Crystal structure of *catena*-(5-(4-carboxyphenyl)-10,15,20-tris(4-carboxylatophenyl)porphyrin-aqua-dimethylformamide-dysprosium(III)-nickel(II) — dimethylformamide — water (1:1:1), $[(C_{48}H_{25}N_4O_8Ni)Dy(H_2O)(C_3H_7NO)] \cdot C_3H_7NO \cdot H_2O$

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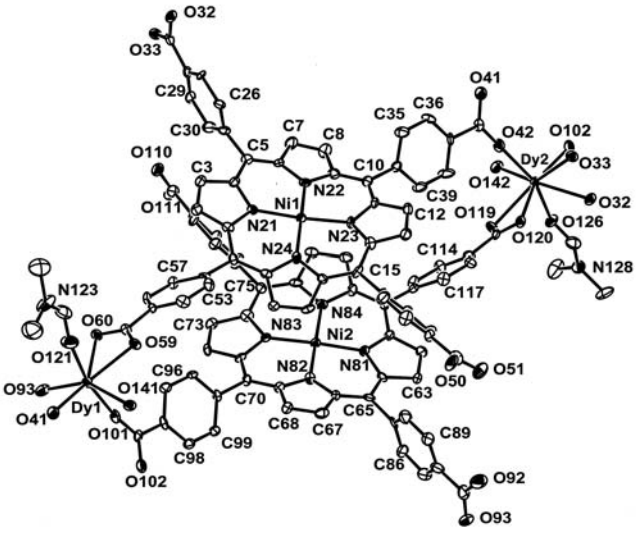

Abstract

$C_{108}H_{82}Dy_2N_{12}Ni_2O_{22}$, monoclinic, $P2_1$ (no. 4), a = 8.7602(1) Å, b = 27.8308(8) Å, c = 21.2201(6) Å, β = 97.680(2)°, V = 5127.1 Å^3, Z = 2, $R_{gf}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.108, T = 110 K.

Source of material

The porphyrin (Frontier Scientific) and all the other reactants and solvents were obtained commercially. The analyzed product was obtained by hydrothermal reaction: 1.54 mg (0.0026 mmol) of dysprosium(III) oxalate hydrate and 7.8 mg (0.031 mmol) of nickel(II) acetate tetrahydrate were mixed together in 25 ml of concentrated hydrochloric acid until a clear green solution was obtained. The latter was then added to a solution of 4 mg (0.005 mmol) of the 5,10,15,20-tetra(4-carboxyphenyl)-porphyrin (H_4TCPP) disolved in 5 ml of *N*,*N*-dimethylformamide (DMF). Crystals suitable for the X-ray diffraction analysis were obtained after 5 days. During the reaction the free-base porphyrin starting material was core-metalated by the nickel ions.

Experimental details

All the intensity statistics tests indicate clearly and decisively a non-centrosymmetric structure. The PLATON structure validation procedure also confirms that the chosen $P2_1$ space-group is correct. All the hydrogen atoms were located in calculated positions. While the DMF crystallization solvent was well defined, the disordered water solvent could not be precisely modeled by discrete atoms. Correspondingly, the contribution of the disordered non-coordinated water solvent in this structure to the diffraction pattern was subtracted by the Squeeze procedure, using the PLATON software [1]. There are most probably 2 water molecules per asymmetric unit. The robust lanthanoid-porphyrin framework has been characterized, however, with good precision.

Discussion

This study is part of an extended research project directed at the design and evaluation of porphyrin-based framework solids [2,3]. In this context, the H_4TCPP ligand bears multiple diverging molecular recognition sites for metal coordination in different directions, and is perfectly suitable when reacted with complimentary metal ion connectors for the formulation of single-framework architectures [2-4]. We found recently that lanthanoid ions provide a very attractive interface for coordination polymerization with the H_4TCPP building blocks (whether in a free-base or core-metalated form) in three dimensions [5,6]. This is due to their large size, spatial divergence of the valent orbitals, high coordination numbers, and oxophilic nature. Here we report on the crystal structure of a new metal organic framework composed of the Ni-HTCPP ligand and trivalent Dy ions, the intercoordination of which is characterized by a continuous 3D coordination polymerization scheme and an open architecture.

The intra-lattice voids are accommodated by DMF and water crystallization solvent. Charge balance is achieved by triple deprotonation of the porphyrin tetra-acid ligand. The Dy:metallo-porphyrin stochiometry is 1:1. The asymmetric unit of this structure consists of two Ni-HTCPP^{3-} ligands and two solvated $Dy^{3+}(H_2O)$(DMF) ions, as well as two molecules of non-coordinated DMF crystallization solvent. The metallo-porphyrin ligand adopts a saddle-type conformation. The Dy ions are characterized by a coordination number of either 7 or 8, linking to either five (Dy1) or six (Dy2) O-sites of neighboring porphyrin entities. Each one of the latter coordinates in turn to four different metal ions. All the Dy—O coordination distances are within the range of 2.217(6) - 2.545(5) Å. The resulting structure represents a single-framework coordination polymer perforated by open channels (accommodated by solvent of crystallization) which propagate parallel to [100]. The supramolecular framework is composed of layered assemblies of metal-intercoordinated porphyrin moieties, which are held together along the normal direction by construction pillars of the $Dy(COO^-)_n$ connecting synthons. It is stable upon heating to above 200 °C and expulsion

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of the crystallization solvent. These results add to our earlier findings on closely related lanthanoid-TCPP frameworks reported before [4,5].

