bonded 1,10-phenanthrolinium cations. Direct N—H···O hydrogen bonds between the 1,10-phenanthrolinium and violurate ions are not encountered.

1. Chemical context

Violuric acid (systematic name: 6-hydroxy-5-nitroso-1H-pyrimidine-2,4-dione) is a derivative of barbituric acid and was first described by the German chemist Adolf von Baeyer more than 150 years ago (Baeyer, 1863). While free violuric acid is colourless, violurate salts typically exhibit an intense colour (Liebing *et al.*, 2019, and references therein). Coloured organic salts of violuric acid were reported as early as in 1909 (Hantzsch & Issaias, 1909; Zerewitinoff, 1909), but their crystal structures have only been investigated since 2006 (for more details, see: Section 4).

For the system violuric acid, 1,10-phenanthroline as an organic base and water as solvent, a pK_{a1} value of 4.35 can be assumed for violuric acid (Moratal *et al.*, 1985) and a pK_a value of 4.84 for the conjugate acid of 1,10-phenanthroline (Haynes, 2016). Hence, we can estimate $\Delta pK_a = pK_a$(protonated base) $- pK_a$(acid) $= 4.84 - 4.35 = 0.49$. In the ΔpK_a range between -1 and 4, the position of the acid proton, and thus the formation of a salt or a co-crystal (Aitipamula *et al.*, 2012), is difficult to predict (Cruz-Cabeza, 2012). In fact, the title compound represents a multicomponent crystal that can be regarded as a co-crystal salt hydrate, $C_{12}H_9N_2^+ \cdot C_4H_2N_3O_4^- \cdot C_4H_3N_3O_4 \cdot 5H_2O$.
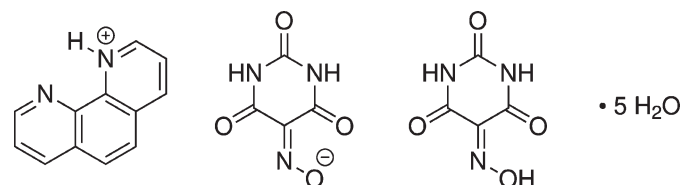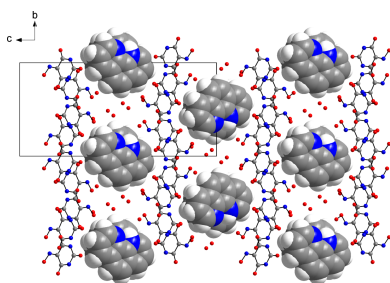
Table 1
Selected geometric parameters (Å, °).

C15—N15	1.342 (5)	C25—N25	1.284 (5)
N15—O15	1.274 (4)	N25—O25	1.345 (4)
C2—N1—C1A	122.8 (4)	C9—N10—C10A	116.4 (4)

2. Structural commentary

The asymmetric unit (Fig. 1) comprises a 1,10-phenanthrolinium cation, a violurate anion, a co-crystallized violuric acid molecule and five water molecules of crystallization (for two of the water molecules, associated with O4 and O5, hydrogen atoms could not be located). Thus, the title compound represents a multicomponent crystal with eight independent residues (Z^R = 8; Grothe *et al.*, 2016). The parameter Z^R, *i.e.* the number of crystallographically independent molecules of any type is also known as Z'' (Steed & Steed, 2015). Inspired by the work by Aitipamula *et al.* (2012), Grothe *et al.* (2016) proposed a classification system for multicomponent crystals comprising seven categories. Accordingly, the title compound belongs to the class *co-crystal salt solvates*, which necessarily exhibit $Z^R \geq 4$.

In the phenanthrolinium cation, the C2—N1—C1A angle is significantly larger by 6.4° than the C9—N10—C10A angle (Table 1), which corroborates the assignment of the site of protonation at N1. Likewise, the N—O and C—N bond lengths in the oxime (C25=N25—O25—H25) and the oximate (C15=N15—O15) moieties of the violuric acid and the violurate residue (Fig. 1; Table 1), lend support to the assignments of the sites of protonation and deprotonation, respectively.
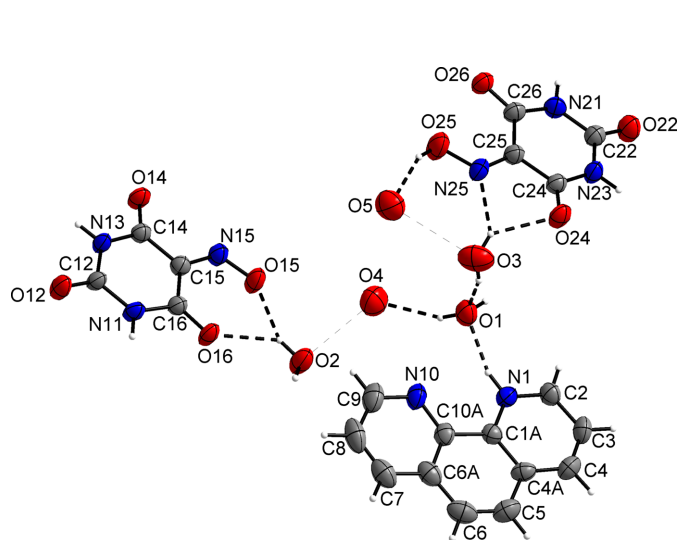
Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.88 (2)	1.89 (2)	2.730 (5)	161 (4)
N11—H11···O14[i]	0.88 (2)	2.12 (2)	2.997 (4)	173 (4)
N13—H13···O16[ii]	0.85 (2)	1.98 (2)	2.835 (4)	177 (4)
N21—H21···O24[iii]	0.87 (2)	1.99 (2)	2.858 (4)	172 (4)
N23—H23···O26[iv]	0.88 (2)	2.03 (2)	2.900 (4)	173 (4)
O1—H1A···O4	0.80 (2)	2.05 (3)	2.809 (5)	157 (5)
O1—H1B···O15[v]	0.85 (2)	1.87 (2)	2.719 (4)	177 (5)
O2—H2A···O12[i]	0.84 (2)	2.02 (3)	2.825 (4)	160 (5)
O2—H2B···O15	0.86 (2)	2.08 (3)	2.811 (5)	143 (4)
O2—H2B···O16	0.86 (2)	2.15 (4)	2.832 (4)	136 (4)
O3—H3A···N25	0.84 (2)	2.32 (4)	3.007 (5)	139 (5)
O3—H3A···O24	0.84 (2)	2.33 (4)	3.006 (5)	137 (5)
O3—H3B···O1	0.81 (2)	2.04 (4)	2.784 (6)	153 (6)
O25—H25···O5	0.82	1.92	2.692 (5)	156
O4···O2			2.694 (5)	
O4···O5[vi]			2.816 (6)	
O4···O4[v]			2.844 (7)	
O5···O5[vi]			2.837 (8)	
O5···O3			2.850 (6)	

