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Dimethylammonium 2,4,5-tricarboxybenzoate: an example of the decarbonylation of *N*,*N*-dimethylformamide in the presence of a metal and a benzenepolycarboxylic acid. Is zirconium(IV) the *Tsotsi*?

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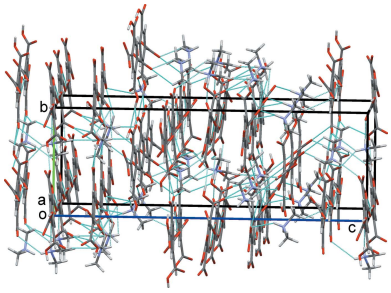
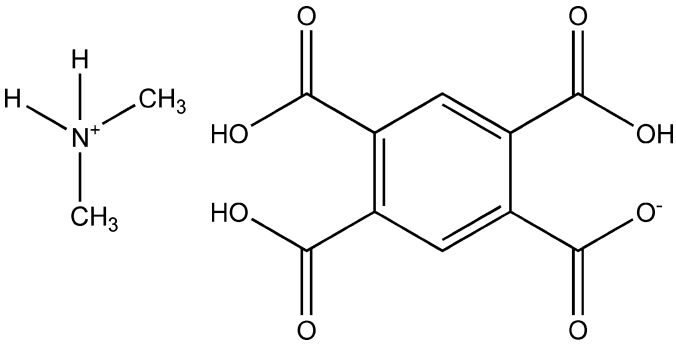
The title salt, $C_2H_8N^+\cdot C_{10}H_5O_8^-$, was the unexpected product of an attempt to prepare a Zr^{IV} metal–organic framework with benzene-1,2,4,5-tetracarboxylic acid (1,2,4,5-H_3B4C). In the reaction, the DMF solvent has been decarbonylated, forming the dimethylammonium cation, with one proton lost from the tetracarboxylic acid. It is proposed that the Zr^{IV} salt acts as a *Tsotsi* or robber, plundering CO from the DMF molecule. The resulting salt crystallizes with two cations and two anions in the asymmetric unit. An intramolecular hydrogen bond forms between a carboxylic acid substituent and the carboxylate group of each of the monodeprotonated (1,2,4,5-H_3B4C$^-$) anions. In the crystal, an extensive array of O—H···O, N—H···O and C—H···O hydrogen bonds generates a three-dimensional network, with columns of cations and anions forming along the *b* axis.

1. Chemical context

The term *Tsotsi* is South African township slang for a street gangster or hoodlum who is known to mug unsuspecting passers-by and steal their goods. Identifying a possible *Tsotsi* on the street is part of everyday township life. We attempted to grow a single crystal of a zirconium-based metal–organic framework incorporating 1,2,4,5-benzenetetracarboxylic acid that we had previously synthesized in powder form, in a dimethylformamide, DMF, solution. Instead this yielded crystals of the unanticipated title compound (I). The unexpected decarbonylation of *N*,*N*-dimethylformamide (DMF) has led us to ponder the possible characteristics of the reagents used that led to this 'plundering' of the DMF. Decarbonylation of DMF has previously been shown to occur under slow evaporation conditions in the presence of coordination complexes (Siddiqui *et al.*, 2012; Chen *et al.*, 2007; Karpova *et al.*, 2004). In these reports, the nitrate salts of Mg^{II} (Siddiqui *et al.*, 2012), Pb^{II} (Chen *et al.*, 2007), Ho^{III} and the chloride salt of Nd^{III} (Karpova *et al.*, 2004) ions were suggested to play a unique catalytic role in the observed decarbonylation reaction. The form of the metals in these reactions was thought to be as six-coordinate metal complexes This suggests that, in the decarbonylation reaction observed here, the active decarbonylation agent could be the chloride salt of Zr^{IV} as this is also likely to be six-coordinate in solution.





The other potential decarbonylation catalyst in this reaction is the benzenetetracarboxylic acid. However, Dale and coworkers have studied the slow evaporation reactions of 1,4-benzenedicarboxylic acid (terephthalic acid; 1,4-H_2B2C), 1,2,3-benzenetricarboxylic acid (hemimellitic acid; 1,2,3-H_3B3C) and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid; 1,2,4,5-H_4B4C) in the absence of metal complexes and no decarbonylation of DMF was observed (Dale & Elsegood, 2004).

Clearly this further implicates the zirconium(IV) as the *Tsotsi* in this decarbonylation reaction, stealing CO from the DMF and forming the dimethylammonium cation (Fig. 1). While the detailed mechanism of the decarbonylation process remains unclear, it is most likely that the formation of this salt is initiated by the zirconium(IV) *Tsotsi*.

2. Structural commentary

The asymmetric unit of the title salt $C_2H_8N^+$ $C_{10}H_5O_8^-$, (I), consists of two anions, 1 and 2 and two cations, 3 and 4, differentiated by the leading numbers in the numbering scheme, Fig. 2. Within the asymmetric unit, both cations and anions are linked by strong N—H···O and weaker C—H···O hydrogen bonds, Table 1, Fig. 3. Bond distances and angles in the approximately tetrahedral dimethylammonium cations are unremarkable.

The benzene rings of the anions are inclined to one another by 6.56 (3)°. In both anions, the two carboxylate substituents lie reasonably close to the benzene ring planes, inclined at 16.16 (19)° for 1 and 6.01 (5)° for 2. One carboxylic acid substituent in each cation also lies close to these planes,

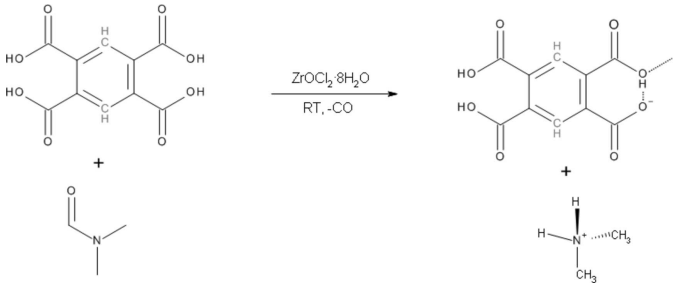


Figure 1
The reaction procedure used in the preparation of (I).

