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# *N*,*N*′,*N*″-Tris(2-nitrobenzyl)-2,2′,2″-nitrilotriethanaminium trichloride 1.41-hydrate

**Perla Elizondo,* Sylvain Bernès, Blanca Nájera and Francisco Góngora**

DEP Facultad de Ciencias Químicas, UANL, Guerrero y Progreso S/N, Col. Treviño, 64570 Monterrey, NL, Mexico
Correspondence e-mail: sylvain_bernes@Hotmail.com

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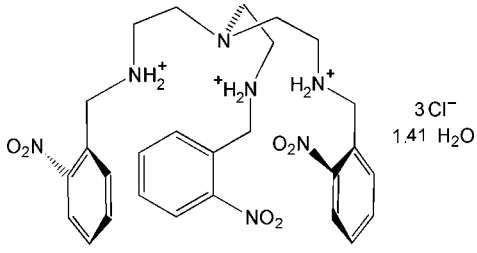
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.006 Å; disorder in solvent or counterion; $R$ factor = 0.056; $wR$ factor = 0.175; data-to-parameter ratio = 15.3.

The title compound, $C_{27}H_{36}N_7O_6^{3+}\cdot 3Cl^-\cdot 1.41H_2O$, is the hydrochloride of a tripodal amine, and was structurally characterized because the free base, used as a ligand in podate complexes, is an oily material. In the cation, the secondary amine groups are protonated, and, despite the induced Coulombic repulsions, a claw-like conformation is stabilized, with a cavity approximating $C_3$ point symmetry. Such a topology, with the lone pair of the tertiary N atom placed inside the cavity, allows the encapsulation of guest species. Indeed, three chloride counter-ions balance the charges, one of which is located inside the cation cavity and is strongly bonded to the $NH_2^+$ groups. The asymmetric unit is completed by two water molecules with occupancies 0.793 (11) and 0.621 (9). The crystal structure is formed by a complex network of efficient N—H···Cl and O—H···Cl hydrogen bonds. One nitro group also forms weak contacts with a water molecule.

## Related literature

For related tripodal amine structures, see: Hossain *et al.* (2004); Coyle *et al.* (2006); McKee *et al.* (2006); Lakshminarayanan *et al.* (2007); For the role of electron-withdrawing groups in these molecules, see: Bryantsev & Hay (2005).




## Experimental

### Crystal data

$C_{27}H_{36}N_7O_6^{3+}\cdot 3Cl^-\cdot 1.41H_2O$
$M_r$ = 686.47
Monoclinic, $P2_1/n$
$a$ = 9.131 (2) Å
$b$ = 13.009 (4) Å
$c$ = 28.071 (7) Å
$\beta$ = 94.190 (9)°
$V$ = 3326 (2) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.33 mm$^{-1}$
$T$ = 298 K
0.50 × 0.42 × 0.24 mm

### Data collection

Siemens P4 diffractometer
Absorption correction: $\psi$ scan (*XSCANS*; Siemens, 1996)
$T_{min}$ = 0.819, $T_{max}$ = 0.924
16115 measured reflections
6712 independent reflections
4181 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.042
3 standard reflections
every 97 reflections
intensity decay: 3.5%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.175
$S$ = 1.03
6712 reflections
438 parameters
12 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.34 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.34 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2*D*···Cl1 | 0.906 (10) | 2.255 (11) | 3.155 (2) | 172 (3) |
| N12—H12*D*···Cl1 | 0.902 (10) | 2.396 (19) | 3.225 (3) | 153 (3) |
| N22—H22*D*···Cl1 | 0.900 (10) | 2.279 (11) | 3.176 (3) | 174 (3) |
| N12—H12*C*···Cl3 | 0.897 (10) | 2.161 (11) | 3.054 (3) | 174 (3) |
| N22—H22*C*···Cl2 | 0.899 (10) | 2.335 (14) | 3.209 (3) | 164 (3) |
| O8—H81···Cl1 | 0.850 (10) | 2.35 (5) | 3.115 (5) | 150 (9) |
| O8—H82···Cl2 | 0.850 (10) | 2.46 (4) | 3.265 (5) | 159 (10) |
| O7—H72···Cl3 | 0.851 (10) | 2.28 (3) | 3.102 (6) | 163 (9) |
| N2—H2*C*···Cl2$^{i}$ | 0.897 (10) | 2.221 (14) | 3.089 (3) | 163 (3) |
| O7—H71···O6$^{ii}$ | 0.851 (10) | 2.45 (8) | 2.965 (7) | 119 (8) |

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

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2103).

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# supporting information

*Acta Cryst.* (2009). E**65**, o1616–o1617 [doi:10.1107/S1600536809022399]

## *N*,*N*′,*N*′′-Tris(2-nitrobenzyl)-2,2′,2′′-nitrilotriethanaminium trichloride 1.41-hydrate

**Perla Elizondo, Sylvain Bernès, Blanca Nájera and Francisco Góngora**

### S1. Comment

Tris(2-aminoethyl)amine (*tren*) derivatives are common starting materials for the synthesis of tripodal ligands used as podants in coordination chemistry (Coyle *et al.*, 2006). They are also used as anions receptors aiming at the design of molecules acting as selective anion bindig sites (Hossain *et al.*, 2004). On the other hand, for *tren*-based molecules bearing an aryl group, it has been shown that substitution of aryl with electron withdrawing groups enhances the stability of anions complexes (Bryantsev & Hay, 2005). Following this idea, we prepared tris[(2-nitrobenzylamino)ethyl]amine by reduction of the corresponding Schiff base, tris[(2-nitrobenzylideneamino)ethyl]amine, which had been previously characterized by X-ray diffraction (McKee *et al.*, 2006). However, as the free base is an oil, we transformed the amine into its hydrochloride salt, (I), and now report its X-ray structure.