Table 1. Data collection and handling.

Crystal:	red plate, size 0.10 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	18.80 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ/ω
$2\theta_{max}$:	51.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	33676, 16870
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 14075
$N(param)_{refined}$:	1324
Programs:	PLATON [1], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	2*a*	0.6560	0.7908	0.9486	0.025
H(3)	2*a*	0.7740	0.8448	0.8756	0.026
H(7)	2*a*	0.8124	0.8329	0.6281	0.034
H(8)	2*a*	0.8223	0.7639	0.5543	0.033
H(12)	2*a*	0.9394	0.5792	0.6025	0.031
H(13)	2*a*	0.8707	0.5219	0.6835	0.029
H(17)	2*a*	0.4979	0.5433	0.8611	0.025
H(18)	2*a*	0.4396	0.6115	0.9284	0.020
H(26)	2*a*	1.0465	0.8428	0.8143	0.023
H(27)	2*a*	1.1506	0.9204	0.8124	0.027
H(29)	2*a*	0.7705	0.9664	0.7040	0.028
H(30)	2*a*	0.6613	0.8882	0.7051	0.033
H(35)	2*a*	1.0794	0.7087	0.5618	0.034
H(36)	2*a*	1.1401	0.7019	0.4580	0.025
H(38)	2*a*	0.7802	0.6147	0.4130	0.052
H(39)	2*a*	0.7164	0.6216	0.5157	0.052
H(44)	2*a*	0.8114	0.5041	0.8627	0.037
H(45)	2*a*	0.8025	0.4221	0.8711	0.035
H(47)	2*a*	0.5541	0.4169	0.6994	0.036
H(48)	2*a*	0.5650	0.4995	0.6908	0.021
H(50)	2*a*	0.7259	0.3050	0.8413	0.043
H(53)	2*a*	0.6481	0.6493	1.0026	0.026
H(54)	2*a*	0.5592	0.6519	1.1024	0.030
H(56)	2*a*	0.3077	0.7693	1.0454	0.022
H(57)	2*a*	0.3825	0.7629	0.9449	0.022
H(62)	2*a*	0.3099	0.4804	0.5566	0.028
H(63)	2*a*	0.2109	0.4267	0.6355	0.029
H(67)	2*a*	0.1737	0.4499	0.8820	0.030
H(68)	2*a*	0.1225	0.5215	0.9464	0.029
H(72)	2*a*	–0.0018	0.7057	0.8866	0.024
H(73)	2*a*	0.0934	0.7586	0.8090	0.025
H(77)	2*a*	0.4437	0.7326	0.6256	0.026
H(78)	2*a*	0.4928	0.6621	0.5597	0.028
H(86)	2*a*	–0.0451	0.4156	0.7091	0.035
H(87)	2*a*	–0.0798	0.3327	0.7139	0.046
H(89)	2*a*	0.3475	0.3214	0.8186	0.041
H(90)	2*a*	0.3709	0.4048	0.8136	0.036
H(95)	2*a*	0.1983	0.6666	0.9728	0.021
H(96)	2*a*	0.1327	0.6761	1.0749	0.024
H(98)	2*a*	–0.1918	0.5712	1.0364	0.025
H(99)	2*a*	–0.1380	0.5659	0.9335	0.024
H(104)	2*a*	0.1424	0.7722	0.6292	0.031
H(105)	2*a*	0.1681	0.8565	0.6194	0.028
H(107)	2*a*	0.4487	0.8600	0.7874	0.029
H(108)	2*a*	0.4109	0.7770	0.8004	0.027
H(111)	2*a*	0.2606	0.9711	0.6481	0.042
H(113)	2*a*	0.2702	0.6179	0.4810	0.027
H(114)	2*a*	0.3629	0.6094	0.3858	0.027
H(116)	2*a*	0.6677	0.5085	0.4615	0.028
H(117)	2*a*	0.5765	0.5157	0.5597	0.028
H(122)	2*a*	0.5531	0.7545	1.2834	0.052
H(12A)	2*a*	0.6999	0.8126	1.3847	0.090
H(12B)	2*a*	0.7878	0.7727	1.3488	0.090
H(12C)	2*a*	0.7909	0.7701	1.4243	0.090
H(12D)	2*a*	0.5870	0.6991	1.4461	0.100
H(12E)	2*a*	0.4181	0.7181	1.4198	0.100
H(12F)	2*a*	0.5334	0.7513	1.4658	0.100
H(127)	2*a*	0.5616	0.4906	0.1795	0.039
H(12G)	2*a*	0.2474	0.5525	0.0653	0.077
H(12H)	2*a*	0.2938	0.5772	0.1333	0.077
H(12I)	2*a*	0.1546	0.5396	0.1231	0.077
H(13A)	2*a*	0.3965	0.4369	0.1266	0.063
H(13B)	2*a*	0.2765	0.4568	0.0690	0.063
H(13C)	2*a*	0.2257	0.4514	0.1383	0.063
H(14M)	2*a*	0.3408	0.5987	1.2771	0.024
H(14N)	2*a*	0.1712	0.5819	1.2651	0.024
H(14P)	2*a*	0.5758	0.6605	0.2107	0.025
H(14R)	2*a*	0.7066	0.6850	0.2216	0.025
H(132)	2*a*	0.4731	0.8838	–0.0259	0.085
H(13D)	2*a*	0.4641	0.9933	–0.0174	0.099
H(13E)	2*a*	0.5195	0.9503	0.0303	0.099
H(13F)	2*a*	0.3786	0.9837	0.0435	0.099
H(13G)	2*a*	0.1135	0.9332	–0.0750	0.099
H(13H)	2*a*	0.1869	0.9859	–0.0722	0.099
H(13I)	2*a*	0.1228	0.9641	–0.0110	0.099
H(137)	2*a*	0.6839	0.8347	0.0624	0.072
H(13J)	2*a*	0.8024	0.7652	0.0779	0.089
H(13K)	2*a*	0.9830	0.7720	0.1002	0.089
H(13L)	2*a*	0.9234	0.7529	0.0301	0.089
H(14G)	2*a*	1.0051	0.8704	0.0015	0.105
H(14H)	2*a*	1.0256	0.8174	–0.0252	0.105
H(14I)	2*a*	1.1135	0.8326	0.0429	0.105