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O13^{i}	0.91	1.86	2.762 (4)	169
N3—H3B···O27	0.91	1.99	2.798 (5)	147
N4—H4A···O26^{ii}	0.91	2.32	3.025 (4)	134
N4—H4A···O27^{ii}	0.91	2.49	2.918 (4)	110
N4—H4A···O12^{iii}	0.91	2.19	2.830 (5)	127
N4—H4B···O16	0.91	1.99	2.879 (5)	167
O11—H11A···O15^{iv}	0.84	1.73	2.560 (4)	171
O14—H14A···O17^{v}	0.84	2.55	3.119 (4)	126
O14—H14A···O18^{v}	0.84	1.77	2.583 (4)	161
O17—H17A···O16	0.84	1.57	2.409 (4)	176
O22—H22A···O23	0.88	1.49	2.370 (4)	179
O25—H25A···O21^{v}	0.84	1.75	2.572 (4)	164
O25—H25A···O22^{v}	0.84	2.59	3.181 (4)	129
O28—H28···O24^{i}	0.84	1.74	2.571 (3)	168
C32—H32C···O15	0.98	2.54	3.234 (6)	128
C41—H41C···O11^{i}	0.98	2.41	3.235 (5)	142
C42—H42C···O21	0.98	2.57	3.519 (6)	164

Symmetry codes: (i) $x, y-1, z$; (ii) $x-1, y, z$; (iii) $y-1, -x+1, z-\frac{1}{4}$; (iv) $x, y+1, z$; (v) $x+1, y, z$.

[5.85 (8)° for 1 and 6.25 (9)° for 2]. This planarity is doubtless aided by the two intramolecular O17—H17A···O16 and O22—H22A···O23 hydrogen bonds that form between a carboxylate oxygen and the OH group of an adjacent carboxylic acid substituent in each of the discrete anions, Fig. 2. Each encloses an $S7$ ring. The other two carboxylic acid substituents in both anions lie well out of the benzene ring planes with dihedral angles ranging from 75.4 (4) to 37.23 (15)°.

3. Supramolecular features

In the crystal structure, a myriad of classical O—H···O and N—H···O hydrogen bonds are found together with non-

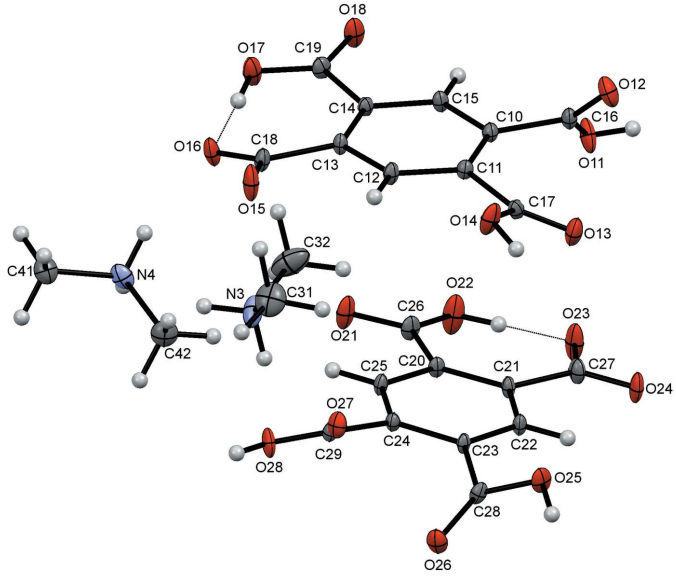


Figure 2
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are drawn as dashed lines.

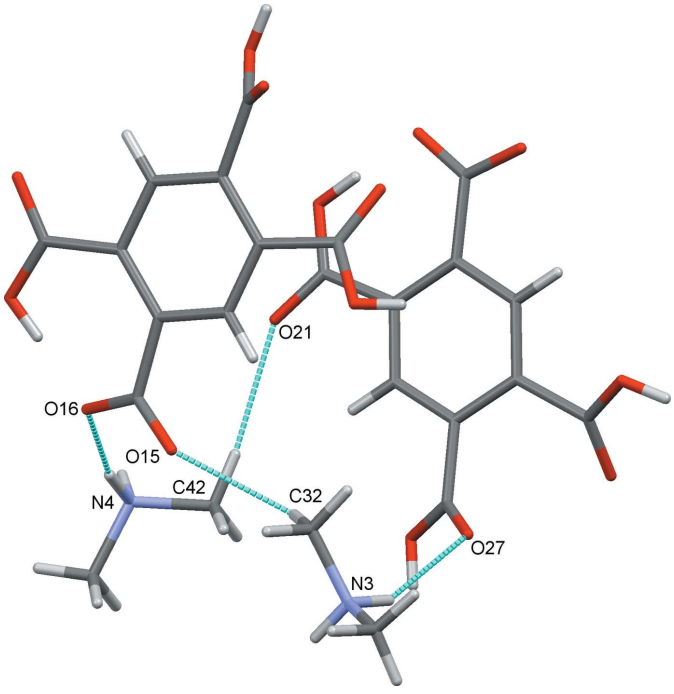


Figure 3
The asymmetric unit of (I), showing the hydrogen bonds formed between the cations and anions. In this and subsequent figures, hydrogen bonds are shown as blue dashed lines.