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

3. Supramolecular features

The predominant supramolecular features of the crystal structure are N—H···O and O—H···O hydrogen bonds (Fig. 2). Table 2 lists the corresponding hydrogen-bond parameters, which are within expected ranges (Thakuria *et al.*, 2017). The violurate and the violuric acid residues each form linear polymeric strands through N—H···O hydrogen bonds with a common $R_2^2(8)$ motif (Allen *et al.*, 1999; Deepa *et al.*, 2014), extending parallel to the *b*-axis direction by application of the 2_1 screw axis symmetry. Thus, there are two distinct

Figure 1
The asymmetric unit of the title compound, showing the molecular entities with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius, and dashed lines represent hydrogen bonds. The water hydrogen atoms bound to O4 and O5 could not be located unambiguously and were therefore excluded from the structure model.
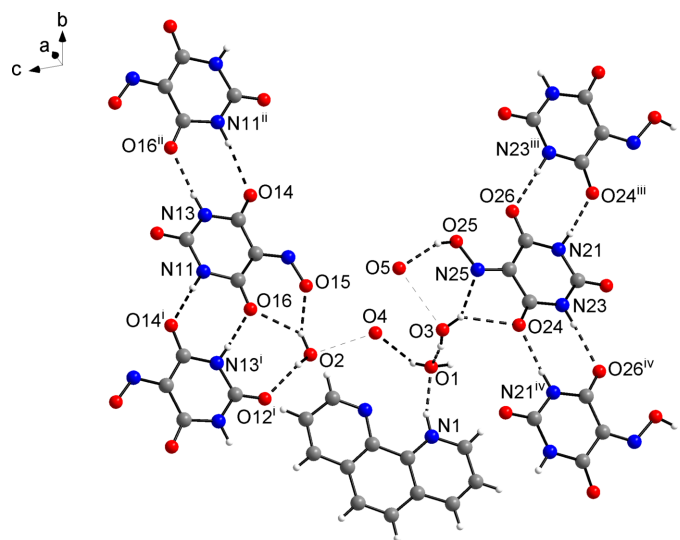

Figure 2
Section of the crystal structure of the title compound (viewed approximately along the *a*-axis direction towards the origin), illustrating some of the key hydrogen-bonding features (dashed lines); symmetry codes refer to Table 2. The water hydrogen atoms bound to O4 and O5 could not be located unambiguously and were therefore excluded from the structure model.
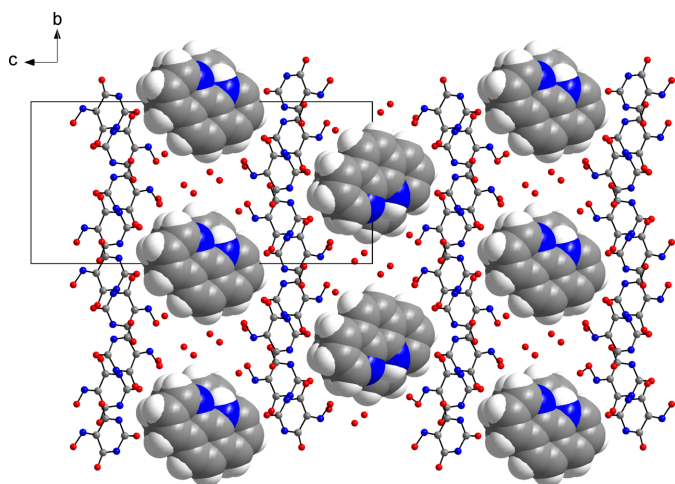
Figure 3
Packing diagram of the title compound viewed along the *a*-axis direction, showing the channel structure formed by the hydrogen-bonded network. Except for the phenanthrolinium cations (space-filling representation), hydrogen atoms were omitted for clarity. Colour scheme: C, grey; H, white; N, blue; O, red.

hydrogen-bonded tapes, one of which features inter-anionic hydrogen bonds (Martín-Fernández *et al.*, 2024). Neutral and anionic hydrogen-bonded tapes stack in an alternating fashion parallel to the *a*-axis direction, with the molecular planes extending parallel to (10$\bar{3}$).

