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Acta Cryst. (1988). **C44**, 614–616

Structure of a New Polymorphic Form of Tris(cyclopentadienyl)lanthanum(III)

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(Received 5 October 1987; accepted 25 November 1987)

Abstract. [La(C₅H₅)₃], *M*_r = 334.20, monoclinic, *P*2₁/*c*, *a* = 15.237 (2), *b* = 9.790 (2), *c* = 16.721 (4) Å, β = 93.93 (3)°, *V* = 2489 (2) Å³, *Z* = 8, *D*_x = 1.784 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 3.4171 mm⁻¹, *F*(000) = 1296, *T* = 295 (1) K, *R* = 0.028 for 2129 observed reflections. Each La atom is η⁵ bonded to three cyclopentadienide rings and η¹ bonded to a ring of an adjacent (C₅H₅)₃La molecule. This sharing of one C atom between the molecular units produces zigzag polymeric chains along the *b* axis of the unit cell.

Introduction. Molecular and crystal structures of a number of tris(cyclopentadienyl) complexes of the lanthanoids, (C₅H₅)₃Ln, have been reported in the literature. They show various polymeric arrangements of (C₅H₅)₃Ln units. The first (rather inaccurate) structure of (C₅H₅)₃Sm (Wong, Lee & Lee, 1969) revealed a complex polymeric chain structure in which each metal ion forms contacts with four disordered rings. (C₅H₅)₃Pr (Hinrichs, Melzer, Rehwoaldt, Jahn & Fischer, 1983) also exhibits an infinite chain arrangement but each Pr ion is η⁵ coordinated to three close-lying C₅H₅ ligands and η² coordinated to a fourth bridging C₅H₅ ligand. The La derivative (Eggers, Kopf & Fischer, 1986) was found to be isotypic with (C₅H₅)₃Pr. The structures of (C₅H₅)₃Er and its isotype (C₅H₅)₃Tm (Eggers, Hinrichs, Kopf, Jahn & Fischer,

1986) in contrast shows molecules containing just three η⁵ C₅H₅ ligands bonded to the metal ion.

On the other hand, (C₅H₅)₃Lu, which is isotypic with (C₅H₅)₃Sc (Eggers, Schultze, Kopf & Fischer, 1986), shows an infinite chain arrangement in which each Lu atom is bounded in a pentahapto fashion to two rings and in a monohapto fashion to two other bridging rings.

A novel experimental technique of preparation allowed us to obtain single crystals of a polymorphic variety of (C₅H₅)₃La. Its characterization by X-ray diffraction is reported here.

Experimental. Tris(cyclopentadienyl)lanthanum was prepared under argon atmosphere, by reaction of (cyclopentadienyl)potassium with lanthanum trichloride in tetrahydrofuran. The THF adduct was removed under controlled conditions [10⁻⁴ torr (~10⁻² Pa), 363 K]. Colourless prismatic single crystals obtained by extraction with *n*-pentane followed by recrystallization. Crystals sealed in thin-walled glass capillaries under argon. The specimen selected for X-ray analysis was 0.25 × 0.25 × 0.30 mm.

Intensity data recorded on an Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo *K*α radiation. Cell parameters refined by least squares from angle data of 25 reflections. Space group unambiguously determined from systematic absences. 3632 unique reflections measured (θ–2θ scan mode) in range

Table 1. Atomic positional and isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + abc\cos\gamma B(1,2) + accos\beta B(1,3) + bccos\alpha B(2,3)].$$