classical C—H···O hydrogen bonds. These are detailed in Table 1. Each individual anion of type 1 binds to four other type 1 anions through O—H···O hydrogen bonds. Each also binds to four cations, two of type 3 and two of type 4, through

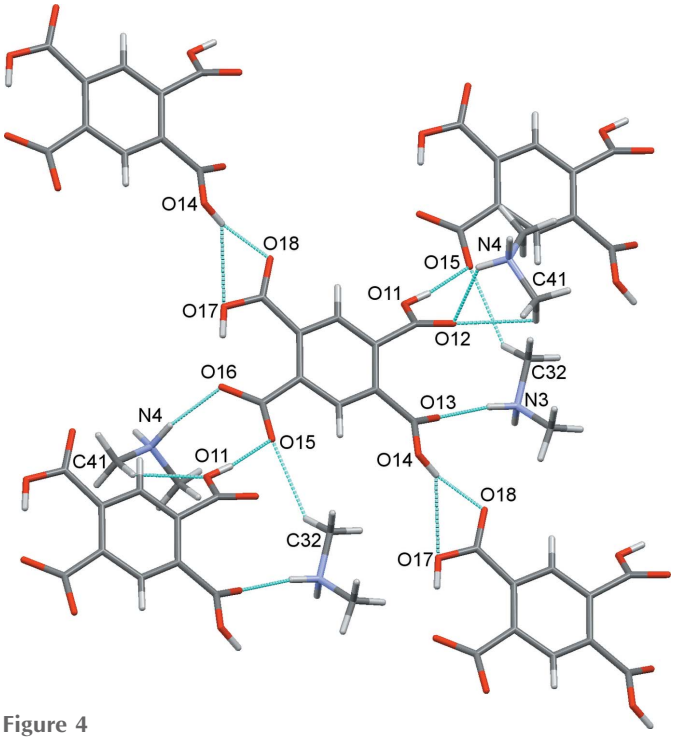


Figure 4
The immediate environment of anion 1.

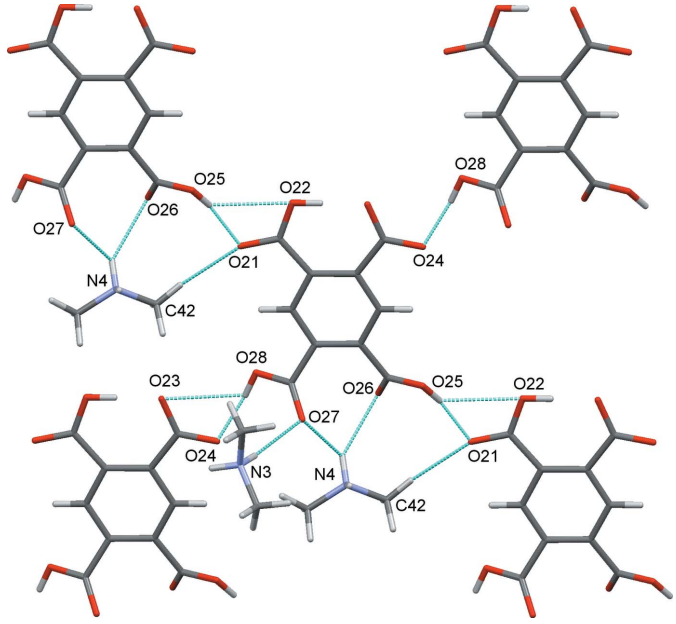


Figure 5
The immediate environment of anion 2.

N—H···O and C—H···O hydrogen bonds, Fig. 4. Similarly, each type 2 anion binds to four other discrete type 2 anions and to three cations one of type 3 and two of type 4, Fig. 5.

Layers built from alternating rows of cations and anions form in the *ab* plane, Fig. 6. These layers are further linked by N—H···O and C—H···O contacts to form a three-dimensional network comprised of linked columns of cations and anions, Fig. 7.

4. Database survey

A search of the Cambridge Structural Database (Version 5.37, update November 2015; Groom *et al.*, 2016) for 1,2,4,5-H_3B4C^- anion yielded 46 hits and of these 35 are purely organic compounds. One particular compound, YIRFOV, reports a 1,2,4,5-H_3B4C^- salt with a tetramethylammonium

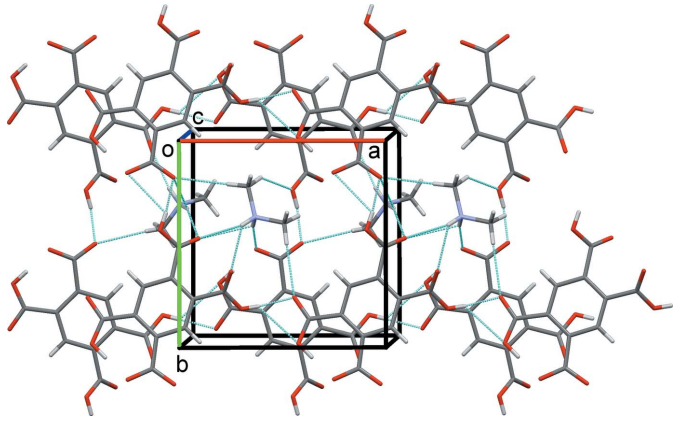


Figure 6
Sheets formed in the *ab* plane by the cations and anions of (I).