These stacks of hydrogen-bonded tapes are separated by **c**/2 at *x*, *y*, $\frac{1}{4}$ and *x*, *y*, $\frac{3}{4}$, and are joined by the water molecules through hydrogen-bonding, which results in an intricate tri-periodic network. The water molecules are clustered at *x*, 0, 0 and *x*, $\frac{1}{2}$, $\frac{1}{2}$ The water molecule associated with O2 joins two violurate anions by a donating bifurcated hydrogen bond to the oximate oxygen atom O15 and the carbonyl oxygen O16, and a single O—H···O hydrogen bond to the carbonyl oxygen O12 of an adjacent molecule. The water molecule associated with O3 forms a donating bifurcated hydrogen bond to the
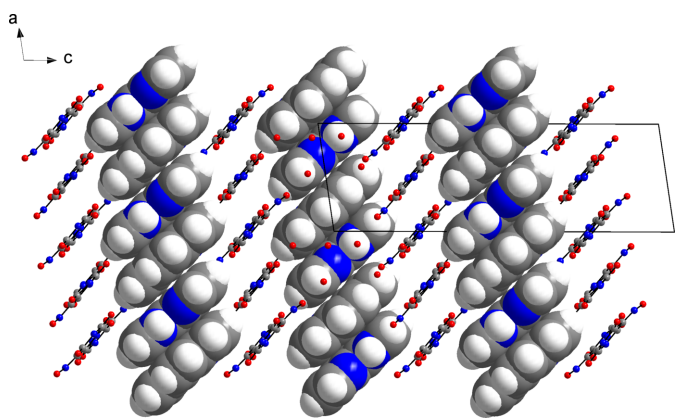

Figure 4
Packing diagram of the title compound viewed along the *b*-axis direction, showing the layer structure of phenanthrolinium cations, violurate anions and violuric acid molecules. Representations and colour codes are as in Fig. 3.

carbonyl oxygen O24 and the oxime nitrogen N25 of the neutral violuric acid molecule, while the oxime hydroxy group (O25) donates a hydrogen bond to the water oxygen atom O5. The donor functions of the latter and of O4 are unclear because their H atoms were not localized. However, the distances to possible acceptor O atoms indicate that there are several possibilities for hydrogen bonds of medium strength (Table 2).

Within the hydrogen-bonded network, the phenanthrolinium cations reside face-to-face stacked in channels extending parallel to the *a*-axis direction (Fig. 3), and each forms an N—H···O hydrogen bond to a water molecule but neither to the violurate nor to violuric acid moieties. A view along the *b*-axis direction reveals a layered arrangement of the phenanthrolinium cations, violurate anions and violuric acid molecules (Fig. 4). Within a stack, the mean planes through the phenanthrolinium ions related by inversion symmetry are separated by 3.46 and 3.55 Å in an alternating fashion.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.45 with March 2024 updates; Groom *et al.*, 2016) revealed more than 60 entries for violuric acid or its monoanion (excluding metal-containing structures), of which some are duplicates. For the polymorphs of violuric acid monohydrate, see: Nichol & Clegg (2005*a*) and Guille *et al.* (2007), and references cited therein. The structure of violuric acid methanol solvate was also reported by Nichol & Clegg (2005*b*). The crystal structure of unsolvated free violuric acid is hitherto unknown, as far as we are able to ascertain. For the structure of ammonium violurate, see: Nichol & Clegg (2007), and for structures of multicomponent crystals of violuric acid and organic nitrogen bases, see: Nichol & Clegg (2006), Kolev *et al.* (2009), Ivanova & Spiteller (2010), Ivanova *et al.* (2010), Koleva *et al.* (2010), Ivanova & Spiteller (2014), Liebing *et al.* (2019) and Ivanova & Spiteller (2019).

The structures most related to the title compound are piperidinium violurate sesquihydrate (CSD refcode: FUFPIG; Kolev *et al.*, 2009), 1,2,3,4-tetrahydroisoquinolinium violurate monohydrate (FUFPOM; Kolev *et al.*, 2009) and ephedrinium violurate dihydrate (WURCUI; Ivanova *et al.*, 2010), which likewise feature hydrogen-bonded tapes of violurate residues with an $R_2^2(8)$ motif, propagating by 2_1 screw symmetry.

We note that the CSD also contains a variety of structures of violurate metal complexes, including alkali metal and alkaline earth metal salts. These are beyond the scope of this survey, and we direct the interested reader to the review by Lorenz *et al.* (2019) for the coordination chemistry of violurate anions.

5. Synthesis and crystallization

1,10-Phenanthroline (170 mg, 0.94 mmol) and violuric acid (175 mg, 1.11 mmol) were mixed in 20 ml of water under continuous stirring at elevated temperature (323–353 K) for 24 h. A red precipitate was obtained after leaving the resulting

Seidel and Kolev • $C_{12}H_9N_2^+ \cdot C_4H_2N_3O_4^- \cdot C_4H_3N_3O_4 \cdot 5H_2O$ **3 of 5**

solution at 298 K for about two weeks. The product was filtered off and air-dried. Red crystals of the title compound suitable for X-ray diffraction analysis were grown from a solution of the sample in doubly distilled water at room temperature over a period of three weeks.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Carbon-bound H atoms and the oxime hydroxy H25 atom were placed in geometrically calculated positions with $d(C-H) = 0.93$ Å and $d(O-H) = 0.82$ Å, respectively, and refined with a riding model. Nitrogen-bound H atoms were located in a difference-Fourier map and their positions refined with the N—H distances restrained to a target value of 0.86 (2) Å. The water H atoms bound to O1, O2 and O3 were located in difference-Fourier maps, and the corresponding O—H distances were restrained to a target value of 0.82 (2) Å. The 1,3-H,H distances of the water molecules were restrained to be similar with a standard deviation of 0.04 Å. $U_{iso}(H)$ was set $1.2U_{eq}(C,N,O)$ for all H atoms. The water H atoms bound to O4 and O5 could not be located with certainty and were therefore excluded from the structural model, but are included in the chemical formula for calculation of crystal data. Two reflections (011 and $\overline{2}$06) were obstructed by the beam stop and were omitted from the refinement.

