Crystal structure of tris[bis(pentamethylene)urea]trinitrato-lanthanum(III), $La(NO_3)_3[(C_5H_{10}N)_2CO]_3$

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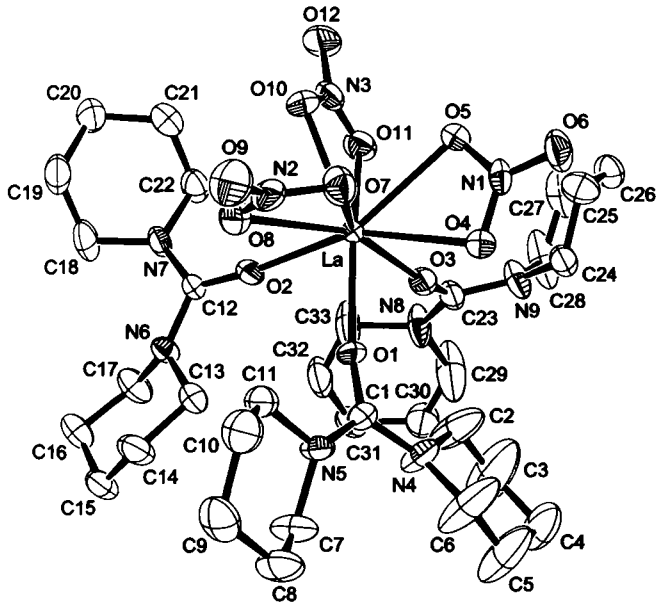

Abstract

$C_{33}H_{60}LaN_9O_{12}$, monoclinic, $P12_1/c1$ (no. 14), $a = 10.158(3)$ Å, $b = 21.971(5)$ Å, $c = 19.301(3)$ Å, $\beta = 104.13(2)°$, $V = 4177.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.045$, $wR_{ref}(F^2) = 0.140$, $T = 293$ K.

Source of material

The title compound was obtained in a systematic investigation of lanthanide nitrate complexes with bis(pentamethylene)urea (BPMU). It was prepared by reaction of hydrated lanthanum trinitrate and BPMU in absolute ethanol.

Discussion

The structural chemistry of lanthanides highlights a wide variety of coordination numbers and relations, due to the lack of strong crystal field effects for the 4*f* electron configurations and to their large ionic radii. In particular, in the nitrate complexes we could observe different coordination modes of this ligand, either as monodentate, bridging or chelating.

The structure of the title compound consists of well isolated molecules where the lanthanum is nine-coordinated to three bidentate nitrato moieties and three oxygen atoms from the BPMU ligand in a distorted tricapped trigonal prism geometry. The three BPMU oxygens form one base of the prism while each of the nitrate oxygens are one in the opposite prism base and the second in capping position. A comparison with the isostructural Nd derivative [1] shows a reduction of the cell parameters (0.01 Å for *a*,*b* and 0.15 Å for *c*), with a volume reduction of 25 Å^3, imputable to the known lanthanide contraction effect. The La—O bond lengths range between 2.600(6) Å and 2.630(6) Å for the three bidentate nitrates (with an average value of 2.610 Å), values that are 0.16 Å (on average) larger than the La—O bond lengths for the BPMU ligand oxygens (range from 2.449(6) Å to 2.458(5) Å, average value of 2.453 Å). Moreover, the La—O distances for the six nitrate oxygens show a slightly asymmetric distribution, with a difference of 0.02 Å between oxygens belonging to the same nitrate ligand, a value in agreement with that found in the Nd-BPMU derivative [1]. The O–La–O angles vary from 48.3(2)° to 156.3(2)°.

Table 1. Data collection and handling.

Crystal:	white prism, size 0.09 × 0.12 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.9 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	43.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6032, 5120
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4009
$N(param)_{refined}$:	497
Programs:	SIR92 [2], SHELXL-97 [3], ORTEP-3 [4], WinGX [5]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	4*e*	0.5266	0.1572	0.5828	0.205
H(2B)	4*e*	0.4199	0.1098	0.5955	0.205
H(3A)	4*e*	0.5416	0.0655	0.5472	0.309
H(3B)	4*e*	0.5452	0.1184	0.4940	0.309
H(4A)	4*e*	0.3484	0.0288	0.4816	0.173
H(4B)	4*e*	0.4269	0.0487	0.4245	0.173
H(5A)	4*e*	0.2956	0.1311	0.3914	0.236
H(5B)	4*e*	0.1899	0.0831	0.4039	0.236
H(6A)	4*e*	0.1800	0.1191	0.4970	0.242
H(6B)	4*e*	0.1742	0.1729	0.4437	0.242
H(7A)	4*e*	0.2628	0.2492	0.4243	0.113
H(7B)	4*e*	0.2961	0.3170	0.4481	0.113
H(8A)	4*e*	0.0972	0.3156	0.3595	0.124
H(8B)	4*e*	0.0332	0.2679	0.4023	0.124
H(9A)	4*e*	−0.0544	0.3612	0.4205	0.126
H(9B)	4*e*	0.0908	0.3905	0.4415	0.126
H(10A)	4*e*	0.0286	0.3740	0.5459	0.123
H(10B)	4*e*	−0.0155	0.3069	0.5241	0.123
H(11A)	4*e*	0.2497	0.3499	0.5652	0.091
H(11B)	4*e*	0.1826	0.3025	0.6068	0.091
H(13A)	4*e*	0.5000	0.3398	0.6128	0.095
H(13B)	4*e*	0.6053	0.3159	0.5716	0.095