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Dy(1)	2*a*	0.18551(4)	0.68853(1)	1.24622(2)	0.0217(2)	0.0178(2)	0.0191(2)	0.0027(2)	0.0070(1)	0.0021(2)
Dy(2)	2*a*	0.76994(4)	0.57830(1)	0.25166(2)	0.0182(2)	0.0136(2)	0.0165(2)	0.0007(2)	0.0036(1)	–0.0003(2)
Ni(1)	2*a*	0.7244(1)	0.68611(4)	0.75987(4)	0.0186(5)	0.0151(6)	0.0139(5)	–0.0019(5)	0.0044(3)	0.0004(5)
C(1)	2*a*	0.6496(8)	0.7385(3)	0.8760(4)	0.018(4)	0.020(5)	0.016(5)	0.003(3)	0.003(3)	0.007(4)
C(2)	2*a*	0.6779(8)	0.7830(3)	0.9072(4)	0.020(4)	0.025(5)	0.017(5)	–0.001(3)	–0.002(3)	–0.004(4)
C(3)	2*a*	0.7420(8)	0.8125(3)	0.8674(4)	0.023(4)	0.017(5)	0.024(5)	0.000(3)	0.001(3)	–0.003(4)
C(4)	2*a*	0.7520(8)	0.7860(3)	0.8111(4)	0.016(4)	0.013(5)	0.024(5)	0.000(3)	0.000(3)	–0.001(4)
C(5)	2*a*	0.7913(9)	0.8060(3)	0.7543(4)	0.021(4)	0.019(5)	0.012(5)	–0.002(3)	0.001(3)	0.004(4)
C(6)	2*a*	0.7850(9)	0.7800(3)	0.6991(4)	0.016(4)	0.016(5)	0.024(5)	–0.007(3)	0.006(3)	–0.004(4)
C(7)	2*a*	0.806(1)	0.7998(3)	0.6383(4)	0.042(5)	0.018(5)	0.026(5)	–0.004(4)	0.010(4)	0.003(4)
C(8)	2*a*	0.813(1)	0.7622(3)	0.5984(4)	0.045(6)	0.020(5)	0.017(5)	0.001(4)	0.004(4)	0.007(4)
C(9)	2*a*	0.8052(9)	0.7192(3)	0.6349(4)	0.022(4)	0.025(5)	0.017(5)	–0.004(4)	0.004(3)	0.000(4)
C(10)	2*a*	0.8434(8)	0.6739(3)	0.6149(4)	0.020(4)	0.025(6)	0.016(5)	–0.006(3)	0.001(3)	–0.008(4)
C(11)	2*a*	0.8359(9)	0.6340(3)	0.6516(4)	0.030(5)	0.017(5)	0.021(5)	–0.007(4)	0.012(4)	–0.011(4)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12)	2*a*	0.8872(9)	0.5871(3)	0.6376(4)	0.036(5)	0.021(6)	0.023(5)	0.000(4)	0.013(4)	–0.006(4)
C(13)	2*a*	0.8504(9)	0.5554(3)	0.6818(4)	0.030(5)	0.019(5)	0.024(5)	–0.001(4)	0.006(4)	–0.002(4)
C(14)	2*a*	0.7747(8)	0.5831(4)	0.7251(4)	0.021(4)	0.025(6)	0.010(4)	0.005(4)	–0.004(3)	–0.001(4)
C(15)	2*a*	0.6986(9)	0.5637(3)	0.7726(4)	0.028(5)	0.009(5)	0.018(5)	0.000(3)	–0.006(3)	–0.001(4)
C(16)	2*a*	0.6301(8)	0.5928(3)	0.8145(4)	0.018(4)	0.025(6)	0.016(5)	–0.004(3)	0.006(3)	–0.005(4)
C(17)	2*a*	0.5328(8)	0.5755(3)	0.8581(4)	0.024(4)	0.014(4)	0.024(4)	–0.008(4)	0.001(3)	0.006(4)
C(18)	2*a*	0.4989(8)	0.6127(3)	0.8940(3)	0.025(4)	0.018(5)	0.008(4)	–0.004(3)	0.005(3)	0.004(3)
C(19)	2*a*	0.5693(9)	0.6544(3)	0.8707(4)	0.018(4)	0.020(5)	0.014(4)	0.000(3)	0.004(3)	0.006(4)
C(20)	2*a*	0.5778(8)	0.6994(3)	0.9013(4)	0.018(4)	0.016(5)	0.014(4)	0.004(3)	0.003(3)	0.001(3)
N(21)	2*a*	0.7006(7)	0.7395(3)	0.8161(3)	0.021(4)	0.015(4)	0.017(4)	–0.001(3)	0.008(3)	0.003(3)