	x	y	z	B_{eq}
La(1)	0.33659 (2)	0.23895 (4)	0.81940 (3)	1.904 (9)
La(2)	0.16422 (3)	0.74114 (4)	0.91531 (2)	1.825 (9)
Ring A				
C(1)	0.2404 (5)	-0.0082 (8)	0.8436 (5)	3.7 (2)
C(2)	0.2973 (6)	0.0107 (8)	0.9143 (6)	5.1 (2)
C(3)	0.2647 (6)	0.1220 (8)	0.9577 (5)	5.2 (2)
C(4)	0.1882 (5)	0.1708 (9)	0.9108 (5)	4.5 (2)
C(5)	0.1738 (5)	0.0948 (9)	0.8434 (6)	4.7 (2)
Ring B				
C(6)	0.5202 (5)	0.187 (1)	0.8254 (6)	5.7 (3)
C(7)	0.5132 (5)	0.327 (1)	0.8199 (6)	5.3 (2)
C(8)	0.4841 (5)	0.3716 (9)	0.8906 (6)	5.6 (2)
C(9)	0.4712 (5)	0.257 (1)	0.9442 (5)	8.0 (4)
C(10)	0.4957 (5)	0.1420 (9)	0.8983 (6)	5.2 (2)
Ring C				
C(11)	0.3878 (6)	0.243 (1)	0.6603 (5)	5.3 (3)
C(12)	0.3322 (6)	0.1272 (9)	0.6617 (5)	5.0 (2)
C(13)	0.2462 (5)	0.1774 (9)	0.6675 (5)	4.2 (2)
C(14)	0.2494 (5)	0.3175 (9)	0.6719 (5)	3.9 (2)
C(15)	0.3360 (6)	0.3609 (9)	0.6671 (1)	4.5 (2)
Ring D				
C(16)	0.2834 (5)	0.6014 (9)	0.8123 (5)	4.8 (2)
C(17)	0.3377 (6)	0.6707 (9)	0.8691 (6)	5.0 (2)
C(18)	0.3335 (5)	0.6144 (9)	0.9448 (6)	4.7 (2)
C(19)	0.2715 (5)	0.5001 (8)	0.9359 (5)	4.0 (2)
C(20)	0.2419 (5)	0.4952 (8)	0.8543 (5)	3.5 (2)
Ring E				
C(21)	0.0920 (8)	0.688 (1)	1.0596 (5)	7.5 (3)
C(22)	0.1839 (8)	0.681 (1)	1.0800 (6)	8.4 (3)
C(23)	0.2157 (6)	0.813 (1)	1.0766 (5)	5.5 (2)
C(24)	0.1443 (6)	0.8968 (8)	1.0553 (5)	4.8 (2)
C(25)	0.0669 (6)	0.821 (1)	1.0453 (5)	5.8 (2)
Ring F				
C(26)	0.0699 (5)	0.6638 (9)	0.7700 (5)	4.0 (2)
C(27)	0.0246 (5)	0.6001 (9)	0.8324 (5)	4.6 (2)
C(28)	-0.0172 (5)	0.707 (1)	0.8758 (6)	5.2 (2)
C(29)	0.0034 (5)	0.8313 (9)	0.8382 (5)	4.8 (2)
C(30)	0.0553 (5)	0.8033 (9)	0.7754 (5)	4.7 (2)

Table 2. Selected distances (\AA) and angles ($^\circ$) in $(\text{C}_5\text{H}_5)_3\text{La}$ with *e.s.d.*'s in parentheses

La(1)–C(1)	2.872 (7)	La(2)–C(16)	2.927 (8)
–C(2)	2.829 (7)	–C(17)	2.887 (8)
–C(3)	2.865 (8)	–C(18)	2.874 (8)
–C(4)	2.892 (7)	–C(19)	2.878 (7)
–C(5)	2.905 (8)	–C(20)	2.899 (7)
–C(6)	2.839 (8)	–C(21)	2.767 (9)
–C(7)	2.825 (8)	–C(22)	2.81 (1)
–C(8)	2.792 (9)	–C(23)	2.844 (8)
–C(9)	2.830 (8)	–C(24)	2.827 (7)
–C(10)	2.842 (9)	–C(25)	2.826 (8)
–C(11)	2.823 (9)	–C(26)	2.840 (7)
–C(12)	2.851 (8)	–C(27)	2.819 (8)
–C(13)	2.869 (8)	–C(28)	2.819 (8)
–C(14)	2.826 (8)	–C(29)	2.831 (8)
–C(15)	2.812 (8)	–C(30)	2.840 (8)
–C(16)	3.640 (9)	–C(1)	3.999 (8)
–C(19)	3.404 (8)	–C(2)	3.329 (9)
–C(20)	2.972 (7)	–C(5)	3.671 (9)
–RcA*	2.609 (8)	–RcD	2.630 (8)
–RcB	2.563 (9)	–RcE	2.554 (9)
–RcC	2.575 (9)	–RcF	2.561 (8)
RcA–La(1)–RcB	117.3 (2)	RcD–La(2)–RcE	116.5 (2)
RcA–La(1)–RcC	115.7 (2)	RcD–La(2)–RcF	114.5 (3)
RcA–La(1)–C(20)	95.6 (2)	RcD–La(2)–C(1)	96.0 (2)
RcB–La(1)–RcC	116.4 (2)	RcE–La(2)–RcF	117.5 (3)
RcB–La(1)–C(20)	109.5 (2)	RcE–La(2)–C(1)	110.5 (2)
RcC–La(1)–C(20)	97.6 (2)	RcF–La(2)–C(1)	97.5 (3)
La(2)–La(1)–La(2)	114.149 (9)	La(1)–La(2)–La(1)	114.149 (9)

* RcA denotes centroid of ring A, RcB centroid of ring B etc.