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(14A)	4e	0.4634	0.3841	0.4981	0.110
H(14B)	4e	0.4906	0.4337	0.5584	0.110
H(15A)	4e	0.6155	0.4592	0.4790	0.104
H(15B)	4e	0.6797	0.3938	0.4836	0.104
H(16A)	4e	0.8377	0.4584	0.5540	0.113
H(16B)	4e	0.7311	0.4801	0.5957	0.113
H(17A)	4e	0.8371	0.3607	0.6011	0.108
H(17B)	4e	0.8740	0.4077	0.6641	0.108
H(18A)	4e	0.7756	0.4614	0.7298	0.121
H(18B)	4e	0.9168	0.4477	0.7825	0.121
H(20A)	4e	0.9356	0.4463	0.9155	0.133
H(20B)	4e	0.8056	0.4600	0.9436	0.133
H(19A)	4e	0.6739	0.4683	0.8256	0.127
H(19B)	4e	0.7949	0.5147	0.8370	0.127
H(21A)	4e	0.8431	0.3542	0.9431	0.137
H(21B)	4e	0.7030	0.3704	0.8911	0.137
H(22A)	4e	0.9437	0.3461	0.8477	0.100
H(22B)	4e	0.8165	0.3030	0.8339	0.100
H(24A)	4e	0.5755	−0.0094	0.7167	0.087

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(24B)	4e	0.5177	0.0560	0.7231	0.087
H(25A)	4e	0.5051	−0.0028	0.8200	0.111
H(25B)	4e	0.5986	0.0541	0.8442	0.111
H(27A)	4e	0.8486	0.0381	0.8749	0.159
H(27B)	4e	0.9065	−0.0264	0.8652	0.159
H(26A)	4e	0.7092	−0.0318	0.9023	0.106
H(26B)	4e	0.6954	−0.0651	0.8288	0.106
H(28A)	4e	0.8427	−0.0192	0.7468	0.183
H(28B)	4e	0.9220	0.0405	0.7760	0.183
H(29A)	4e	0.9887	0.0780	0.6912	0.305
H(29B)	4e	0.8507	0.0587	0.6406	0.305
H(30A)	4e	0.8705	0.1093	0.5642	0.155
H(30B)	4e	1.0200	0.0909	0.5993	0.155
H(31A)	4e	0.9714	0.1954	0.5576	0.120
H(31B)	4e	1.0829	0.1844	0.6289	0.120
H(32A)	4e	0.9546	0.2556	0.6619	0.181
H(32B)	4e	0.8206	0.2297	0.6134	0.181
H(33A)	4e	0.7990	0.2203	0.7094	0.201
H(33B)	4e	0.9505	0.2024	0.7412	0.201