N(22)	2*a*	0.7793(7)	0.7300(3)	0.6962(3)	0.014(3)	0.024(5)	0.018(4)	–0.007(3)	0.002(3)	–0.001(3)
N(23)	2*a*	0.7740(7)	0.6322(2)	0.7083(3)	0.022(4)	0.013(4)	0.015(4)	0.005(3)	0.003(3)	–0.003(3)
N(24)	2*a*	0.6446(7)	0.6422(3)	0.8197(3)	0.024(4)	0.020(4)	0.013(4)	–0.001(3)	0.004(3)	–0.005(3)
C(25)	2*a*	0.8432(9)	0.8571(3)	0.7564(4)	0.022(4)	0.021(5)	0.021(5)	–0.007(4)	0.009(3)	0.002(4)
C(26)	2*a*	0.9898(8)	0.8675(3)	0.7906(4)	0.014(4)	0.020(5)	0.026(5)	0.000(3)	0.007(3)	0.003(4)
C(27)	2*a*	1.0517(9)	0.9138(3)	0.7899(4)	0.022(4)	0.016(5)	0.029(5)	–0.011(4)	0.007(4)	–0.014(4)
C(28)	2*a*	0.9694(8)	0.9496(3)	0.7567(4)	0.018(4)	0.013(5)	0.020(5)	0.005(3)	0.005(3)	–0.001(4)
C(29)	2*a*	0.828(1)	0.9410(3)	0.7260(5)	0.034(5)	0.009(5)	0.029(6)	0.002(3)	0.013(4)	0.003(4)
C(30)	2*a*	0.7622(9)	0.8938(3)	0.7262(4)	0.022(4)	0.026(6)	0.035(6)	–0.004(4)	0.005(4)	0.001(4)
C(31)	2*a*	1.0474(8)	0.9976(3)	0.7557(4)	0.018(4)	0.023(5)	0.019(5)	0.006(3)	0.005(3)	–0.004(4)
O(32)	2*a*	1.1852(6)	1.0001(2)	0.7817(3)	0.029(3)	0.010(3)	0.028(3)	0.001(2)	0.004(2)	0.002(2)
O(33)	2*a*	0.9809(6)	1.0333(2)	0.7281(3)	0.016(3)	0.023(4)	0.028(4)	0.002(2)	0.004(2)	0.002(3)
C(34)	2*a*	0.8871(8)	0.6681(3)	0.5498(4)	0.025(4)	0.014(4)	0.016(4)	–0.002(3)	0.002(3)	0.001(3)
C(35)	2*a*	1.0148(8)	0.6901(4)	0.5316(4)	0.025(4)	0.041(6)	0.017(5)	–0.014(5)	0.000(3)	–0.004(5)
C(36)	2*a*	1.0524(8)	0.6857(3)	0.4694(3)	0.018(4)	0.030(5)	0.016(4)	–0.003(4)	0.006(3)	0.011(4)
C(37)	2*a*	0.9648(9)	0.6585(3)	0.4257(4)	0.026(5)	0.016(5)	0.021(5)	0.004(3)	0.010(3)	–0.008(4)
C(38)	2*a*	0.841(1)	0.6345(4)	0.4431(4)	0.040(5)	0.066(8)	0.026(6)	–0.040(5)	0.009(4)	–0.020(5)
C(39)	2*a*	0.802(1)	0.6389(4)	0.5045(4)	0.052(6)	0.054(7)	0.028(6)	–0.038(5)	0.022(4)	–0.023(5)
C(40)	2*a*	1.0025(8)	0.6534(3)	0.3597(4)	0.020(4)	0.020(5)	0.011(4)	0.005(3)	–0.003(3)	0.000(4)
O(41)	2*a*	1.1170(6)	0.6768(2)	0.3467(3)	0.042(3)	0.027(5)	0.027(4)	–0.006(3)	0.016(3)	–0.004(3)
O(42)	2*a*	0.9206(6)	0.6261(2)	0.3217(3)	0.028(3)	0.029(4)	0.020(3)	0.000(3)	0.005(2)	–0.006(3)
C(43)	2*a*	0.6913(8)	0.5103(3)	0.7770(4)	0.018(4)	0.014(5)	0.022(5)	0.002(3)	–0.001(3)	–0.001(4)
C(44)	2*a*	0.7582(9)	0.4862(3)	0.8285(5)	0.036(5)	0.024(6)	0.033(6)	–0.006(4)	0.003(4)	–0.005(4)
C(45)	2*a*	0.753(1)	0.4378(3)	0.8341(5)	0.046(6)	0.019(6)	0.021(5)	0.004(4)	0.001(4)	0.010(4)
