

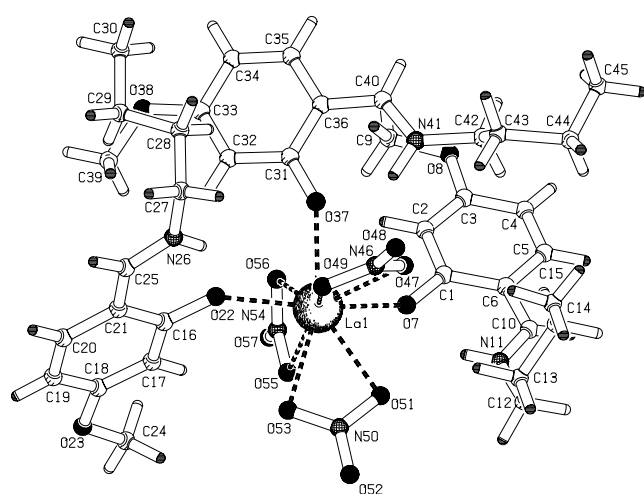
# Crystal structure of tris(*N*-(*n*-butyl)-4-methoxy-2-hydroxybenzaldimine)-tris(nitrato)lanthanum(III), La(C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>

L. Van Meervelt<sup>\*I</sup>, K. Uytterhoeven<sup>I</sup>, R. Van Deun<sup>II</sup> and K. Binnemans<sup>II</sup>

<sup>I</sup> K. U. Leuven, Chemistry Department, Biomolecular Architecture, Celestijnenlaan 200F, B-3001 Leuven (Heverlee), Belgium

<sup>II</sup> K. U. Leuven, Chemistry Department, Coordination Chemistry, Celestijnenlaan 200F, B-3001 Leuven (Heverlee), Belgium

Received July 16, 2003, accepted and available on-line November 4, 2003; CCDC-No. 1267/1122



## Abstract

C<sub>36</sub>H<sub>51</sub>LaN<sub>6</sub>O<sub>15</sub>, triclinic,  $P\bar{1}$  (No. 2),  $a = 11.455(2)$  Å,  $b = 13.859(3)$  Å,  $c = 14.101(4)$  Å,  $\alpha = 98.50(2)^\circ$ ,  $\beta = 98.87(1)^\circ$ ,  $\gamma = 92.52(2)^\circ$ ,  $V = 2182.4$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.035$ ,  $wR_{\text{ref}}(F^2) = 0.082$ ,  $T = 289$  K.

## Source of material

The synthesis of the complex is described in [1]. Suitable crystals were obtained by crystallisation from a 1:1 dichloromethane-hexane mixture.

## Experimental details

Hydrogen atoms were refined in the riding mode with a fixed isotropic temperature factor 1.2 or 1.5 times  $U_{\text{eq}}$  of the parent atom.

## Discussion

The liquid-crystalline behaviour of complexes of the type [Ln(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>], where Ln is a trivalent rare-earth ion and LH is the Schiff's base 4-alkoxy-*N*-alkyl-2-hydroxybenzaldimine, has been described in detail [1–3]. Crystal structures of [Nd(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>] and [Dy(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>], where LH is the short-chain Schiff's base 4-methoxy-*N*-butyl-2-hydroxybenzaldimine have been reported in [1]. Both structures are isostructural, as is the structure of complex [Eu(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>] with the same ligand, which has been described in [4]. In this report we describe the crystal structure of the analogous La(III) complex [La(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>].

The La atom has coordination number 9, which corresponds in this case to a distorted monocapped square antiprismatic environment. Three ligands LH coordinate to the La atom, as well

as three nitrate ions. The nitrate ions coordinate in a bidentate fashion, but the ligands LH do not. The ligands are present in a zwitterionic form, resulting from the migration of the phenol proton towards the imine nitrogen, which thus has a positive charge. As a result, the Schiff's base ligands coordinate in a monodentate way to the La ion, through the phenol oxygen only. An intramolecular hydrogen bond between the protonated imine nitrogen atom and the deprotonated phenol oxygen atom is formed.

