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Crystal structure of 3-[({2-[bis(2-hydroxybenzyl)-amino]ethyl}(2-hydroxybenzyl)amino)methyl]-2-hydroxy-5-methylbenzaldehyde

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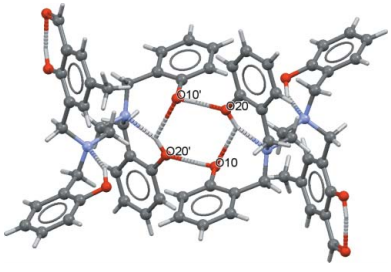
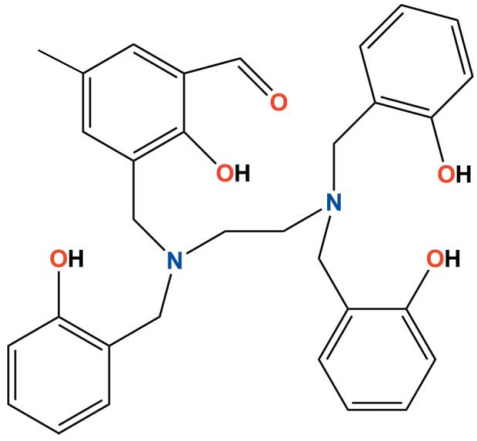
The non-symmetric title molecule, $C_{32}H_{34}N_2O_5$, is based on a tetrasubstituted ethylenediamine backbone. The molecular structure consists of three hydroxybenzyl groups and one 2-hydroxy-5-methylbenzaldehyde group bonded to the N atoms of the diamine unit. The ethylenediamine skeleton shows a regular extended conformation, while the spatial orientation of the phenol arms is governed by hydrogen bonds. In the 2-hydroxy-5-methylbenzaldehyde group, an intramolecular $S(6)$ O—H···O hydrogen bond is observed between the alcohol and aldehyde functions, and the neighbouring phenol arm participates in an intramolecular $S(6)$ O—H···N hydrogen bond. The third phenol group is involved in a bifurcated intramolecular hydrogen bond with graph-set notation $S(6)$ for O—H···N and O—H···O intramolecular hydrogen bonds between neighbouring amine and phenol arms, respectively. Finally, the fourth phenol group acts as an acceptor in a bifurcated intramolecular hydrogen bond and also acts as donor in an intermolecular hydrogen bond, which connects inversion-related molecules into dimers with $R_4^4(8)$ ring motifs.

1. Chemical context

The preparation of non-symmetric compounds has always been of interest in organic synthesis, as well as in coordination chemistry. Compounds containing tetrasubstituted ethylenediamine groups have attracted significant interest because of their coordination versatility towards metal ions, their easy preparation and their biological activity (Musa *et al.*, 2014). With respect to medical applications, high *in vitro* cytotoxic activity of free ethylenediamine-type compounds against different types of cancer cells, such as HL-60 leukemic and B16 human melanoma cells lines, has been reported (Dencic *et al.*, 2012; Lazić *et al.*, 2010). In addition, metal complexes containing substituted ethylenediamine have also found valuable applications in pharmacological research as potential anticancer agents (Ansari *et al.*, 2009), radiopharmaceuticals for tumor imaging (Boros *et al.*, 2011; Price *et al.*, 2012) and artificial nucleases (Raman *et al.*, 2011). In this paper, we report the synthesis and crystal structure of the non-symmetric molecule 3-[({2-[bis(2-hydroxybenzyl)amino]ethyl}(2-hydroxybenzyl)amino)methyl]-2-hydroxy-5-methylbenzaldehyde, (I), which is a potential hexadentate ligand with an N_2O_4-donor set which could stabilize complexes containing high-oxidation-state metal ions, such as Tc^{III}, Ga^{III} and In^{III} ions, that are widely used in radiopharmaceuticals for diagnostic imaging and related research.





2. Structural commentary

Compound (I) is a non-symmetric molecule based on a tetrasubstituted ethylenediamine backbone (Fig. 1). The structure consists of three hydroxybenzyl groups and one 2-hydroxy-5-methylbenzaldehyde group bonded to nitrogen atoms of the diamine unit. The ethylenediamine skeleton shows a regular extended 'zigzag' conformation [with an N1—C2—C3—N4 torsion angle of 174.78 (13)°], while the pendant phenol arms are randomly oriented but governed by hydrogen bonds (Table 1). Three intramolecular hydrogen bonds with an $S(6)$ graph-set motif are observed in the molecular structure of (I) (Fig. 2). One of these occurs between the neighbouring alcohol and aldehyde groups. In addition, intramolecular O—H···N and O—H···O interactions, which include bifurcated hydrogen bonds, are observed, involving O—H functions as donors and the amine sites and one phenolic oxygen atom as acceptors. All bond lengths and angles found for (I) are in the expected range for organic compounds (Bruno *et al.*, 2004).