C(46)	2*a*	0.6755(9)	0.4117(3)	0.7848(4)	0.033(5)	0.008(5)	0.025(5)	0.005(3)	0.010(4)	0.005(4)
C(47)	2*a*	0.608(1)	0.4349(3)	0.7333(5)	0.028(5)	0.019(6)	0.042(6)	0.000(4)	0.002(4)	–0.002(4)
C(48)	2*a*	0.6138(8)	0.4839(3)	0.7279(4)	0.023(4)	0.011(5)	0.018(5)	0.003(3)	0.001(3)	0.005(4)
C(49)	2*a*	0.667(1)	0.3572(4)	0.7870(4)	0.027(5)	0.034(6)	0.024(6)	0.008(4)	–0.002(4)	0.004(5)
O(50)	2*a*	0.7227(7)	0.3380(2)	0.8422(3)	0.058(4)	0.010(3)	0.041(5)	0.000(3)	0.007(3)	0.002(3)
O(51)	2*a*	0.6152(7)	0.3326(2)	0.7407(3)	0.045(4)	0.020(4)	0.047(5)	0.003(3)	–0.005(3)	0.001(3)
C(52)	2*a*	0.5230(8)	0.7050(3)	0.9631(4)	0.010(4)	0.020(5)	0.015(4)	–0.007(3)	0.003(3)	0.003(3)
C(53)	2*a*	0.5754(8)	0.6732(3)	1.0105(4)	0.017(4)	0.023(5)	0.025(5)	0.010(3)	–0.001(3)	–0.002(4)
C(54)	2*a*	0.5242(8)	0.6750(3)	1.0707(4)	0.027(4)	0.027(6)	0.021(5)	0.003(4)	0.002(3)	0.010(4)
C(55)	2*a*	0.4232(8)	0.7104(3)	1.0832(3)	0.018(4)	0.015(4)	0.008(4)	–0.002(3)	0.004(3)	–0.002(3)
C(56)	2*a*	0.3739(8)	0.7439(3)	1.0365(4)	0.024(4)	0.016(5)	0.015(5)	0.005(3)	0.005(3)	–0.004(4)
C(57)	2*a*	0.4208(8)	0.7405(3)	0.9770(4)	0.022(4)	0.017(5)	0.015(5)	0.006(3)	0.000(3)	0.002(3)
C(58)	2*a*	0.3558(8)	0.7087(3)	1.1449(4)	0.013(4)	0.024(5)	0.015(5)	0.003(3)	–0.001(3)	–0.001(4)
O(59)	2*a*	0.3794(5)	0.6718(2)	1.1795(3)	0.016(3)	0.021(4)	0.025(3)	0.006(2)	0.006(2)	0.006(3)
O(60)	2*a*	0.2677(6)	0.7419(2)	1.1593(3)	0.025(3)	0.019(4)	0.026(3)	0.001(2)	0.011(2)	0.003(3)
Ni(2)	2*a*	0.2226(1)	0.59199(3)	0.73652(5)	0.0185(5)	0.0141(6)	0.0161(6)	–0.0014(4)	0.0035(4)	0.0000(4)
C(61)	2*a*	0.2981(9)	0.5360(3)	0.6245(4)	0.020(4)	0.013(5)	0.013(5)	–0.002(3)	0.000(3)	0.000(3)
C(62)	2*a*	0.2858(9)	0.4893(3)	0.5973(4)	0.029(5)	0.027(6)	0.017(5)	–0.006(4)	0.010(3)	–0.003(4)
C(63)	2*a*	0.2333(9)	0.4600(3)	0.6402(4)	0.026(5)	0.019(5)	0.029(5)	–0.006(4)	0.011(4)	–0.012(4)
C(64)	2*a*	0.2181(8)	0.4896(3)	0.6945(4)	0.020(4)	0.029(6)	0.011(5)	–0.007(4)	0.009(3)	–0.006(4)
C(65)	2*a*	0.1879(8)	0.4712(3)	0.7526(4)	0.013(4)	0.018(5)	0.033(6)	–0.003(3)	0.011(3)	0.002(4)
C(66)	2*a*	0.1792(9)	0.4998(3)	0.8051(4)	0.023(4)	0.016(5)	0.022(5)	–0.003(3)	0.010(3)	–0.006(4)
C(67)	2*a*	0.1651(9)	0.4823(3)	0.8679(4)	0.024(4)	0.019(5)	0.033(6)	–0.002(3)	0.003(4)	0.007(4)
C(68)	2*a*	0.1372(9)	0.5216(3)	0.9029(4)	0.027(5)	0.022(5)	0.025(5)	–0.005(4)	0.005(4)	–0.008(4)
C(69)	2*a*	0.1336(8)	0.5632(3)	0.8626(4)	0.021(4)	0.016(5)	0.010(4)	–0.001(3)	–0.001(3)	0.001(3)
