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$La(NO_2)_3$, a novel (3,9)-connected lanthanide-based network

Qing-Qing Kang, La-Sheng Long, Rong-Bin Huang* and Lan-Sun Zheng

Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

Correspondence e-mail: rbhuang@xmu.edu.cn

Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(O–N) = 0.005 Å
R factor = 0.013
wR factor = 0.029
Data-to-parameter ratio = 8.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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A novel (3,9)-connected lanthanide-based network of lanthanum trinitrite, $La(NO_2)_3$, was synthesized and characterized by single-crystal X-ray diffraction. The central La^{III} atom is coordinated by nine O atoms from nine nitrite anions. These unidentate O atoms are arranged in a capped trigonal prism. The resulting [LaO_9] polyhedron shows 3m symmetry.

Comment

Assemblies of coordination polymers are of a great current interest, not only because of their potential application in the field of materials chemistry (Seo *et al.*, 2000), but also for their intriguing architectures, new topologies and intertwining phenomena (Carlucci *et al.*, 2002). By the careful design of tailored ligands, various novel supramolecular architectures have been constructed (Zaworotko, 1994). All of these extraordinary structures are of fundamental importance in structure design and in the understanding of structure property correlations. Considering the existing coordination systems, one notes that there has been little progress concerning the synthesis of high-connected networks.

Lanthanide ions possess larger radii and higher coordination numbers, thus lanthanide-based networks may generate high-connecting topological structures as in the case of eight-connected lanthanide coordination polymers (Long *et al.*, 2001). This is especially true when linear ligands were used, since steric hindrance between the ligands is reduced to a

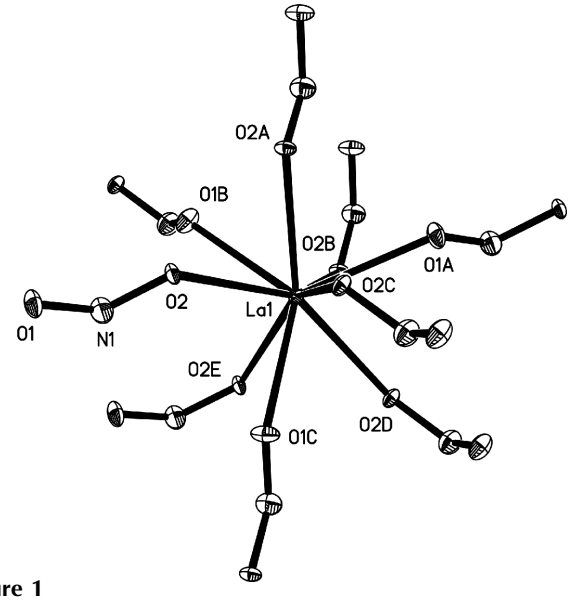

Figure 1
*ORTEP*II plot (Johnson, 1976), showing the coordination environment of La^{III} atoms and the connected mode of the nitrite anions in (I). Displacement ellipsoids are drawn at the 50% probability level.

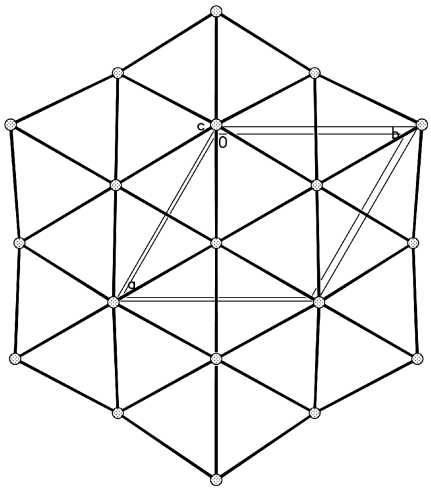

Figure 2
Plot showing the 3^6 topological net in (I), in which the lines represent nitrite anions and the dotted spheres represent La^{III} atoms.

