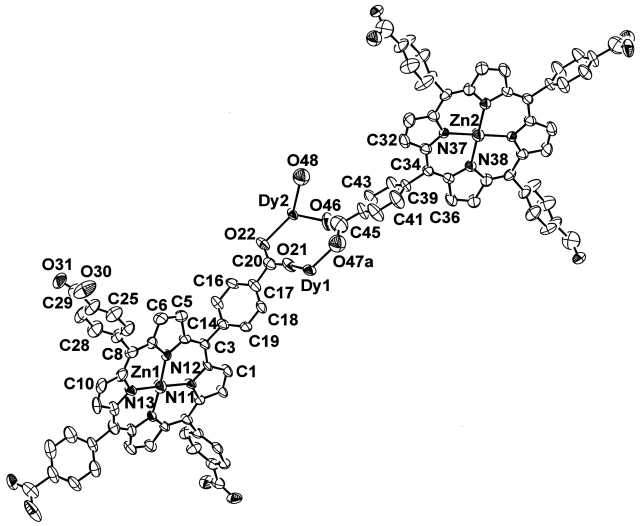
Crystal structure of *catena*-tris(5,10,15,20-(4-carboxylatophenyl)-porphyrin)-aqua-tetradysprosium-trizinc solvate, $(C_{48}H_{24}N_4O_8Zn)_3Dy_4(H_2O) \cdot (solvent)_x$

Sumod George and Israel Goldberg*

School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel

Received February 8, 2011, accepted and available on-line July 13, 2011; CCDC no. 1267/3400



Abstract

$C_{144}H_{72}Dy_4N_{12}O_{25}Zn_3$, orthorhombic, *Cccm* (no. 66), a = 16.7295(3) Å, b = 32.1935(5) Å, c = 33.4739(7) Å, V = 18028.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.072, $wR_{ref}(F^2)$ = 0.187, T = 110 K.

Source of material

The porphyrin (Frontier Scientific) and all the other reactants and solvents were obtained commercially. The target product was obtained by hydrothermal reaction. 1.12 mg (0.002 mmol) of dysprosium(III) oxalate hydrate and 3.32 mg (0.015 mmol) of zinc(II) acetate dihydrate were mixed together, and concentrated hydrochloric acid was added (45 ml) until a clear solution was obtained. In a second vessel, 3 mg (0.0038 mmol) of the 5,10,15,20-tetra(4-carboxy)porphyrin (H_4TCPP) was dissolved in a mixture of 4 ml of *N*,*N*-dimethylformamide (DMF) and 65 ml of 4-acetylpyridine. The organic and inorganic solutions were mixed to react in hydrothermal conditions in a stainless-steel vessel for 3 days, to yield crystalline material of $[(Dy)_4$:(Zn-TCPP)$_3]$ · (DMF/*N*-acetylpyridine)$_x$ suitable for crystallographic analysis. During the reaction the free-base starting porphyrin was core-metalated by the zinc ions.

Experimental details

All the hydrogen atoms were located in calculated positions, except for those of the Dy-coordinated water ligand (of partial occupancy). The crystallization solvent (possibly a mixture of DMF and *N*-acetylpyridine) could not be identified at all, being disordered within the wide intra-lattice channels. Correspondingly, the contribution to the diffraction pattern was subtracted by the Squeeze procedure, using the PLATON software [1]. Nevertheless, the robust lanthanoid-porphyrin framework has been characterized with acceptable reliability. Due to partial disorder of the Dy2-coordinated water species and one of the carboxylate groups, along with high content of disordered solvent affecting the quality of the diffracted intensities, the final *R*-factor is somewhat high.

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.

The intra-lattice voids in the title structure are accommodated by a mixture of DMF and *N*-acetylpyridine crystallization solvent moieties. Charge balance is achieved by deprotonation of the porphyrin tetra-acid ligand. The Dy : metalloporphyrin stochiometry is 4 : 3. The asymmetric unit consists of two zinc-porphyrin ligands located on special positions (one strictly planar on 2/*m* center of inversion and the other slightly deformed in a saddle-like shape on a mirror plane), and two hydrated Dy ions located on twofold rotation axes. The Dy ions have coordination numbers of either 6 (Dy1) or 7 (Dy2), with six of their coordination sites used to link the carboxylate groups of adjacent porphyrin moieties (at Dy—O distance range of 2.236(5) - 2.342(5) Å). The remaining coordination site on Dy2 is occupied by water. Each of the carboxy groups of a given porphyrin moiety bridges two different metal ions. Their diverging orientation in four different directions leads to the formation of a single-framework coordination polymer with open intra-lattice channels propagating parallel to [100]. The solvent-accessible void accounts for about 45 % of the crystal volume. This framework solid 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

* Correspondence author (e-mail: goldberg@post.tau.ac.il)

above 200 °C and expulsion of the crystallization solvent. This study supplements our earlier findings on closely related lanthanoid-TCPP frameworks reported before [4,5].

