

mixture of L (0.0777 g, 0.1 mmol) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.0433 g, 0.1 mmol) in ethyl acetate at room temperature, then recrystallized from methanol/ethyl acetate (1 : 1, V/V) by slow evaporation to give colorless transparent crystal suitable for structure determination.

Structure measurement for the lanthanum complex ($[\text{La}(\text{NO}_3)_3\text{L}] \cdot 3.75\text{H}_2\text{O}$) was performed on a Siemens P4 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm) at 291(2) K, using the $\omega/2\theta$ scan technique. A summary of crystallographic data and the details of the structure refinements are listed in Table 1. Empirical absorption correction was applied. The structure was solved by direct method and refined by full-matrix least square techniques with all ordered non-hydrogen atoms treated anisotropically. Some carbon atoms of a benzyl group were disordered in the lattice owing to fast thermal movement. All hydrogen atoms were generated theoretically. All the calculations were performed with the program package Siemens SHELXTL-97.⁶

Table 1 Crystallographic data, data collection and the structure refinement for the complex $[\text{La}(\text{NO}_3)_3\text{L}] \cdot 3.75\text{H}_2\text{O}$

Formula	$\text{C}_{48}\text{H}_{55.50}\text{LaN}_7\text{O}_{18.75}$
M_r	1169.40
Crystal size/mm ³	0.56 × 0.46 × 0.28
Crystal system	Monoclinic
Space group	$P2_1/n$
$a/\text{nm}; \alpha/^\circ$	1.0644(3); 90
$b/\text{nm}; \beta/^\circ$	2.3889(5); 90.65
$c/\text{nm}; \gamma/^\circ$	2.1917(5); 90
V/nm^3	5.573(2)
Z	1
$D_c/(\text{g} \cdot \text{cm}^{-3})$	1.394
hkl range	0—12, 0—28, —26—26
$F(000)$	2389
No. of refs.	11043
No. of independent refs.	9793
R_1	0.0487
$wR [I > 2\sigma(I)]$	0.1266

Figure 1 shows molecular structure of the La(III) complex. Selected bond lengths and bond angles are given in Table 2.

The complex is composed of a neutral $[\text{La}(\text{NO}_3)_3\text{L}]$ entity and some water molecules. Each La(III) ion binds to 9 oxygen atoms, three of which belong to carbonyl groups from three tripodal ligands [O(2), O(4) and O(6)] and six to three bidentate nitrate groups [O(7), O(8), O(10), O(11), O(13) and O(14)] (see Figure 1). In general, multidentate tripodal ligands have the ability to be employed as cup-like hosts for 3d and/or 4f metal ions and to form the mononuclear, homopolynuclear (4f, 4f) or heteropolynuclear (3d, 4f) complexes.^{7,8} The poten-

tial heptadentate L is a multidentate hard-oxygen donor-containing ligand and we wish that it might be used as an excellent chelator for lanthanide ions. To our surprise, L acts as tridentate bridging spacer in the complex due to steric hindrance and links the La(III) ions to form a two-dimensional sheet of 4.8^2 topology assembled by coordination bond (La—O) (Figure 2, Scheme 2). 2D sheet of 4.8^2 framework, predicted by Wells,⁹ belongs to a rather unusual topology and only one¹⁰ of which consisting of Er(III) ions and 4,4'-bipyridine-*N,N'*-dioxide was observed previously for coordination framework in lanthanide complexes. This net consists of three connected nodes shared by a tetragonal square unit and two octagons. The former is a 32-membered ring with 2 metal ions and 2 ligands and the latter is a 64-membered ring with 4 metal ions and 4 ligands. Interpenetration may lead to the formation of 3D network but that is prevented by 4-membered ring motifs of adjacent layers occupying the large cavities. On the one hand, there is a marked difference between Ref. 4 and this article, that is, the apical atoms or groups are different and it is obvious to find that the structure of the lanthanide complex would change from 3D-network to 2D-sheet of 4.8^2 net directed by coordination and hydrogen bonds when substituting nitrogen atoms for propyl groups in spite of

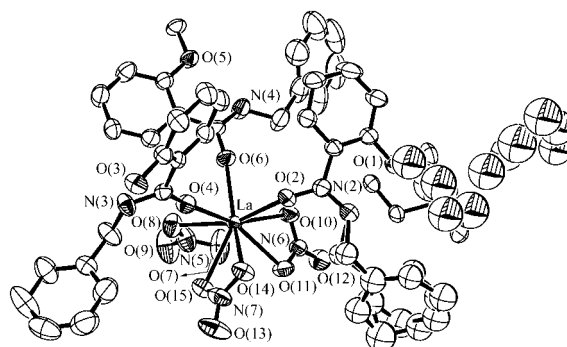


Figure 1 Molecular structure of the $[\text{La}(\text{NO}_3)_3\text{L}] \cdot 3.75\text{H}_2\text{O}$ complex with thermal ellipsoids at the 50% possibility level. Only the nitrogen atoms and oxygen atoms have been labeled for clarity.

