IUCrData

ISSN 2414-3146

Tetraaqua[2,6-diacetylpyridine bis(semicarbazone)]samarium(III) trinitrate

Michael Gioia, Guy Crundwell* and Barry L. Westcott

Central Connecticut State University, Department of Chemistry & Biochemistry, 1619 Stanley Street, New Britain, CT 06050, USA. *Correspondence e-mail: crundwellg@ccsu.edu

Received 8 October 2018
Accepted 15 October 2018

Edited by J. Simpson, University of Otago, New Zealand

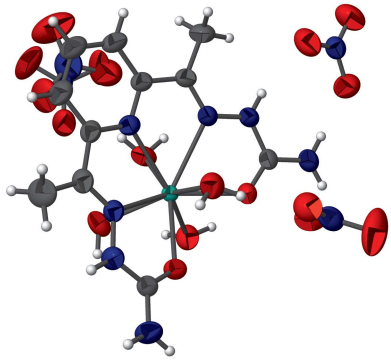
Keywords: crystal structure; lanthanide(III) salts; DAPSC.

CCDC reference: 1873366

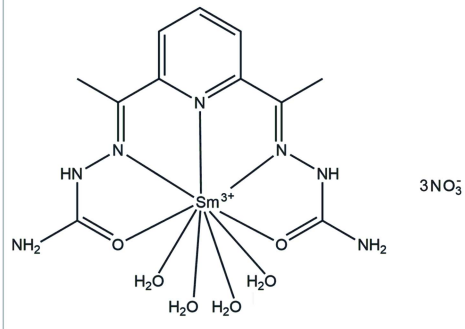
Structural data: full structural data are available from iucrdata.iucr.org

The structure of tetraaqua[2,6-diacetylpyridine bis(semicarbazone)]-samarium(III) trinitrate, $[Sm(C_{11}H_{15}N_7O_2)(H_2O)_4](NO_3)_3$, has monoclinic ($P2_1/c$) symmetry. The 2,6-diacetylpyridine (DAPSC) ligand is pentadentate. The coordination of the DAPSC ligand and four coordinated water molecules around the metal cation is best described as a distorted tricapped trigonal prism. The structure displays intermolecular hydrogen bonding. The structure is isomorphous with many other published lanthanide(III) nitrate salts with the DAPSC ligand, 2,6-diacetylpyridinebis(semicarbazone). One of the three nitrate counter-anions is disordered, which is consistent with the structures of other +3 lanthanide nitrate salts with DAPSC. Refinement of occupancies for the disordered nitrate group gave major and minor occupancies of 54.9 (14) and 45.1 (14)%, respectively.

3D view



Chemical scheme



Structure description

2,6-Diacetylpyridinebis(semicarbazone), DAPSC, is a potential pentadentate ligand that has gained interest in the design of single molecule magnets (Qian *et al.*, 2013). DAPSC has also gained interest as a potential antimicrobial agent in its metal-coordinated form. Kasuga and coworkers studied several semicarbazones and their zinc complexes as potential antibacterial agents. Whereas DAPSC alone showed no ability to inhibit the growth of several bacteria, its zinc salts with nitrate and acetate anions showed modest ability to inhibit the growth of *E. coli* and *P. aeuginosa* (Gram-negative) and of *S. aureus* and *B. subtilis* (Gram-positive) bacteria (Kasuga *et al.*, 2003). Compared to the other zinc semicarbazone structures in the study, the authors postulated that antibacterial activity is enhanced when the metal–semicarbazone complex has extensive hydrogen-bonding interactions between the coordinated water molecules and the counter-anions (Kasuga *et al.*, 2003). The authors also proposed a relationship between increased antibacterial

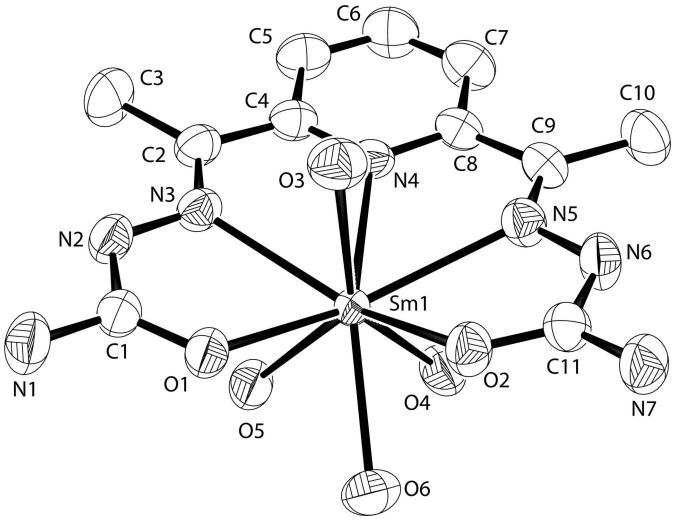


Figure 1
An *ORTEP* plot (Farrugia, 2012) of tetraaqua[2,6-diacetylpyridinebis(-semicarbazone)]samarium(III) trinitrate with 50% probability ellipsoids. Hydrogen atoms and the nitrate anions omitted for clarity.

activity and coordination number during a study of bismuth(III) semicarbazone complexes where an eight-coordinate Bi^{III} DAPSC complex was more active in its inhibition of bacteria than bismuth(III) carbazones with lower coordination numbers (Nomiya *et al.*, 2004).