Table 1. Data collection and handling.

Crystal:	red prism, size 0.30 × 0.35 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	20.84 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, $\Delta\varphi = 1°$, φ
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	51367, 1046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5704
$N(param)_{refined}$:	432
Programs:	PLATON [1], SHELX [7]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	16*m*		0.3616	–0.1823	–0.0366	0.061
H(5)	16*m*		0.3399	–0.0648	–0.1466	0.063
H(6)	16*m*		0.3569	0.0102	–0.1457	0.069
H(10)	16*m*		0.4424	0.1202	–0.0354	0.069
H(15)	16*m*		0.2354	–0.1180	–0.1167	0.066
H(16)	16*m*		0.2160	–0.1612	–0.1711	0.062
H(18)	16*m*		0.4364	–0.2050	–0.1590	0.057
H(19)	16*m*		0.4532	–0.1659	–0.1011	0.053
H(24)	16*m*		0.4897	0.0587	–0.1362	0.074
H(25)	16*m*		0.4874	0.1137	–0.1823	0.084
H(27)	16*m*		0.2967	0.1613	–0.1272	0.101
H(28)	16*m*		0.3001	0.1070	–0.0809	0.093
H(32)	16*m*		0.4478	–0.3494	–0.4632	0.070
H(36)	16*m*		0.4833	–0.4633	–0.3526	0.094
H(40)	16*m*		0.5502	–0.3149	–0.3532	0.118
H(41)	16*m*		0.5729	–0.3639	–0.4030	0.100
H(43)	16*m*		0.3313	–0.3532	–0.3374	0.075
H(44)	16*m*		0.3541	–0.4079	–0.3815	0.082
O(47A)	16*m*	0.50	0.4910(9)	–0.2776(5)	–0.2970(5)	0.093(4)
O(47B)	16*m*	0.50	0.4730(8)	–0.2615(4)	–0.3154(4)	0.074(4)
O(48)	8*k*	0.50	¼	–¼	–0.3551(6)	0.088(5)

