

Hydrogen-bonded three-dimensional network of a lanthanum(III) exocyclic complex with 5,10,15,20-tetra-4-pyridylporphyrin

Sophia Lipstman and Israel Goldberg*

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

Correspondence e-mail: goldberg@post.tau.ac.il

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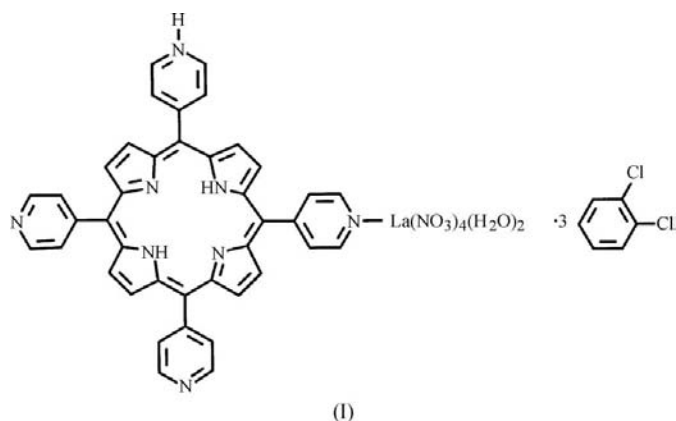
In the complex diaquatetranitrato[5-(pyridinium-4-yl)-10,15,20-tri-4-pyridylporphyrin]lanthanum(III) 1,2-dichlorobenzene trisolvate, $[\text{La}(\text{NO}_3)_4(\text{C}_{40}\text{H}_{27}\text{N}_8)(\text{H}_2\text{O})_2] \cdot 3\text{C}_6\text{H}_4\text{Cl}_2$, the lanthanum ion is coordinated to one of the peripheral pyridyl substituents of the porphyrin entity. Units of the complex are interlinked to one another in three dimensions by a network of $\text{O}-\text{H} \cdots \text{N}$, $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds between the water ligands, nitrate ions, and pyridyl and pyridinium groups of adjacent species. This is the first structural report of an exocyclic complex of the tetrapyridylporphyrin ligand with any lanthanide ion and its self-assembly into a three-dimensional architecture sustained by hydrogen bonds.

Comment

The tetrapyridylporphyrin (TPyP) and tetra(carboxyphenyl)porphyrin (TCPP) ligands have been utilized extensively as building blocks in the design of framework solids (Goldberg, 2008, 2005, 2000, and references therein). Of particular interest is the coordination polymerization of these scaffolds through exocyclic metal ion connectors, which often results in the formation of open but robust architectures (Suslick *et al.*, 2005). The use of lanthanide ions to this end is rather rare. Only recently have hybrid organic-inorganic networks composed of TCPPs and various lanthanide ions been reported (George *et al.*, 2006; Lipstman *et al.*, 2007; Muniappan *et al.*, 2007). The metal ions are oxophilic and coordinate readily to the peripheral carboxyphenyl functions, an interaction which is facilitated by deprotonation of the latter and ion pairing between the component species. Although a few coordination polymers and complexes of some lanthanide ions with bipyridyls are known (Sharma & Rogers, 1999, and references therein), analogous compounds with the TPyP unit have not been obtained thus far. This can be attributed to the relatively low affinity of the lanthanides for

coordination by neutral *N*-pyridyl groups and the need to incorporate additional counter-ions into the lattice. A number of double-decker-type compounds in which lanthanide ions are sandwiched between, and coordinated by, the central pyrrole rings of two TPyPs (Ikeda *et al.*, 2000; Magnera *et al.*, 1997), or between one TPyP and one phthalocyanine ring (Bian *et al.*, 2003; Sun *et al.*, 2003), have also been described.