Herein we report the room temperature crystal structure of a samarium(III) nitrate complex with DAPSC. Tetraaqua[2,6-diacetylpyridinebis(semicarbazone)]samarium(III) trinitrate (Fig. 1) is isomorphous with other previously published lanthanium(III) nitrate DAPSC complexes such as dysprosium(III) (Sasnovskaya *et al.*, 2018), gadolinium(III) (Sommerer *et al.*, 1993), europium(III), and holmium (III) (Palenik *et al.*, 2006). All cations in these complexes with DAPSC have four coordinated water molecules such that their coordination geometry is best described as a distorted tricapped trigonal prism. The DAPSC ligand is nearly planar. The r.m.s. deviation of the thirteen atoms Sm1, O1, C1, N2, N3, C4, N4, C8, C9, N5, N6, C11, O2 is only 0.221 (3). Like the other salts, the samarium salt also has a nitrate disorder which was modeled. One of the three nitrate groups displays disorder over two orientations giving major and minor occupancies of 54.9 (14) and 45.1(14)%, respectively. The four coordinated water molecules are involved in an extensive hydrogen-bonding network (Table 1) with the three nitrate counter-anions as well. Fig. 2 shows the packing highlighting the hydrogen-bond interactions.

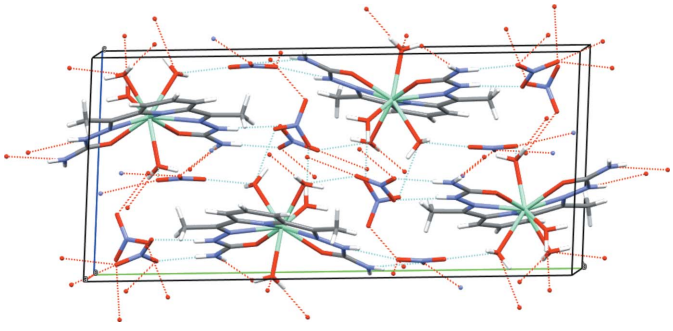


Figure 2
Packing (Mercury; Macrae *et al.*, 2008) as viewed along the (100) direction showing the counter-anions as well as hydrogen-bonding interactions (dashed lines). The minor component of the disordered nitrate group was omitted for clarity.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3*A*···O9	0.86	2.04	2.895 (6)	173
O4—H4*B*···O14	0.88	2.33	3.050 (15)	139
O4—H4*B*···O13	0.88	1.82	2.638 (11)	155
O4—H4*B*···O15*B*	0.88	2.11	2.805 (19)	135
O4—H4*B*···N10	0.88	2.42	3.278 (9)	164
O4—H4*A*···O14^{i}	0.88	1.89	2.706 (9)	153
O4—H4*A*···O15*B*^{i}	0.88	1.96	2.735 (19)	147
O4—H4*A*···O14*B*^{i}	0.88	2.47	3.239 (17)	146
O4—H4*A*···N10*B*^{i}	0.88	2.57	3.420 (15)	164
O5—H5*A*···O12^{ii}	0.90	2.21	2.957 (6)	141
O5—H5*B*···O7^{iii}	0.90	1.93	2.767 (5)	155
O5—H5*B*···N8^{iii}	0.90	2.63	3.511 (5)	170
O5—H5*B*···O8^{iii}	0.90	2.66	3.455 (6)	149
O6—H6*A*···O8^{iv}	0.94	2.34	3.055 (6)	133
O6—H6*A*···O9^{iv}	0.94	2.33	3.192 (6)	154
O6—H6*B*···O8^{iii}	0.93	1.89	2.812 (6)	171
N1—H1*A*···O10^{iv}	0.86	2.11	2.938 (6)	162
N1—H1*B*···O13^{v}	0.86	1.93	2.780 (8)	173
N1—H1*B*···O13*B*^{v}	0.86	2.18	2.936 (13)	146
N2—H2···O15^{v}	0.86	2.06	2.914 (11)	175
N2—H2···O13*B*^{v}	0.86	2.03	2.801 (13)	149
O3—H3*A*···O2	0.86	2.53	2.833 (5)	102
O3—H3*B*···N3	0.86	2.56	2.858 (5)	101
O4—H4*A*···N5	0.88	2.52	2.831 (5)	101
N6—H6···O11	0.86	2.19	3.031 (5)	166
N7—H7*A*···O2^{iv}	0.86	2.29	3.095 (5)	156
N7—H7*B*···O10	0.86	2.16	2.995 (6)	163

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

Synthesis and crystallization

2,6-diacetylpyridine, semicarbazide hydrochloride and samarium(III) nitrate were obtained from Sigma Aldrich and used without further purification. All other solvents and chemicals used were reagent grade.