C(70)	2*a*	0.0894(9)	0.6087(3)	0.8788(4)	0.023(5)	0.017(5)	0.010(4)	0.000(3)	0.001(3)	–0.003(3)
C(71)	2*a*	0.1013(8)	0.6484(3)	0.8404(4)	0.018(4)	0.010(5)	0.018(5)	–0.003(3)	–0.002(3)	0.002(4)
C(72)	2*a*	0.0549(8)	0.6963(3)	0.8535(4)	0.026(4)	0.021(6)	0.014(4)	0.001(4)	0.008(3)	–0.007(4)
C(73)	2*a*	0.1052(8)	0.7247(3)	0.8113(4)	0.020(4)	0.015(5)	0.026(5)	0.004(3)	–0.002(3)	0.003(4)
C(74)	2*a*	0.1802(9)	0.6957(3)	0.7698(4)	0.026(4)	0.019(5)	0.016(4)	0.004(4)	0.000(3)	0.011(4)
C(75)	2*a*	0.2587(8)	0.7135(3)	0.7217(4)	0.012(4)	0.019(5)	0.023(5)	0.004(3)	0.000(3)	–0.001(4)
C(76)	2*a*	0.3209(7)	0.6832(4)	0.6806(4)	0.012(4)	0.029(5)	0.020(5)	–0.008(4)	–0.002(3)	0.000(4)
C(77)	2*a*	0.4109(8)	0.7005(3)	0.6312(4)	0.023(4)	0.023(6)	0.018(5)	–0.003(3)	0.004(3)	0.008(4)
C(78)	2*a*	0.4378(8)	0.6622(3)	0.5954(4)	0.023(4)	0.026(5)	0.020(5)	–0.006(3)	0.005(3)	0.003(4)
C(79)	2*a*	0.3666(9)	0.6210(3)	0.6216(4)	0.024(5)	0.025(6)	0.013(5)	–0.003(4)	–0.001(3)	–0.010(4)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(80)	2*a*	0.3620(7)	0.5760(3)	0.5954(3)	0.014(4)	0.025(5)	0.020(4)	0.001(4)	0.003(3)	–0.008(4)
N(81)	2*a*	0.2537(8)	0.5373(2)	0.6837(3)	0.027(4)	0.012(4)	0.018(4)	–0.002(3)	0.008(3)	0.001(3)
N(82)	2*a*	0.1678(7)	0.5493(3)	0.8027(3)	0.020(4)	0.020(4)	0.016(4)	0.004(3)	0.000(3)	0.000(3)
N(83)	2*a*	0.1719(7)	0.6476(2)	0.7851(3)	0.012(3)	0.012(4)	0.021(4)	–0.001(3)	0.001(3)	–0.001(3)
N(84)	2*a*	0.3002(7)	0.6337(3)	0.6750(3)	0.015(4)	0.020(4)	0.025(4)	0.000(3)	0.001(3)	0.001(3)
C(85)	2*a*	0.1669(9)	0.4170(3)	0.7571(4)	0.027(5)	0.019(5)	0.026(5)	0.005(4)	0.021(4)	–0.002(4)
C(86)	2*a*	0.0345(9)	0.3962(3)	0.7305(4)	0.030(5)	0.018(5)	0.040(6)	0.000(4)	0.007(4)	–0.005(4)
C(87)	2*a*	0.012(1)	0.3472(4)	0.7339(5)	0.031(5)	0.044(8)	0.043(7)	–0.011(5)	0.013(4)	–0.011(5)
C(88)	2*a*	0.1318(9)	0.3188(3)	0.7681(5)	0.023(5)	0.032(6)	0.041(7)	–0.001(4)	0.016(4)	0.003(5)
C(89)	2*a*	0.267(1)	0.3403(3)	0.7966(5)	0.036(5)	0.023(6)	0.045(6)	0.000(4)	0.016(4)	–0.003(5)
C(90)	2*a*	0.282(1)	0.3895(3)	0.7924(4)	0.028(5)	0.029(6)	0.034(6)	0.005(4)	0.007(4)	–0.001(4)
C(91)	2*a*	0.114(1)	0.2640(3)	0.7694(5)	0.054(7)	0.013(5)	0.054(7)	0.007(5)	0.029(5)	0.004(5)
O(92)	2*a*	0.2347(8)	0.2416(2)	0.7887(4)	0.040(4)	0.023(4)	0.114(7)	0.002(3)	0.022(4)	–0.001(4)
O(93)	2*a*	–0.0176(7)	0.2481(2)	0.7534(3)	0.045(4)	0.025(4)	0.048(5)	–0.015(3)	0.015(3)	–0.005(3)
