

Preliminary communication

Studies on organolanthanide complexes

XXXIX[†]. Synthesis and molecular structure of (MeCp)₃La (MeCp = CH₃C₅H₄): a tetrameric complex of the type [(MeCp)₃La]₄Zuwei Xie, F. Ekkehardt Hahn¹ and Changtao Qian^{*}*Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032 (People's Republic of China)*

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Abstract

Reaction of LaCl₃ with excess Na(MeCp) in THF, followed by sublimation, affords (MeCp)₃La. The complex crystallizes as a tetramer [(MeCp)₃La]₄ in the monoclinic space group *P*2₁/*c* with unit cell dimensions *a* 9.6785(14), *b* 26.058(5), *c* 12.506(2) Å, *β* 97.724(13)° and *Z* = 2 (tetramers).

Up to now, the molecular structures of the following tricyclopentadienyl lanthanide complexes have been reported: Cp₃Sc [2], Cp₃Pr [3], Cp₃Nd [4], Cp₃La [5], Cp₃Er [6], Cp₃Tm [6], Cp₃Yb [7], Cp₃Lu [8], (MeCp)₃Nd [9], (MeCp)₃Yb [10], (MeCp)₃Ce [11], and [(Me₃Si)₂C₅H₃]₃Ce [11]. The results of above structural analyses suggest that the solid-state structures of the trivalent lanthanide metalloenes are dependent on the lanthanide metals as well as the size of the substituents on the cyclopentadienyl rings. For example, (MeCp)₃Nd is tetrameric while Cp₃Nd is a polymer [9,10]; (MeCp)₃Ce is tetrameric while [(Me₃Si)₂C₅H₃]₃Ce and (Me₃SiC₅H₄)₃Ce are monomers [11]. An interesting question is how is the molecular structure of (MeCp)₃La compared to the polymeric η²:η⁵-Cp₃La [5].

We report the crystal structure of solvent-free (MeCp)₃La (**1**) prepared by the reaction of LaCl₃ with excess (MeCp)Na in THF, followed by vacuum sublimation [12*]. Single crystals suitable for an X-ray study were obtained from a toluene solution at room temperature.

[†] For Part XXXVIII see ref. 1.

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* Reference number with asterisk indicates a note in the list of references.