The asymmetric unit (Fig. 1) contains one cation and three chloride ions balancing the charges, as expected. Two sites are occupied by water molecules, for which occupancies converged to 0.79 (11) and 0.621 (9). All atoms are placed in general positions. The presence of lattice water molecules is confirmed by IR spectroscopy, as well as by the consistent network of hydrogen bonds involving all H atoms of water molecules. The three secondary amine groups of the *tren* derivative are protonated, generating strong Coulombic repulsions within the cation. However, a claw-like conformation is stabilized, since a $Cl^-$ ion is placed inside the cavity and forms three strong hydrogen bonds with all $NH_2^+$ groups. Such a behaviour is not systematically observed with closely related cations. For example, tris(2-benzylammonioethyl)amine cation has been crystallized with bromide or phosphate, and X-ray studies revealed that in both cases cations approximate a trigonal planar shape (Hossain *et al.*, 2004). In the same way, the free Schiff base used as starting material for (I) is a planar molecule with crystallographic $C_3$ symmetry (space group $R\bar{3}$, McKee *et al.*, 2006). In contrast, the same cation including pentafluorobenzyl groups in place of benzyl encapsulates $Cl^-$ or $Br^-$ ions (Lakshminarayanan *et al.*, 2007), as (I) does.

The supramolecular network formed by cations, anions, and water molecules in (I) is a complex arrangement of N—H···Cl and O—H···Cl hydrogen bonds. The most important, as commented above, are the $NH_2^+$···Cl1 strong hydrogen bonds allowing the anion encapsulation in the cationic cavity. Chloride ions placed outside this cavity are also connected to $NH_2^+$ functional groups *via* hydrogen bonds, one of which being intermolecular. In the asymmetric unit, water molecules also serve as donor for O—H···Cl hydrogen bonds (Fig. 2). One nitro group also forms weak intermolecular contacts with the water molecule O7.

### S2. Experimental

Tris[(2-nitrobenzylideneamino)ethyl]amine (12.461 g, 27 mmol) was dispersed in methanol (40 ml). To achieve selective reduction, an amount of $NaBH_4$ (3.643 g, 96 mmol) was added in small portions at 298 K under stirring. After reduction was completed, solvent was removed and then the reduction product, tris[(2-nitrobenzylamino)ethyl]amine, was

extracted with $CHCl_3$ (2 × 10 ml) and water (20 ml). The organic phase was dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the free base as a pale yellow oil (yield: 91%). This compound was dissolved in ethanol and HCl was added until the title white salt [m.p. 503.5–504.5 K (dec.)] had completely precipitated. Suitable single crystals were obtained by evaporation of an ethanol-water (19:1) mixture.

### S3. Refinement

From the IR spectrum of the single-crystal used for X-ray diffraction, it was assumed that an amount of water was present in the sample. Sites for disordered water molecules and chloride ions were inferred from H atoms positions, found in a difference map. Occupancies for water molecules were refined, and converged to 0.79 (1) and 0.621 (9) for O7 and O8. Some O atoms belonging to nitro groups display high displacement parameters, but attempts to resolve disordered sites were unsuccessful. N–bonded H atoms were found in a difference map, confirming the charge of the cation to be +3. All O– and N–bonded H atoms were refined freely, although the geometry was restrained to suitable target values: O—H = 0.85 (1) Å, H···H = 1.34 (2) Å, and N—H = 0.90 (1) Å. Other H atoms were placed in idealized positions and refined as riding to their parent atoms, with bond lengths fixed to 0.97 (methylene) or 0.93 Å (aromatic). Isotropic displacement parameters for H atoms were calculated as $U_{iso}$(H) = 1.5 $U_{eq}$(carrier atom) for water molecules and $U_{iso}$(H) = 1.2 $U_{eq}$(carrier atom) otherwise.

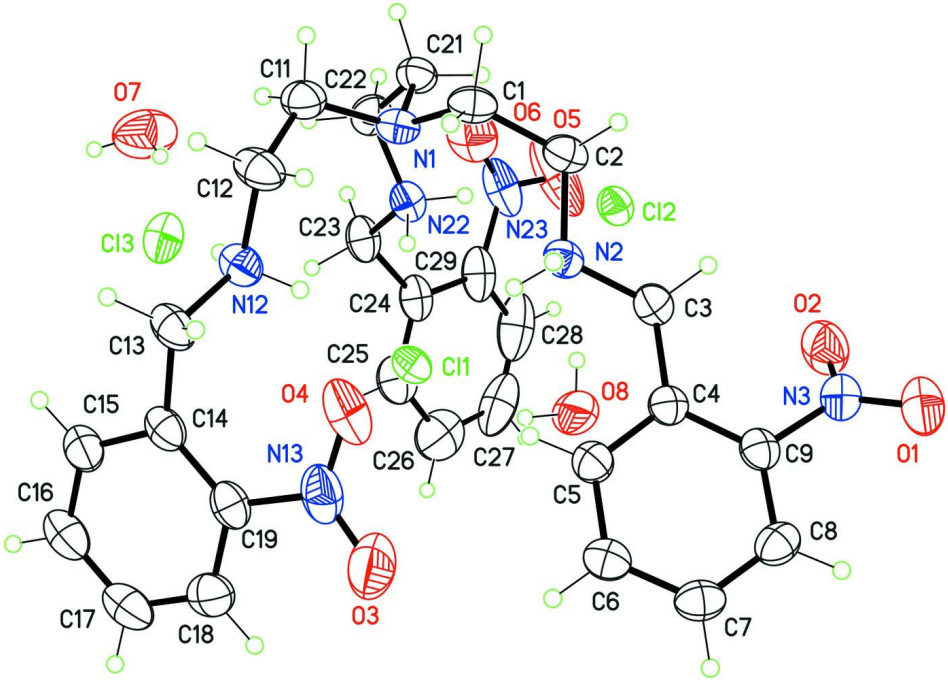


**Figure 1**

The asymmetric unit of (I). Displacement ellipsoids are shown at the 25% probability level.