C(94)	2*a*	0.0389(8)	0.6154(3)	0.9428(3)	0.024(4)	0.019(5)	0.004(4)	0.004(3)	0.004(3)	0.002(3)
C(95)	2*a*	0.1178(8)	0.6477(3)	0.9858(4)	0.018(4)	0.013(4)	0.023(5)	–0.006(3)	0.006(3)	0.001(3)
C(96)	2*a*	0.0812(8)	0.6527(3)	1.0471(4)	0.025(4)	0.016(5)	0.019(5)	–0.002(3)	0.003(3)	0.004(4)
C(97)	2*a*	–0.0330(8)	0.6230(3)	1.0683(4)	0.021(4)	0.018(4)	0.020(5)	0.015(3)	0.007(3)	0.002(3)
C(98)	2*a*	–0.1130(8)	0.5909(3)	1.0235(4)	0.018(4)	0.020(5)	0.023(5)	–0.002(3)	0.001(3)	–0.001(4)
C(99)	2*a*	–0.0806(8)	0.5872(3)	0.9626(4)	0.016(4)	0.024(6)	0.018(4)	–0.005(3)	–0.001(3)	–0.006(4)
C(100)	2*a*	–0.0560(8)	0.6237(3)	1.1362(4)	0.017(4)	0.011(5)	0.024(5)	0.007(3)	0.000(3)	–0.003(4)
O(101)	2*a*	0.0113(6)	0.6556(2)	1.1719(3)	0.028(3)	0.028(4)	0.017(3)	0.006(3)	0.007(2)	–0.002(3)
O(102)	2*a*	–0.1378(6)	0.5912(2)	1.1554(3)	0.040(3)	0.018(4)	0.028(4)	0.004(3)	0.018(3)	0.000(3)
C(103)	2*a*	0.2773(9)	0.7661(3)	0.7166(4)	0.030(5)	0.015(5)	0.025(6)	–0.008(4)	0.005(4)	0.007(4)
C(104)	2*a*	0.2031(9)	0.7900(3)	0.6616(4)	0.045(5)	0.020(5)	0.011(4)	–0.005(4)	0.002(3)	0.000(4)
C(105)	2*a*	0.2201(9)	0.8403(3)	0.6554(4)	0.037(5)	0.010(5)	0.021(5)	0.003(4)	0.000(3)	0.006(4)
C(106)	2*a*	0.3122(9)	0.8658(3)	0.7017(4)	0.029(5)	0.022(5)	0.033(6)	–0.001(3)	0.009(4)	–0.005(4)
C(107)	2*a*	0.3852(8)	0.8424(3)	0.7557(4)	0.021(4)	0.017(5)	0.033(5)	–0.003(3)	0.000(3)	–0.012(4)
C(108)	2*a*	0.3641(9)	0.7925(3)	0.7629(4)	0.029(4)	0.018(5)	0.019(5)	–0.002(4)	0.002(3)	0.003(4)
C(109)	2*a*	0.3400(9)	0.9174(3)	0.6934(4)	0.023(5)	0.011(5)	0.041(6)	0.007(3)	0.008(4)	0.006(4)
O(110)	2*a*	0.4370(7)	0.9397(2)	0.7284(3)	0.021(3)	0.024(4)	0.050(4)	0.001(3)	0.002(3)	–0.012(3)
O(111)	2*a*	0.2512(7)	0.9381(2)	0.6466(3)	0.042(4)	0.017(4)	0.029(4)	–0.003(2)	0.003(3)	0.008(3)
C(112)	2*a*	0.4178(8)	0.5692(3)	0.5325(4)	0.024(4)	0.013(5)	0.024(5)	–0.007(3)	0.008(3)	–0.004(4)
C(113)	2*a*	0.3524(9)	0.5961(3)	0.4777(4)	0.036(5)	0.014(5)	0.015(5)	0.005(3)	–0.001(3)	0.003(3)
C(114)	2*a*	0.4070(8)	0.5908(3)	0.4211(4)	0.026(4)	0.031(6)	0.008(4)	0.002(3)	–0.001(3)	–0.002(4)
C(115)	2*a*	0.5263(8)	0.5588(3)	0.4132(4)	0.016(4)	0.020(5)	0.026(5)	0.000(3)	0.004(3)	0.002(4)
C(116)	2*a*	0.5880(8)	0.5308(3)	0.4661(4)	0.019(4)	0.023(5)	0.030(6)	–0.001(3)	0.010(3)	–0.001(4)
C(117)	2*a*	0.5347(8)	0.5353(3)	0.5250(4)	0.027(4)	0.025(6)	0.016(5)	0.005(4)	–0.004(3)	0.004(4)
C(118)	2*a*	0.5993(9)	0.5583(3)	0.3535(4)	0.023(4)	0.011(5)	0.013(5)	–0.003(3)	0.004(3)	–0.004(4)