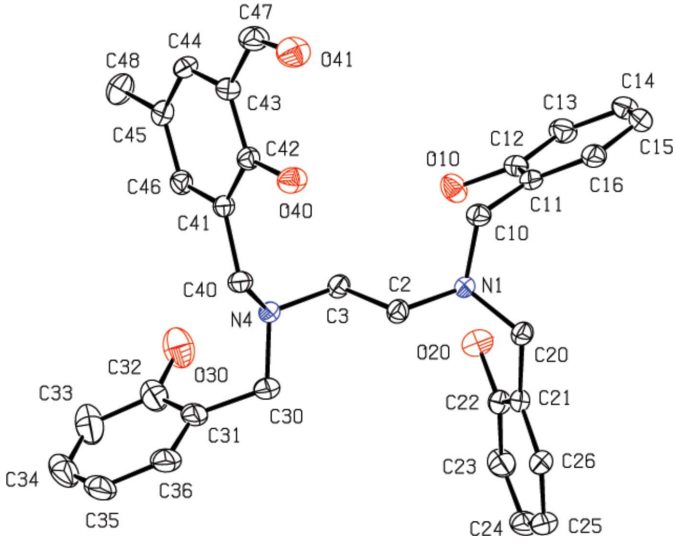


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 40% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
O10—H10···O20^{i}	0.93	1.80	2.7230 (16)	177
O20—H20···N1	0.94	1.75	2.5928 (17)	148
O20—H20···O10	0.94	2.43	3.0362 (19)	122
O30—H30···N4	0.93	1.94	2.784 (2)	149
O40—H40···O41	0.93	1.76	2.6146 (19)	151

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

3. Supramolecular features

In the crystal of (I), inversion dimers with $R_4^4(8)$ ring motifs are formed by pairs of O—H···O hydrogen bonds (Fig. 3, Table 1). The approximate planes of the ring motifs of the dimers are arranged as stacks along [010] (Fig. 4). No π–π stacking interactions are observed.

4. Database survey

A search for similar structures in the current version of the Cambridge Structural Database (Version 5.35, November 2013; Groom & Allen, 2014) resulted in four entries but only three different structures: (i) HUNDIE (CCDC 727272) and HUNDOK (CCDC 727273) (Boyle *et al.*, 2009); (ii) USODUC (CCDC 809654) (Wang *et al.*, 2011*a*) and (iii) USODUC01 (CCDC 809654) (Wang *et al.*, 2011*b*). All of these structures are symmetric molecules and the phenol groups have an additional one or two substituents in the *para* and *ortho* positions with respect to the O–H function. As observed in (I), the spatial orientations of the phenol arms are influenced by intra- and intermolecular hydrogen bonding. There are no significant differences in the geometrical parameters;

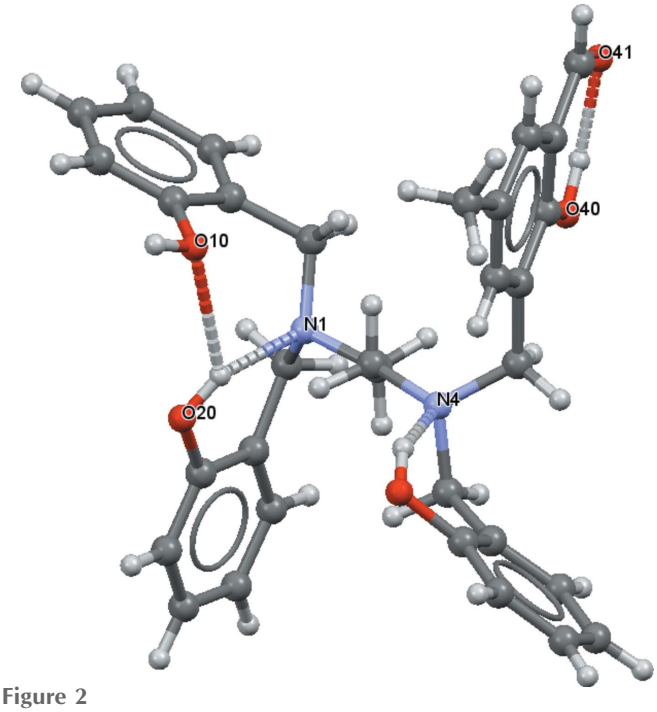


Figure 2
The intramolecular hydrogen bonds (dashed lines) observed in (I).

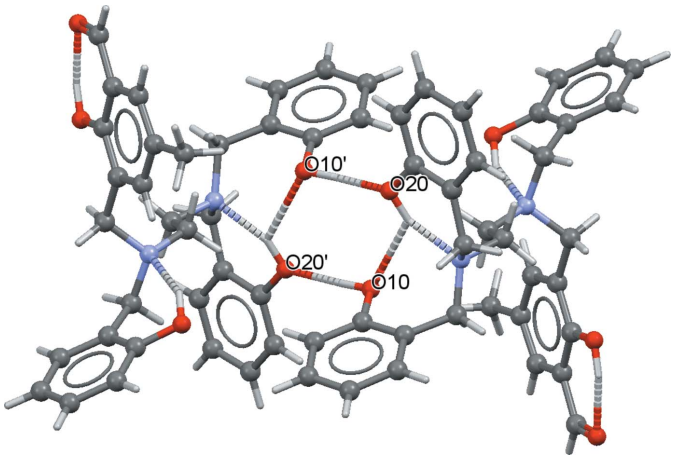


Figure 3
An inversion dimer of (I) formed by intermolecular O—H···O hydrogen bonds (dashed lines). [Symmetry code: (′) $-x+1, -y, -z$.]

however, the crystal packing shows distinguishable three-dimensional arrangements due to differences in molecular symmetry and intermolecular interactions.