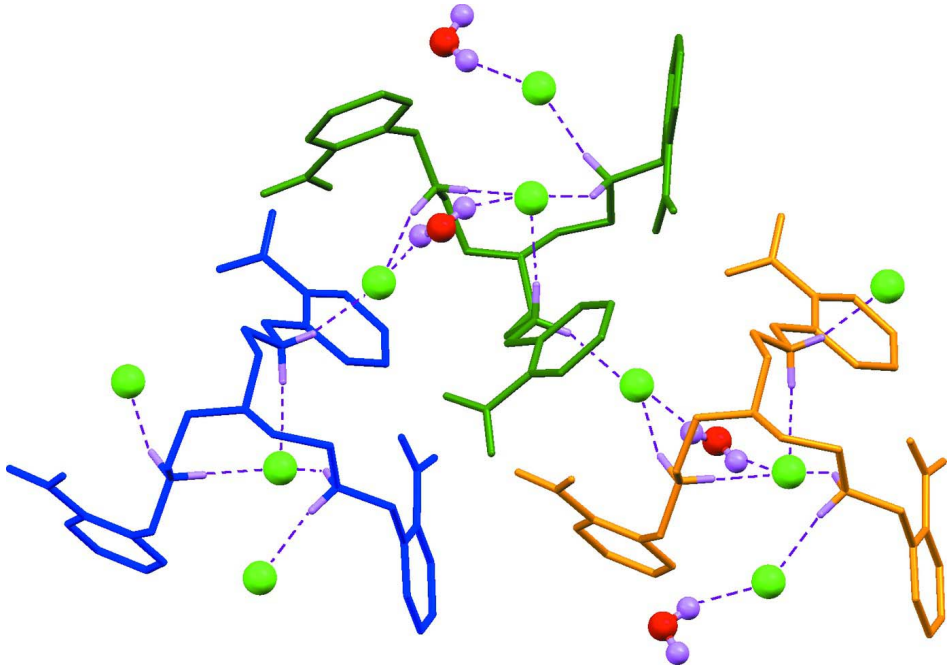

**Figure 2**

A part of the crystal structure of (I). Three symmetry-related cations are represented, omitting H atoms not involved in the supramolecular network. Hydrogen bonds are represented by dashed lines, and weak contacts involving nitro groups have been omitted for clarity. Symmetry codes for cations: green *x*, *y*, *z*; gold 3/2 - *x*, 1/2 + *y*, 1/2 - *z*; blue 3/2 - *x*, -1/2 + *y*, 1/2 - *z*.

### *N,N′,N″*-Tris(2-nitrobenzyl)-2,2′,2″- nitrilotriethanaminium trichloride 1.41-hydrate

*Crystal data*

$C_{27}H_{36}N_7O_6^{3+}\cdot 3Cl^-\cdot 1.41H_2O$
$M_r = 686.47$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 9.131\ (2)$ Å
$b = 13.009\ (4)$ Å
$c = 28.071\ (7)$ Å
$\beta = 94.190\ (9)°$
$V = 3326\ (2)$ Å$^3$
$Z = 4$
$F(000) = 1441$
$D_x = 1.371$ Mg m$^{-3}$
Melting point: 503.5–504.5 (dec.) K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 69 reflections
$\theta = 4.6–12.5°$
$\mu = 0.33$ mm$^{-1}$
$T = 298$ K
Block, colorless
0.50 × 0.42 × 0.24 mm

*Data collection*

Siemens P4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$2\theta/\omega$ scans
Absorption correction: $\psi$ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.819$, $T_{max} = 0.924$
16115 measured reflections
6712 independent reflections
4181 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 26.3°$, $\theta_{min} = 2.1°$
$h = -11\rightarrow 10$
$k = -16\rightarrow 1$
$l = -34\rightarrow 34$
3 standard reflections every 97 reflections
intensity decay: 3.5%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.175$
$S = 1.03$
6712 reflections
438 parameters
12 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 1.5076P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ e Å$^{-3}$

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| N1 | 0.9829 (3) | 0.79136 (19) | 0.17125 (9) | 0.0624 (6) | |
| C1 | 0.9926 (4) | 0.8169 (3) | 0.22199 (11) | 0.0701 (8) | |
| H1A | 0.9977 | 0.8911 | 0.2253 | 0.084* | |
| H1B | 1.0831 | 0.7887 | 0.2368 | 0.084* | |
| C2 | 0.8671 (4) | 0.7782 (3) | 0.24840 (11) | 0.0690 (8) | |
| H2A | 0.8467 | 0.7074 | 0.2393 | 0.083* | |
| H2B | 0.8945 | 0.7797 | 0.2824 | 0.083* | |
| N2 | 0.7313 (3) | 0.8412 (2) | 0.23819 (8) | 0.0586 (6) | |
| H2C | 0.758 (3) | 0.9045 (12) | 0.2481 (11) | 0.070* | |
| H2D | 0.706 (3) | 0.844 (2) | 0.2064 (4) | 0.070* | |
| C3 | 0.6071 (4) | 0.7981 (2) | 0.26312 (11) | 0.0668 (8) | |
| H3A | 0.6416 | 0.7807 | 0.2956 | 0.080* | |
| H3B | 0.5740 | 0.7352 | 0.2472 | 0.080* | |
| C4 | 0.4792 (3) | 0.8706 (2) | 0.26437 (10) | 0.0588 (7) | |
| C5 | 0.4586 (4) | 0.9520 (2) | 0.23318 (11) | 0.0682 (8) | |
| H5A | 0.5256 | 0.9624 | 0.2102 | 0.082* | |
| C6 | 0.3408 (4) | 1.0185 (3) | 0.23509 (13) | 0.0733 (9) | |
| H6A | 0.3284 | 1.0714 | 0.2129 | 0.088* | |
| C7 | 0.2432 (4) | 1.0077 (3) | 0.26895 (13) | 0.0736 (9) | |
| H7A | 0.1651 | 1.0533 | 0.2702 | 0.088* | |
| C8 | 0.2608 (4) | 0.9293 (3) | 0.30119 (12) | 0.0725 (9) | |
| H8A | 0.1957 | 0.9216 | 0.3249 | 0.087* | |
| C9 | 0.3756 (4) | 0.8620 (2) | 0.29820 (10) | 0.0623 (8) | |
| N3 | 0.3838 (4) | 0.7755 (3) | 0.33158 (12) | 0.0856 (9) | |
| O1 | 0.3524 (4) | 0.7895 (3) | 0.37214 (12) | 0.1437 (14) | |
| O2 | 0.4250 (4) | 0.6941 (2) | 0.31824 (11) | 0.1107 (10) | |
| C11 | 1.0831 (4) | 0.8554 (3) | 0.14559 (14) | 0.0763 (9) | |
| H11A | 1.0975 | 0.8234 | 0.1151 | 0.092* | |
| H11B | 1.1777 | 0.8573 | 0.1637 | 0.092* | |
| C12 | 1.0314 (4) | 0.9638 (3) | 0.13682 (15) | 0.0869 (11) | |
| H12A | 1.0114 | 0.9950 | 0.1670 | 0.104* | |
| H12B | 1.1091 | 1.0030 | 0.1235 | 0.104* | |
| N12 | 0.8964 (3) | 0.9694 (2) | 0.10352 (11) | 0.0709 (7) | |