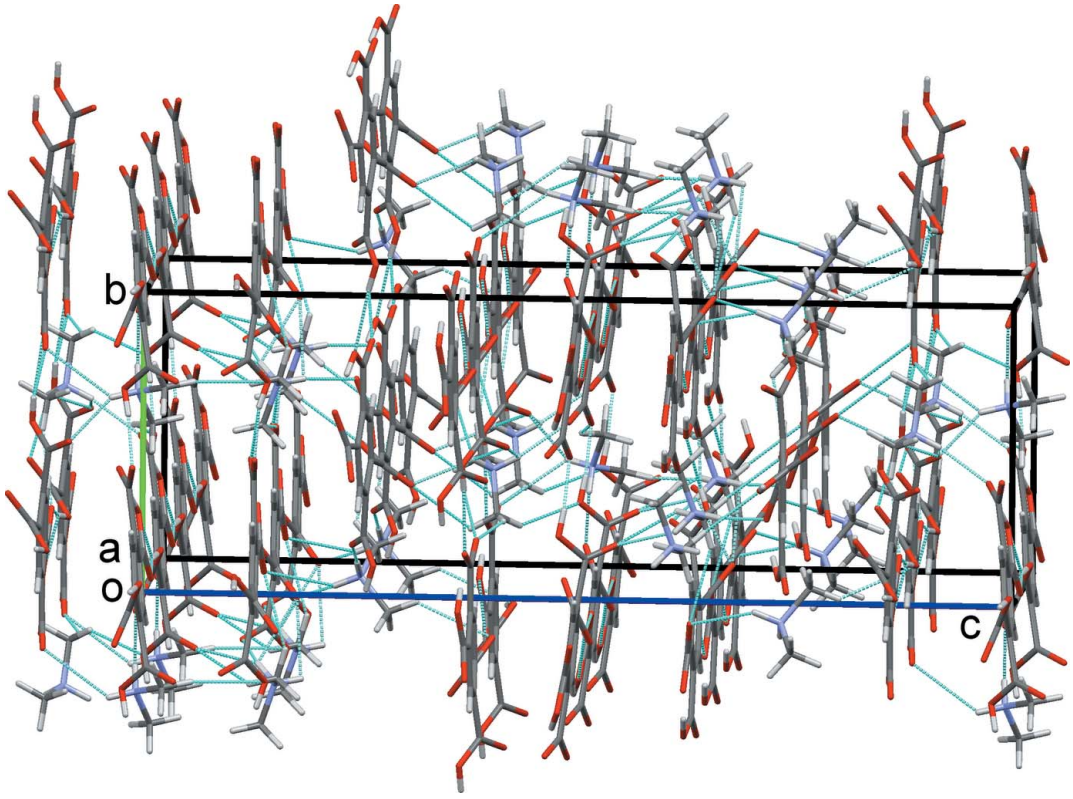


Figure 7
Overall packing for (I), viewed along the *a*-axis direction.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_2H_8N^+\cdot C_{10}H_5O_8^-$
M_r	299.23
Crystal system, space group	Tetragonal, $P4_1$
Temperature (K)	200
a, c (Å)	9.6621 (5), 27.8940 (17)
V (Å^3)	2604.1 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	0.42 × 0.32 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2010)
T_{min}, T_{max}	0.946, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	47565, 6473, 6118
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.134, 1.15
No. of reflections	6473
No. of parameters	388
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.27
Absolute structure	Flack x determined using 2780 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.14 (15)

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ShelXle* (Hübschle *et al.*, 2011), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

cation (Cunha-Silva *et al.*, 2008). This is very similar to the structure reported here. The principal difference between these structures is that the asymmetric unit of YIRFOV comprises one tetramethylammonium cation, one 1,2,4,5-H_3B4C$^-$ anion co-crystallized with half a fully protonated 1,2,4,5-H_4B4C molecule that lies on a centre of inversion. In YIRFOV, the crystal packing is also mediated by an extensive hydrogen-bonding network.

5. Synthesis and crystallization

A 2 mL aqueous solution of $ZrOCl_2\cdot 8H_2O$ (0.04 g, 0.124 mmol) was suspended in 0.5 mL *N*,*N*-dimethylformamide (DMF). A 2 mL aqueous solution of 1,2,4,5-H_4B4C 0.032 g, 0.124 mmol) was similarly suspended in 0.5 mL DMF and the two solutions were combined in a small sample vial. This was placed inside a larger sample vial. 0.5 mL of deionized water was added before it was covered and left until crystallization was complete. After three weeks, yellow–brown cubic crystals formed. These were isolated and used for the X-ray crystallographic analysis.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions and were included in the refinement in the riding-model approximation, with U_{iso}(H)

set to $1.2U_{eq}$(C). The hydrogen atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density, with U_{iso}(H) = $1.5U_{eq}$(C). The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C—-O bond to best fit the experimental electron density with U_{iso}(H) set to $1.5U_{eq}$(O).

Acknowledgements

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supporting information

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Dimethylammonium 2,4,5-tricarboxybenzoate: an example of the decarbonylation of *N*,*N*-dimethylformamide in the presence of a metal and a benzenepolycarboxylic acid. Is zirconium(IV) the *Tsotsi*?

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Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *APEX2* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b) and *ShelXle* (Hübschle *et al.*, 2011); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

Dimethylammonium 2,4,5-tricarboxybenzoate

Crystal data

$C_2H_8N^+·C_{10}H_5O_8^-$
M_r = 299.23
Tetragonal, $P4_1$
a = 9.6621 (5) Å
c = 27.8940 (17) Å
V = 2604.1 (3) Å^3
Z = 8
$F(000)$ = 1248
D_x = 1.526 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9896 reflections
θ = 2.2–28.3°
μ = 0.13 mm^{-1}
T = 200 K
Block, pale yellow
0.42 × 0.32 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (SADABS; Bruker, 2010)
T_{min} = 0.946, T_{max} = 1.000
47565 measured reflections
6473 independent reflections
6118 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 28.3°, θ_{min} = 2.1°
h = −12→12
k = −12→12
l = −37→37

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.134
S = 1.15
6473 reflections
388 parameters
2 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 1.8024P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Absolute structure: Flack *x* determined using 2780 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.14 (15)

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.