5. Synthesis and crystallization

The title compound was obtained from a nucleophilic substitution reaction between *N*,*N*,*N*′-tris(2-hydroxybenzyl)-1,2-diaminoethane (Schmitt *et al.*, 2002) and chloromethyl-4-methyl-6-formylphenol. These precursors were prepared following the methodologies already described in the literature (Schmitt *et al.*, 2002; Thoer *et al.*, 1988). A solution of 2-chloromethyl-4-methyl-6-formylphenol (1.19 g, 6.6 mmol) in tetrahydrofuran (40 ml) was added slowly to a cooled solution of *N*,*N*,*N*′-tris(2-hydroxybenzyl)-1,2-diaminoethane (2.50 g, 6.6 mmol) in tetrahydrofuran (40 ml) containing triethylamine (0.96 ml, 6.6 mmol). The reaction was kept cooled during addition time, and the resulting solution stirred for 24 h. Yellow mixture oil/solid was obtained after evaporation of the solvent. A solution of this mixture in CH_2Cl_2 (50 ml) was washed with a saturated solution of $NaHCO_3$ (3 × 50 ml) and filtered off in the presence of $NaSO_4$. The solvent was removed, and a straw-yellow solid was obtained. This solid was refluxed in *n*-hexane/$CHCl_3$ (1:1, 100 ml). After cooling the solid was filtered off, washed with *n*-hexane (80 ml), dried and recrystallized from an ethyl acetate solution to afford 3-[({2-[bis(2-hydroxybenzyl)amino]ethyl}(2-hydroxybenzyl)amino)-methyl]-2-hydroxy-5-methylbenzaldehyde, (I).

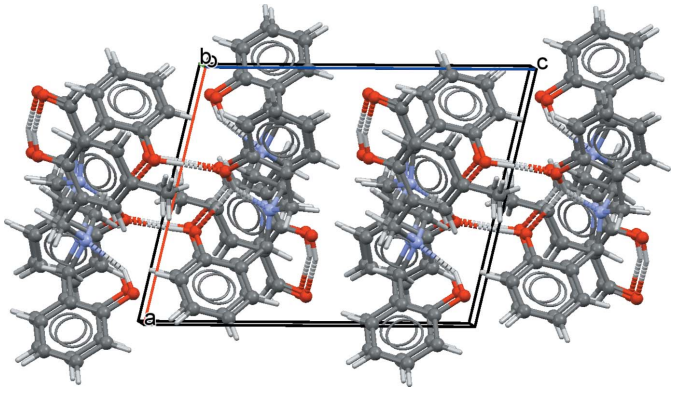


Figure 4
Partial packing of (I), showing dimers stacked along [010].

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{32}H_{34}N_2O_5$
M_r	526.61
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	190
a, b, c (Å)	10.1635 (5), 11.0440 (6), 13.5439 (7)
α, β, γ (°)	113.549 (2), 98.381 (2), 99.451 (3)
V (Å^3)	1336.64 (12)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.15 × 0.08 × 0.04
Data collection	
Diffractometer	Bruker APEXII DUO
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17177, 8122, 5175
R_{int}	0.031
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.166, 1.02
No. of reflections	8122
No. of parameters	353
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.42, −0.25

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008).

The formation of (I) was indicated by the presence of the band at 1655 cm^{-1} in the IR spectrum, which is typical for stretching vibrations ν(C═O) of free aldehyde. In the ^{1}H NMR spectrum, the signal at 9.81 p.p.m. related to one aldehyde proton is further evidence for product formation. Yield 90%, m.p. 444.8–445.4 K. IR (KBr, cm^{-1}): ν(O—H) 3273, ν(C—H$_{ar}$ and C—H$_{alif}$) 3042–2718, ν(C═O)1655, ν(C═C) 1615–1457, δ(O—H) 1365, δ(C—O) 1252, δ(C—H$_{ar}$) 757; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, p.p.m.): 2.29 (*s*, 3H, CH_3), 2.78 (*s*, 4H, $CH_{2\text{-en}}$), 3.58 (*s*, 2H, CH_2), 3.61–3.77 (*m*, 6 H, CH_2), 6.69–6.87 (*m*, 6H, CH_{ar}), 6.91 (*d*, 2H, CH_{ar}), 6.99 (*d*, 2 H, CH_{ar}), 7.07–7.19 (*m*, 2H, CH_{ar}), 7.24 (*d*, 2H, CH_{ar}), 9.81 (*s*, 1H, CH_{ald}); ^{13}C NMR (400 MHz, DMSO-d_6, δ p.p.m.): 20.0, 48.6, 48.8, 53.5, 54.3, 115.2, 121.7, 122.7, 123.2, 124.5, 127.6, 128.4, 128.7, 129.8, 130.8, 136.7, 156.2, 156.5, 158.7, 191.6. Negative HPLC/ESI–MS (*m*/*z*): [*M*−H] calculated for $C_{32}H_{35}N_2O_5^-$, 527.25; found, 527.19. Colourless blocks were grown by slow evaporation of the solvent from a saturated solution of (I) in ethyl acetate.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in idealized