Preparation of DAPSC

1.954 g of 2,6-diacetylpyridine (11.97 mmol) were dissolved in 100 ml of 95% ethanol. 2.670 g (23.94 mmol) semicarbazide hydrochloride and 1.964 g (23.94 mmol) sodium acetate were added to this solution and stirred, and deionized water was added until the solids dissolved completely. The solution was then heated, and a precipitate formed within 1 min. The white precipitate was removed by vacuum filtration. Yield 2.57 g or 56% DAPSC.

Preparation of $[Sm(DAPSC)(H_2O)_4](NO_3)_3$

Approximately 1.55 mmol DAPSC and 0.75 mmol $Sm(NO_3)_3{\cdot}xH_2O$ were dissolved in 40 ml of deionized water. The solution was then stirred and heated to 52°C for 1 h. The solution was filtered hot and left in an open beaker to evaporate slowly. After several days, X-ray quality crystals were obtained and removed through filtration. Samples selected for study displayed uniform birefringence.

Refinement

Crystal and refinement details are shown in Table 2. A disordered nitrate group was refined by restraining N—O and O—O distances along with allowing the site occupancy for each portion of the disordered group to refine. Refinement of occupancies for the disordered nitrate group gave major and minor occupancies of 54.9(14) and 45.1(14)%, respectively.

Funding information

The authors would like to thank CSU–AAUP for the research funding.

References

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Kasuga, N. C., Sekino, K., Ishikawa, M., Honda, A., Yokoyama, M., Nakano, S., Shimada, N., Koumo, C. & Nomiya, K. (2003). *J. Inorg. Biochem.* **96**, 298–310.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Nomiya, K., Sekino, K., Ishikawa, M., Honda, A., Yokoyama, M., Kasuga, N. C., Yokoyama, H., Nakano, S. & Onodera, K. (2004). *J. Inorg. Biochem.* **98**, 601–615.
Palenik, R. C., Abboud, K. A., Summers, S. P., Reitfort, L. L. & Palenik, G. J. (2006). *Inorg. Chim. Acta*, **359**, 4645–4650.
Qian, K., Huang, X.-C., Zhou, C., You, X.-Z., Wang, X.-Y. & Dunbar, K. R. (2013). *J. Am. Chem. Soc.* **135**, 13302–13305.
Rigaku OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Sasnovskaya, V. D., Kopotkov, V. A., Kazakova, A. V., Talantsev, A. D., Morgunov, R. B., Simonov, S. V., Zorina, L. V., Mironov, V. S. & Yagubskii, E. B. (2018). *New J. Chem.* **42**, 14883–14893.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Sm(C_{11}H_{15}N_7O_2)(H_2O)_4](NO_3)_3$
M_r	685.74
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	10.0164 (5), 22.7494 (3), 15.0848 (8)
β (°)	138.151 (10)
V (Å^3)	2293.3 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.66
Crystal size (mm)	0.34 × 0.30 × 0.28
Data collection	
Diffractometer	Rigaku Oxford Diffraction Xcalibur Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.580, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	123615, 9028, 6975
R_{int}	0.097
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.854
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.127, 1.03
No. of reflections	9028
No. of parameters	378
No. of restraints	12
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.71, −1.43

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

Sommerer, S. O., Westcott, B. L., Cundari, T. R. & Krause, J. A. (1993). *Inorg. Chim. Acta*, **209**, 101–104.

full crystallographic data

IUCrData (2018). **3**, x181454 [https://doi.org/10.1107/S2414314618014542]

Tetraaqua[2,6-diacetylpyridine bis(semicarbazone)]samarium(III) trinitrate

Michael Gioia, Guy Crundwell and Barry L. Westcott

Tetraaqua[2,6-diacetylpyridine bis(semicarbazone)]samarium(III) trinitrate

Crystal data

$[Sm(C_{11}H_{15}N_7O_2)(H_2O)_4](NO_3)_3$
M_r = 685.74
Monoclinic, $P2_1/c$
a = 10.0164 (5) Å
b = 22.7494 (3) Å
c = 15.0848 (8) Å
β = 138.151 (10)°
V = 2293.3 (3) Å^3
Z = 4
$F(000)$ = 1364
D_x = 1.986 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 23000 reflections
θ = 4.3–32.9°
μ = 2.66 mm^{-1}
T = 293 K
Block, yellow
0.34 × 0.30 × 0.28 mm

Data collection

Rigaku Oxford Diffraction Xcalibur Sapphire3 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.1790 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)
T_{min} = 0.580, T_{max} = 1.000
123615 measured reflections
9028 independent reflections
6975 reflections with $I > 2\sigma(I)$
R_{int} = 0.097
θ_{max} = 37.4°, θ_{min} = 4.1°
h = −15→15
k = −35→34
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.127
S = 1.03
9028 reflections
378 parameters
12 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
$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 3.2075P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.71 e Å^{-3}
$\Delta\rho_{min}$ = −1.43 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.