| | | | | | |
|---|---|---|---|---|---|
| H12C | 0.907 (4) | 0.923 (2) | 0.0803 (9) | 0.085* | |
| H12D | 0.825 (3) | 0.943 (3) | 0.1206 (11) | 0.085* | |
| C13 | 0.8715 (4) | 1.0771 (3) | 0.08618 (13) | 0.0800 (10) | |
| H13A | 0.9484 | 1.0955 | 0.0657 | 0.096* | |
| H13B | 0.8785 | 1.1233 | 0.1134 | 0.096* | |
| C14 | 0.7249 (4) | 1.0919 (2) | 0.05908 (11) | 0.0671 (8) | |
| C15 | 0.7256 (4) | 1.0997 (3) | 0.01013 (12) | 0.0784 (10) | |
| H15A | 0.8139 | 1.0911 | −0.0039 | 0.094* | |
| C16 | 0.6024 (6) | 1.1193 (3) | −0.01819 (15) | 0.0926 (12) | |
| H16A | 0.6072 | 1.1236 | −0.0511 | 0.111* | |
| C17 | 0.4729 (5) | 1.1328 (3) | 0.00097 (16) | 0.0919 (12) | |
| H17A | 0.3891 | 1.1470 | −0.0188 | 0.110* | |
| C18 | 0.4635 (4) | 1.1258 (3) | 0.04915 (17) | 0.0858 (11) | |
| H18A | 0.3737 | 1.1342 | 0.0623 | 0.103* | |
| C19 | 0.5905 (4) | 1.1060 (2) | 0.07840 (12) | 0.0712 (9) | |
| N13 | 0.5780 (6) | 1.1031 (2) | 0.12976 (14) | 0.0969 (11) | |
| O3 | 0.4647 (6) | 1.1270 (4) | 0.14496 (16) | 0.1638 (18) | |
| O4 | 0.6834 (5) | 1.0783 (2) | 0.15623 (10) | 0.1092 (10) | |
| C21 | 1.0212 (4) | 0.6829 (2) | 0.16548 (11) | 0.0679 (8) | |
| H21A | 0.9807 | 0.6430 | 0.1906 | 0.081* | |
| H21B | 1.1272 | 0.6756 | 0.1689 | 0.081* | |
| C22 | 0.9657 (4) | 0.6407 (3) | 0.11834 (13) | 0.0758 (9) | |
| H22A | 0.9985 | 0.6840 | 0.0931 | 0.091* | |
| H22B | 1.0057 | 0.5724 | 0.1144 | 0.091* | |
| N22 | 0.8036 (3) | 0.63543 (19) | 0.11434 (9) | 0.0648 (7) | |
| H22C | 0.774 (4) | 0.596 (2) | 0.1381 (9) | 0.078* | |
| H22D | 0.756 (3) | 0.6949 (15) | 0.1190 (12) | 0.078* | |
| C23 | 0.7439 (4) | 0.5962 (3) | 0.06626 (11) | 0.0769 (10) | |
| H23A | 0.7383 | 0.6529 | 0.0437 | 0.092* | |
| H23B | 0.8114 | 0.5457 | 0.0549 | 0.092* | |
| C24 | 0.5961 (5) | 0.5488 (3) | 0.06750 (11) | 0.0737 (9) | |
| C25 | 0.4793 (6) | 0.6015 (4) | 0.04688 (14) | 0.0959 (12) | |
| H25A | 0.4936 | 0.6668 | 0.0345 | 0.115* | |
| C26 | 0.3370 (7) | 0.5587 (6) | 0.04397 (18) | 0.1311 (19) | |
| H26A | 0.2571 | 0.5950 | 0.0301 | 0.157* | |
| C27 | 0.3195 (8) | 0.4606 (7) | 0.0625 (2) | 0.138 (3) | |
| H27A | 0.2270 | 0.4303 | 0.0608 | 0.166* | |
| C28 | 0.4359 (10) | 0.4094 (5) | 0.0827 (2) | 0.140 (3) | |
| H28A | 0.4229 | 0.3436 | 0.0946 | 0.168* | |
| C29 | 0.5702 (6) | 0.4512 (3) | 0.08602 (12) | 0.0939 (13) | |
| N23 | 0.6930 (7) | 0.3884 (2) | 0.10924 (12) | 0.1083 (15) | |
| O5 | 0.6572 (7) | 0.3081 (3) | 0.12602 (13) | 0.205 (3) | |
| O6 | 0.8142 (6) | 0.4235 (3) | 0.11446 (16) | 0.1383 (14) | |
| Cl1 | 0.61515 (8) | 0.83642 (6) | 0.12955 (2) | 0.0618 (2) | |
| Cl2 | 0.66871 (10) | 0.53719 (6) | 0.20643 (3) | 0.0696 (2) | |
| Cl3 | 0.91772 (12) | 0.82403 (9) | 0.01891 (4) | 0.0971 (3) | |
| O7 | 1.0384 (7) | 0.6272 (5) | −0.0268 (2) | 0.166 (3) | 0.793 (11) |
| H71 | 1.046 (14) | 0.658 (7) | −0.0533 (19) | 0.249* | 0.793 (11) |