positions with distances of 0.95 (CH_{Ar}), 0.99 (CH_2) or 0.98 Å (CH_3) with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$. The hydrogen atoms of the alcohol groups were located from a Fourier difference map and treated with a riding-model approximation with $U_{iso}(H) = 1.5U_{eq}(O)$.

Acknowledgements

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supporting information

Acta Cryst. (2014). E**70**, 562-565 [doi:10.1107/S1600536814024465]

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Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

3-[({2-[Bis(2-hydroxybenzyl)amino]ethyl}(2-hydroxybenzyl)amino)methyl]-2-hydroxy-5-methylbenzaldehyde

Crystal data

$C_{32}H_{34}N_2O_5$
M_r = 526.61
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 10.1635 (5) Å
b = 11.0440 (6) Å
c = 13.5439 (7) Å
α = 113.549 (2)°
β = 98.381 (2)°
γ = 99.451 (3)°
V = 1336.64 (12) Å^3
Z = 2
$F(000)$ = 560
D_x = 1.308 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4159 reflections
θ = 2.4–30.3°
μ = 0.09 mm^{-1}
T = 190 K
Prismatic, colourless
0.15 × 0.08 × 0.04 mm

Data collection

Bruker APEXII DUO diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
17177 measured reflections
8122 independent reflections
5175 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 30.6°, θ_{min} = 1.7°
h = −13→14
k = −15→15
l = −9→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.166
S = 1.02
8122 reflections
353 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0806P)^2 + 0.2575P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.55546 (13)	0.19576 (13)	0.30195 (10)	0.0231 (3)
C2	0.46867 (17)	0.29324 (17)	0.32893 (12)	0.0268 (3)
H2A	0.5193	0.3775	0.3954	0.032*
H2B	0.3853	0.2536	0.3460	0.032*
C3	0.42744 (17)	0.32788 (16)	0.23213 (12)	0.0258 (3)
H3A	0.5117	0.3735	0.2200	0.031*
H3B	0.3865	0.2416	0.1646	0.031*
N4	0.33030 (13)	0.41522 (13)	0.24463 (11)	0.0258 (3)
C10	0.69979 (16)	0.26500 (17)	0.31867 (13)	0.0280 (3)
H10A	0.7441	0.3071	0.3987	0.034*
H10B	0.7017	0.3390	0.2948	0.034*
C11	0.78117 (16)	0.17145 (16)	0.25636 (13)	0.0263 (3)
C12	0.74930 (16)	0.11211 (18)	0.14067 (13)	0.0288 (3)
C13	0.82640 (18)	0.02915 (19)	0.08148 (15)	0.0350 (4)
H13	0.8023	−0.0122	0.0028	0.042*
C14	0.93856 (18)	0.0067 (2)	0.13728 (16)	0.0368 (4)
H14	0.9915	−0.0497	0.0967	0.044*
C15	0.97344 (18)	0.06622 (19)	0.25181 (16)	0.0350 (4)
H15	1.0507	0.0515	0.2901	0.042*
C16	0.89474 (17)	0.14765 (18)	0.31045 (14)	0.0312 (4)
H16	0.9188	0.1880	0.3891	0.037*
C20	0.54425 (17)	0.11170 (17)	0.36403 (13)	0.0268 (3)
H20A	0.5551	0.1718	0.4434	0.032*
H20B	0.6192	0.0640	0.3576	0.032*
C21	0.40800 (16)	0.00815 (16)	0.32108 (13)	0.0259 (3)
C22	0.34574 (17)	−0.05756 (17)	0.20764 (14)	0.0296 (3)
C23	0.22507 (19)	−0.15869 (19)	0.16750 (17)	0.0394 (4)
H23	0.1832	−0.2018	0.0905	0.047*
C24	0.1654 (2)	−0.1970 (2)	0.23937 (19)	0.0457 (5)
H24	0.0838	−0.2678	0.2113	0.055*
C25	0.2237 (2)	−0.1331 (2)	0.35144 (19)	0.0439 (5)
H25	0.1822	−0.1592	0.4007	0.053*
C26	0.34370 (18)	−0.03025 (19)	0.39182 (16)	0.0338 (4)
H26	0.3827	0.0149	0.4693	0.041*
C30	0.20423 (18)	0.36075 (19)	0.27170 (17)	0.0364 (4)
H30A	0.2235	0.3827	0.3516	0.044*