**Table 1.** Data collection and handling.

Crystal:	transparent block, size 0.10 × 0.10 × 0.40 mm
Wavelength:	Mo $K_{\alpha}$ radiation (0.71073 Å)
$\mu$ :	10.49 cm <sup>-1</sup>
Diffractometer, scan mode:	Siemens P4-PC, $\omega$
$2\theta_{\text{max}}$ :	44.36°
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ :	6405, 5408
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 4579
$N(\text{param})_{\text{refined}}$ :	538
Programs:	SHELXS-97 [5], SHELXL-97 [6], PLATON [7]

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	$x$	$y$	$z$	$U_{\text{iso}}$
H(2)	2i	0.7528	0.1955	0.5341	0.064
H(4)	2i	0.8773	-0.0579	0.4345	0.091
H(5)	2i	0.7459	-0.1411	0.5013	0.083
H(9A)	2i	0.8468	0.2446	0.4155	0.149
H(9B)	2i	0.9826	0.2412	0.4115	0.149
H(9C)	2i	0.9376	0.2507	0.5118	0.149
H(10)	2i	0.5941	-0.1471	0.5949	0.066
H(11)	2i	0.5181	0.0121	0.6641	0.071
H(12A)	2i	0.4442	-0.1693	0.6856	0.080
H(12B)	2i	0.3633	-0.0815	0.6992	0.080
H(13A)	2i	0.4952	-0.0129	0.8411	0.081
H(13B)	2i	0.4332	-0.1129	0.8509	0.081
H(14A)	2i	0.6677	-0.0878	0.8189	0.098
H(14B)	2i	0.6060	-0.1898	0.8230	0.098
H(15A)	2i	0.6598	-0.0375	0.9820	0.179
H(15B)	2i	0.7230	-0.1357	0.9712	0.179
H(15C)	2i	0.5905	-0.1362	0.9872	0.179
H(17)	2i	0.3881	0.4619	0.6502	0.061
H(19)	2i	0.2792	0.7152	0.7686	0.069
H(20)	2i	0.4145	0.7154	0.9063	0.064
H(24A)	2i	0.3031	0.5181	0.5089	0.120
H(24B)	2i	0.1691	0.5381	0.4837	0.120
H(24C)	2i	0.2072	0.4609	0.5512	0.120
H(25)	2i	0.5707	0.6456	0.9972	0.063
H(26)	2i	0.6400	0.4800	0.9230	0.067

\* Correspondence author

(e-mail: Luc.VanMeervelt@chem.kuleuven.ac.be)

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(27A)	2i	0.7432	0.4722	1.0726	0.081
H(27B)	2i	0.7244	0.5837	1.1004	0.081
H(28A)	2i	0.9216	0.5523	1.0762	0.072
H(28B)	2i	0.8724	0.5152	0.9664	0.072
H(29A)	2i	0.8590	0.7088	1.0566	0.095
H(29B)	2i	0.8158	0.6708	0.9458	0.095
H(30A)	2i	1.0546	0.6852	1.0367	0.159
H(30B)	2i	1.0006	0.7530	0.9639	0.159
H(30C)	2i	1.0132	0.6422	0.9268	0.159
H(32)	2i	0.7480	0.4916	0.7394	0.067
H(34)	2i	1.0789	0.5493	0.6974	0.089
H(35)	2i	1.1224	0.3925	0.7079	0.084
H(39A)	2i	0.7225	0.6265	0.6515	0.158

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(39B)	2i	0.7795	0.7308	0.6987	0.158
H(39C)	2i	0.7515	0.6542	0.7649	0.158
H(40)	2i	1.0686	0.2333	0.7294	0.082
H(41)	2i	0.8480	0.2000	0.7680	0.085
H(42A)	2i	0.8911	0.0305	0.7099	0.105
H(42B)	2i	1.0267	0.0634	0.7270	0.105
H(43A)	2i	0.8964	0.0657	0.8776	0.140
H(43B)	2i	1.0349	0.0838	0.8890	0.140
H(44A)	2i	0.9624	-0.0902	0.8992	0.205
H(44B)	2i	0.9217	-0.1023	0.7864	0.205
H(45A)	2i	1.1130	-0.0670	0.7691	0.213
H(45B)	2i	1.0985	-0.1618	0.8157	0.213
H(45C)	2i	1.1508	-0.0634	0.8813	0.213