Acknowledgements

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_9N_2^+\cdot C_4H_2N_3O_4^-\cdot C_4H_3N_3O_4\cdot 5H_2O$
M_r	584.47
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	294
a, b, c (Å)	8.247 (3), 12.0714 (16), 25.771 (4)
β (°)	98.572 (16)
V (Å^3)	2537.1 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	$0.29 \times 0.25 \times 0.22$
Data collection	
Diffractometer	Siemens P4
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	5990, 4453, 2259
R_{int}	0.050
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.187, 1.01
No. of reflections	4453
No. of parameters	404
No. of restraints	14
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.21

Computer programs: *XSCANS* (Siemens, 1994), *SHELXS97* (Sheldrick, 2008), *SHELXL2019/3* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2018), *PLATON* (Spek, 2020), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

References

Aitipamula, S., Banerjee, R., Bansal, A. K., Biradha, K., Cheney, M. L., Choudhury, A. R., Desiraju, G. R., Dikundwar, A. G., Dubey, R., Duggirala, N., Ghogale, P. P., Ghosh, S., Goswami, P. K., Goud, N. R., Jetti, R. R. K. R., Karpinski, P., Kaushik, P., Kumar, D., Kumar, V., Moulton, B., Mukherjee, A., Mukherjee, G., Myerson, A. S., Puri, V., Ramanan, A., Rajamannar, T., Reddy, C. M., Rodriguez-Hornedo, N., Rogers, R. D., Row, T. N. G., Sanphui, P., Shan, N., Shete, G., Singh, A., Sun, C. C., Swift, J. A., Thaimattam, R., Thakur, T. S., Kumar Thaper, R., Thomas, S. P., Tothadi, S., Vangala, V. R., Variankaval, N., Vishweshwar, P., Weyna, D. R. & Zaworotko, M. J. (2012). *Cryst. Growth Des.* **12**, 2147–2152.
Allen, F. H., Motherwell, W. D. S., Raithby, P. R., Shields, G. P. & Taylor, R. (1999). *New J. Chem.* **23**, 25–34.
Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
Baeyer, A. (1863). *Justus Liebigs Ann. Chem.* **127**, 199–236.
Brandenburg, K. (2018). *DIAMOND.* Crystal Impact GbR, Bonn, Germany.
Cruz-Cabeza, A. (2012). *CrystEngComm*, **14**, 6362–7365.
Deepa, P., Vijay Solomon, R., Angeline Vedha, S., Kolandaivel, P. & Venuvanalingam, P. (2014). *Mol. Phys.* **112**, 3195–3205.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Grothe, E., Meekes, H., Vlieg, E., ter Horst, J. H. & de Gelder, R. (2016). *Cryst. Growth Des.* **16**, 3237–3243.
Guille, K., Harrington, R. W. & Clegg, W. (2007). *Acta Cryst.* C**63**, o327–o329.
Hantzsch, A. & Issaias, B. (1909). *Ber. Dtsch. Chem. Ges.* **42**, 1000–1007.
Haynes, W. M. (2016). *CRC Handbook of Chemistry and Physics*, 97th ed., p. 3.444. Boca Raton: CRC Press.
Ivanova, B., Kolev, T., Lamshöft, M., Mayer-Figge, H., Seidel, R., Sheldrick, W. S. & Spiteller, M. (2010). *J. Mol. Struct.* **971**, 8–11.
Ivanova, B. & Spiteller, M. (2014). *Food. Meas.* **8**, 343–355.
Ivanova, B. & Spiteller, M. (2019). *Chem. Pap.* **73**, 2821–2844.
Ivanova, B. B. & Spiteller, M. (2010). *Cryst. Growth Des.* **10**, 2470–2474.
Koleva, B. B., Bakalska, R., Seidel, R. W., Kolev, T., Mayer-Figge, H., Sheldrick, W. S. & Spiteller, M. (2010). *J. Mol. Struct.* **965**, 89–97.
Kolev, T., Koleva, B. B., Seidel, R. W., Spiteller, M. & Sheldrick, W. S. (2009). *Cryst. Growth Des.* **9**, 3348–3352.
Liebing, P., Stein, F., Hilfert, L., Lorenz, V., Oliynyk, K. & Edelmann, F. T. (2019). *Z. Anorg. Allge Chem.* **645**, 36–43.
Lorenz, V., Liebing, P., Engelhardt, F., Stein, F., Kühling, M., Schröder, L. & Edelmann, F. T. (2019). *J. Coord. Chem.* **72**, 1–34.
Martín-Fernández, C., Montero-Campillo, M. M. & Alkorta, I. (2024). *J. Phys. Chem. Lett.* **15**, 4105–4110.
Moratal, J. M., Prades, A., Julve, M. & Faus, J. (1985). *Thermochim. Acta*, **89**, 343–350.
Nichol, G. S. & Clegg, W. (2005*a*). *Acta Cryst.* E**61**, o3788–o3790.
Nichol, G. S. & Clegg, W. (2005*b*). *Acta Cryst.* C**61**, o718–o721.
Nichol, G. S. & Clegg, W. (2006). *Cryst. Growth Des.* **6**, 451–460.
Nichol, G. S. & Clegg, W. (2007). *Acta Cryst.* C**63**, o609–o612.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Siemens (1994). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

Steed, K. M. & Steed, J. W. (2015). *Chem. Rev.* **115**, 2895–2933.

Thakuria, R., Sarma, B. & Nangia, A. (2017). *Hydrogen Bonding in Molecular Crystals.* In *Comprehensive Supramolecular Chemistry II*, vol. 7, edited by J. L. Atwood, J. L., pp. 25–48. Oxford: Elsevier.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zerewitinoff, Th. (1909). *Ber. Dtsch. Chem. Ges.* **42**, 4802–4808.