H30B	0.1767	0.2604	0.2293	0.044*
C31	0.08900 (18)	0.41958 (19)	0.24471 (18)	0.0404 (4)
C32	0.0497 (2)	0.4116 (2)	0.13898 (18)	0.0453 (5)
C33	−0.0650 (2)	0.4543 (2)	0.1098 (2)	0.0613 (7)
H33	−0.0926	0.4460	0.0368	0.074*
C34	−0.1378 (2)	0.5087 (2)	0.1875 (3)	0.0637 (7)
H34	−0.2174	0.5359	0.1672	0.076*
C35	−0.0980 (2)	0.5243 (2)	0.2931 (3)	0.0603 (7)
H35	−0.1472	0.5660	0.3467	0.072*
C36	0.0148 (2)	0.4792 (2)	0.3227 (2)	0.0499 (5)
H36	0.0416	0.4889	0.3962	0.060*
C40	0.39032 (17)	0.55858 (16)	0.32520 (14)	0.0286 (3)
H40A	0.4334	0.5613	0.3967	0.034*
H40B	0.3159	0.6066	0.3376	0.034*
C41	0.49612 (16)	0.63311 (16)	0.28855 (13)	0.0247 (3)
C42	0.62638 (16)	0.70468 (16)	0.35788 (12)	0.0260 (3)
C43	0.71949 (16)	0.78163 (17)	0.32493 (13)	0.0284 (3)
C44	0.68364 (17)	0.78221 (17)	0.22159 (13)	0.0293 (3)
H44	0.7473	0.8341	0.1998	0.035*
C45	0.55741 (18)	0.70888 (17)	0.15050 (13)	0.0290 (3)
C46	0.46489 (17)	0.63763 (17)	0.18737 (13)	0.0277 (3)
H46	0.3762	0.5900	0.1406	0.033*
C47	0.85585 (19)	0.8554 (2)	0.39565 (15)	0.0385 (4)
H47	0.9159	0.9059	0.3704	0.046*
C48	0.5214 (2)	0.7027 (2)	0.03654 (14)	0.0406 (4)
H48A	0.5719	0.7864	0.0368	0.061*
H48B	0.4226	0.6935	0.0152	0.061*
H48C	0.5462	0.6241	−0.0166	0.061*
O10	0.64008 (13)	0.13999 (14)	0.09024 (10)	0.0368 (3)
H10	0.6275	0.1024	0.0139	0.044*
O20	0.40399 (13)	−0.02278 (13)	0.13465 (9)	0.0364 (3)
H20	0.4684	0.0616	0.1734	0.044*
O30	0.12438 (17)	0.36127 (17)	0.06209 (13)	0.0586 (4)
H30	0.2124	0.3804	0.1050	0.070*
O40	0.66072 (13)	0.69757 (14)	0.45562 (10)	0.0380 (3)
H40	0.7520	0.7475	0.4859	0.046*
O41	0.89821 (14)	0.85675 (16)	0.48535 (11)	0.0491 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0239 (6)	0.0241 (6)	0.0259 (6)	0.0070 (5)	0.0077 (5)	0.0144 (5)
C2	0.0319 (8)	0.0270 (8)	0.0272 (7)	0.0117 (7)	0.0117 (6)	0.0142 (6)
C3	0.0303 (8)	0.0247 (8)	0.0257 (7)	0.0085 (6)	0.0090 (6)	0.0128 (6)
N4	0.0230 (6)	0.0211 (6)	0.0359 (7)	0.0052 (5)	0.0086 (5)	0.0144 (5)
C10	0.0237 (8)	0.0273 (8)	0.0306 (8)	0.0022 (6)	0.0043 (6)	0.0125 (6)
C11	0.0215 (7)	0.0259 (8)	0.0335 (8)	0.0023 (6)	0.0066 (6)	0.0162 (7)
C12	0.0231 (8)	0.0338 (9)	0.0340 (8)	0.0060 (7)	0.0087 (6)	0.0189 (7)