Table 3. Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
La(1)	2i	0.56017(3)	0.26811(2)	0.72623(2)	0.0398(2)	0.0395(2)	0.0522(2)	0.0062(1)	0.0127(1)	0.0031(1)
C(1)	2i	0.6686(4)	0.0791(3)	0.5715(3)	0.050(3)	0.052(3)	0.034(2)	0.012(2)	0.004(2)	-0.002(2)
C(2)	2i	0.7507(4)	0.1278(4)	0.5289(3)	0.061(3)	0.050(3)	0.050(3)	0.016(3)	0.010(3)	0.003(2)
C(3)	2i	0.8279(5)	0.0773(4)	0.4797(4)	0.066(4)	0.069(4)	0.056(3)	0.018(3)	0.014(3)	0.013(3)
C(4)	2i	0.8249(6)	-0.0242(4)	0.4691(4)	0.084(4)	0.076(4)	0.075(4)	0.029(4)	0.034(4)	0.004(3)
C(5)	2i	0.7469(5)	-0.0732(4)	0.5087(4)	0.079(4)	0.051(3)	0.073(4)	0.020(3)	0.009(3)	-0.007(3)
C(6)	2i	0.6670(4)	-0.0247(3)	0.5607(3)	0.057(3)	0.047(3)	0.046(3)	0.009(3)	0.002(3)	-0.006(2)
O(7)	2i	0.5956(3)	0.1271(2)	0.6191(2)	0.068(2)	0.048(2)	0.062(2)	0.008(2)	0.024(2)	-0.005(2)
O(8)	2i	0.9096(4)	0.1189(3)	0.4365(3)	0.082(3)	0.094(3)	0.094(3)	0.023(2)	0.043(2)	0.029(2)
C(9)	2i	0.9200(6)	0.2222(5)	0.4445(5)	0.109(6)	0.098(5)	0.105(5)	0.004(4)	0.047(5)	0.032(4)
C(10)	2i	0.5904(5)	-0.0796(4)	0.6053(3)	0.061(3)	0.046(3)	0.051(3)	0.004(3)	-0.004(3)	-0.002(2)
N(11)	2i	0.5159(4)	-0.0449(3)	0.6589(3)	0.070(3)	0.047(2)	0.059(3)	-0.003(3)	0.010(2)	0.003(2)
C(12)	2i	0.4442(5)	-0.1002(4)	0.7104(4)	0.064(4)	0.061(3)	0.074(4)	-0.011(3)	0.011(3)	0.008(3)
C(13)	2i	0.4904(5)	-0.0827(4)	0.8183(4)	0.073(4)	0.057(3)	0.075(4)	0.005(3)	0.017(3)	0.016(3)
C(14)	2i	0.6092(6)	-0.1206(4)	0.8483(4)	0.083(4)	0.078(4)	0.085(4)	0.005(4)	0.010(4)	0.023(3)
C(15)	2i	0.6493(7)	-0.1062(5)	0.9571(5)	0.139(7)	0.111(6)	0.101(6)	0.005(5)	-0.016(5)	0.031(5)
C(16)	2i	0.4774(4)	0.5089(3)	0.7855(3)	0.043(3)	0.037(3)	0.054(3)	0.006(2)	0.013(2)	0.006(2)
C(17)	2i	0.3949(4)	0.5127(3)	0.7022(3)	0.056(3)	0.043(3)	0.051(3)	0.003(2)	0.013(3)	-0.002(2)
C(18)	2i	0.3244(4)	0.5884(3)	0.6951(3)	0.050(3)	0.047(3)	0.052(3)	0.002(2)	0.013(3)	0.012(2)
C(19)	2i	0.3297(5)	0.6648(3)	0.7728(4)	0.066(4)	0.044(3)	0.068(4)	0.019(3)	0.019(3)	0.011(3)
C(20)	2i	0.4101(4)	0.6642(3)	0.8549(4)	0.063(3)	0.040(3)	0.058(3)	0.011(3)	0.018(3)	0.002(2)
C(21)	2i	0.4866(4)	0.5879(3)	0.8636(3)	0.046(3)	0.037(3)	0.046(3)	0.000(2)	0.010(2)	0.004(2)
O(22)	2i	0.5451(3)	0.4361(2)	0.7923(2)	0.063(2)	0.045(2)	0.068(2)	0.016(2)	0.005(2)	-0.003(2)
O(23)	2i	0.2424(3)	0.5973(3)	0.6166(3)	0.068(2)	0.074(2)	0.060(2)	0.012(2)	0.004(2)	0.018(2)
C(24)	2i	0.2294(5)	0.5224(4)	0.5332(4)	0.087(4)	0.091(4)	0.054(3)	-0.001(4)	-0.003(3)	0.003(3)
C(25)	2i	0.5704(4)	0.5921(3)	0.9488(4)	0.058(3)	0.042(3)	0.059(3)	0.004(3)	0.021(3)	0.002(2)
N(26)	2i	0.6476(4)	0.5277(3)	0.9659(3)	0.055(3)	0.057(3)	0.053(3)	0.004(2)	0.005(2)	0.000(2)
C(27)	2i	0.7411(5)	0.5344(4)	1.0488(4)	0.067(4)	0.072(4)	0.061(3)	0.008(3)	-0.001(3)	0.017(3)
C(28)	2i	0.8604(4)	0.5605(4)	1.0228(4)	0.050(3)	0.068(3)	0.059(3)	0.004(3)	0.002(3)	0.010(3)
C(29)	2i	0.8741(5)	0.6632(4)	1.0014(5)	0.084(5)	0.068(4)	0.085(4)	-0.001(3)	0.007(4)	0.012(3)
C(30)	2i	0.9969(6)	0.6882(5)	0.9803(5)	0.106(6)	0.099(5)	0.114(6)	-0.025(4)	0.024(5)	0.024(4)
C(31)	2i	0.8475(4)	0.3733(4)	0.7425(3)	0.041(3)	0.065(3)	0.049(3)	-0.001(3)	-0.002(2)	0.011(2)
C(32)	2i	0.8229(4)	0.4708(4)	0.7334(3)	0.049(3)	0.064(3)	0.053(3)	0.000(3)	0.009(2)	0.006(3)
C(33)	2i	0.9073(5)	0.5343(4)	0.7159(4)	0.066(4)	0.064(4)	0.058(3)	-0.010(3)	-0.001(3)	0.012(3)
C(34)	2i	1.0209(5)	0.5047(5)	0.7078(4)	0.061(4)	0.081(4)	0.084(4)	-0.014(3)	0.017(3)	0.026(3)
C(35)	2i	1.0470(5)	0.4117(5)	0.7149(4)	0.046(3)	0.096(5)	0.070(4)	0.001(3)	0.010(3)	0.015(3)
C(36)	2i	0.9615(5)	0.3437(4)	0.7328(4)	0.050(3)	0.071(4)	0.054(3)	-0.001(3)	0.000(3)	0.014(3)
O(37)	2i	0.7680(3)	0.3136(2)	0.7600(3)	0.042(2)	0.062(2)	0.092(3)	0.001(2)	0.009(2)	0.022(2)
O(38)	2i	0.8909(4)	0.6283(3)	0.7034(3)	0.098(3)	0.068(3)	0.100(3)	-0.010(3)	0.015(3)	0.023(2)
C(39)	2i	0.7770(7)	0.6627(5)	0.7047(6)	0.115(6)	0.071(4)	0.131(6)	0.018(4)	0.011(5)	0.023(4)
C(40)	2i	0.9922(5)	0.2478(5)	0.7383(4)	0.048(3)	0.090(5)	0.067(4)	0.008(3)	0.003(3)	0.018(3)
N(41)	2i	0.9235(4)	0.1777(4)	0.7545(4)	0.053(3)	0.063(3)	0.093(4)	0.019(3)	-0.001(3)	0.012(3)
C(42)	2i	0.9533(6)	0.0730(5)	0.7524(5)	0.071(4)	0.097(5)	0.087(5)	0.019(4)	-0.005(4)	0.008(4)
C(43)	2i	0.9655(7)	0.0483(6)	0.8485(5)	0.137(7)	0.126(6)	0.108(6)	0.059(6)	0.055(5)	0.038(5)
C(44)	2i	0.9790(9)	-0.0684(7)	0.8401(8)	0.19(1)	0.132(8)	0.25(1)	0.099(8)	0.109(9)	0.119(8)
C(45)	2i	1.0947(8)	-0.0920(6)	0.8254(6)	0.163(9)	0.137(7)	0.144(8)	0.076(7)	0.032(7)	0.051(6)
N(46)	2i	0.6613(4)	0.1932(4)	0.9124(4)	0.081(3)	0.074(3)	0.065(3)	0.023(3)	0.015(3)	0.021(3)
O(47)	2i	0.6722(3)	0.1469(2)	0.8316(3)	0.066(2)	0.055(2)	0.065(2)	0.015(2)	0.016(2)	0.008(2)