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 $F^2 > 2\text{sigma}(F^2)$ 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}	Occ. (<1)
Sm1	0.43786 (2)	0.39014 (2)	0.21680 (2)	0.02632 (6)	
O1	0.1686 (4)	0.33450 (12)	0.1319 (3)	0.0427 (6)	
O2	0.2300 (4)	0.47121 (12)	0.0923 (3)	0.0427 (6)	
O3	0.2453 (5)	0.37078 (16)	−0.0110 (3)	0.0520 (7)	
H3A	0.1393	0.3921	−0.0633	0.078*	
H3B	0.2007	0.3354	−0.0319	0.078*	
O4	0.7198 (5)	0.43890 (15)	0.4159 (3)	0.0520 (7)	
H4A	0.7277	0.4753	0.4004	0.078*	
H4B	0.8312	0.4230	0.4514	0.078*	
O5	0.5973 (5)	0.33437 (13)	0.4133 (3)	0.0497 (7)	
H5A	0.5071	0.3152	0.4018	0.074*	
H5B	0.6561	0.3581	0.4821	0.074*	
O6	0.3400 (5)	0.43687 (15)	0.3072 (3)	0.0531 (8)	
H6A	0.3160	0.4773	0.2902	0.080*	
H6B	0.4425	0.4369	0.3999	0.080*	
N1	0.0147 (6)	0.24779 (17)	0.0794 (5)	0.0550 (10)	
H1A	−0.0845	0.2645	0.0564	0.066*	
H1B	0.0166	0.2102	0.0742	0.066*	
N2	0.3166 (5)	0.25034 (14)	0.1562 (4)	0.0428 (7)	
H2	0.3179	0.2126	0.1530	0.051*	
N3	0.4651 (5)	0.28430 (14)	0.1948 (3)	0.0381 (6)	
N4	0.7029 (5)	0.36044 (15)	0.2395 (3)	0.0388 (6)	
N5	0.5609 (5)	0.46636 (15)	0.1683 (4)	0.0411 (7)	
N6	0.4595 (5)	0.51843 (15)	0.1209 (4)	0.0452 (8)	
H6	0.5039	0.5498	0.1178	0.054*	
N7	0.1732 (6)	0.56525 (16)	0.0225 (4)	0.0510 (9)	
H7A	0.0595	0.5665	−0.0071	0.061*	
H7B	0.2161	0.5956	0.0155	0.061*	
C1	0.1656 (6)	0.28011 (16)	0.1229 (4)	0.0380 (7)	
C2	0.6125 (7)	0.26076 (18)	0.2265 (4)	0.0421 (8)	
C3	0.6383 (10)	0.1961 (2)	0.2250 (7)	0.0695 (16)	
H3C	0.7503	0.1823	0.3144	0.104*	
H3D	0.6616	0.1886	0.1747	0.104*	
H3E	0.5194	0.1759	0.1848	0.104*	
C4	0.7537 (6)	0.30343 (19)	0.2572 (4)	0.0408 (8)	
C5	0.9236 (7)	0.2862 (2)	0.2931 (5)	0.0538 (11)	
H5	0.9588	0.2467	0.3063	0.065*	
C6	1.0377 (8)	0.3290 (3)	0.3083 (6)	0.0609 (13)	
H6C	1.1538	0.3186	0.3355	0.073*	
C7	0.9796 (8)	0.3867 (2)	0.2833 (6)	0.0542 (12)	