In the above context we report here the first complex of the TPyP entity with a lanthanum ion, where the coordination takes place on the porphyrin periphery between the metal ion and one of the pyridyl substituents of TPyP. The reaction between TPyP and lanthanum trinitrate hexahydrate is associated with protonation of another pyridyl group (at N34) and formation of the $\text{TPyPH}^+ - \{\text{La}(\text{NO}_3)_4(\text{H}_2\text{O})_2\}^-$ complex, which crystallizes as the title 1,2-dichlorobenzene trisolvate, (I). Similar behaviour of La^{III} ions complexed with four (rather than three) bidentate anions has been observed before (Sharma & Rogers, 1999).



The molecular structure of (I) is shown in Fig. 1. The lanthanum cation is 11-coordinate, where in addition to the nitrate ions it binds to one pyridyl and two water ligands (Table 1). A large excess of the lanthanum salt was used in the

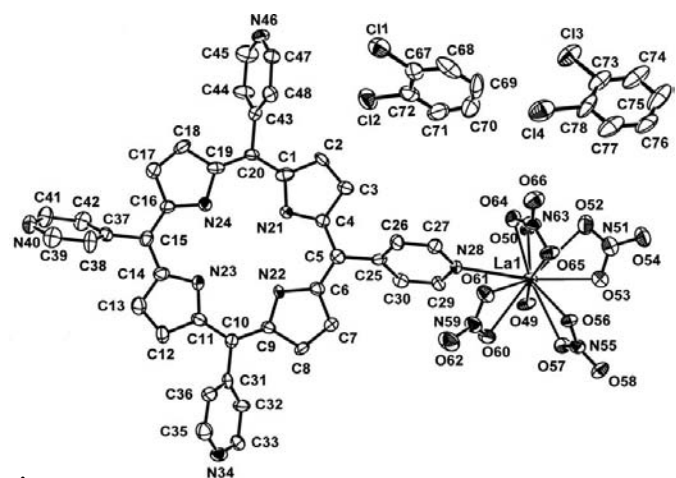
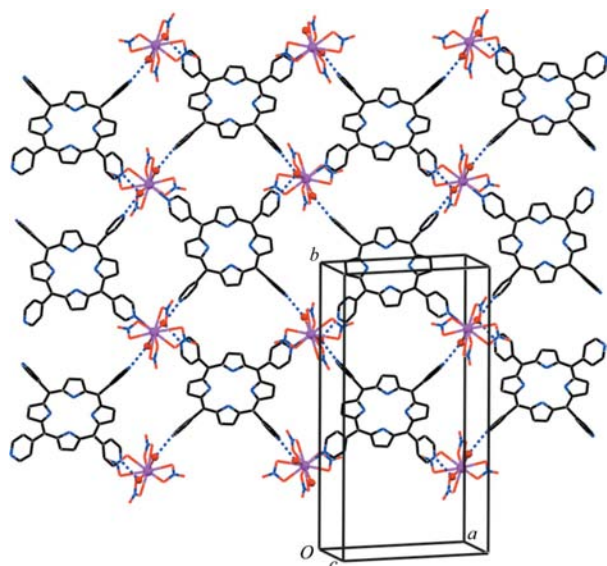


Figure 1

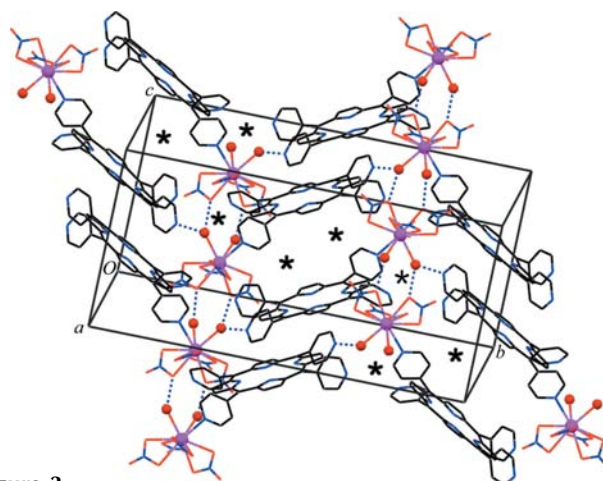
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. H atoms have been omitted. The porphyrin ring exhibits a shallow saddle conformation. One of the three solvent molecules is not included (see *Experimental*).