C13	0.0317 (9)	0.0410 (10)	0.0359 (9)	0.0095 (8)	0.0128 (7)	0.0182 (8)
C14	0.0283 (9)	0.0389 (10)	0.0515 (10)	0.0116 (8)	0.0183 (8)	0.0235 (9)
C15	0.0233 (8)	0.0389 (10)	0.0512 (10)	0.0082 (7)	0.0082 (7)	0.0278 (9)
C16	0.0243 (8)	0.0341 (9)	0.0363 (8)	0.0027 (7)	0.0034 (6)	0.0193 (7)
C20	0.0279 (8)	0.0285 (8)	0.0280 (7)	0.0070 (6)	0.0057 (6)	0.0165 (6)
C21	0.0248 (8)	0.0242 (8)	0.0342 (8)	0.0090 (6)	0.0088 (6)	0.0165 (6)
C22	0.0294 (8)	0.0240 (8)	0.0371 (8)	0.0085 (7)	0.0097 (7)	0.0136 (7)
C23	0.0314 (9)	0.0274 (9)	0.0484 (10)	0.0037 (7)	0.0034 (8)	0.0088 (8)
C24	0.0287 (9)	0.0303 (10)	0.0757 (14)	0.0027 (8)	0.0142 (9)	0.0218 (10)
C25	0.0371 (10)	0.0409 (11)	0.0705 (14)	0.0126 (9)	0.0256 (10)	0.0352 (10)
C26	0.0336 (9)	0.0351 (9)	0.0443 (9)	0.0121 (7)	0.0149 (7)	0.0255 (8)
C30	0.0277 (9)	0.0319 (9)	0.0552 (11)	0.0045 (7)	0.0136 (8)	0.0242 (8)
C31	0.0225 (8)	0.0279 (9)	0.0699 (13)	0.0010 (7)	0.0098 (8)	0.0226 (9)
C32	0.0336 (10)	0.0280 (10)	0.0612 (12)	0.0057 (8)	0.0007 (9)	0.0106 (9)
C33	0.0442 (13)	0.0331 (11)	0.0821 (17)	0.0056 (10)	−0.0162 (11)	0.0127 (11)
C34	0.0277 (10)	0.0339 (12)	0.113 (2)	0.0043 (9)	0.0014 (12)	0.0225 (13)
C35	0.0338 (11)	0.0353 (11)	0.116 (2)	0.0094 (9)	0.0324 (13)	0.0314 (13)
C36	0.0362 (11)	0.0367 (11)	0.0832 (15)	0.0069 (9)	0.0258 (10)	0.0292 (11)
C40	0.0279 (8)	0.0253 (8)	0.0348 (8)	0.0062 (6)	0.0134 (7)	0.0135 (7)
C41	0.0255 (7)	0.0207 (7)	0.0305 (7)	0.0079 (6)	0.0109 (6)	0.0114 (6)
C42	0.0273 (8)	0.0266 (8)	0.0261 (7)	0.0077 (6)	0.0079 (6)	0.0125 (6)
C43	0.0243 (8)	0.0284 (8)	0.0317 (8)	0.0038 (6)	0.0058 (6)	0.0134 (7)
C44	0.0302 (8)	0.0262 (8)	0.0360 (8)	0.0048 (7)	0.0112 (7)	0.0175 (7)
C45	0.0336 (9)	0.0260 (8)	0.0300 (8)	0.0092 (7)	0.0077 (6)	0.0140 (6)
C46	0.0253 (8)	0.0251 (8)	0.0311 (8)	0.0057 (6)	0.0032 (6)	0.0119 (6)
C47	0.0283 (9)	0.0394 (10)	0.0428 (10)	−0.0015 (8)	0.0034 (7)	0.0184 (8)
C48	0.0518 (12)	0.0422 (11)	0.0324 (9)	0.0116 (9)	0.0078 (8)	0.0215 (8)
O10	0.0338 (7)	0.0523 (8)	0.0295 (6)	0.0177 (6)	0.0082 (5)	0.0200 (6)
O20	0.0418 (7)	0.0324 (7)	0.0269 (6)	0.0004 (6)	0.0070 (5)	0.0086 (5)
O30	0.0575 (10)	0.0587 (10)	0.0500 (9)	0.0222 (8)	−0.0007 (7)	0.0155 (8)
O40	0.0342 (7)	0.0497 (8)	0.0323 (6)	0.0037 (6)	0.0048 (5)	0.0235 (6)
O41	0.0367 (7)	0.0579 (9)	0.0432 (8)	−0.0025 (7)	−0.0056 (6)	0.0230 (7)

Geometric parameters (Å, º)

N1—C2	1.471 (2)	C26—H26	0.9500
N1—C10	1.478 (2)	C30—C31	1.497 (3)
N1—C20	1.4828 (19)	C30—H30A	0.9900
C2—C3	1.528 (2)	C30—H30B	0.9900
C2—H2A	0.9900	C31—C32	1.392 (3)
C2—H2B	0.9900	C31—C36	1.398 (3)
C3—N4	1.471 (2)	C32—O30	1.370 (3)
C3—H3A	0.9900	C32—C33	1.390 (3)
C3—H3B	0.9900	C33—C34	1.372 (4)
N4—C40	1.476 (2)	C33—H33	0.9500
N4—C30	1.483 (2)	C34—C35	1.361 (4)
C10—C11	1.500 (2)	C34—H34	0.9500
C10—H10A	0.9900	C35—C36	1.392 (3)