H7	1.0520	0.4156	0.2895	0.065*	
C8	0.8098 (6)	0.4013 (2)	0.2484 (4)	0.0413 (8)	
C9	0.7288 (6)	0.46160 (19)	0.2099 (4)	0.0411 (8)	
C10	0.8339 (8)	0.5109 (2)	0.2159 (6)	0.0581 (12)	
H10A	0.7642	0.5470	0.1925	0.087*	
H10B	0.8367	0.5034	0.1547	0.087*	
H10C	0.9684	0.5139	0.3043	0.087*	
C11	0.2812 (6)	0.51712 (17)	0.0783 (4)	0.0395 (8)	
O7	−0.1567 (6)	0.37785 (16)	−0.3329 (4)	0.0583 (9)	
O8	−0.3794 (8)	0.4429 (3)	−0.4153 (4)	0.1019 (19)	
O9	−0.1190 (6)	0.43889 (19)	−0.2064 (4)	0.0661 (10)	
N8	−0.2184 (6)	0.41941 (17)	−0.3193 (4)	0.0478 (8)	
O10	0.3359 (7)	0.6816 (2)	0.0444 (5)	0.0779 (12)	
O11	0.5420 (7)	0.63334 (18)	0.0667 (5)	0.0734 (11)	
O12	0.5472 (8)	0.72787 (19)	0.0658 (5)	0.0800 (13)	
N9	0.4759 (6)	0.68165 (16)	0.0580 (4)	0.0472 (8)	
N10	1.1785 (13)	0.4007 (4)	0.5921 (13)	0.057 (3)	0.549 (14)
O13	1.0404 (14)	0.3721 (4)	0.5584 (10)	0.081 (3)	0.549 (14)
O14	1.140 (2)	0.4516 (4)	0.5481 (15)	0.088 (5)	0.549 (14)
O15	1.3432 (14)	0.3775 (4)	0.6638 (14)	0.124 (6)	0.549 (14)
N10B	1.218 (2)	0.4132 (7)	0.583 (2)	0.079 (5)	0.451 (14)
O13B	1.172 (3)	0.3651 (5)	0.5935 (18)	0.118 (6)	0.451 (14)
O14B	1.385 (2)	0.4221 (7)	0.633 (2)	0.140 (8)	0.451 (14)
O15B	1.102 (3)	0.4556 (8)	0.532 (3)	0.118 (9)	0.451 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sm1	0.02879 (9)	0.02325 (9)	0.03029 (9)	0.00034 (5)	0.02301 (8)	0.00002 (5)
O1	0.0467 (15)	0.0318 (13)	0.0576 (17)	−0.0029 (11)	0.0412 (14)	−0.0039 (11)
O2	0.0433 (14)	0.0350 (13)	0.0496 (16)	0.0043 (11)	0.0346 (14)	0.0061 (11)
O3	0.0559 (18)	0.0561 (18)	0.0452 (16)	0.0046 (15)	0.0380 (16)	0.0020 (14)
O4	0.0573 (18)	0.0544 (18)	0.0499 (17)	−0.0153 (14)	0.0417 (16)	−0.0069 (14)
O5	0.068 (2)	0.0384 (15)	0.0420 (15)	−0.0060 (13)	0.0408 (16)	−0.0023 (12)
O6	0.064 (2)	0.0532 (18)	0.0533 (17)	0.0096 (15)	0.0470 (17)	0.0002 (14)
N1	0.052 (2)	0.0370 (18)	0.079 (3)	−0.0106 (15)	0.050 (2)	−0.0113 (17)
N2	0.0464 (18)	0.0312 (15)	0.0522 (19)	−0.0010 (13)	0.0371 (17)	−0.0042 (13)
N3	0.0413 (16)	0.0341 (15)	0.0409 (16)	0.0036 (12)	0.0312 (15)	0.0001 (12)
N4	0.0414 (16)	0.0418 (17)	0.0428 (16)	0.0025 (13)	0.0343 (15)	−0.0002 (13)
N5	0.0413 (16)	0.0389 (16)	0.0457 (17)	0.0035 (13)	0.0332 (15)	0.0058 (13)
N6	0.0455 (18)	0.0329 (16)	0.060 (2)	0.0027 (13)	0.0403 (18)	0.0087 (14)
N7	0.059 (2)	0.0358 (17)	0.068 (2)	0.0100 (15)	0.050 (2)	0.0116 (16)
C1	0.0399 (18)	0.0333 (17)	0.0417 (18)	−0.0013 (14)	0.0307 (17)	−0.0017 (14)
C2	0.050 (2)	0.0363 (18)	0.046 (2)	0.0067 (16)	0.0371 (19)	0.0014 (15)
C3	0.089 (4)	0.034 (2)	0.113 (5)	0.011 (2)	0.083 (4)	0.003 (3)
C4	0.0411 (19)	0.045 (2)	0.0402 (19)	0.0071 (15)	0.0313 (17)	0.0031 (15)
C5	0.049 (2)	0.057 (3)	0.062 (3)	0.012 (2)	0.043 (2)	0.003 (2)
C6	0.049 (2)	0.070 (3)	0.076 (3)	0.007 (2)	0.050 (3)	0.002 (3)