| | | | | | |
|---|---|---|---|---|---|
| H72 | 1.006 (12) | 0.673 (5) | −0.009 (3) | 0.249* | 0.793 (11) |
| O8 | 0.3919 (5) | 0.6773 (5) | 0.1646 (2) | 0.121 (3) | 0.621 (9) |
| H81 | 0.426 (9) | 0.723 (5) | 0.147 (3) | 0.182* | 0.621 (9) |
| H82 | 0.461 (7) | 0.633 (6) | 0.168 (4) | 0.182* | 0.621 (9) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0575 (14) | 0.0559 (14) | 0.0721 (15) | 0.0051 (12) | −0.0083 (12) | −0.0021 (12) |
| C1 | 0.0607 (19) | 0.0697 (19) | 0.077 (2) | 0.0053 (16) | −0.0152 (16) | −0.0118 (16) |
| C2 | 0.070 (2) | 0.071 (2) | 0.0636 (18) | 0.0112 (17) | −0.0087 (15) | −0.0050 (15) |
| N2 | 0.0642 (15) | 0.0621 (14) | 0.0480 (12) | 0.0035 (12) | −0.0052 (11) | −0.0073 (11) |
| C3 | 0.076 (2) | 0.0637 (18) | 0.0605 (17) | 0.0026 (16) | 0.0023 (15) | 0.0007 (14) |
| C4 | 0.0616 (18) | 0.0628 (17) | 0.0509 (15) | −0.0004 (14) | −0.0026 (13) | −0.0095 (13) |
| C5 | 0.072 (2) | 0.0675 (19) | 0.0659 (18) | 0.0044 (17) | 0.0064 (15) | 0.0024 (15) |
| C6 | 0.073 (2) | 0.0644 (19) | 0.081 (2) | 0.0048 (17) | −0.0035 (18) | 0.0015 (16) |
| C7 | 0.0618 (19) | 0.073 (2) | 0.084 (2) | 0.0042 (17) | −0.0072 (18) | −0.0149 (18) |
| C8 | 0.0571 (19) | 0.088 (2) | 0.073 (2) | −0.0054 (18) | 0.0035 (15) | −0.0145 (18) |
| C9 | 0.0652 (19) | 0.0674 (18) | 0.0530 (16) | −0.0069 (16) | −0.0055 (14) | −0.0046 (14) |
| N3 | 0.087 (2) | 0.096 (2) | 0.075 (2) | 0.0044 (19) | 0.0149 (16) | 0.0109 (18) |
| O1 | 0.163 (3) | 0.182 (4) | 0.091 (2) | 0.048 (3) | 0.042 (2) | 0.042 (2) |
| O2 | 0.139 (3) | 0.0850 (19) | 0.109 (2) | 0.0062 (19) | 0.0188 (19) | 0.0254 (17) |
| C11 | 0.060 (2) | 0.075 (2) | 0.092 (2) | −0.0038 (17) | −0.0063 (17) | 0.0100 (18) |
| C12 | 0.078 (2) | 0.072 (2) | 0.105 (3) | −0.0145 (18) | −0.030 (2) | 0.0173 (19) |
| N12 | 0.0734 (18) | 0.0586 (16) | 0.0781 (19) | −0.0116 (14) | −0.0118 (15) | 0.0082 (13) |
| C13 | 0.085 (2) | 0.066 (2) | 0.084 (2) | −0.0186 (18) | −0.0207 (18) | 0.0212 (17) |
| C14 | 0.077 (2) | 0.0526 (17) | 0.0688 (19) | −0.0149 (16) | −0.0133 (16) | 0.0096 (14) |
| C15 | 0.087 (2) | 0.076 (2) | 0.071 (2) | −0.0080 (19) | −0.0006 (18) | 0.0149 (17) |
| C16 | 0.115 (4) | 0.082 (3) | 0.077 (2) | −0.007 (2) | −0.020 (2) | 0.0171 (19) |
| C17 | 0.099 (3) | 0.070 (2) | 0.101 (3) | −0.009 (2) | −0.035 (3) | 0.016 (2) |
| C18 | 0.078 (2) | 0.0571 (19) | 0.123 (3) | −0.0040 (18) | 0.007 (2) | 0.013 (2) |
| C19 | 0.095 (3) | 0.0479 (16) | 0.0705 (19) | −0.0080 (16) | 0.0032 (18) | 0.0081 (14) |
| N13 | 0.143 (4) | 0.0622 (18) | 0.088 (2) | −0.004 (2) | 0.030 (3) | 0.0144 (17) |
| O3 | 0.183 (4) | 0.170 (4) | 0.150 (3) | 0.037 (3) | 0.090 (3) | 0.048 (3) |
| O4 | 0.182 (3) | 0.0783 (18) | 0.0662 (16) | −0.005 (2) | −0.0007 (18) | 0.0081 (13) |
| C21 | 0.0662 (19) | 0.0653 (19) | 0.0718 (19) | 0.0132 (16) | 0.0023 (15) | 0.0041 (15) |
| C22 | 0.080 (2) | 0.067 (2) | 0.082 (2) | 0.0100 (17) | 0.0165 (18) | −0.0071 (17) |
| N22 | 0.088 (2) | 0.0529 (14) | 0.0541 (14) | 0.0044 (13) | 0.0074 (13) | −0.0057 (11) |
| C23 | 0.110 (3) | 0.066 (2) | 0.0553 (17) | −0.0139 (19) | 0.0089 (17) | −0.0046 (15) |
| C24 | 0.110 (3) | 0.0599 (18) | 0.0524 (17) | −0.0175 (19) | 0.0113 (18) | −0.0092 (14) |
| C25 | 0.123 (4) | 0.096 (3) | 0.068 (2) | −0.014 (3) | 0.001 (2) | −0.013 (2) |
| C26 | 0.125 (5) | 0.181 (6) | 0.086 (3) | −0.011 (4) | −0.003 (3) | −0.042 (4) |
| C27 | 0.138 (5) | 0.185 (7) | 0.098 (4) | −0.088 (5) | 0.044 (4) | −0.053 (4) |
| C28 | 0.207 (7) | 0.133 (5) | 0.087 (3) | −0.087 (5) | 0.055 (4) | −0.043 (3) |
| C29 | 0.152 (4) | 0.077 (2) | 0.0545 (19) | −0.039 (3) | 0.022 (2) | −0.0207 (18) |
| N23 | 0.213 (5) | 0.0461 (18) | 0.0650 (18) | −0.013 (3) | 0.006 (3) | −0.0040 (14) |
| O5 | 0.416 (8) | 0.075 (2) | 0.113 (3) | −0.073 (3) | −0.056 (4) | 0.0271 (19) |
| O6 | 0.187 (4) | 0.079 (2) | 0.151 (3) | 0.034 (3) | 0.029 (3) | 0.007 (2) |