Refinement. Carbon and nitrogen-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U(H) set to 1.2 U_{eq}(C) and U_{eq}(N) respectively.
The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C-C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite (Sheldrick, 2008)), with U(H) set to 1.5Ueq(C).
The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C—O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite (Sheldrick, 2008)), with U(H) set to 1.5U_{eq}(C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O11	0.5156 (3)	1.2649 (3)	0.49062 (12)	0.0377 (7)
H11A	0.5377	1.3476	0.4959	0.057*
O12	0.6526 (3)	1.2222 (3)	0.55294 (12)	0.0349 (6)
O13	0.8393 (3)	1.0813 (3)	0.48959 (12)	0.0340 (7)
O14	0.8840 (3)	0.8724 (3)	0.51895 (13)	0.0363 (7)
H14A	0.9655	0.8913	0.5107	0.054*
O15	0.5589 (3)	0.5243 (3)	0.50160 (14)	0.0406 (8)
O16	0.3406 (3)	0.5520 (3)	0.48128 (12)	0.0321 (6)
O17	0.1613 (3)	0.7171 (3)	0.49938 (13)	0.0365 (7)
H17A	0.2233	0.6602	0.4919	0.055*
O18	0.1428 (3)	0.9376 (3)	0.51382 (13)	0.0351 (7)
O21	0.5303 (3)	0.7790 (3)	0.38363 (14)	0.0370 (7)
O22	0.5504 (3)	1.0018 (3)	0.37440 (17)	0.0500 (10)
H22A	0.6137	1.0670	0.3758	0.075*
O23	0.7235 (3)	1.1753 (3)	0.37790 (17)	0.0455 (9)
O24	0.9469 (3)	1.1983 (2)	0.38543 (13)	0.0318 (6)
O25	1.2733 (2)	0.8364 (3)	0.39696 (10)	0.0276 (6)
H25A	1.3548	0.8232	0.3875	0.041*
O26	1.2263 (3)	0.6532 (3)	0.35071 (11)	0.0291 (6)
O27	1.0649 (3)	0.4957 (3)	0.41643 (10)	0.0265 (5)
O28	0.8825 (3)	0.4524 (2)	0.36955 (11)	0.0286 (6)
H28	0.9106	0.3703	0.3714	0.043*
N3	0.9720 (4)	0.3343 (4)	0.49322 (15)	0.0420 (9)
H3A	0.9185	0.2571	0.4910	0.050*
H3B	1.0072	0.3520	0.4636	0.050*
N4	0.3409 (3)	0.3907 (4)	0.39447 (13)	0.0310 (7)
H4A	0.2799	0.4288	0.3734	0.037*
H4B	0.3290	0.4338	0.4232	0.037*
C10	0.5492 (3)	1.0341 (3)	0.51166 (12)	0.0190 (6)

C11	0.6516 (3)	0.9326 (3)	0.50839 (12)	0.0180 (6)
C12	0.6134 (3)	0.7951 (3)	0.50505 (13)	0.0203 (6)
H12	0.6836	0.7263	0.5043	0.024*
C13	0.4749 (3)	0.7538 (3)	0.50279 (12)	0.0181 (6)
C14	0.3713 (3)	0.8560 (3)	0.50605 (12)	0.0182 (6)
C15	0.4121 (3)	0.9940 (3)	0.51066 (13)	0.0193 (6)
H15	0.3426	1.0631	0.5132	0.023*
C16	0.5807 (3)	1.1841 (3)	0.52053 (13)	0.0214 (6)
C17	0.8019 (3)	0.9708 (3)	0.50521 (13)	0.0207 (6)
C18	0.4570 (4)	0.5988 (3)	0.49537 (14)	0.0238 (7)
C19	0.2155 (3)	0.8358 (4)	0.50648 (14)	0.0239 (7)
C20	0.7591 (3)	0.8638 (3)	0.38189 (13)	0.0186 (6)
C21	0.8632 (3)	0.9671 (3)	0.38146 (13)	0.0185 (6)
C22	1.0014 (3)	0.9250 (3)	0.38182 (13)	0.0200 (6)
H22	1.0716	0.9938	0.3817	0.024*
C23	1.0406 (3)	0.7872 (3)	0.38235 (12)	0.0158 (6)
C24	0.9378 (3)	0.6852 (3)	0.38409 (12)	0.0173 (6)
C25	0.7998 (3)	0.7253 (3)	0.38374 (13)	0.0194 (6)
H25	0.7304	0.6558	0.3848	0.023*
C26	0.6027 (3)	0.8836 (4)	0.38037 (15)	0.0249 (7)
C27	0.8424 (4)	1.1233 (3)	0.38165 (15)	0.0266 (7)
C28	1.1904 (3)	0.7498 (3)	0.37547 (13)	0.0201 (6)
C29	0.9707 (3)	0.5344 (3)	0.39091 (12)	0.0186 (6)
C31	1.0866 (6)	0.3067 (6)	0.5262 (2)	0.0530 (13)
H31A	1.1372	0.2244	0.5154	0.080*
H31B	1.0499	0.2906	0.5585	0.080*
H31C	1.1492	0.3864	0.5267	0.080*
C32	0.8850 (6)	0.4510 (7)	0.5079 (3)	0.0627 (16)
H32A	0.9411	0.5354	0.5093	0.094*
H32B	0.8457	0.4323	0.5397	0.094*
H32C	0.8099	0.4633	0.4847	0.094*
C41	0.3069 (5)	0.2421 (4)	0.40027 (17)	0.0353 (9)
H41A	0.3220	0.1939	0.3698	0.053*
H41B	0.2097	0.2326	0.4098	0.053*
H41C	0.3664	0.2017	0.4250	0.053*
C42	0.4831 (4)	0.4183 (5)	0.37732 (19)	0.0395 (10)
H42A	0.4988	0.3687	0.3471	0.059*
H42B	0.5498	0.3865	0.4014	0.059*
H42C	0.4949	0.5179	0.3721	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.0440 (17)	0.0134 (11)	0.0557 (19)	−0.0008 (11)	−0.0229 (14)	−0.0006 (12)
O12	0.0337 (14)	0.0235 (13)	0.0475 (17)	0.0014 (11)	−0.0156 (13)	−0.0105 (12)
O13	0.0244 (13)	0.0226 (12)	0.0550 (18)	−0.0073 (10)	0.0025 (12)	0.0038 (12)
O14	0.0114 (11)	0.0270 (13)	0.070 (2)	−0.0007 (10)	−0.0005 (12)	0.0107 (14)
O15	0.0245 (13)	0.0136 (11)	0.084 (3)	−0.0006 (10)	−0.0132 (15)	−0.0025 (13)