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)	8*h*	½	–0.23308(2)	–¼	0.0681(4)	0.0537(3)	0.0235(2)	0	0.0012(2)	0
Dy(2)	8*k*	¼	–¼	–0.28377(1)	0.0918(4)	0.0233(2)	0.0252(2)	–0.0013(2)	0	0
Zn(1)	8*l*	0.38507(8)	–0.02997(4)	0	0.079(1)	0.0450(7)	0.0544(8)	–0.0006(7)	0	0
Zn(2)	4*c*	½	–½	–½	0.086(1)	0.049(1)	0.044(1)	0.006(1)	0	0
C(1)	16*m*	0.3650(4)	–0.1593(2)	–0.0200(2)	0.103(6)	0.021(3)	0.028(4)	–0.006(3)	0.003(4)	0.000(3)
C(2)	16*m*	0.3711(4)	–0.1172(2)	–0.0327(2)	0.075(5)	0.027(3)	0.018(3)	0.004(3)	0.002(3)	–0.008(3)
C(3)	16*m*	0.3621(4)	–0.1038(2)	–0.0721(2)	0.076(5)	0.031(3)	0.020(3)	–0.006(3)	0.000(3)	–0.002(3)
C(4)	16*m*	0.3634(4)	–0.0631(2)	–0.0836(2)	0.063(5)	0.036(4)	0.021(3)	0.000(3)	–0.003(3)	0.007(3)
C(5)	16*m*	0.3514(4)	–0.0486(2)	–0.1243(2)	0.069(5)	0.052(5)	0.036(4)	0.004(4)	–0.003(4)	0.006(4)
C(6)	16*m*	0.3618(5)	–0.0073(2)	–0.1238(2)	0.088(6)	0.046(4)	0.039(4)	–0.007(4)	–0.008(4)	0.018(4)
C(7)	16*m*	0.3815(4)	0.0047(2)	–0.0836(2)	0.062(5)	0.028(3)	0.043(4)	0.003(3)	–0.005(4)	0.005(3)
C(8)	16*m*	0.3973(4)	0.0449(2)	–0.0717(2)	0.056(5)	0.040(4)	0.055(5)	–0.009(3)	–0.016(4)	0.008(4)
C(9)	16*m*	0.4092(4)	0.0572(2)	–0.0321(2)	0.060(5)	0.039(4)	0.059(5)	0.003(3)	–0.006(4)	0.015(4)
C(10)	16*m*	0.4291(4)	0.0980(2)	–0.0189(2)	0.069(5)	0.020(3)	0.084(6)	–0.002(3)	–0.009(4)	0.010(3)
N(11)	8*l*	0.3743(5)	–0.0911(2)	0	0.062(5)	0.032(4)	0.019(4)	–0.009(4)	0	0
N(12)	16*m*	0.3803(3)	–0.0294(1)	–0.0584(2)	0.057(4)	0.025(3)	0.031(3)	0.004(3)	0.001(3)	0.005(2)
N(13)	8*l*	0.4016(5)	0.0305(2)	0	0.063(6)	0.035(4)	0.026(4)	–0.005(4)	0	0
C(14)	16*m*	0.3464(4)	–0.1358(2)	–0.1042(2)	0.066(5)	0.038(4)	0.023(4)	–0.003(3)	0.001(3)	0.000(3)
C(15)	16*m*	0.2757(5)	–0.1360(2)	–0.1245(2)	0.065(5)	0.049(4)	0.050(5)	–0.004(4)	0.005(4)	–0.022(4)
C(16)	16*m*	0.2650(4)	–0.1605(2)	–0.1581(2)	0.049(5)	0.070(5)	0.035(4)	0.000(4)	–0.006(3)	–0.018(4)
C(17)	16*m*	0.3261(5)	–0.1857(2)	–0.1711(2)	0.078(6)	0.036(4)	0.033(4)	–0.014(4)	0.005(4)	–0.007(3)
C(18)	16*m*	0.3957(5)	–0.1877(2)	–0.1501(2)	0.079(6)	0.036(4)	0.029(4)	0.006(4)	0.008(4)	–0.006(3)
C(19)	16*m*	0.4067(4)	–0.1635(2)	–0.1161(2)	0.072(5)	0.036(4)	0.024(4)	0.000(3)	–0.006(3)	0.007(3)
C(20)	16*m*	0.3188(5)	–0.2075(2)	–0.2101(2)	0.064(5)	0.039(4)	0.039(4)	–0.016(4)	0.003(4)	–0.002(3)
O(21)	16*m*	0.3755(3)	–0.2290(2)	–0.2236(1)	0.074(4)	0.059(3)	0.039(3)	–0.011(3)	0.015(3)	–0.015(2)
O(22)	16*m*	0.2516(3)	–0.2054(2)	–0.2285(2)	0.075(4)	0.053(3)	0.046(3)	–0.011(3)	–0.003(3)	–0.021(2)
C(23)	16*m*	0.3959(5)	0.0786(2)	–0.1041(2)	0.065(5)	0.036(4)	0.066(5)	–0.005(4)	–0.005(4)	0.025(4)
C(24)	16*m*	0.4513(5)	0.0793(2)	–0.1343(3)	0.064(6)	0.037(4)	0.083(6)	–0.009(4)	–0.010(5)	0.015(4)
C(25)	16*m*	0.4493(5)	0.1121(3)	–0.1622(3)	0.075(6)	0.065(5)	0.070(6)	–0.008(5)	0.002(5)	0.040(5)
C(26)	16*m*	0.3924(5)	0.1408(2)	–0.1603(3)	0.063(6)	0.048(5)	0.094(7)	–0.008(4)	–0.009(5)	0.037(5)
C(27)	16*m*	0.3343(6)	0.1402(3)	–0.1290(3)	0.085(7)	0.059(5)	0.109(9)	0.013(5)	–0.017(6)	0.029(6)
C(28)	16*m*	0.3379(5)	0.1087(2)	–0.1011(3)	0.085(7)	0.057(5)	0.089(7)	–0.006(5)	–0.002(5)	0.024(5)
C(29)	16*m*	0.3876(7)	0.1764(3)	–0.1910(3)	0.094(8)	0.079(7)	0.068(7)	–0.020(6)	–0.006(6)	0.025(5)
O(30)	16*m*	0.4497(4)	0.1811(2)	–0.2122(2)	0.095(5)	0.104(5)	0.132(6)	–0.036(4)	–0.027(5)	0.082(5)
O(31)	16*m*	0.3238(4)	0.1965(2)	–0.1929(2)	0.126(6)	0.065(4)	0.061(4)	0.036(4)	–0.003(4)	0.026(3)
C(32)	16*m*	0.4571(5)	–0.3726(2)	–0.4802(2)	0.081(5)	0.033(4)	0.061(5)	0.000(4)	–0.002(4)	–0.011(3)
C(33)	16*m*	0.4734(4)	–0.4128(2)	–0.4683(2)	0.050(5)	0.043(4)	0.033(4)	–0.001(3)	–0.001(3)	–0.001(3)
C(34)	16*m*	0.4777(4)	–0.4262(2)	–0.4274(2)	0.040(4)	0.049(4)	0.038(4)	0.007(3)	–0.003(3)	–0.013(3)
C(35)	16*m*	0.4892(4)	–0.4657(2)	–0.4152(2)	0.074(5)	0.047(5)	0.031(4)	0.013(4)	–0.009(4)	–0.008(3)
C(36)	16*m*	0.4918(6)	–0.4800(2)	–0.3749(2)	0.149(9)	0.062(5)	0.024(4)	0.038(6)	0.003(5)	–0.010(4)
N(37)	8*l*	0.4813(4)	–0.4387(2)	–½	0.035(5)	0.035(4)	0.030(4)	0.006(3)	0	0
N(38)	8*i*	½	–½	–0.4403(2)	0.051(5)	0.039(4)	0.035(4)	0.002(4)	0	0