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|---|---|---|---|---|---|---|
| Cl1 | 0.0686 (5) | 0.0594 (4) | 0.0555 (4) | 0.0021 (4) | −0.0085 (3) | 0.0005 (3) |
| Cl2 | 0.0815 (5) | 0.0606 (4) | 0.0665 (5) | 0.0027 (4) | 0.0050 (4) | 0.0078 (3) |
| Cl3 | 0.1002 (7) | 0.1081 (8) | 0.0858 (6) | −0.0133 (6) | 0.0264 (5) | 0.0007 (5) |
| O7 | 0.139 (5) | 0.212 (6) | 0.145 (5) | 0.047 (4) | 0.003 (4) | −0.046 (4) |
| O8 | 0.077 (3) | 0.125 (5) | 0.163 (5) | −0.006 (3) | 0.025 (3) | 0.052 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C1 | 1.459 (4) | C14—C19 | 1.389 (5) |
| N1—C11 | 1.465 (4) | C15—C16 | 1.354 (5) |
| N1—C21 | 1.466 (4) | C15—H15A | 0.9300 |
| C1—C2 | 1.497 (5) | C16—C17 | 1.346 (6) |
| C1—H1A | 0.9700 | C16—H16A | 0.9300 |
| C1—H1B | 0.9700 | C17—C18 | 1.364 (6) |
| C2—N2 | 1.497 (4) | C17—H17A | 0.9300 |
| C2—H2A | 0.9700 | C18—C19 | 1.396 (5) |
| C2—H2B | 0.9700 | C18—H18A | 0.9300 |
| N2—C3 | 1.485 (4) | C19—N13 | 1.455 (5) |
| N2—H2C | 0.897 (10) | N13—O3 | 1.190 (5) |
| N2—H2D | 0.906 (10) | N13—O4 | 1.216 (5) |
| C3—C4 | 1.504 (4) | C21—C22 | 1.487 (5) |
| C3—H3A | 0.9700 | C21—H21A | 0.9700 |
| C3—H3B | 0.9700 | C21—H21B | 0.9700 |
| C4—C5 | 1.378 (4) | C22—N22 | 1.478 (5) |
| C4—C9 | 1.393 (4) | C22—H22A | 0.9700 |
| C5—C6 | 1.385 (5) | C22—H22B | 0.9700 |
| C5—H5A | 0.9300 | N22—C23 | 1.507 (4) |
| C6—C7 | 1.357 (5) | N22—H22C | 0.899 (10) |
| C6—H6A | 0.9300 | N22—H22D | 0.900 (10) |
| C7—C8 | 1.365 (5) | C23—C24 | 1.487 (5) |
| C7—H7A | 0.9300 | C23—H23A | 0.9700 |
| C8—C9 | 1.372 (5) | C23—H23B | 0.9700 |
| C8—H8A | 0.9300 | C24—C25 | 1.361 (6) |
| C9—N3 | 1.463 (4) | C24—C29 | 1.398 (5) |
| N3—O2 | 1.193 (4) | C25—C26 | 1.411 (7) |
| N3—O1 | 1.208 (4) | C25—H25A | 0.9300 |
| C11—C12 | 1.501 (5) | C26—C27 | 1.391 (9) |
| C11—H11A | 0.9700 | C26—H26A | 0.9300 |
| C11—H11B | 0.9700 | C27—C28 | 1.345 (9) |
| C12—N12 | 1.493 (4) | C27—H27A | 0.9300 |
| C12—H12A | 0.9700 | C28—C29 | 1.338 (8) |
| C12—H12B | 0.9700 | C28—H28A | 0.9300 |
| N12—C13 | 1.495 (4) | C29—N23 | 1.498 (7) |
| N12—H12C | 0.897 (10) | N23—O6 | 1.196 (6) |
| N12—H12D | 0.902 (10) | N23—O5 | 1.202 (5) |
| C13—C14 | 1.503 (5) | O7—H71 | 0.851 (10) |
| C13—H13A | 0.9700 | O7—H72 | 0.851 (10) |
| C13—H13B | 0.9700 | O8—H81 | 0.850 (10) |