O16	0.0201 (12)	0.0194 (12)	0.0567 (18)	−0.0025 (9)	−0.0041 (12)	−0.0130 (12)
O17	0.0174 (12)	0.0261 (13)	0.066 (2)	−0.0019 (10)	0.0030 (13)	−0.0130 (13)
O18	0.0132 (11)	0.0260 (13)	0.066 (2)	0.0014 (10)	−0.0006 (12)	−0.0076 (13)
O21	0.0109 (11)	0.0223 (13)	0.078 (2)	−0.0005 (9)	−0.0032 (13)	0.0035 (14)
O22	0.0147 (12)	0.0226 (13)	0.113 (3)	0.0058 (10)	−0.0048 (16)	0.0069 (16)
O23	0.0191 (13)	0.0148 (12)	0.102 (3)	0.0052 (9)	−0.0021 (16)	−0.0011 (15)
O24	0.0222 (12)	0.0108 (10)	0.0624 (19)	−0.0022 (9)	−0.0031 (13)	0.0014 (11)
O25	0.0095 (10)	0.0280 (13)	0.0454 (16)	−0.0009 (9)	−0.0013 (10)	−0.0052 (11)
O26	0.0186 (11)	0.0230 (12)	0.0457 (16)	0.0041 (10)	0.0020 (11)	−0.0069 (11)
O27	0.0216 (12)	0.0175 (11)	0.0405 (15)	0.0036 (9)	−0.0048 (10)	0.0043 (10)
O28	0.0314 (13)	0.0099 (10)	0.0445 (16)	−0.0022 (9)	−0.0115 (11)	−0.0007 (10)
N3	0.051 (2)	0.0303 (17)	0.045 (2)	−0.0167 (16)	−0.0150 (18)	0.0110 (15)
N4	0.0235 (15)	0.0280 (16)	0.0414 (19)	0.0082 (12)	−0.0053 (13)	−0.0080 (14)
C10	0.0182 (14)	0.0144 (13)	0.0243 (16)	−0.0007 (11)	−0.0005 (12)	−0.0010 (11)
C11	0.0137 (13)	0.0149 (13)	0.0255 (16)	0.0009 (11)	−0.0005 (11)	0.0005 (11)
C12	0.0129 (14)	0.0152 (14)	0.0328 (18)	−0.0002 (11)	−0.0014 (12)	−0.0004 (12)
C13	0.0130 (13)	0.0119 (13)	0.0295 (17)	−0.0008 (11)	−0.0020 (12)	−0.0005 (11)
C14	0.0127 (13)	0.0161 (14)	0.0258 (16)	−0.0010 (11)	0.0010 (11)	−0.0023 (12)
C15	0.0124 (13)	0.0149 (14)	0.0305 (16)	0.0009 (10)	−0.0018 (12)	−0.0035 (12)
C16	0.0165 (14)	0.0143 (13)	0.0333 (18)	−0.0014 (11)	0.0003 (13)	−0.0035 (12)
C17	0.0147 (14)	0.0178 (14)	0.0297 (17)	−0.0020 (11)	0.0027 (12)	−0.0058 (12)
C18	0.0212 (15)	0.0131 (13)	0.0370 (19)	−0.0018 (12)	0.0005 (14)	0.0002 (13)
C19	0.0128 (14)	0.0244 (16)	0.0344 (19)	−0.0008 (12)	−0.0003 (13)	−0.0047 (14)
C20	0.0102 (12)	0.0152 (14)	0.0304 (17)	0.0013 (10)	−0.0002 (12)	−0.0016 (12)
C21	0.0153 (14)	0.0102 (12)	0.0299 (16)	0.0005 (10)	−0.0018 (12)	−0.0015 (12)
C22	0.0145 (13)	0.0118 (13)	0.0336 (17)	−0.0023 (10)	0.0007 (13)	−0.0016 (12)
C23	0.0092 (12)	0.0124 (13)	0.0258 (15)	−0.0009 (10)	−0.0019 (11)	−0.0008 (11)
C24	0.0134 (13)	0.0133 (13)	0.0253 (15)	−0.0013 (11)	0.0008 (12)	−0.0014 (12)
C25	0.0130 (13)	0.0139 (14)	0.0312 (17)	−0.0029 (11)	−0.0001 (12)	0.0007 (12)
C26	0.0106 (13)	0.0223 (15)	0.042 (2)	0.0011 (11)	−0.0007 (13)	−0.0013 (15)
C27	0.0236 (16)	0.0138 (14)	0.042 (2)	0.0024 (12)	−0.0014 (15)	−0.0009 (14)
C28	0.0112 (13)	0.0157 (14)	0.0334 (18)	0.0017 (10)	0.0010 (12)	0.0054 (12)
C29	0.0158 (14)	0.0135 (13)	0.0267 (16)	−0.0007 (11)	0.0006 (12)	0.0008 (11)
C31	0.051 (3)	0.052 (3)	0.056 (3)	0.004 (2)	−0.015 (2)	0.013 (2)
C32	0.043 (3)	0.076 (4)	0.069 (4)	0.015 (3)	0.019 (3)	0.024 (3)
C41	0.034 (2)	0.032 (2)	0.039 (2)	0.0016 (16)	−0.0071 (17)	−0.0011 (17)
C42	0.028 (2)	0.039 (2)	0.051 (3)	0.0064 (17)	0.0007 (18)	−0.001 (2)