Figure 2

The two-dimensional square-grid network motif observed in (I). Note that every $\{\text{La}(\text{NO}_3)_4(\text{H}_2\text{O})_2\}$ connecting node is associated with four neighbouring porphyrin units either *via* coordination or hydrogen bonds (denoted by dashed lines). H atoms have been omitted and the La and water O atoms are shown as small spheres.

reaction mixture, anticipating simultaneous coordination of the metal ions to the four pyridyl corners of the porphyrin. Instead, such coordination occurred only at one out of the four sites. In the resulting complex, the H atoms of the two water ligands and the NH34 pyridinium group, along with the O atoms of the four nitrate ions, constitute complementary divergent molecular-recognition sites for supramolecular associations. All five of the potential H-atom donors are utilized in intermolecular hydrogen bonding.

The supramolecular organization of (I) can be best described in a modular way. The $\{\text{La}(\text{NO}_3)_4(\text{H}_2\text{O})_2\}^-$ ion is associated in four equatorial directions with four different TPyPs. This involves a direct $\text{La}-\text{N}_{\text{py}}$ coordination, two $\text{O}-\text{H}(\text{water})\cdots\text{N}_{\text{py}}$ hydrogen bonds from the two water ligands to porphyrin units, and an additional $\text{N}_{\text{py}}-\text{H}^+\cdots\text{O}_{\text{water}}$ hydrogen bond in the fourth direction (Table 2). As a result, the molecular units assemble into undulating two-dimensional supramolecular square-grid-type layers (Fig. 2). The mean plane of the layers, which are stacked along the *c* axis, is parallel to $(\bar{2}01)$. Additional hydrogen bonds operate between the $\{\text{La}(\text{NO}_3)_4(\text{H}_2\text{O})_2\}$ connecting nodes of subsequent layers in the stack. The two water ligands donate their H atoms to the nitrate groups of the layer above, while two of the nitrate groups act as acceptors in hydrogen bonds with the water ligands from the layer below (Table 2). The crystal structure (Fig. 3) consists of alternating zones of the porphyrin moieties (centred at $y = 0$ and $\frac{1}{2}$), and the $\{\text{La}(\text{NO}_3)_4(\text{H}_2\text{O})_2\}$ connectors (centred at $y = \frac{1}{4}$ and $\frac{3}{4}$) aligned perpendicular to the *b* axis. Molecules of the 1,2-dichlorobenzene solvent are enclathrated within the interstitial voids. They are positioned at the interface between porphyrin ligands of neighbouring layers, as well as between adjacent pillars of the metallic bridges in any given zone (Fig. 3). The supramolecular framework is held together


Figure 3

The crystal packing of (I), showing (edge-on) the stacked arrangement of the undulating layers depicted in Fig. 2. Note the interlayer hydrogen-bonding interactions (dashed lines) from the water ligands of one layer to the nitrate anions of adjacent layers. Asterisks (*) indicate the approximate locations of the 1,2-dichlorobenzene solvent molecules. H atoms have been omitted and the La and water O atoms are shown as small spheres.

by the inorganic pillars in a similar way to that observed in the coordination polymers of TCPP with solvated lanthanide ions (Lipstman *et al.*, 2007; Muniappan *et al.*, 2007).

In summary, this study confirms earlier observations (Sharma & Rogers, 1999) that lanthanide ions can be utilized in the formation of networked architectures involving not only coordination forces but also hydrogen bonds. It also indicates for the first time that, in addition to the TCPP building blocks, the TPyP moieties may also coordinate to lanthanides. In the former case, charge balance is achieved by deprotonation of the carboxylic acid groups. In structures with pyridylporphyrins, the hydrogen-bonding sites of suitable counterions and water ligands located in the coordination environment of the metal centres provide additional/alternative means for supramolecular aggregation. This is well demonstrated by the three-dimensional supramolecular architecture of (I).