Crystal structure of 1,10-phenanthrolinium violurate violuric acid pentahydrate

Rüdiger W. Seidel and Tsonko M. Kolev

Computing details

1,10-Phenanthrolinium 6-hydroxy-5-(oxidoimino)-1,3-diazinane-2,4-dione–\ 6-hydroxy-5-(hydroxyimino)-1,3-diazinane-2,4-dione–water (1/1/5)

Crystal data

$C_{12}H_9N_2^+ \cdot C_4H_2N_3O_4^- \cdot C_4H_3N_3O_4 \cdot 5H_2O$	$F(000) = 1216$
$M_r = 584.47$	$D_x = 1.530$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.247$ (3) Å	Cell parameters from 16 reflections
$b = 12.0714$ (16) Å	$\theta = 12.0$–$26.1°$
$c = 25.771$ (4) Å	$\mu = 0.13$ mm^{-1}
$\beta = 98.572$ (16)°	$T = 294$ K
$V = 2537.1$ (12) Å^3	Prism, red
$Z = 4$	$0.29 \times 0.25 \times 0.22$ mm

Data collection

Siemens P4 diffractometer	$R_{int} = 0.050$
Radiation source: sealed X-ray tube	$\theta_{max} = 25.0°$, $\theta_{min} = 2.3°$
ω scans	$h = -9 \rightarrow 1$
5990 measured reflections	$k = -1 \rightarrow 14$
4453 independent reflections	$l = -30 \rightarrow 30$
2259 reflections with $I > 2\sigma(I)$	3 standard reflections every 15 min
	intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.067$	Hydrogen site location: mixed
$wR(F^2) = 0.187$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.01$	
4453 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.7605P]$
404 parameters	where $P = (F_o^2 + 2F_c^2)/3$
14 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.27$ e Å^{-3}
	$\Delta\rho_{min} = -0.21$ 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*	$U_{iso}*/U_{eq}$
C1A	0.1694 (5)	−0.0134 (4)	0.46997 (15)	0.0351 (10)
C2	−0.0174 (5)	0.0453 (4)	0.39698 (16)	0.0420 (11)
H2	−0.067421	0.103132	0.376762	0.050*
C3	−0.0579 (6)	−0.0633 (4)	0.38352 (18)	0.0492 (12)
H3	−0.134885	−0.079078	0.354276	0.059*
C4	0.0162 (6)	−0.1461 (4)	0.41353 (17)	0.0475 (12)
H4	−0.009583	−0.219140	0.404186	0.057*
C4A	0.1305 (5)	−0.1251 (3)	0.45819 (17)	0.0406 (11)
C5	0.2093 (6)	−0.2071 (4)	0.49225 (19)	0.0565 (14)
H5	0.185146	−0.281281	0.485187	0.068*
C6	0.3184 (6)	−0.1803 (4)	0.5347 (2)	0.0582 (14)
H6	0.367223	−0.236401	0.556320	0.070*
C6A	0.3608 (5)	−0.0673 (4)	0.54709 (17)	0.0484 (12)
C7	0.4758 (6)	−0.0371 (5)	0.58985 (18)	0.0604 (15)
H7	0.530675	−0.090678	0.611739	0.072*
C8	0.5062 (6)	0.0729 (6)	0.59896 (19)	0.0675 (16)
H8	0.580971	0.095392	0.627666	0.081*
C9	0.4234 (6)	0.1524 (5)	0.56446 (19)	0.0617 (15)
H9	0.446266	0.226869	0.571235	0.074*
C10A	0.2859 (5)	0.0173 (4)	0.51489 (17)	0.0403 (11)
C12	0.5769 (5)	0.7219 (3)	0.78082 (16)	0.0367 (10)
C14	0.3737 (5)	0.8194 (3)	0.71811 (15)	0.0349 (10)
C15	0.3164 (5)	0.7134 (3)	0.69627 (15)	0.0356 (10)
C16	0.3938 (5)	0.6117 (3)	0.71692 (16)	0.0360 (10)
N11	0.5144 (4)	0.6237 (3)	0.76025 (14)	0.0404 (9)
H11	0.560 (5)	0.561 (2)	0.7729 (15)	0.048*
N13	0.5025 (5)	0.8154 (3)	0.75876 (14)	0.0394 (9)
H13	0.546 (5)	0.875 (2)	0.7721 (15)	0.047*
N15	0.1919 (4)	0.7205 (3)	0.65645 (13)	0.0432 (9)
C22	−0.1051 (6)	0.5632 (4)	0.22527 (16)	0.0419 (11)
C24	0.1034 (5)	0.4561 (3)	0.28192 (16)	0.0361 (10)
C25	0.1608 (5)	0.5592 (3)	0.30845 (16)	0.0389 (11)
C26	0.0898 (6)	0.6672 (3)	0.28899 (17)	0.0408 (11)
N1	0.0931 (4)	0.0670 (3)	0.43884 (14)	0.0389 (9)
H1	0.117 (5)	0.1369 (18)	0.4449 (16)	0.047*
N10	0.3159 (5)	0.1267 (3)	0.52332 (14)	0.0494 (10)
N21	−0.0407 (5)	0.6588 (3)	0.24939 (14)	0.0428 (10)
H21	−0.088 (5)	0.719 (2)	0.2359 (15)	0.051*
N23	−0.0273 (5)	0.4667 (3)	0.24254 (14)	0.0437 (10)
H23	−0.054 (5)	0.403 (2)	0.2268 (15)	0.052*
N25	0.2728 (5)	0.5426 (3)	0.34791 (14)	0.0478 (10)
O1	0.1190 (4)	0.2924 (3)	0.43698 (12)	0.0570 (10)
H1A	0.115 (6)	0.317 (4)	0.4657 (10)	0.068*
H1B	0.039 (4)	0.314 (4)	0.4145 (14)	0.068*
O2	0.1342 (5)	0.3996 (3)	0.62720 (15)	0.0669 (11)