Geometric parameters (Å, º)

O11—C16	1.304 (5)	C11—C12	1.382 (4)
O11—H11A	0.8400	C11—C17	1.501 (4)
O12—C16	1.198 (5)	C12—C13	1.398 (4)
O13—C17	1.208 (4)	C12—H12	0.9500
O14—C17	1.297 (4)	C13—C14	1.409 (4)
O14—H14A	0.8400	C13—C18	1.522 (4)
O15—C18	1.232 (5)	C14—C15	1.396 (4)
O16—C18	1.274 (4)	C14—C19	1.518 (4)

O17—C19	1.276 (4)	C15—H15	0.9500
O17—H17A	0.8400	C20—C25	1.396 (4)
O18—C19	1.226 (4)	C20—C21	1.418 (4)
O21—C26	1.233 (4)	C20—C26	1.523 (4)
O22—C26	1.260 (4)	C21—C22	1.396 (4)
O22—H22A	0.8788	C21—C27	1.522 (4)
O23—C27	1.258 (4)	C22—C23	1.384 (4)
O24—C27	1.248 (4)	C22—H22	0.9500
O25—C28	1.304 (4)	C23—C24	1.400 (4)
O25—H25A	0.8400	C23—C28	1.504 (4)
O26—C28	1.211 (4)	C24—C25	1.388 (4)
O27—C29	1.214 (4)	C24—C29	1.504 (4)
O28—C29	1.307 (4)	C25—H25	0.9500
O28—H28	0.8400	C31—H31A	0.9800
N3—C31	1.463 (6)	C31—H31B	0.9800
N3—C32	1.465 (8)	C31—H31C	0.9800
N3—H3A	0.9100	C32—H32A	0.9800
N3—H3B	0.9100	C32—H32B	0.9800
N4—C42	1.479 (6)	C32—H32C	0.9800
N4—C41	1.481 (5)	C41—H41A	0.9800
N4—H4A	0.9100	C41—H41B	0.9800
N4—H4B	0.9100	C41—H41C	0.9800
C10—C15	1.381 (4)	C42—H42A	0.9800
C10—C11	1.396 (4)	C42—H42B	0.9800
C10—C16	1.501 (4)	C42—H42C	0.9800

C16—O11—H11A	109.5	C22—C21—C20	118.3 (3)
C17—O14—H14A	109.5	C22—C21—C27	114.6 (3)
C19—O17—H17A	109.5	C20—C21—C27	127.2 (3)
C26—O22—H22A	111.4	C23—C22—C21	122.9 (3)
C28—O25—H25A	109.5	C23—C22—H22	118.6
C29—O28—H28	109.5	C21—C22—H22	118.6
C31—N3—C32	113.5 (5)	C22—C23—C24	118.9 (3)
C31—N3—H3A	108.9	C22—C23—C28	119.6 (3)
C32—N3—H3A	108.9	C24—C23—C28	121.2 (3)
C31—N3—H3B	108.9	C25—C24—C23	119.0 (3)
C32—N3—H3B	108.9	C25—C24—C29	118.3 (3)
H3A—N3—H3B	107.7	C23—C24—C29	122.5 (3)
C42—N4—C41	114.6 (3)	C24—C25—C20	122.6 (3)
C42—N4—H4A	108.6	C24—C25—H25	118.7
C41—N4—H4A	108.6	C20—C25—H25	118.7
C42—N4—H4B	108.6	O21—C26—O22	121.7 (3)
C41—N4—H4B	108.6	O21—C26—C20	117.3 (3)
H4A—N4—H4B	107.6	O22—C26—C20	121.0 (3)
C15—C10—C11	118.7 (3)	O24—C27—O23	120.9 (3)
C15—C10—C16	118.0 (3)	O24—C27—C21	118.0 (3)
C11—C10—C16	123.1 (3)	O23—C27—C21	121.1 (3)
C12—C11—C10	119.4 (3)	O26—C28—O25	125.5 (3)

C12—C11—C17	119.4 (3)	O26—C28—C23	122.2 (3)
C10—C11—C17	121.1 (3)	O25—C28—C23	112.2 (3)
C11—C12—C13	122.2 (3)	O27—C29—O28	124.7 (3)
C11—C12—H12	118.9	O27—C29—C24	122.0 (3)
C13—C12—H12	118.9	O28—C29—C24	113.1 (3)
C12—C13—C14	118.5 (3)	N3—C31—H31A	109.5
C12—C13—C18	113.3 (3)	N3—C31—H31B	109.5
C14—C13—C18	128.2 (3)	H31A—C31—H31B	109.5
C15—C14—C13	118.3 (3)	N3—C31—H31C	109.5
C15—C14—C19	113.7 (3)	H31A—C31—H31C	109.5
C13—C14—C19	127.9 (3)	H31B—C31—H31C	109.5
C10—C15—C14	122.8 (3)	N3—C32—H32A	109.5
C10—C15—H15	118.6	N3—C32—H32B	109.5
C14—C15—H15	118.6	H32A—C32—H32B	109.5
O12—C16—O11	125.4 (3)	N3—C32—H32C	109.5
O12—C16—C10	122.5 (3)	H32A—C32—H32C	109.5
O11—C16—C10	112.0 (3)	H32B—C32—H32C	109.5
O13—C17—O14	124.8 (3)	N4—C41—H41A	109.5
O13—C17—C11	121.9 (3)	N4—C41—H41B	109.5
O14—C17—C11	113.2 (3)	H41A—C41—H41B	109.5
O15—C18—O16	122.8 (3)	N4—C41—H41C	109.5
O15—C18—C13	117.7 (3)	H41A—C41—H41C	109.5
O16—C18—C13	119.4 (3)	H41B—C41—H41C	109.5
O18—C19—O17	120.8 (3)	N4—C42—H42A	109.5
O18—C19—C14	117.8 (3)	N4—C42—H42B	109.5
O17—C19—C14	121.5 (3)	H42A—C42—H42B	109.5
C25—C20—C21	118.4 (3)	N4—C42—H42C	109.5
C25—C20—C26	113.6 (3)	H42A—C42—H42C	109.5
C21—C20—C26	128.0 (3)	H42B—C42—H42C	109.5