C7	0.042 (2)	0.068 (3)	0.061 (3)	0.0018 (19)	0.041 (2)	0.003 (2)
C8	0.0386 (19)	0.050 (2)	0.0419 (19)	0.0009 (16)	0.0320 (18)	0.0024 (16)
C9	0.0390 (19)	0.047 (2)	0.0412 (19)	−0.0019 (15)	0.0312 (17)	0.0029 (15)
C10	0.057 (3)	0.058 (3)	0.077 (3)	−0.005 (2)	0.055 (3)	0.004 (2)
C11	0.0425 (19)	0.0373 (18)	0.0403 (18)	0.0044 (15)	0.0313 (17)	0.0054 (14)
O7	0.070 (2)	0.0537 (18)	0.060 (2)	0.0003 (17)	0.051 (2)	−0.0055 (16)
O8	0.098 (3)	0.119 (4)	0.050 (2)	0.053 (3)	0.043 (2)	0.016 (2)
O9	0.065 (2)	0.089 (3)	0.0483 (18)	−0.0188 (19)	0.0434 (18)	−0.0213 (18)
N8	0.055 (2)	0.047 (2)	0.0429 (18)	−0.0066 (16)	0.0369 (18)	−0.0027 (15)
O10	0.078 (3)	0.075 (3)	0.108 (4)	0.015 (2)	0.077 (3)	0.013 (2)
O11	0.114 (3)	0.050 (2)	0.102 (3)	0.015 (2)	0.094 (3)	0.009 (2)
O12	0.106 (3)	0.059 (2)	0.096 (3)	−0.015 (2)	0.081 (3)	−0.005 (2)
N9	0.056 (2)	0.0414 (18)	0.0499 (19)	0.0048 (15)	0.0409 (18)	0.0029 (14)
N10	0.054 (5)	0.038 (6)	0.046 (4)	0.018 (4)	0.027 (4)	0.000 (4)
O13	0.060 (5)	0.047 (4)	0.100 (7)	0.000 (4)	0.049 (5)	0.017 (4)
O14	0.072 (6)	0.019 (4)	0.090 (7)	−0.004 (3)	0.036 (5)	0.003 (4)
O15	0.057 (6)	0.062 (6)	0.185 (13)	0.017 (4)	0.070 (7)	0.018 (6)
N10B	0.098 (12)	0.056 (9)	0.096 (11)	0.009 (9)	0.076 (10)	−0.003 (8)
O13B	0.121 (15)	0.040 (6)	0.181 (16)	0.022 (7)	0.109 (13)	0.031 (7)
O14B	0.095 (9)	0.117 (14)	0.206 (19)	−0.033 (9)	0.111 (12)	−0.052 (12)
O15B	0.132 (15)	0.092 (12)	0.19 (2)	0.034 (10)	0.140 (17)	0.042 (12)

Geometric parameters (Å, º)

Sm1—O1	2.317 (3)	N7—C11	1.312 (5)
Sm1—O2	2.332 (3)	N7—H7A	0.8600
Sm1—O4	2.364 (3)	N7—H7B	0.8600
Sm1—O3	2.418 (3)	C2—C4	1.476 (6)
Sm1—O5	2.427 (3)	C2—C3	1.497 (6)
Sm1—O6	2.438 (3)	C3—H3C	0.9600
Sm1—N3	2.473 (3)	C3—H3D	0.9600
Sm1—N4	2.504 (3)	C3—H3E	0.9600
Sm1—N5	2.530 (3)	C4—C5	1.404 (6)
O1—C1	1.243 (4)	C5—C6	1.385 (8)
O2—C11	1.249 (5)	C5—H5	0.9300
O3—H3A	0.8584	C6—C7	1.371 (7)
O3—H3B	0.8585	C6—H6C	0.9300
O4—H4A	0.8808	C7—C8	1.395 (6)
O4—H4B	0.8797	C7—H7	0.9300
O5—H5A	0.8970	C8—C9	1.476 (6)
O5—H5B	0.8972	C9—C10	1.494 (6)
O6—H6A	0.9362	C10—H10A	0.9600
O6—H6B	0.9325	C10—H10B	0.9600
N1—C1	1.333 (5)	C10—H10C	0.9600
N1—H1A	0.8600	O7—N8	1.228 (5)
N1—H1B	0.8600	O8—N8	1.227 (6)
N2—N3	1.363 (5)	O9—N8	1.250 (5)
N2—C1	1.367 (5)	O10—N9	1.257 (6)