H2A	0.204 (5)	0.353 (3)	0.640 (2)	0.080*
H2B	0.176 (6)	0.462 (2)	0.638 (2)	0.080*
O3	0.4014 (5)	0.3233 (4)	0.39153 (19)	0.0802 (12)
H3A	0.372 (7)	0.364 (4)	0.3655 (16)	0.096*
H3B	0.324 (5)	0.293 (5)	0.402 (2)	0.096*
O4	0.1337 (5)	0.4343 (3)	0.52391 (14)	0.0822 (12)
O5	0.5317 (5)	0.5145 (3)	0.44781 (14)	0.0823 (12)
O12	0.6901 (4)	0.7252 (2)	0.81696 (12)	0.0543 (9)
O14	0.3169 (4)	0.9110 (2)	0.70432 (11)	0.0466 (8)
O15	0.1345 (4)	0.6320 (2)	0.63379 (12)	0.0563 (9)
O16	0.3588 (4)	0.5181 (2)	0.70065 (12)	0.0480 (8)
O22	−0.2202 (4)	0.5645 (3)	0.19080 (12)	0.0596 (10)
O24	0.1668 (4)	0.3658 (2)	0.29265 (12)	0.0484 (8)
O25	0.3305 (5)	0.6316 (3)	0.37618 (14)	0.0714 (11)
H25	0.407415	0.612960	0.398400	0.086*
O26	0.1407 (4)	0.7577 (2)	0.30519 (12)	0.0496 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1A	0.031 (2)	0.038 (2)	0.036 (2)	0.001 (2)	0.0031 (19)	0.002 (2)
C2	0.039 (3)	0.044 (3)	0.040 (2)	0.003 (2)	−0.004 (2)	0.001 (2)
C3	0.046 (3)	0.056 (3)	0.043 (3)	−0.008 (2)	−0.004 (2)	−0.012 (2)
C4	0.051 (3)	0.036 (3)	0.055 (3)	−0.006 (2)	0.007 (2)	−0.008 (2)
C4A	0.036 (3)	0.032 (2)	0.053 (3)	0.002 (2)	0.006 (2)	0.007 (2)
C5	0.058 (3)	0.039 (3)	0.072 (4)	−0.001 (3)	0.010 (3)	0.001 (3)
C6	0.057 (3)	0.056 (3)	0.063 (3)	0.014 (3)	0.013 (3)	0.018 (3)
C6A	0.039 (3)	0.064 (3)	0.041 (3)	0.006 (3)	0.003 (2)	0.008 (2)
C7	0.050 (3)	0.086 (4)	0.043 (3)	0.008 (3)	0.000 (2)	0.008 (3)
C8	0.046 (3)	0.111 (5)	0.041 (3)	−0.002 (3)	−0.006 (2)	−0.012 (3)
C9	0.053 (3)	0.073 (4)	0.057 (3)	−0.017 (3)	0.001 (3)	−0.017 (3)
C10A	0.033 (2)	0.047 (3)	0.040 (2)	−0.005 (2)	0.002 (2)	−0.003 (2)
C12	0.036 (2)	0.026 (2)	0.044 (2)	−0.003 (2)	−0.005 (2)	0.002 (2)
C14	0.038 (2)	0.028 (2)	0.037 (2)	0.0017 (19)	0.001 (2)	0.0002 (19)
C15	0.035 (2)	0.032 (2)	0.038 (2)	0.002 (2)	0.001 (2)	0.0001 (19)
C16	0.038 (2)	0.030 (2)	0.038 (2)	−0.002 (2)	0.000 (2)	0.002 (2)
N11	0.041 (2)	0.025 (2)	0.050 (2)	−0.0004 (17)	−0.0092 (18)	0.0050 (17)
N13	0.044 (2)	0.0263 (19)	0.042 (2)	−0.0032 (17)	−0.0122 (18)	−0.0005 (16)
N15	0.046 (2)	0.034 (2)	0.044 (2)	−0.0012 (18)	−0.0115 (18)	−0.0002 (17)
C22	0.048 (3)	0.035 (3)	0.041 (3)	0.000 (2)	0.002 (2)	−0.001 (2)
C24	0.037 (2)	0.029 (2)	0.041 (2)	0.000 (2)	0.002 (2)	0.001 (2)
C25	0.042 (3)	0.031 (2)	0.041 (2)	−0.001 (2)	−0.002 (2)	0.002 (2)
C26	0.048 (3)	0.029 (2)	0.044 (3)	0.002 (2)	0.003 (2)	0.000 (2)
N1	0.038 (2)	0.033 (2)	0.045 (2)	−0.0025 (18)	0.0027 (18)	−0.0018 (18)
N10	0.046 (2)	0.053 (3)	0.046 (2)	−0.010 (2)	−0.003 (2)	−0.010 (2)
N21	0.048 (2)	0.033 (2)	0.044 (2)	0.0075 (18)	−0.0046 (19)	0.0037 (18)
N23	0.052 (2)	0.030 (2)	0.044 (2)	−0.0008 (19)	−0.0091 (19)	−0.0052 (17)
N25	0.056 (2)	0.037 (2)	0.047 (2)	−0.0108 (19)	−0.005 (2)	−0.0056 (18)