O(119)	2*a*	0.5466(5)	0.5864(2)	0.3099(2)	0.021(3)	0.026(4)	0.021(3)	0.006(2)	0.010(2)	0.007(3)
O(120)	2*a*	0.7187(6)	0.5332(2)	0.3488(3)	0.028(3)	0.009(3)	0.022(3)	0.004(2)	0.006(2)	0.003(3)
O(121)	2*a*	0.3943(7)	0.7155(3)	1.3086(3)	0.040(4)	0.064(5)	0.033(4)	–0.022(3)	0.008(3)	–0.008(4)
C(122)	2*a*	0.514(1)	0.7405(4)	1.3187(5)	0.026(5)	0.051(8)	0.055(8)	0.002(4)	0.012(5)	0.004(6)
N(123)	2*a*	0.5861(9)	0.7485(3)	1.3753(4)	0.044(5)	0.043(6)	0.045(6)	–0.013(4)	–0.030(4)	–0.010(4)
C(124)	2*a*	0.728(1)	0.7785(5)	1.3840(7)	0.042(7)	0.07(1)	0.07(1)	0.001(7)	–0.007(7)	0.01(1)
C(125)	2*a*	0.526(2)	0.7274(5)	1.4316(6)	0.08(1)	0.08(1)	0.056(9)	–0.012(9)	0.017(8)	0.005(8)
O(126)	2*a*	0.5486(6)	0.5574(2)	0.1804(3)	0.022(3)	0.019(4)	0.032(4)	–0.001(2)	–0.006(2)	–0.005(3)
C(127)	2*a*	0.4992(9)	0.5174(4)	0.1653(5)	0.020(5)	0.038(7)	0.040(6)	0.002(4)	0.003(4)	0.003(5)
N(128)	2*a*	0.3633(7)	0.5086(3)	0.1300(4)	0.022(4)	0.033(5)	0.031(5)	–0.002(3)	–0.002(3)	–0.007(4)
C(129)	2*a*	0.256(1)	0.5477(4)	0.1114(5)	0.041(6)	0.037(7)	0.069(8)	0.014(5)	–0.021(5)	–0.011(6)
C(130)	2*a*	0.311(1)	0.4593(4)	0.1147(5)	0.044(6)	0.035(7)	0.044(6)	–0.024(5)	–0.005(5)	–0.005(5)
O(141)	2*a*	0.2430(6)	0.6050(2)	1.2615(3)	0.021(3)	0.018(3)	0.029(4)	0.000(2)	0.005(2)	0.005(3)
O(142)	2*a*	0.6752(6)	0.6540(2)	0.2266(3)	0.027(3)	0.019(3)	0.031(4)	–0.002(2)	0.001(2)	–0.002(3)
O(131)	2*a*	0.282(1)	0.8633(4)	–0.0737(4)	0.073(7)	0.077(7)	0.075(7)	0.013(5)	–0.006(5)	–0.017(5)
C(132)	2*a*	0.370(2)	0.8932(5)	–0.0407(6)	0.079(9)	0.056(9)	0.08(1)	–0.004(7)	0.011(7)	–0.019(8)
N(133)	2*a*	0.324(1)	0.9365(4)	–0.0265(5)	0.068(7)	0.076(9)	0.045(6)	–0.019(5)	–0.003(5)	0.002(5)
C(134)	2*a*	0.430(2)	0.9685(6)	0.0104(6)	0.07(1)	0.07(2)	0.037(8)	–0.02(1)	0.016(7)	–0.018(9)
C(135)	2*a*	0.175(1)	0.9565(4)	–0.0479(6)	0.065(8)	0.060(9)	0.071(9)	0.024(6)	0.003(6)	–0.004(7)
O(136)	2*a*	0.753(1)	0.8908(3)	0.0241(4)	0.072(7)	0.050(6)	0.076(6)	0.020(5)	–0.016(5)	–0.020(5)
C(137)	2*a*	0.768(1)	0.8482(5)	0.0443(5)	0.074(8)	0.06(1)	0.036(7)	0.011(6)	–0.018(5)	–0.021(6)
N(138)	2*a*	0.8914(9)	0.8207(3)	0.0422(4)	0.043(5)	0.036(6)	0.055(6)	0.003(4)	–0.024(4)	–0.002(4)
C(139)	2*a*	0.901(1)	0.7744(4)	0.0642(5)	0.063(7)	0.043(8)	0.064(8)	0.016(6)	–0.016(6)	0.004(6)
C(140)	2*a*	1.019(1)	0.8365(5)	0.0132(6)	0.065(8)	0.08(1)	0.062(9)	–0.003(7)	–0.019(6)	0.016(7)

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