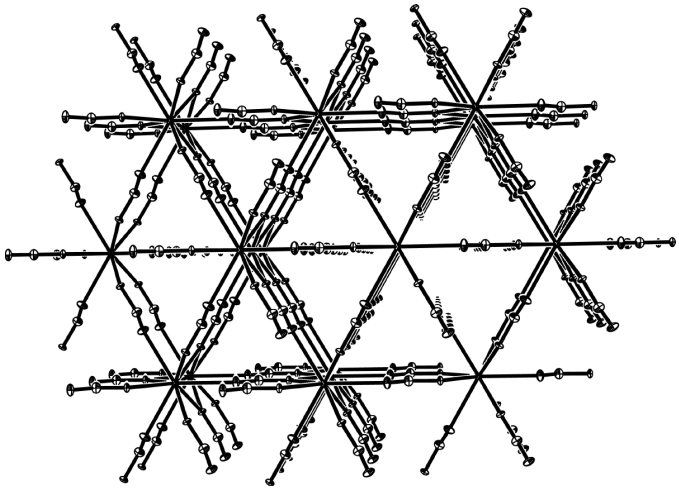

Figure 3
*ORTEP*II plot (Johnson, 1976), showing the (3,9)-connected network of (I), viewed along the *c* axis. Displacement ellipsoids are drawn at the 50% probability level.

lower extent in the high-connected network. Based on this consideration, as well as our interest in pursuing novel topological structures of coordination polymers (Yang *et al.*, 2002), we were encouraged to use lanthanide ions, Ln^{3+}, and a simple ligand, the nitrite anion, to construct a coordination polymer, *viz*. $La(NO_2)_3$ (I).

Each La^{III} atom in (I) is nine-coordinated by nine nitrite anions with each nitrite anion adopting a 3-connected mode, as shown in Fig. 1. The La—O bond lengths range from 2.491 (3) Å to 2.589 (3) Å, and are comparable to those encountered for ninefold lanthanum-oxygen coordination (2.512(2)-2.780 (2) Å) (Long *et al.*, 2000). The La···La distance of 4.0954 (15) Å is shorter than those reported for other ninefold lanthanum-oxygen coordination polymers (4.5–4.7 Å) (Long *et al.*, 2000), and indicates that the metal···metal distances are primarily governed by the nature and mode of the coordination of the bridging groups (Sun *et al.*, 2002). The assembly of the three-dimensional network of (I) can be viewed as follows: Firstly, each lanthanum ion is six-coordinated by six nitrite anions with each nitrite anion connected to two lanthanum atoms, resulting in a 3^6 layer structure, as shown in Fig. 2. Secondly, the 3^6 layer structure is connected by three μ_2-oxygen bridges from adjacent layers, generating a (3, 9)-connected network, as shown in Fig. 3. Although many coordination polymers have been reported, they usually exhibit low-connected networks based on three- to four-connected nodes. Examples of high-connected topological networks have been rarely reported. To the best of our knowledge, only two eight- and one nine-connected topologies have recently been reported (Long *et al.*, 2001), while the (3, 9)-connected network in (I) has not been found so far.

Experimental

The title compound was synthesized by the hydrothermal reaction of $LaCl_3{\cdot}H_2O$ (0.41 g, 1 mmol, Aldrich 99.99%), $NaNO_2$ (0.21 g, 3 mmol, Aldrich 99.99%) and 10 ml deionized water for 6 d at 393 K, followed by slow cooling to room temperature over a 30 h period. Needle-like colorless crystals of (I) were obtained in about 62% yield (0.17 g).

Crystal data

$La(NO_2)_3$
M_r = 276.94
Trigonal, *R*3*m*
a = 10.6226 (19) Å
c = 4.0954 (15) Å
V = 400.21 (18) Å^3
Z = 3
D_x = 3.447 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 746 reflections
θ = 3.8–28.0°
μ = 7.99 mm^{-1}
T = 273 (2) K
Needle, colorless
0.12 × 0.01 × 0.01 mm

Data collection

Bruker SMART APEX 2000 diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.447, T_{max} = 0.924
738 measured reflections
195 independent reflections
195 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.0°
h = −13 → 13
k = −10 → 13
l = −3 → 5

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.013
$wR(F^2)$ = 0.029
S = 1.14
195 reflections
22 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0156P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.025
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Absolute structure: Flack (1983), 40 Friedel pairs
Flack parameter = 0.06 (5)

Table 1
Selected geometric parameters (Å, °).

La1—O1^{i}	2.491 (3)	La1···La1^{ii}	4.0954 (15)
La1—O2^{ii}	2.569 (3)	O1—N1	1.226 (5)
La1—O2	2.589 (3)	O2—N1	1.268 (4)
O1—N1—O2	124.0 (4)		

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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