N2—H2	0.8600	O11—N9	1.238 (5)
N3—C2	1.282 (5)	O12—N9	1.226 (6)
N4—C4	1.345 (5)	N10—O15	1.229 (8)
N4—C8	1.347 (5)	N10—O13	1.243 (9)
N5—C9	1.290 (5)	N10—O14	1.247 (9)
N5—N6	1.365 (5)	N10B—O14B	1.234 (10)
N6—C11	1.376 (5)	N10B—O13B	1.242 (10)
N6—H6	0.8600	N10B—O15B	1.243 (10)
O1—Sm1—O2	90.78 (10)	C8—N4—Sm1	120.7 (3)
O1—Sm1—O4	139.06 (11)	C9—N5—N6	121.3 (4)
O2—Sm1—O4	99.03 (12)	C9—N5—Sm1	122.8 (3)
O1—Sm1—O3	75.33 (12)	N6—N5—Sm1	114.5 (3)
O2—Sm1—O3	73.21 (12)	N5—N6—C11	115.2 (3)
O4—Sm1—O3	145.52 (12)	N5—N6—H6	122.4
O1—Sm1—O5	79.97 (11)	C11—N6—H6	122.4
O2—Sm1—O5	141.02 (11)	C11—N7—H7A	120.0
O4—Sm1—O5	67.49 (11)	C11—N7—H7B	120.0
O3—Sm1—O5	137.95 (11)	H7A—N7—H7B	120.0
O1—Sm1—O6	76.13 (11)	O1—C1—N1	122.0 (4)
O2—Sm1—O6	67.41 (12)	O1—C1—N2	121.5 (4)
O4—Sm1—O6	71.45 (12)	N1—C1—N2	116.5 (3)
O3—Sm1—O6	130.31 (12)	N3—C2—C4	114.2 (4)
O5—Sm1—O6	73.61 (12)	N3—C2—C3	124.6 (4)
O1—Sm1—N3	66.00 (11)	C4—C2—C3	121.0 (4)
O2—Sm1—N3	141.57 (11)	C2—C3—H3C	109.5
O4—Sm1—N3	118.73 (12)	C2—C3—H3D	109.5
O3—Sm1—N3	71.51 (12)	H3C—C3—H3D	109.5
O5—Sm1—N3	67.49 (11)	C2—C3—H3E	109.5
O6—Sm1—N3	129.07 (12)	H3C—C3—H3E	109.5
O1—Sm1—N4	127.38 (10)	H3D—C3—H3E	109.5
O2—Sm1—N4	122.90 (11)	N4—C4—C5	121.1 (4)
O4—Sm1—N4	79.15 (12)	N4—C4—C2	116.1 (3)
O3—Sm1—N4	77.72 (12)	C5—C4—C2	122.6 (4)
O5—Sm1—N4	91.48 (12)	C6—C5—C4	118.8 (4)
O6—Sm1—N4	150.29 (12)	C6—C5—H5	120.6
N3—Sm1—N4	62.86 (11)	C4—C5—H5	120.6
O1—Sm1—N5	146.23 (11)	C7—C6—C5	120.0 (5)
O2—Sm1—N5	63.90 (11)	C7—C6—H6C	120.0
O4—Sm1—N5	70.59 (12)	C5—C6—H6C	120.0
O3—Sm1—N5	76.05 (12)	C6—C7—C8	118.6 (5)
O5—Sm1—N5	133.78 (11)	C6—C7—H7	120.7
O6—Sm1—N5	110.36 (12)	C8—C7—H7	120.7
N3—Sm1—N5	120.15 (12)	N4—C8—C7	122.0 (4)
N4—Sm1—N5	61.93 (11)	N4—C8—C9	116.0 (4)
C1—O1—Sm1	121.9 (3)	C7—C8—C9	121.9 (4)
C11—O2—Sm1	124.4 (3)	N5—C9—C8	113.9 (4)
Sm1—O3—H3A	109.6	N5—C9—C10	124.9 (4)

Sm1—O3—H3B	109.8	C8—C9—C10	121.2 (4)
H3A—O3—H3B	104.1	C9—C10—H10A	109.5
Sm1—O4—H4A	111.3	C9—C10—H10B	109.5
Sm1—O4—H4B	110.7	H10A—C10—H10B	109.5
H4A—O4—H4B	103.0	C9—C10—H10C	109.5
Sm1—O5—H5A	111.6	H10A—C10—H10C	109.5
Sm1—O5—H5B	111.5	H10B—C10—H10C	109.5
H5A—O5—H5B	102.4	O2—C11—N7	124.0 (4)
Sm1—O6—H6A	113.8	O2—C11—N6	119.5 (4)
Sm1—O6—H6B	112.7	N7—C11—N6	116.4 (4)
H6A—O6—H6B	100.4	O8—N8—O7	121.4 (4)
C1—N1—H1A	120.0	O8—N8—O9	117.8 (5)
C1—N1—H1B	120.0	O7—N8—O9	120.8 (4)
H1A—N1—H1B	120.0	O12—N9—O11	121.7 (5)
N3—N2—C1	115.7 (3)	O12—N9—O10	121.0 (4)
N3—N2—H2	122.2	O11—N9—O10	117.3 (4)
C1—N2—H2	122.2	O15—N10—O13	119.4 (10)
C2—N3—N2	120.6 (3)	O15—N10—O14	123.1 (11)
C2—N3—Sm1	124.6 (3)	O13—N10—O14	117.5 (9)
N2—N3—Sm1	114.5 (2)	O14B—N10B—O13B	122.0 (13)
C4—N4—C8	119.4 (4)	O14B—N10B—O15B	117.9 (13)
C4—N4—Sm1	119.5 (3)	O13B—N10B—O15B	119.7 (13)