O1	0.064 (2)	0.051 (2)	0.048 (2)	0.0016 (18)	−0.0149 (19)	−0.0008 (18)
O2	0.076 (3)	0.039 (2)	0.074 (3)	−0.0058 (19)	−0.028 (2)	−0.0016 (19)
O3	0.067 (3)	0.072 (3)	0.098 (3)	0.015 (2)	0.002 (2)	0.032 (2)
O4	0.105 (3)	0.064 (2)	0.074 (3)	0.003 (2)	0.003 (2)	−0.008 (2)
O5	0.077 (3)	0.086 (3)	0.077 (3)	0.000 (2)	−0.014 (2)	0.014 (2)
O12	0.056 (2)	0.0371 (18)	0.059 (2)	−0.0008 (16)	−0.0269 (17)	0.0014 (15)
O14	0.055 (2)	0.0242 (16)	0.0548 (19)	0.0045 (15)	−0.0115 (16)	0.0014 (14)
O15	0.063 (2)	0.0365 (18)	0.058 (2)	−0.0032 (17)	−0.0255 (17)	−0.0053 (16)
O16	0.057 (2)	0.0224 (16)	0.0574 (19)	0.0007 (15)	−0.0162 (16)	−0.0039 (15)
O22	0.061 (2)	0.050 (2)	0.059 (2)	0.0040 (18)	−0.0194 (19)	−0.0003 (17)
O24	0.055 (2)	0.0269 (17)	0.058 (2)	0.0069 (15)	−0.0088 (16)	−0.0053 (15)
O25	0.084 (3)	0.047 (2)	0.069 (2)	−0.007 (2)	−0.033 (2)	−0.0034 (19)
O26	0.061 (2)	0.0300 (17)	0.0527 (19)	−0.0019 (16)	−0.0078 (16)	−0.0001 (15)

Geometric parameters (Å, º)

C1A—N1	1.353 (5)	C14—C15	1.449 (6)
C1A—C4A	1.408 (6)	C15—N15	1.342 (5)
C1A—C10A	1.438 (5)	C15—C16	1.448 (6)
C2—N1	1.330 (5)	C16—O16	1.224 (5)
C2—C3	1.384 (6)	C16—N11	1.388 (5)
C2—H2	0.9300	N11—H11	0.884 (19)
C3—C4	1.353 (6)	N13—H13	0.852 (19)
C3—H3	0.9300	N15—O15	1.274 (4)
C4—C4A	1.398 (6)	C22—O22	1.200 (5)
C4—H4	0.9300	C22—N23	1.372 (5)
C4A—C5	1.415 (6)	C22—N21	1.378 (5)
C5—C6	1.347 (7)	C24—O24	1.222 (5)
C5—H5	0.9300	C24—N23	1.372 (5)
C6—C6A	1.433 (7)	C24—C25	1.465 (6)
C6—H6	0.9300	C25—N25	1.284 (5)
C6A—C7	1.391 (6)	C25—C26	1.485 (6)
C6A—C10A	1.400 (6)	C26—O26	1.222 (5)
C7—C8	1.366 (7)	C26—N21	1.372 (5)
C7—H7	0.9300	N1—H1	0.876 (19)
C8—C9	1.413 (7)	N21—H21	0.873 (19)
C8—H8	0.9300	N23—H23	0.879 (19)
C9—N10	1.314 (6)	N25—O25	1.345 (4)
C9—H9	0.9300	O1—H1A	0.803 (19)
C10A—N10	1.355 (6)	O1—H1B	0.850 (19)
C12—O12	1.217 (4)	O2—H2A	0.837 (19)
C12—N13	1.367 (5)	O2—H2B	0.858 (19)
C12—N11	1.367 (5)	O3—H3A	0.841 (19)
C14—O14	1.232 (5)	O3—H3B	0.813 (19)
C14—N13	1.377 (5)	O25—H25	0.8200
N1—C1A—C4A	119.2 (4)	N13—C14—C15	115.7 (4)
N1—C1A—C10A	119.2 (4)	N15—C15—C16	125.5 (4)

C4A—C1A—C10A	121.6 (4)	N15—C15—C14	114.1 (4)
N1—C2—C3	120.0 (4)	C16—C15—C14	120.4 (3)
N1—C2—H2	120.0	O16—C16—N11	118.4 (4)
C3—C2—H2	120.0	O16—C16—C15	126.0 (4)
C4—C3—C2	119.0 (4)	N11—C16—C15	115.5 (4)
C4—C3—H3	120.5	C12—N11—C16	125.9 (3)
C2—C3—H3	120.5	C12—N11—H11	119 (3)
C3—C4—C4A	121.9 (4)	C16—N11—H11	115 (3)
C3—C4—H4	119.1	C12—N13—C14	126.4 (4)
C4A—C4—H4	119.1	C12—N13—H13	113 (3)
C4—C4A—C1A	117.1 (4)	C14—N13—H13	120 (3)
C4—C4A—C5	125.1 (4)	O15—N15—C15	119.1 (3)
C1A—C4A—C5	117.8 (4)	O22—C22—N23	122.1 (4)
C6—C5—C4A	121.7 (5)	O22—C22—N21	122.1 (4)
C6—C5—H5	119.2	N23—C22—N21	115.7 (4)
C4A—C5—H5	119.2	O24—C24—N23	120.9 (4)
C5—C6—C6A	121.4 (5)	O24—C24—C25	123.7 (4)
C5—C6—H6	119.3	N23—C24—C25	115.4 (4)
C6A—C6—H6	119.3	N25—C25—C24	112.4 (4)
C7—C6A—C10A	117.9 (5)	N25—C25—C26	127.3 (4)
C7—C6A—C6	122.8 (5)	C24—C25—C26	120.3 (4)
C10A—C6A—C6	119.4 (4)	O26—C26—N21	120.8 (4)
C8—C7—C6A	118.5 (5)	O26—C26—C25	124.9 (4)
C8—C7—H7	120.8	N21—C26—C25	114.4 (4)
C6A—C7—H7	120.8	C2—N1—C1A	122.8 (4)
C7—C8—C9	119.5 (5)	C2—N1—H1	116 (3)
C7—C8—H8	120.2	C1A—N1—H1	121 (3)
C9—C8—H8	120.2	C9—N10—C10A	116.4 (4)
N10—C9—C8	123.6 (5)	C26—N21—C22	127.2 (4)
N10—C9—H9	118.2	C26—N21—H21	119 (3)
C8—C9—H9	118.2	C22—N21—H21	113 (3)
N10—C10A—C6A	124.2 (4)	C22—N23—C24	126.7 (4)
N10—C10A—C1A	117.7 (4)	C22—N23—H23	121 (3)
C6A—C10A—C1A	118.2 (4)	C24—N23—H23	112 (3)
O12—C12—N13	122.5 (4)	C25—N25—O25	117.4 (4)
O12—C12—N11	121.8 (4)	H1A—O1—H1B	112 (4)
N13—C12—N11	115.7 (3)	H2A—O2—H2B	105 (4)
O14—C14—N13	117.9 (4)	H3A—O3—H3B	112 (5)
O14—C14—C15	126.3 (4)	N25—O25—H25	109.5
N1—C2—C3—C4	0.1 (7)	N13—C12—N11—C16	5.8 (6)
C2—C3—C4—C4A	1.0 (7)	O16—C16—N11—C12	174.6 (4)
C3—C4—C4A—C1A	−1.8 (7)	C15—C16—N11—C12	−7.6 (6)
C3—C4—C4A—C5	178.1 (5)	O12—C12—N13—C14	−179.7 (4)
N1—C1A—C4A—C4	1.5 (6)	N11—C12—N13—C14	−0.7 (7)
C10A—C1A—C4A—C4	−179.7 (4)	O14—C14—N13—C12	177.2 (4)
N1—C1A—C4A—C5	−178.4 (4)	C15—C14—N13—C12	−1.8 (6)
C10A—C1A—C4A—C5	0.3 (7)	C16—C15—N15—O15	−0.4 (7)