C10—H10B	0.9900	C35—H35	0.9500
C11—C16	1.395 (2)	C36—H36	0.9500
C11—C12	1.397 (2)	C40—C41	1.507 (2)
C12—O10	1.361 (2)	C40—H40A	0.9900
C12—C13	1.389 (2)	C40—H40B	0.9900
C13—C14	1.387 (3)	C41—C46	1.384 (2)
C13—H13	0.9500	C41—C42	1.400 (2)
C14—C15	1.383 (3)	C42—O40	1.3556 (18)
C14—H14	0.9500	C42—C43	1.407 (2)
C15—C16	1.389 (2)	C43—C44	1.397 (2)
C15—H15	0.9500	C43—C47	1.456 (2)
C16—H16	0.9500	C44—C45	1.380 (2)
C20—C21	1.509 (2)	C44—H44	0.9500
C20—H20A	0.9900	C45—C46	1.400 (2)
C20—H20B	0.9900	C45—C48	1.505 (2)
C21—C26	1.393 (2)	C46—H46	0.9500
C21—C22	1.401 (2)	C47—O41	1.222 (2)
C22—O20	1.369 (2)	C47—H47	0.9500
C22—C23	1.385 (2)	C48—H48A	0.9800
C23—C24	1.382 (3)	C48—H48B	0.9800
C23—H23	0.9500	C48—H48C	0.9800
C24—C25	1.377 (3)	O10—H10	0.9269
C24—H24	0.9500	O20—H20	0.9386
C25—C26	1.390 (3)	O30—H30	0.9332
C25—H25	0.9500	O40—H40	0.9349

C2—N1—C10	111.44 (12)	C25—C26—H26	119.3
C2—N1—C20	112.03 (12)	C21—C26—H26	119.3
C10—N1—C20	111.35 (12)	N4—C30—C31	111.34 (14)
N1—C2—C3	110.69 (12)	N4—C30—H30A	109.4
N1—C2—H2A	109.5	C31—C30—H30A	109.4
C3—C2—H2A	109.5	N4—C30—H30B	109.4
N1—C2—H2B	109.5	C31—C30—H30B	109.4
C3—C2—H2B	109.5	H30A—C30—H30B	108.0
H2A—C2—H2B	108.1	C32—C31—C36	118.15 (19)
N4—C3—C2	116.14 (12)	C32—C31—C30	120.33 (18)
N4—C3—H3A	108.3	C36—C31—C30	121.5 (2)
C2—C3—H3A	108.3	O30—C32—C33	119.1 (2)
N4—C3—H3B	108.3	O30—C32—C31	120.03 (18)
C2—C3—H3B	108.3	C33—C32—C31	120.9 (2)
H3A—C3—H3B	107.4	C34—C33—C32	119.3 (3)
C3—N4—C40	114.03 (13)	C34—C33—H33	120.3
C3—N4—C30	112.54 (12)	C32—C33—H33	120.3
C40—N4—C30	109.74 (13)	C35—C34—C33	121.2 (2)
N1—C10—C11	113.43 (13)	C35—C34—H34	119.4
N1—C10—H10A	108.9	C33—C34—H34	119.4
C11—C10—H10A	108.9	C34—C35—C36	119.9 (2)
N1—C10—H10B	108.9	C34—C35—H35	120.0

C11—C10—H10B	108.9	C36—C35—H35	120.0
H10A—C10—H10B	107.7	C35—C36—C31	120.4 (2)
C16—C11—C12	117.97 (15)	C35—C36—H36	119.8
C16—C11—C10	121.94 (15)	C31—C36—H36	119.8
C12—C11—C10	119.96 (14)	N4—C40—C41	113.41 (13)
O10—C12—C13	122.45 (15)	N4—C40—H40A	108.9
O10—C12—C11	116.65 (15)	C41—C40—H40A	108.9
C13—C12—C11	120.90 (15)	N4—C40—H40B	108.9
C14—C13—C12	119.98 (16)	C41—C40—H40B	108.9
C14—C13—H13	120.0	H40A—C40—H40B	107.7
C12—C13—H13	120.0	C46—C41—C42	118.20 (14)
C15—C14—C13	120.14 (17)	C46—C41—C40	120.76 (14)
C15—C14—H14	119.9	C42—C41—C40	120.98 (14)
C13—C14—H14	119.9	O40—C42—C41	119.10 (14)
C14—C15—C16	119.55 (16)	O40—C42—C43	121.17 (14)
C14—C15—H15	120.2	C41—C42—C43	119.73 (14)
C16—C15—H15	120.2	C44—C43—C42	119.95 (15)
C15—C16—C11	121.45 (16)	C44—C43—C47	119.64 (15)
C15—C16—H16	119.3	C42—C43—C47	120.34 (15)
C11—C16—H16	119.3	C45—C44—C43	121.23 (15)
N1—C20—C21	111.67 (12)	C45—C44—H44	119.4
N1—C20—H20A	109.3	C43—C44—H44	119.4
C21—C20—H20A	109.3	C44—C45—C46	117.50 (15)
N1—C20—H20B	109.3	C44—C45—C48	121.42 (16)
C21—C20—H20B	109.3	C46—C45—C48	121.06 (16)
H20A—C20—H20B	107.9	C41—C46—C45	123.31 (15)
C26—C21—C22	117.90 (16)	C41—C46—H46	118.3
C26—C21—C20	121.25 (15)	C45—C46—H46	118.3
C22—C21—C20	120.77 (14)	O41—C47—C43	124.37 (17)
O20—C22—C23	119.00 (16)	O41—C47—H47	117.8
O20—C22—C21	120.26 (15)	C43—C47—H47	117.8
C23—C22—C21	120.74 (17)	C45—C48—H48A	109.5
C24—C23—C22	120.06 (18)	C45—C48—H48B	109.5
C24—C23—H23	120.0	H48A—C48—H48B	109.5
C22—C23—H23	120.0	C45—C48—H48C	109.5
C25—C24—C23	120.42 (18)	H48A—C48—H48C	109.5
C25—C24—H24	119.8	H48B—C48—H48C	109.5
C23—C24—H24	119.8	C12—O10—H10	112.6
C24—C25—C26	119.46 (18)	C22—O20—H20	109.6
C24—C25—H25	120.3	C32—O30—H30	103.6
C26—C25—H25	120.3	C42—O40—H40	104.9
C25—C26—C21	121.40 (18)		