C1—N2—N3—C2	−179.1 (4)	C2—C4—C5—C6	174.1 (5)
C1—N2—N3—Sm1	6.2 (4)	C4—C5—C6—C7	−2.6 (8)
C9—N5—N6—C11	179.2 (4)	C5—C6—C7—C8	2.8 (9)
Sm1—N5—N6—C11	−14.3 (5)	C4—N4—C8—C7	−3.9 (6)
Sm1—O1—C1—N1	177.1 (3)	Sm1—N4—C8—C7	169.0 (4)
Sm1—O1—C1—N2	−3.5 (5)	C4—N4—C8—C9	172.0 (4)
N3—N2—C1—O1	−2.2 (6)	Sm1—N4—C8—C9	−15.2 (5)
N3—N2—C1—N1	177.1 (4)	C6—C7—C8—N4	0.4 (8)
N2—N3—C2—C4	176.1 (4)	C6—C7—C8—C9	−175.2 (5)
Sm1—N3—C2—C4	−9.9 (5)	N6—N5—C9—C8	−175.8 (4)
N2—N3—C2—C3	0.1 (7)	Sm1—N5—C9—C8	18.9 (5)
Sm1—N3—C2—C3	174.1 (4)	N6—N5—C9—C10	2.2 (7)
C8—N4—C4—C5	4.0 (6)	Sm1—N5—C9—C10	−163.2 (4)
Sm1—N4—C4—C5	−168.9 (3)	N4—C8—C9—N5	−2.2 (6)
C8—N4—C4—C2	−171.2 (4)	C7—C8—C9—N5	173.7 (4)
Sm1—N4—C4—C2	15.8 (5)	N4—C8—C9—C10	179.8 (4)
N3—C2—C4—N4	−4.3 (5)	C7—C8—C9—C10	−4.4 (7)
C3—C2—C4—N4	171.9 (4)	Sm1—O2—C11—N7	−171.0 (3)
N3—C2—C4—C5	−179.5 (4)	Sm1—O2—C11—N6	10.1 (6)
C3—C2—C4—C5	−3.3 (7)	N5—N6—C11—O2	4.2 (6)
N4—C4—C5—C6	−0.8 (7)	N5—N6—C11—N7	−174.8 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O9	0.86	2.04	2.895 (6)	173
O4—H4*B*···O14	0.88	2.33	3.050 (15)	139
O4—H4*B*···O13	0.88	1.82	2.638 (11)	155
O4—H4*B*···O15*B*	0.88	2.11	2.805 (19)	135
O4—H4*B*···N10	0.88	2.42	3.278 (9)	164
O4—H4*A*···O14^{i}	0.88	1.89	2.706 (9)	153
O4—H4*A*···O15*B*^{i}	0.88	1.96	2.735 (19)	147
O4—H4*A*···O14*B*^{i}	0.88	2.47	3.239 (17)	146
O4—H4*A*···N10*B*^{i}	0.88	2.57	3.420 (15)	164
O5—H5*A*···O12^{ii}	0.90	2.21	2.957 (6)	141
O5—H5*B*···O7^{iii}	0.90	1.93	2.767 (5)	155
O5—H5*B*···N8^{iii}	0.90	2.63	3.511 (5)	170
O5—H5*B*···O8^{iii}	0.90	2.66	3.455 (6)	149
O6—H6*A*···O8^{iv}	0.94	2.34	3.055 (6)	133
O6—H6*A*···O9^{iv}	0.94	2.33	3.192 (6)	154
O6—H6*B*···O8^{iii}	0.93	1.89	2.812 (6)	171
N1—H1*A*···O10^{iv}	0.86	2.11	2.938 (6)	162
N1—H1*B*···O13^{v}	0.86	1.93	2.780 (8)	173
N1—H1*B*···O13*B*^{v}	0.86	2.18	2.936 (13)	146
N2—H2···O15^{v}	0.86	2.06	2.914 (11)	175
N2—H2···O13*B*^{v}	0.86	2.03	2.801 (13)	149
O3—H3*A*···O2	0.86	2.53	2.833 (5)	102
O3—H3*B*···N3	0.86	2.56	2.858 (5)	101
O4—H4*A*···N5	0.88	2.52	2.831 (5)	101
N6—H6···O11	0.86	2.19	3.031 (5)	166
N7—H7*A*···O2^{iv}	0.86	2.29	3.095 (5)	156
N7—H7*B*···O10	0.86	2.16	2.995 (6)	163

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