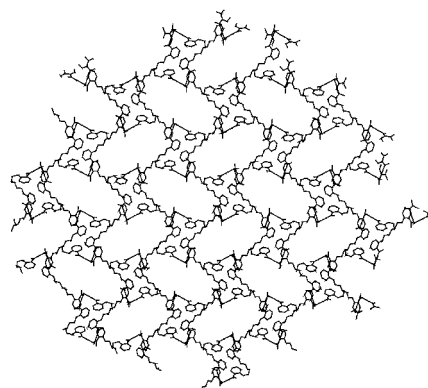
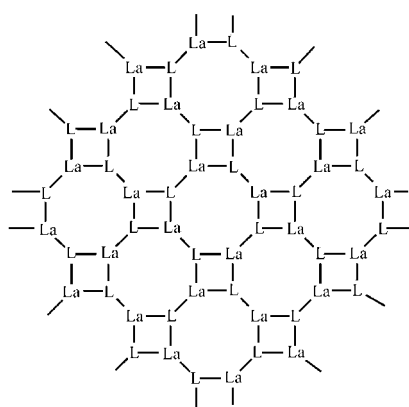


Figure 2 View of 4.8^2 net in La(III) complex. Nitrate groups, water molecules, *N*-benzyl group and all hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (nm) and bond angles ($^{\circ}$) of the $[\text{La}(\text{NO}_3)_3\text{L}]$ complex

Bond lengths					
La—O(2)	0.2416(4)	La—O(7)	0.2553(4)	La—O(11)	0.2516(4)
La—O(4)	0.2390(4)	La—O(8)	0.2548(4)	La—O(13)	0.2588(4)
La—O(6)	0.2403(4)	La—O(10)	0.2591(4)	La—O(14)	0.2552(5)
Mean La—O (C=O)	0.2403			Mean NO_3^- La—(NO_3^-)	0.2558
Bond angles					
O(2)-La-O(7)	123.99(15)	O(2)-La-O(8)	74.10(13)	O(2)-La-O(10)	74.55(14)
O(2)-La-O(11)	82.76(14)	O(2)-La-O(13)	160.48(15)	O(2)-La-O(14)	141.69(15)
O(2)-La-N(5)	99.00(16)	O(2)-La-N(6)	79.90(14)	O(2)-La-N(7)	161.27(15)
O(4)-La-O(2)	92.60(14)	O(4)-La-O(6)	81.41(13)	O(4)-La-O(7)	81.74(14)
O(4)-La-O(8)	75.59(14)	O(4)-La-O(10)	157.04(13)	O(4)-La-O(11)	148.83(13)
O(4)-La-O(13)	76.77(15)	O(4)-La-O(14)	124.79(15)	O(4)-La-N(5)	77.67(14)
O(4)-La-N(6)	170.56(14)	O(4)-La-N(7)	100.58(16)	O(6)-La-O(2)	84.82(14)
O(6)-La-O(7)	147.11(15)	O(6)-La-O(8)	147.76(14)	O(6)-La-O(10)	78.58(13)
O(6)-La-O(11)	28.42(13)	O(6)-La-O(13)	77.50(15)	O(6)-La-O(14)	92.22(19)
O(6)-La-N(5)	158.86(14)	O(6)-La-N(6)	103.42(14)	O(6)-La-N(7)	84.06(17)
O(7)-La-O(10)	121.21(14)	O(7)-La-O(13)	71.25(16)	O(7)-La-N(5)	25.24(14)
O(7)-La-N(6)	97.63(14)	O(7)-La-N(7)	71.58(16)	O(8)-La-O(7)	50.41(14)
O(8)-La-O(10)	117.38(14)	O(8)-La-O(13)	117.78(15)	O(8)-La-O(14)	119.44(19)
O(8)-La-N(5)	25.17(14)	O(8)-La-N(6)	96.69(15)	O(8)-La-N(7)	121.95(15)
O(10)-La-N(5)	122.52(14)	O(10)-La-N(6)	25.02(12)	O(10)-La-N(7)	88.49(16)
O(11)-La-O(7)	75.67(14)	O(11)-La-O(8)	73.49(14)	O(11)-La-O(10)	49.85(12)
O(11)-La-O(13)	114.75(15)	O(11)-La-O(14)	69.36(17)	O(11)-La-N(5)	72.71(14)
O(11)-La-N(6)	25.05(12)	O(11)-La-N(7)	92.43(17)	O(13)-La-O(10)	109.40(15)
O(13)-La-N(5)	94.69(18)	O(13)-La-N(6)	112.04(14)	O(13)-La-N(7)	24.02(14)
O(14)-La-O(7)	74.79(19)	O(14)-La-O(10)	67.45(16)	O(14)-La-O(13)	48.56(15)

Scheme 2 Schematic representation of a two-dimensional 4.8^2 net

different lanthanide ions. On the other hand, in comparison with Ref. 7a, it is clear to find that the structure of lanthanide complexes varies from discrete mononuclear to 2D net and the heptadentate tripodal ligands act as heptadentate or tridentate ligands, respectively, most

due to the difference in rigidity derived from three arms. As a whole, these amide-type tripodal ligands show strong terminal group and skeletal effects in the process of coordination with the lanthanide ions.¹¹

The average distance of La—O (L, C=O) (0.2403 nm) is shorter than that of La—O (NO_3^-) (0.2558 nm), showing that coordination ability of carbonyl oxygen atoms is stronger than that of nitrate group.

Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with supplementary publication No. 218043. Copies of the data can be obtained free of charge on application to CCDC. E-mail: deposit@ccdc.cam.ac.uk.

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