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}
La	4e	0.47884(5)	0.22669(2)	0.75132(2)	0.0724(4)	0.0348(3)	0.0371(3)	−0.0039(2)	0.0161(2)	0.0021(2)
O(1)	4e	0.3723(6)	0.2320(2)	0.6229(3)	0.097(4)	0.056(4)	0.032(3)	0.002(3)	0.004(3)	−0.002(2)
O(2)	4e	0.6376(6)	0.3033(3)	0.7266(3)	0.085(4)	0.064(4)	0.048(3)	−0.018(3)	0.018(3)	0.007(3)
O(3)	4e	0.6323(6)	0.1499(3)	0.7228(3)	0.077(4)	0.057(4)	0.066(4)	0.005(3)	0.029(3)	0.003(3)
O(4)	4e	0.3140(6)	0.1335(3)	0.7238(3)	0.092(4)	0.060(4)	0.053(4)	−0.009(3)	0.014(3)	0.000(3)
O(5)	4e	0.4014(6)	0.1495(3)	0.8356(3)	0.091(4)	0.061(4)	0.052(3)	−0.011(3)	0.023(3)	0.005(3)
O(6)	4e	0.2492(7)	0.0793(3)	0.8047(4)	0.113(5)	0.063(4)	0.130(6)	−0.030(4)	0.053(5)	0.006(4)
O(7)	4e	0.2382(7)	0.2585(3)	0.7623(4)	0.091(5)	0.063(5)	0.102(5)	0.010(3)	0.032(4)	0.010(4)
O(8)	4e	0.3606(8)	0.3337(3)	0.7457(4)	0.111(6)	0.063(4)	0.085(5)	0.012(4)	0.029(4)	0.006(3)
O(9)	4e	0.1517(9)	0.3492(4)	0.7492(5)	0.136(7)	0.094(6)	0.138(7)	0.054(5)	0.046(6)	0.002(5)
O(10)	4e	0.5270(8)	0.2706(3)	0.8802(3)	0.113(5)	0.076(5)	0.045(3)	−0.006(4)	0.014(3)	−0.011(3)
O(11)	4e	0.6790(7)	0.2081(3)	0.8633(4)	0.089(5)	0.084(5)	0.068(4)	−0.001(4)	0.014(4)	0.014(4)
O(12)	4e	0.6926(9)	0.2447(4)	0.9694(4)	0.174(8)	0.122(6)	0.045(4)	−0.028(6)	−0.014(5)	0.010(4)
N(1)	4e	0.3191(7)	0.1191(3)	0.7881(4)	0.068(5)	0.032(4)	0.090(6)	−0.002(3)	0.026(4)	0.005(4)
N(2)	4e	0.248(1)	0.3139(4)	0.7526(4)	0.104(7)	0.066(6)	0.068(5)	0.027(5)	0.028(5)	−0.008(4)
N(3)	4e	0.634(1)	0.2400(4)	0.9056(4)	0.110(7)	0.068(6)	0.051(5)	−0.026(5)	0.005(5)	0.015(4)
N(4)	4e	0.3376(8)	0.1742(4)	0.5238(4)	0.099(6)	0.080(6)	0.066(5)	0.039(5)	−0.022(4)	−0.034(4)
N(5)	4e	0.2319(7)	0.2674(3)	0.5214(3)	0.074(4)	0.067(5)	0.038(4)	0.019(4)	0.013(3)	−0.002(3)
N(6)	4e	0.6857(6)	0.3728(3)	0.6507(3)	0.058(4)	0.064(4)	0.054(4)	−0.009(3)	0.017(3)	0.015(3)
N(7)	4e	0.7868(8)	0.3773(3)	0.7720(4)	0.093(5)	0.047(4)	0.066(5)	−0.016(4)	0.002(4)	0.018(4)
N(8)	4e	0.835(1)	0.1326(3)	0.6984(6)	0.157(8)	0.044(5)	0.21(1)	−0.010(5)	0.146(8)	−0.005(5)
N(9)	4e	0.7198(8)	0.0547(3)	0.7384(5)	0.087(6)	0.056(5)	0.137(8)	0.006(4)	0.063(5)	0.031(5)
C(1)	4e	0.3159(8)	0.2252(4)	0.5586(4)	0.070(5)	0.054(5)	0.053(6)	0.002(4)	0.017(4)	−0.007(4)
C(2)	4e	0.449(2)	0.1328(7)	0.5591(7)	0.20(2)	0.16(1)	0.11(1)	0.12(1)	−0.05(1)	−0.063(9)
C(3)	4e	0.486(2)	0.0962(8)	0.518(1)	0.22(2)	0.15(2)	0.32(3)	0.11(2)	−0.11(2)	−0.11(2)
C(4)	4e	0.384(2)	0.0635(6)	0.4610(8)	0.17(1)	0.077(8)	0.15(1)	0.041(9)	−0.02(1)	−0.037(8)
C(5)	4e	0.268(2)	0.1070(7)	0.4276(9)	0.20(2)	0.14(1)	0.19(2)	0.08(1)	−0.07(1)	−0.10(1)
C(6)	4e	0.234(2)	0.1424(8)	0.4712(9)	0.17(1)	0.19(2)	0.18(2)	0.09(1)	−0.09(1)	−0.13(1)