C15—C10—C11—C12	−1.0 (5)	C25—C20—C21—C22	1.4 (5)
C16—C10—C11—C12	173.4 (3)	C26—C20—C21—C22	−178.3 (3)
C15—C10—C11—C17	174.9 (3)	C25—C20—C21—C27	−177.2 (4)
C16—C10—C11—C17	−10.6 (5)	C26—C20—C21—C27	3.0 (6)
C10—C11—C12—C13	2.7 (5)	C20—C21—C22—C23	0.3 (5)
C17—C11—C12—C13	−173.3 (3)	C27—C21—C22—C23	179.1 (3)
C11—C12—C13—C14	−2.7 (5)	C21—C22—C23—C24	−2.0 (5)
C11—C12—C13—C18	175.6 (3)	C21—C22—C23—C28	171.1 (3)
C12—C13—C14—C15	0.9 (5)	C22—C23—C24—C25	2.0 (5)
C18—C13—C14—C15	−177.0 (3)	C28—C23—C24—C25	−171.1 (3)
C12—C13—C14—C19	−177.3 (3)	C22—C23—C24—C29	−172.2 (3)
C18—C13—C14—C19	4.7 (6)	C28—C23—C24—C29	14.7 (5)
C11—C10—C15—C14	−0.7 (5)	C23—C24—C25—C20	−0.2 (5)
C16—C10—C15—C14	−175.4 (3)	C29—C24—C25—C20	174.2 (3)
C13—C14—C15—C10	0.7 (5)	C21—C20—C25—C24	−1.5 (5)
C19—C14—C15—C10	179.2 (3)	C26—C20—C25—C24	178.3 (3)
C15—C10—C16—O12	123.0 (4)	C25—C20—C26—O21	4.0 (5)
C11—C10—C16—O12	−51.5 (5)	C21—C20—C26—O21	−176.3 (4)

C15—C10—C16—O11	−53.8 (4)	C25—C20—C26—O22	−173.7 (4)
C11—C10—C16—O11	131.6 (4)	C21—C20—C26—O22	6.1 (6)
C12—C11—C17—O13	150.8 (4)	C22—C21—C27—O24	−4.8 (5)
C10—C11—C17—O13	−25.2 (5)	C20—C21—C27—O24	173.9 (4)
C12—C11—C17—O14	−26.7 (5)	C22—C21—C27—O23	174.9 (4)
C10—C11—C17—O14	157.3 (3)	C20—C21—C27—O23	−6.4 (7)
C12—C13—C18—O15	14.0 (5)	C22—C23—C28—O26	−138.4 (4)
C14—C13—C18—O15	−168.0 (4)	C24—C23—C28—O26	34.7 (5)
C12—C13—C18—O16	−163.2 (4)	C22—C23—C28—O25	38.4 (5)
C14—C13—C18—O16	14.8 (6)	C24—C23—C28—O25	−148.6 (3)
C15—C14—C19—O18	−4.7 (5)	C25—C24—C29—O27	−138.4 (4)
C13—C14—C19—O18	173.7 (4)	C23—C24—C29—O27	35.8 (5)
C15—C14—C19—O17	175.2 (4)	C25—C24—C29—O28	37.1 (5)
C13—C14—C19—O17	−6.4 (6)	C23—C24—C29—O28	−148.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O13^{i}	0.91	1.86	2.762 (4)	169
N3—H3*B*···O27	0.91	1.99	2.798 (5)	147
N4—H4*A*···O26^{ii}	0.91	2.32	3.025 (4)	134
N4—H4*A*···O27^{ii}	0.91	2.49	2.918 (4)	110
N4—H4*A*···O12^{iii}	0.91	2.19	2.830 (5)	127
N4—H4*B*···O16	0.91	1.99	2.879 (5)	167
O11—H11*A*···O15^{iv}	0.84	1.73	2.560 (4)	171
O14—H14*A*···O17^{v}	0.84	2.55	3.119 (4)	126
O14—H14*A*···O18^{v}	0.84	1.77	2.583 (4)	161
O17—H17*A*···O16	0.84	1.57	2.409 (4)	176
O22—H22*A*···O23	0.88	1.49	2.370 (4)	179
O25—H25*A*···O21^{v}	0.84	1.75	2.572 (4)	164
O25—H25*A*···O22^{v}	0.84	2.59	3.181 (4)	129
O28—H28···O24^{i}	0.84	1.74	2.571 (3)	168
C32—H32*C*···O15	0.98	2.54	3.234 (6)	128
C41—H41*C*···O11^{i}	0.98	2.41	3.235 (5)	142
C42—H42*C*···O21	0.98	2.57	3.519 (6)	164

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*−1, *y*, *z*; (iii) *y*−1, −*x*+1, *z*−1/4; (iv) *x*, *y*+1, *z*; (v) *x*+1, *y*, *z*.