Table 3. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
O(48)	2i	0.7040(5)	0.1674(4)	0.9881(3)	0.165(5)	0.133(4)	0.066(3)	0.069(4)	0.009(3)	0.031(3)
O(49)	2i	0.6019(4)	0.2690(3)	0.9118(3)	0.113(3)	0.085(3)	0.061(2)	0.048(3)	0.023(2)	0.014(2)
N(50)	2i	0.3289(4)	0.1858(4)	0.7709(3)	0.045(3)	0.082(4)	0.090(4)	0.007(3)	0.025(3)	0.030(3)
O(51)	2i	0.4067(3)	0.1325(3)	0.7448(3)	0.052(2)	0.055(2)	0.123(3)	0.007(2)	0.035(2)	0.008(2)
O(52)	2i	0.2404(4)	0.1499(4)	0.7923(4)	0.056(3)	0.122(4)	0.169(5)	0.013(3)	0.051(3)	0.060(3)
O(53)	2i	0.3457(4)	0.2747(3)	0.7709(3)	0.070(3)	0.070(3)	0.140(4)	0.018(2)	0.044(3)	0.021(3)
N(54)	2i	0.5015(5)	0.3239(3)	0.5249(4)	0.081(4)	0.055(3)	0.054(3)	0.004(3)	0.002(3)	0.005(2)
O(55)	2i	0.4211(3)	0.2905(3)	0.5646(3)	0.061(2)	0.061(2)	0.065(2)	0.002(2)	0.002(2)	0.002(2)
O(56)	2i	0.6013(4)	0.3455(3)	0.5771(3)	0.075(3)	0.072(2)	0.064(2)	−0.006(2)	0.011(2)	0.017(2)
O(57)	2i	0.4846(5)	0.3339(4)	0.4405(3)	0.135(4)	0.132(4)	0.060(3)	−0.003(3)	−0.002(3)	0.036(3)