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(39)	16*m*	0.4655(5)	–0.3930(2)	–0.3968(2)	0.065(5)	0.042(4)	0.042(4)	0.009(4)	–0.003(4)	–0.020(3)
C(40)	16*m*	0.5094(6)	–0.3331(3)	–0.3600(3)	0.082(8)	0.079(9)	0.09(1)	–0.032(6)	0.019(7)	–0.044(8)
C(41)	16*m*	0.5255(5)	–0.3640(3)	–0.3886(3)	0.062(6)	0.093(7)	0.095(7)	–0.005(5)	0.023(5)	–0.051(6)
C(42)	16*m*	0.4377(5)	–0.3289(2)	–0.3421(3)	0.072(6)	0.047(5)	0.073(6)	–0.002(4)	0.016(5)	–0.033(4)
C(43)	16*m*	0.3804(5)	–0.3558(2)	–0.3501(2)	0.058(5)	0.074(5)	0.056(5)	–0.001(4)	0.019(4)	–0.029(4)
C(44)	16*m*	0.3939(5)	–0.3883(2)	–0.3773(3)	0.066(6)	0.058(5)	0.081(6)	–0.003(4)	0.007(5)	–0.032(5)
C(45)	16*m*	0.4226(7)	–0.2933(3)	–0.3132(3)	0.102(8)	0.087(8)	0.098(8)	–0.017(7)	–0.004(7)	–0.012(7)
O(46)	16*m*	0.3549(4)	–0.2901(2)	–0.2990(2)	0.095(5)	0.053(3)	0.064(4)	0.018(3)	0.034(3)	–0.003(3)

Acknowledgment. This research was supported by The Israel Science Foundation (grant no. 502/08).

References

1. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148-155.
2. Goldberg, I.: Crystal Engineering of nanoporous architectures and chiral porphyrin assemblies. CrystEngComm **10** (2008) 637-645.
3. Goldberg, I.: Crystal engineering of porphyrin framework solids. Chem. Commun. (2005) 1243-1254.
4. Suslick, K. S.; Byrappa, P.; Chou, J.-H.; Kosal, M. E.; Nakagaki, S.; Smitherny, W. D.; Wilson, S. R.: Microporous porphyrin solids. Acc. Chem. Res. **38** (2005) 283-291.
5. Lipstman, S.; Muniappan, S.; George, S.; Goldberg, I.: Framework coordination polymers of tetra(4-carboxyphenyl)porphyrin and lanthanide ions in crystalline solids. Dalton Trans. (2007) 3273-3281.
6. Muniappan, S.; Lipstman, S.; George, S.; Goldberg, I.: Porphyrin framework solids. Synthesis and structure of hybrid coordination polymers of tetra(carboxyphenyl)porphyrins and lanthanide-bridging ions. Inorg. Chem. **46** (2007) 5544-5554.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.