C10—N1—C2—C3	81.42 (15)	C40—N4—C30—C31	72.17 (19)
C20—N1—C2—C3	−153.07 (13)	N4—C30—C31—C32	54.0 (2)
N1—C2—C3—N4	174.78 (13)	N4—C30—C31—C36	−128.35 (18)
C2—C3—N4—C40	72.09 (17)	C36—C31—C32—O30	176.19 (18)
C2—C3—N4—C30	−53.74 (18)	C30—C31—C32—O30	−6.1 (3)

C2—N1—C10—C11	−159.44 (12)	C36—C31—C32—C33	−3.7 (3)
C20—N1—C10—C11	74.67 (16)	C30—C31—C32—C33	174.00 (18)
N1—C10—C11—C16	−117.78 (16)	O30—C32—C33—C34	−178.0 (2)
N1—C10—C11—C12	66.33 (19)	C31—C32—C33—C34	1.9 (3)
C16—C11—C12—O10	−178.35 (15)	C32—C33—C34—C35	1.5 (3)
C10—C11—C12—O10	−2.3 (2)	C33—C34—C35—C36	−2.9 (3)
C16—C11—C12—C13	1.6 (2)	C34—C35—C36—C31	1.0 (3)
C10—C11—C12—C13	177.67 (15)	C32—C31—C36—C35	2.3 (3)
O10—C12—C13—C14	178.56 (17)	C30—C31—C36—C35	−175.38 (17)
C11—C12—C13—C14	−1.4 (3)	C3—N4—C40—C41	67.55 (17)
C12—C13—C14—C15	0.3 (3)	C30—N4—C40—C41	−165.16 (14)
C13—C14—C15—C16	0.5 (3)	N4—C40—C41—C46	54.7 (2)
C14—C15—C16—C11	−0.3 (3)	N4—C40—C41—C42	−128.20 (16)
C12—C11—C16—C15	−0.8 (2)	C46—C41—C42—O40	−177.66 (14)
C10—C11—C16—C15	−176.73 (15)	C40—C41—C42—O40	5.2 (2)
C2—N1—C20—C21	72.32 (16)	C46—C41—C42—C43	1.9 (2)
C10—N1—C20—C21	−162.11 (13)	C40—C41—C42—C43	−175.28 (15)
N1—C20—C21—C26	−146.22 (15)	O40—C42—C43—C44	177.11 (15)
N1—C20—C21—C22	37.1 (2)	C41—C42—C43—C44	−2.4 (2)
C26—C21—C22—O20	179.39 (15)	O40—C42—C43—C47	0.2 (3)
C20—C21—C22—O20	−3.8 (2)	C41—C42—C43—C47	−179.35 (16)
C26—C21—C22—C23	−0.9 (2)	C42—C43—C44—C45	0.3 (3)
C20—C21—C22—C23	175.91 (16)	C47—C43—C44—C45	177.31 (17)
O20—C22—C23—C24	179.02 (16)	C43—C44—C45—C46	2.1 (2)
C21—C22—C23—C24	−0.7 (3)	C43—C44—C45—C48	−176.43 (16)
C22—C23—C24—C25	1.4 (3)	C42—C41—C46—C45	0.7 (2)
C23—C24—C25—C26	−0.4 (3)	C40—C41—C46—C45	177.87 (15)
C24—C25—C26—C21	−1.2 (3)	C44—C45—C46—C41	−2.7 (3)
C22—C21—C26—C25	1.8 (2)	C48—C45—C46—C41	175.86 (16)
C20—C21—C26—C25	−174.92 (16)	C44—C43—C47—O41	−177.20 (19)
C3—N4—C30—C31	−159.71 (15)	C42—C43—C47—O41	−0.3 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10···O20^{i}	0.93	1.80	2.7230 (16)	177
O20—H20···N1	0.94	1.75	2.5928 (17)	148
O20—H20···O10	0.94	2.43	3.0362 (19)	122
O30—H30···N4	0.93	1.94	2.784 (2)	149
O40—H40···O41	0.93	1.76	2.6146 (19)	151

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