C(7)	4e	0.233(1)	0.2838(6)	0.4476(5)	0.094(7)	0.14(1)	0.047(5)	0.022(7)	0.014(5)	0.007(6)
C(8)	4e	0.094(1)	0.3025(6)	0.4071(5)	0.107(8)	0.13(1)	0.060(6)	0.019(7)	−0.005(6)	0.011(6)
C(9)	4e	0.040(1)	0.3537(5)	0.4443(6)	0.098(8)	0.093(8)	0.110(9)	0.022(6)	0.000(7)	0.031(7)
C(10)	4e	0.051(1)	0.3381(5)	0.5217(6)	0.105(8)	0.090(8)	0.12(1)	0.035(6)	0.038(7)	0.005(7)
C(11)	4e	0.186(1)	0.3165(4)	0.5595(5)	0.102(7)	0.065(6)	0.060(5)	0.024(5)	0.022(5)	0.004(5)
C(12)	4e	0.7021(8)	0.3491(3)	0.7170(4)	0.057(5)	0.043(5)	0.049(5)	−0.003(4)	0.017(4)	0.008(4)
C(13)	4e	0.576(1)	0.3515(4)	0.5936(5)	0.108(7)	0.064(6)	0.066(6)	−0.022(5)	0.022(5)	0.011(5)
C(14)	4e	0.532(1)	0.4006(5)	0.5379(5)	0.107(8)	0.097(8)	0.063(6)	−0.018(6)	0.004(5)	0.024(6)
C(15)	4e	0.647(1)	0.4251(5)	0.5106(5)	0.119(8)	0.079(7)	0.067(6)	0.009(6)	0.033(6)	0.026(5)
C(16)	4e	0.761(1)	0.4456(5)	0.5719(6)	0.103(8)	0.089(8)	0.098(8)	−0.008(6)	0.038(7)	0.037(6)
C(17)	4e	0.802(1)	0.3941(5)	0.6242(6)	0.079(6)	0.098(8)	0.101(8)	0.000(6)	0.038(6)	0.038(6)
C(18)	4e	0.820(1)	0.4423(5)	0.7748(7)	0.099(8)	0.063(7)	0.13(1)	−0.028(6)	0.006(7)	0.023(7)
C(20)	4e	0.838(1)	0.4415(5)	0.9052(6)	0.18(1)	0.073(8)	0.077(7)	−0.004(7)	0.013(7)	0.003(6)
C(19)	4e	0.772(1)	0.4718(5)	0.8346(7)	0.14(1)	0.055(6)	0.11(1)	−0.005(6)	−0.003(8)	0.002(6)
C(21)	4e	0.801(2)	0.3747(5)	0.8988(6)	0.18(1)	0.084(8)	0.087(8)	0.001(8)	0.037(8)	0.024(7)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	4*e*	0.845(1)	0.3452(4)	0.8382(5)	0.094(7)	0.064(6)	0.079(7)	–0.002(5)	–0.003(5)	0.015(5)
C(23)	4*e*	0.727(1)	0.1141(4)	0.7202(5)	0.100(7)	0.046(5)	0.082(6)	0.005(5)	0.053(6)	0.006(4)
C(24)	4*e*	0.5910(9)	0.0282(4)	0.7437(5)	0.079(6)	0.063(6)	0.076(6)	–0.008(5)	0.019(5)	0.012(5)
C(25)	4*e*	0.590(1)	0.0160(5)	0.8180(5)	0.084(7)	0.112(9)	0.088(8)	0.011(6)	0.033(6)	0.012(6)
C(27)	4*e*	0.833(1)	0.0016(6)	0.8457(9)	0.080(9)	0.10(1)	0.20(2)	0.011(7)	–0.008(9)	0.04(1)
C(26)	4*e*	0.707(1)	–0.0257(5)	0.8523(6)	0.102(8)	0.075(7)	0.087(7)	0.018(6)	0.021(6)	0.023(5)
C(28)	4*e*	0.840(1)	0.0176(5)	0.774(1)	0.092(9)	0.072(8)	0.33(2)	0.032(6)	0.12(1)	0.06(1)
C(29)	4*e*	0.908(2)	0.0934(6)	0.658(1)	0.39(3)	0.071(9)	0.45(3)	–0.02(1)	0.38(3)	–0.03(1)
C(30)	4*e*	0.945(2)	0.1153(6)	0.6061(7)	0.18(1)	0.11(1)	0.14(1)	–0.033(9)	0.12(1)	–0.026(8)
C(31)	4*e*	0.987(1)	0.1806(5)	0.6063(6)	0.123(9)	0.098(8)	0.100(8)	–0.022(7)	0.065(7)	0.014(7)
C(32)	4*e*	0.905(2)	0.2183(5)	0.6470(9)	0.26(2)	0.059(8)	0.18(2)	–0.028(9)	0.15(2)	0.002(8)
C(33)	4*e*	0.874(2)	0.1966(5)	0.701(1)	0.25(2)	0.055(7)	0.27(2)	–0.029(9)	0.21(2)	–0.013(9)

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