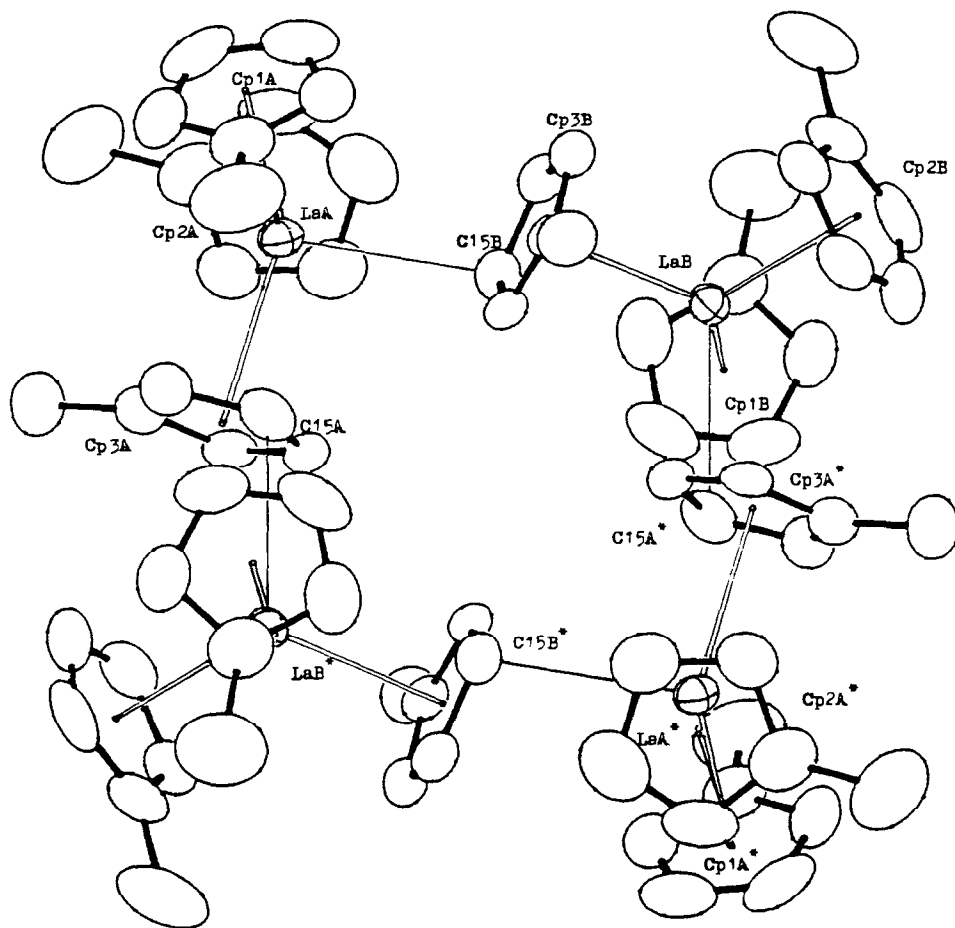


Fig. 1. ORTEP drawing of one tetramer $[(\text{MeCp})_3\text{La}]_4$ (two asymmetric units). Starred atoms represent transformed coordinates of the type $1-x, -y, -z$. Cp denotes the centroids of the cyclopentadienyl rings. Important bond distances (\AA) and angles ($^\circ$): LaA–Cp1A 2.553(7), LaA–Cp2A 2.569(7), LaA–Cp3A 2.637(7), LaB–Cp1B 2.601(7), LaB–Cp2B 2.555(7), LaB–Cp3B 2.630(7), LaA–C15B 2.972(5), LaB–C15A* 3.064(6), Cp1A–LaA–Cp2A 116.5(2), Cp1A–LaA–Cp3A 121.4(2), Cp2A–LaA–Cp3A 113.8(2), Cp1B–LaB–Cp2B 119.5(2), Cp1B–LaB–Cp3B 114.5(2), Cp2B–LaB–Cp3B 115.0(2), LaA–C15A–LaB* 168.8(3), LaB–C15B–LaA 178.5(2).

The X-ray structure analysis [13*] shows that $(\text{MeCp})_3\text{La}$ crystallizes as a tetramer, $[(\text{MeCp})_3\text{La}]_4$. Figure 1 shows one tetramer with the adopted numbering scheme. The structure of **1** differs significantly from that of Cp_3La [5]. The methyl substituent on the cyclopentadienyl ring forces the mode of coordination from an $\eta^2 : \eta^5$ polymer for Cp_3La [5] to an $\eta^1 : \eta^5$ tetramer for **1**.

In $(\text{MeCp})_3\text{La}$, each La atom is surrounded by two terminal η^5 -MeCp groups and a bridging MeCp group which is η^5 -bonded to one lanthanum atom and η^1 -bonded to an adjacent lanthanum atom. Thus the coordination number of the La atoms is ten. The geometry of tetrameric $(\text{MeCp})_3\text{La}$ is nearly identical with those of its cerium and neodymium analogues $(\text{MeCp})_3\text{Ln}$ (Ln = Ce (2), Nd(3)) [9,11]. The average $\eta^1\text{-C-Ln}$ distance is 3.018(7) \AA in **1**, 3.03(3) \AA in **2** and 2.984(3) \AA in **3**.

The Ln–C(η^5 -MeCp) distance in **1** is 2.843(3) Å, in **2** it is 2.83(4) Å and in **3** it is 2.79(4) Å. The Cp–Ln–Cp angles (Cp denotes the centroids of the cyclopentadienyl rings) are almost identical for all three derivatives at 117°. The differences in bond length are most reasonably ascribed to the lanthanide contraction.

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- Reaction of 3.17 g (12.92 mmol) of LaCl₃ with 33.0 ml (50.10 mmol) of Na(MeCp) in 70 ml of THF overnight, followed by sublimation at 200–230°C/10⁻³ mmHg, gave white crystals, 2.50 g (yield 51.5%). Anal. Found: C, 57.22; H, 5.84. C₁₈H₂₁La calc.: C, 57.46; H, 5.63%. MS (EI): 751 (2M⁺ – 1), 673 ([2M – MeCp]⁺), 376 (M⁺), 297 [(MeCp)₂La]⁺, 217 [(MeCp)La]⁺.
- Crystal data for [(MeCp)₃La]₄: C₇₂H₈₄La₄, M = 1505.12. Crystals are monoclinic, space group P2₁/c (no. 14). a 9.6785(14), b 26.058(5), c 12.506(2) Å. β 97.724(13)°. V 3125(2) Å³. d_c 1.60 g cm⁻³ for Z = 2, μ 27.3 cm⁻¹. Data collection on a CAD-4 diffractometer at 24(4)°C with Mo-K_α radiation (λ 0.71073 Å), crystal size 0.35 × 0.38 × 0.42 mm, 2θ range 2° ≤ 2θ ≤ 50°, systematic absences uniquely defined the space group to be P2₁/c. Data reduction with Lorentz, polarization and absorption correction gave 5031 unique reflections. Solution with Patterson methods, refinement with Fourier and least-squares methods gave R = 0.032, R_w = 0.053 and GOF = 2.084 for 4339 reflections F_o² ≥ 3σ(F_o²) and 343 parameters.