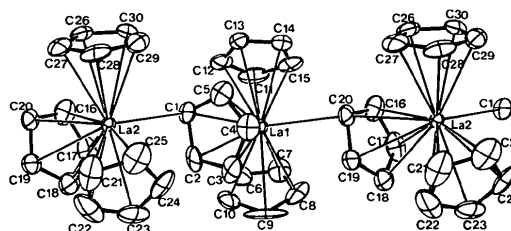


Fig. 1. The structure of $(\text{C}_5\text{H}_5)_3\text{La}$ illustrated by three $(\text{C}_5\text{H}_5)_2\text{La}(\mu\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_5)$ units along a polymeric chain. Atoms are depicted as 40% probability ellipsoids.

$4 \leq 2\theta \leq 45^\circ$, 2627 considered observed [$I \geq 1\sigma(I)$, $+h, -k, \pm l$].

Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors 79.46–99.84%). Structure solved by direct methods and Fourier techniques. Full-matrix least-squares refinement, minimizing $\sum(\Delta F)^2$; $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (A/I)^2]^{1/2}/Lp$ where A , the ignorance factor, is 0.07, on 2129 reflections with $F^2 \geq 3\sigma(F^2)$, index range h 0/+16, k -10/0, l -17/+17. Anisotropic thermal parameters for non-H atoms; H atoms in calculated positions included in final structure-factor calculation with B_{iso} between 3.0 and 7.0 \AA^2 . A secondary-extinction coefficient refined to a value of $g = 8.04 \times 10^{-8}$ $\{F_c = F_o/[1 + g(F_o^2)Lp]\}$. $R = 0.028$, $wR = 0.048$, $S = 1.315$, $(\Delta/\sigma)_{\text{max}} = 0.03$, $\Delta\rho$ in final difference Fourier map within +0.648 and -0.767 $e \text{\AA}^{-3}$. Atomic scattering factors and anomalous-dispersion

terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1979) *SDP* programs.

Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are reported in Table 2. The present structural analysis exhibits two symmetrically independent $(\text{C}_5\text{H}_5)_3\text{La}$ molecules in the asymmetric unit. They are bridged through one cyclopentadienyl ring, as illustrated by Fig. 1, to form infinite zigzag polymeric chains parallel to the b axis of the crystal. The chains are spaced at about half a unit-cell length along both the a and the c axis.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, cyclopentadienyl bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44571 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

From La—C distances (Table 2) it can be concluded that each La atom is coordinated to three cyclopentadienyl rings in a pentahapto fashion and to one other from a neighbouring molecule though only one carbon atom. Indeed the average La—C bond length for the η^5 -C₅H₅ rings is 2.85 (8) Å with a maximum deviation from this mean value of only 0.05 Å.

This value compares favourably with those reported for several pentahapto-cyclopentadienyl lanthanum complexes (Rogers, Atwood, Emad, Sikora & Rausch, 1981; Xing-Fu, Eggers, Kopf, Jahn, Fischer, Apostolidis, Kanellakopoulos, Benetollo, Polo & Bombieri, 1985; Spirlet, Rebizant, Apostolidis & Kanellakopoulos, 1987). The interactions La(1)—C(20) and La(2)—C(1) are only about 0.13 Å greater than the η^5 bonds. They can therefore be considered as η^1 bonds. The next closer La—C approaches differ by 0.55 and 0.48 Å respectively for La(1) and La(2). The coordination polyhedra about the metal ions can be described as distorted tetrahedra, as shown by the angles subtended at the La atoms (Table 2).

The mean C—C bond lengths and the mean C—C—C bond angles in each C₅ ring agree with known values. The bridging C₅H₅ group does not differ from the terminal group with respect to either bond distances and angles.

The first structure reported, by Eggers *et al.* (1986), for (C₅H₅)₃La differs markedly, not only in the cell dimensions and the space group but also in the

molecular geometry and the packing arrangement. In this earlier structure a much wider range of La—C distances [2.560 (6) to 2.999 (6) Å] is observed for the η^5 -cyclopentadienyl ligands. Moreover there are two (instead of one in the present structure analysis) La...C short contacts between adjacent molecules so that the crystal is described as made of zigzag chains of (C₅H₅)₂La(μ - η^5 : η^2 -C₅H₅) units.

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Acta Cryst. (1988). **C44**, 616–618

Structure of Chloromercury(II) Saccharinate

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(Received 6 July 1987; accepted 18 November 1987)

Abstract. C₇H₄ClHgNO₃S, *M*_r = 418.22, orthorhombic, *Pca*2₁, *a* = 20.530 (5), *b* = 4.767 (2), *c* =

9.467 (2) Å, *V* = 926.5 (8) Å³, *Z* = 4, *D*_m (pycnometrically) = 2.98, *D*_x = 3.00 Mg m⁻³, λ(Mo Kα) = 0.7107 Å, μ = 17.11 mm⁻¹, *F*(000) = 760, room temperature, final *R* = 0.028 for 818 independent observed reflections. The structure is built up of the discrete molecules. Mercury has digonal characteristic

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