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|---|---|---|---|
| C14—C15 | 1.378 (5) | O8—H82 | 0.850 (10) |
| | | | |
| C1—N1—C11 | 110.8 (3) | C14—C13—H13B | 108.9 |
| C1—N1—C21 | 109.2 (2) | H13A—C13—H13B | 107.8 |
| C11—N1—C21 | 109.3 (3) | C15—C14—C19 | 116.6 (3) |
| N1—C1—C2 | 114.4 (3) | C15—C14—C13 | 116.4 (3) |
| N1—C1—H1A | 108.7 | C19—C14—C13 | 126.8 (3) |
| C2—C1—H1A | 108.7 | C16—C15—C14 | 122.3 (4) |
| N1—C1—H1B | 108.7 | C16—C15—H15A | 118.8 |
| C2—C1—H1B | 108.7 | C14—C15—H15A | 118.8 |
| H1A—C1—H1B | 107.6 | C17—C16—C15 | 120.5 (4) |
| N2—C2—C1 | 112.0 (3) | C17—C16—H16A | 119.8 |
| N2—C2—H2A | 109.2 | C15—C16—H16A | 119.8 |
| C1—C2—H2A | 109.2 | C16—C17—C18 | 120.5 (4) |
| N2—C2—H2B | 109.2 | C16—C17—H17A | 119.7 |
| C1—C2—H2B | 109.2 | C18—C17—H17A | 119.7 |
| H2A—C2—H2B | 107.9 | C17—C18—C19 | 119.1 (4) |
| C3—N2—C2 | 110.7 (2) | C17—C18—H18A | 120.5 |
| C3—N2—H2C | 114 (2) | C19—C18—H18A | 120.5 |
| C2—N2—H2C | 104 (2) | C14—C19—C18 | 121.0 (3) |
| C3—N2—H2D | 109 (2) | C14—C19—N13 | 121.3 (4) |
| C2—N2—H2D | 111 (2) | C18—C19—N13 | 117.8 (4) |
| H2C—N2—H2D | 109 (3) | O3—N13—O4 | 121.4 (4) |
| N2—C3—C4 | 113.3 (3) | O3—N13—C19 | 118.8 (5) |
| N2—C3—H3A | 108.9 | O4—N13—C19 | 119.8 (4) |
| C4—C3—H3A | 108.9 | N1—C21—C22 | 112.6 (3) |
| N2—C3—H3B | 108.9 | N1—C21—H21A | 109.1 |
| C4—C3—H3B | 108.9 | C22—C21—H21A | 109.1 |
| H3A—C3—H3B | 107.7 | N1—C21—H21B | 109.1 |
| C5—C4—C9 | 115.3 (3) | C22—C21—H21B | 109.1 |
| C5—C4—C3 | 122.5 (3) | H21A—C21—H21B | 107.8 |
| C9—C4—C3 | 122.2 (3) | N22—C22—C21 | 111.1 (3) |
| C4—C5—C6 | 121.7 (3) | N22—C22—H22A | 109.4 |
| C4—C5—H5A | 119.1 | C21—C22—H22A | 109.4 |
| C6—C5—H5A | 119.1 | N22—C22—H22B | 109.4 |
| C7—C6—C5 | 120.9 (3) | C21—C22—H22B | 109.4 |
| C7—C6—H6A | 119.5 | H22A—C22—H22B | 108.0 |
| C5—C6—H6A | 119.5 | C22—N22—C23 | 112.2 (3) |
| C6—C7—C8 | 119.4 (3) | C22—N22—H22C | 109 (2) |
| C6—C7—H7A | 120.3 | C23—N22—H22C | 111 (2) |
| C8—C7—H7A | 120.3 | C22—N22—H22D | 116 (2) |
| C7—C8—C9 | 119.3 (3) | C23—N22—H22D | 106 (2) |
| C7—C8—H8A | 120.4 | H22C—N22—H22D | 102 (3) |
| C9—C8—H8A | 120.4 | C24—C23—N22 | 112.9 (3) |
| C8—C9—C4 | 123.4 (3) | C24—C23—H23A | 109.0 |
| C8—C9—N3 | 117.1 (3) | N22—C23—H23A | 109.0 |
| C4—C9—N3 | 119.5 (3) | C24—C23—H23B | 109.0 |
| O2—N3—O1 | 122.1 (4) | N22—C23—H23B | 109.0 |

| | | | |
|---|---|---|---|
| O2—N3—C9 | 119.0 (3) | H23A—C23—H23B | 107.8 |
| O1—N3—C9 | 118.9 (4) | C25—C24—C29 | 117.9 (4) |
| N1—C11—C12 | 114.5 (3) | C25—C24—C23 | 117.7 (3) |
| N1—C11—H11A | 108.6 | C29—C24—C23 | 124.4 (4) |
| C12—C11—H11A | 108.6 | C24—C25—C26 | 121.0 (5) |
| N1—C11—H11B | 108.6 | C24—C25—H25A | 119.5 |
| C12—C11—H11B | 108.6 | C26—C25—H25A | 119.5 |
| H11A—C11—H11B | 107.6 | C27—C26—C25 | 118.1 (6) |
| N12—C12—C11 | 112.6 (3) | C27—C26—H26A | 121.0 |
| N12—C12—H12A | 109.1 | C25—C26—H26A | 121.0 |
| C11—C12—H12A | 109.1 | C28—C27—C26 | 120.2 (6) |
| N12—C12—H12B | 109.1 | C28—C27—H27A | 119.9 |
| C11—C12—H12B | 109.1 | C26—C27—H27A | 119.9 |
| H12A—C12—H12B | 107.8 | C29—C28—C27 | 121.3 (6) |
| C12—N12—C13 | 110.5 (2) | C29—C28—H28A | 119.4 |
| C12—N12—H12C | 107 (2) | C27—C28—H28A | 119.4 |
| C13—N12—H12C | 114 (2) | C28—C29—C24 | 121.5 (6) |
| C12—N12—H12D | 104 (2) | C28—C29—N23 | 117.5 (5) |
| C13—N12—H12D | 115 (2) | C24—C29—N23 | 121.0 (4) |
| H12C—N12—H12D | 104 (3) | O6—N23—O5 | 124.0 (6) |
| N12—C13—C14 | 113.2 (3) | O6—N23—C29 | 120.1 (4) |
| N12—C13—H13A | 108.9 | O5—N23—C29 | 115.4 (6) |
| C14—C13—H13A | 108.9 | H71—O7—H72 | 104 (3) |
| N12—C13—H13B | 108.9 | H81—O8—H82 | 104 (3) |