Experimental

All reactants and solvents were obtained commercially and used without further purification. TPyP (0.015 mmol) and lanthanum(III) nitrate hexahydrate (0.100 mmol) were dissolved in a 1:1 mixture of 1,2-dichlorobenzene and ethanol (15 ml). The resulting solution was refluxed for 2 h. After filtration, the solution was allowed to evaporate slowly. X-ray quality red crystals of (I) were obtained after five weeks.

Crystal data

$[\text{La}(\text{NO}_3)_4(\text{C}_{40}\text{H}_{27}\text{N}_8)(\text{H}_2\text{O})_2] \cdot 3\text{C}_6\text{H}_4\text{Cl}_2$	$\beta = 112.984 (1)^\circ$
$M_r = 1483.65$	$V = 6099.34 (19) \text{ \AA}^3$
Monoclinic, $P2_1/c$	$Z = 4$
$a = 17.1527 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 28.5415 (6) \text{ \AA}$	$\mu = 1.04 \text{ mm}^{-1}$
$c = 13.5331 (2) \text{ \AA}$	$T = 110 \text{ K}$
	$0.25 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	36533 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	10767 independent reflections
$T_{\min} = 0.798$, $T_{\max} = 0.911$	6137 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.091$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.148$	
$S = 0.94$	$\Delta\rho_{\text{max}} = 0.83 \text{ e } \text{\AA}^{-3}$
10767 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e } \text{\AA}^{-3}$
748 parameters	

Table 1

Selected bond lengths (Å).

La—O49	2.506 (4)	La—O60	2.643 (4)
La—O50	2.583 (4)	La—O65	2.654 (4)
La—O56	2.593 (4)	La—O57	2.720 (4)
La—O61	2.601 (4)	La—N28	2.773 (5)
La—O53	2.602 (5)	La—O52	2.820 (5)
La—O64	2.611 (4)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N34—H34 \cdots O50 ⁱ	0.96 (7)	1.88 (7)	2.810 (7)	163 (6)
O49—H49A \cdots N40 ⁱⁱ	0.82	1.92	2.652 (7)	148
O49—H49B \cdots O65 ⁱⁱⁱ	0.82	2.08	2.899 (5)	172
O50—H50A \cdots O56 ⁱⁱⁱ	0.82	1.93	2.751 (6)	179
O50—H50B \cdots N46 ^{iv}	0.82	1.84	2.658 (6)	179

Symmetry codes: (i) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z - \frac{1}{2}$; (iii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $-x + 2, -y + 2, -z$.

H atoms bound to C atoms were located in calculated positions and constrained to ride on their parent atoms, with $C-H = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Inspection of the contoured representation of the difference electron density indicated that the two pyrrole N-bound H atoms were disordered between the four pyrrole sites. They were then also located in calculated positions and constrained to ride on their parent atoms, with $N-H = 0.88 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The H atoms of the two water ligands were either located in a difference Fourier map (atom O49) or in calculated positions to optimize the hydrogen bonding (atom O50). All O—H bond lengths were constrained at 0.82 \AA but not refined, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Finally, the H atom on the pyridyl group at N34 was located in a difference Fourier map as the highest residual peak. Its atomic coordinates were included in the final refinement with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. One of the 1,2-dichlorobenzene solvent species could not be modelled reliably by discrete atoms, though it was clearly identified in the difference Fourier map. Its contribution was subtracted from the diffraction pattern by the SQUEEZE method, using

PLATON (Spek, 2003). In the unit cell, the sites accessible by these solvent species are centred at $(0, 0, 0)$ and $(0, \frac{1}{2}, 0)$, each of the created voids being characterized by a volume of 444 \AA^3 with residual electron density of 165 e . The other two 1,2-dichlorobenzene molecules of the asymmetric unit included in the structural model also appear to be characterized by partial orientational disorder.

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3203). Services for accessing these data are described at the back of the journal.

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