C4—C4A—C5—C6	180.0 (5)	C14—C15—N15—O15	178.7 (4)
C1A—C4A—C5—C6	−0.1 (7)	O24—C24—C25—N25	−7.2 (6)
C4A—C5—C6—C6A	−0.5 (8)	N23—C24—C25—N25	174.0 (4)
C5—C6—C6A—C7	−178.4 (5)	O24—C24—C25—C26	172.8 (4)
C5—C6—C6A—C10A	0.8 (7)	N23—C24—C25—C26	−6.0 (6)
C10A—C6A—C7—C8	1.7 (7)	N25—C25—C26—O26	7.6 (8)
C6—C6A—C7—C8	−179.0 (5)	C24—C25—C26—O26	−172.4 (4)
C6A—C7—C8—C9	−1.2 (8)	N25—C25—C26—N21	−173.4 (4)
C7—C8—C9—N10	0.3 (8)	C24—C25—C26—N21	6.6 (6)
C7—C6A—C10A—N10	−1.3 (7)	C3—C2—N1—C1A	−0.4 (7)
C6—C6A—C10A—N10	179.4 (5)	C4A—C1A—N1—C2	−0.4 (6)
C7—C6A—C10A—C1A	178.7 (4)	C10A—C1A—N1—C2	−179.2 (4)
C6—C6A—C10A—C1A	−0.6 (6)	C8—C9—N10—C10A	0.1 (7)
N1—C1A—C10A—N10	−1.2 (6)	C6A—C10A—N10—C9	0.4 (7)
C4A—C1A—C10A—N10	−179.9 (4)	C1A—C10A—N10—C9	−179.6 (4)
N1—C1A—C10A—C6A	178.8 (4)	O26—C26—N21—C22	176.0 (4)
C4A—C1A—C10A—C6A	0.0 (6)	C25—C26—N21—C22	−3.0 (7)
O14—C14—C15—N15	1.7 (7)	O22—C22—N21—C26	180.0 (5)
N13—C14—C15—N15	−179.4 (4)	N23—C22—N21—C26	−1.2 (7)
O14—C14—C15—C16	−179.1 (4)	O22—C22—N23—C24	−179.2 (4)
N13—C14—C15—C16	−0.3 (6)	N21—C22—N23—C24	2.0 (7)
N15—C15—C16—O16	1.1 (7)	O24—C24—N23—C22	−177.3 (4)
C14—C15—C16—O16	−177.9 (4)	C25—C24—N23—C22	1.6 (6)
N15—C15—C16—N11	−176.5 (4)	C24—C25—N25—O25	−177.9 (4)
C14—C15—C16—N11	4.5 (6)	C26—C25—N25—O25	2.1 (7)
O12—C12—N11—C16	−175.2 (4)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1	0.88 (2)	1.89 (2)	2.730 (5)	161 (4)
N11—H11⋯O14[i]	0.88 (2)	2.12 (2)	2.997 (4)	173 (4)
N13—H13⋯O16[ii]	0.85 (2)	1.98 (2)	2.835 (4)	177 (4)
N21—H21⋯O24[iii]	0.87 (2)	1.99 (2)	2.858 (4)	172 (4)
N23—H23⋯O26[iv]	0.88 (2)	2.03 (2)	2.900 (4)	173 (4)
O1—H1*A*⋯O4	0.80 (2)	2.05 (3)	2.809 (5)	157 (5)
O1—H1*B*⋯O15[v]	0.85 (2)	1.87 (2)	2.719 (4)	177 (5)
O2—H2*A*⋯O12[i]	0.84 (2)	2.02 (3)	2.825 (4)	160 (5)
O2—H2*B*⋯O15	0.86 (2)	2.08 (3)	2.811 (5)	143 (4)
O2—H2*B*⋯O16	0.86 (2)	2.15 (4)	2.832 (4)	136 (4)
O3—H3*A*⋯N25	0.84 (2)	2.32 (4)	3.007 (5)	139 (5)
O3—H3*A*⋯O24	0.84 (2)	2.33 (4)	3.006 (5)	137 (5)
O3—H3*B*⋯O1	0.81 (2)	2.04 (4)	2.784 (6)	153 (6)
O25—H25⋯O5	0.82	1.92	2.692 (5)	156
O4⋯O2			2.694 (5)	
O4⋯O5[vi]			2.816 (6)	
O4⋯O4[v]			2.844 (7)	

O5···O5[vi]	2.837 (8)
O5···O3	2.850 (6)

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