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|---|---|---|---|
| C11—N1—C1—C2 | 163.5 (3) | C16—C17—C18—C19 | 0.9 (6) |
| C21—N1—C1—C2 | −76.1 (3) | C15—C14—C19—C18 | 0.7 (5) |
| N1—C1—C2—N2 | −75.8 (3) | C13—C14—C19—C18 | 175.6 (3) |
| C1—C2—N2—C3 | 177.4 (2) | C15—C14—C19—N13 | −177.8 (3) |
| C2—N2—C3—C4 | 165.9 (2) | C13—C14—C19—N13 | −2.9 (5) |
| N2—C3—C4—C5 | 19.9 (4) | C17—C18—C19—C14 | −1.0 (5) |
| N2—C3—C4—C9 | −158.0 (3) | C17—C18—C19—N13 | 177.6 (3) |
| C9—C4—C5—C6 | −1.4 (4) | C14—C19—N13—O3 | 171.6 (4) |
| C3—C4—C5—C6 | −179.5 (3) | C18—C19—N13—O3 | −6.9 (5) |
| C4—C5—C6—C7 | 2.0 (5) | C14—C19—N13—O4 | −7.1 (5) |
| C5—C6—C7—C8 | −0.8 (5) | C18—C19—N13—O4 | 174.3 (3) |
| C6—C7—C8—C9 | −1.0 (5) | C1—N1—C21—C22 | 159.9 (3) |
| C7—C8—C9—C4 | 1.7 (5) | C11—N1—C21—C22 | −78.8 (3) |
| C7—C8—C9—N3 | −176.1 (3) | N1—C21—C22—N22 | −67.4 (4) |
| C5—C4—C9—C8 | −0.5 (4) | C21—C22—N22—C23 | 178.1 (3) |
| C3—C4—C9—C8 | 177.6 (3) | C22—N22—C23—C24 | 155.5 (3) |
| C5—C4—C9—N3 | 177.2 (3) | N22—C23—C24—C25 | 107.9 (4) |
| C3—C4—C9—N3 | −4.7 (4) | N22—C23—C24—C29 | −75.9 (4) |
| C8—C9—N3—O2 | 143.3 (4) | C29—C24—C25—C26 | −0.5 (5) |
| C4—C9—N3—O2 | −34.6 (5) | C23—C24—C25—C26 | 176.0 (3) |
| C8—C9—N3—O1 | −38.7 (5) | C24—C25—C26—C27 | −0.5 (6) |
| C4—C9—N3—O1 | 143.5 (4) | C25—C26—C27—C28 | 0.4 (8) |
| C1—N1—C11—C12 | −76.1 (3) | C26—C27—C28—C29 | 0.6 (8) |

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|---|---|---|---|
| C21—N1—C11—C12 | 163.6 (3) | C27—C28—C29—C24 | −1.7 (7) |
| N1—C11—C12—N12 | −66.1 (4) | C27—C28—C29—N23 | 179.9 (5) |
| C11—C12—N12—C13 | −165.5 (3) | C25—C24—C29—C28 | 1.6 (5) |
| C12—N12—C13—C14 | −170.5 (3) | C23—C24—C29—C28 | −174.6 (4) |
| N12—C13—C14—C15 | −104.5 (4) | C25—C24—C29—N23 | 180.0 (3) |
| N12—C13—C14—C19 | 80.5 (4) | C23—C24—C29—N23 | 3.8 (5) |
| C19—C14—C15—C16 | −0.4 (5) | C28—C29—N23—O6 | −177.6 (4) |
| C13—C14—C15—C16 | −175.9 (3) | C24—C29—N23—O6 | 3.9 (6) |
| C14—C15—C16—C17 | 0.4 (6) | C28—C29—N23—O5 | −5.1 (5) |
| C15—C16—C17—C18 | −0.6 (6) | C24—C29—N23—O5 | 176.4 (4) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*D*···Cl1 | 0.91 (1) | 2.26 (1) | 3.155 (2) | 172 (3) |
| N12—H12*D*···Cl1 | 0.90 (1) | 2.40 (2) | 3.225 (3) | 153 (3) |
| N22—H22*D*···Cl1 | 0.90 (1) | 2.28 (1) | 3.176 (3) | 174 (3) |
| N12—H12*C*···Cl3 | 0.90 (1) | 2.16 (1) | 3.054 (3) | 174 (3) |
| N22—H22*C*···Cl2 | 0.90 (1) | 2.34 (1) | 3.209 (3) | 164 (3) |
| O8—H81···Cl1 | 0.85 (1) | 2.35 (5) | 3.115 (5) | 150 (9) |
| O8—H82···Cl2 | 0.85 (1) | 2.46 (4) | 3.265 (5) | 159 (10) |
| O7—H72···Cl3 | 0.85 (1) | 2.28 (3) | 3.102 (6) | 163 (9) |
| N2—H2*C*···Cl2$^{i}$ | 0.90 (1) | 2.22 (1) | 3.089 (3) | 163 (3) |
| O7—H71···O6$^{ii}$ | 0.85 (1) | 2.45 (8) | 2.965 (7) | 119 (8) |

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