*Acknowledgments.* The authors gratefully acknowledge the financial support from FWO-Vlaanderen, K. U. Leuven and IWT (Belgium). KB and RVD are postdoctoral fellows of the FWO-Vlaanderen.

## References

- Binnemans, K.; Galyametdinov, Y. G.; Van Deun, R.; Bruce, D. W.; Collinson, S. R.; Polishchuk, A. P.; Bikchantaev, I.; Haase, W.; Prosvirin, A. V.; Tinchurina, L.; Litvinov, I.; Gubajdullin, A.; Rakhmatullin, A.; Uytterhoeven, K.; Van Meervelt, L.: Rare-Earth-Containing Magnetic Liquid Crystals. *J. Am. Chem. Soc.* **122** (2000) 4335-4344.
- Galyametdinov, Y.; Athanassopoulou, M. A.; Griesar, K.; Kharitonova, O.; Bustamante, E. A. S.; Tinchurina, L.; Ovchinnikov, I.; Haase, W.: Synthesis and magnetic investigations on rare-earth-containing liquid crystals with large magnetic anisotropy. *Chem. Mater.* **8** (1996) 922-926.
- Binnemans, K.; Görlner-Walrand, C.: Lanthanide-containing liquid crystals and surfactants. *Chem. Rev.* **102** (2002) 2303-2346.
- Van Meervelt, L.; Uytterhoeven, K.; Van Deun, R.; Moors, D.; Binnemans, K.: Crystal structure of tris(*N*-(*n*-butyl)-4-methoxy-2-hydroxybenzaldimine)-tris(nitrato)europium(III), Eu(LH)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>. *Z. Kristallogr. NCS* **218** (2003) 118-120.
- Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. A* **46** (1990) 467-473.
- Sheldrick, G. M.: SHELXL-97. Program for the refinement of crystal structures. University of Göttingen, Germany 1997.
- Spek, A. L.: PLATON, Molecular Geometry Program. University of Utrecht, The Netherlands 1998.