Inorganica Chimica Acta, *139* (1987) 203–207

Studies on Rare Earth Allyl Compounds.
IV. The Crystal Structure of $[Li_2(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(\eta^3\text{-}C_3H_5)_4]$*

ZUEN HUANG, MINGQIN CHEN, WENJIE QIU
and WENLING WU

Department of Chemistry, Fudan University, Shanghai, China

Previous reports [1, 2] on the preparation of allyl compounds $Li_2Ln(C_3H_5)_5 \cdot 3C_4H_8O_2$ (Ln = Ce, Pr, Nd, Sm, Gd, Lu), which are very sensitive to air and moisture, raised strong interest in the interactions among these metals and allyl groups and the effect of the dioxanes in these compounds. No crystal structure of an allyl lanthanide has been published, although a few reports [3, 4] about the synthesis of these compounds were presented in the last decade. Therefore a single crystal X-ray structure determination was undertaken.

Experimental

The synthesis of $[Li_2(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(C_3H_5)_4]$ has been described in our previous work [1]. The compound crystallized in the triclinic space group $P\bar{1}$ with $a = 12.297(2)$, $b = 11.319(3)$, $c = 13.592(2)$ Å, $\alpha = 111.24(2)$, $\beta = 79.87(10)$, $\gamma = 115.34(2)°$, $V = 1593.15$ Å^3, $Z = 2$, $D_x = 1.300$ g cm^{-3}. A purple crystal of dimensions 0.15 × 0.3 × 0.4 mm was chosen and sealed into a capillary under N_2 atmosphere. The unit cell parameters were refined from the setting angles of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer controlled by a house computer PDP11/44. Intensities of 6925 reflections with $\theta \leqslant 25°$ were collected, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and ω–2θ scanning mode at 20 °C, 5242 of which were considered observed ($I \geqslant 3\sigma(I)$) after Lorentz, polarization and absorption corrections. The cerium atom was found by the direct method and the remaining atoms were determined by a difference electron density map. A few of them were in some disorder and needed refined occupancy factors. The final full matrix least squares refinement including unit weights gave a conventional factor $R = 0.0495$. The positional parameters of atoms, bond distances and bond angles are listed in Tables I–III. A view of the cation framework and complex anion $[Ce(C_3H_5)_4]^-$ are shown in Figs. 1 and 2.

TABLE I. Positional Parameters and their Estimated Standard Deviations (e.s.d.s) in Parentheses[a]

Atom	*x*	*y*	*z*	B_{eq}	Mult.
Ce	0.14457(3)	0.39972(4)	0.16758(3)	3.673(7)	1.000
C101	0.0393(7)	0.3156(8)	−0.0308(7)	6.4(2)**	1.000
C102	−0.0531(8)	0.2627(8)	0.0338(7)	6.9(2)**	1.000
C103	−0.0894(8)	0.3285(9)	0.1296(8)	7.6(2)**	1.000
C201	0.2807(8)	0.4747(9)	0.3447(7)	7.2(2)**	1.000
C202	0.170(1)	0.474(1)	0.3857(9)	9.6(3)**	1.000
C203	0.054(1)	0.383(1)	0.3690(9)	9.1(3)**	1.000
C301	0.168(1)	0.678(1)	0.2338(9)	9.3(3)**	1.000
C302	0.2323(9)	0.659(1)	0.1404(8)	8.2(3)**	1.000
C303	0.3222(9)	0.612(1)	0.1115(8)	8.2(3)**	1.000
C401	0.148(1)	0.136(2)	0.104(1)	5.7(4)**	0.450
C402	0.258(2)	0.212(2)	0.099(1)	6.3(4)**	0.450
C403	0.311(2)	0.305(2)	0.031(2)	6.5(4)**	0.450
C401*	0.098(1)	0.119(1)	0.134(1)	5.5(3)**	0.550
C402*	0.183(1)	0.160(2)	0.053(1)	6.8(4)**	0.550
C403*	0.294(1)	0.267(1)	0.063(1)	6.2(3)**	0.550
Li1	−0.484(1)	0.166(1)	0.2584(9)	4.4(3)	1.000
Li2	−0.264(1)	−0.172(1)	0.3918(9)	4.7(3)	1.000
C501	−0.5828(7)	0.182(1)	0.4960(7)	7.3(3)	1.000
C502	−0.6243(7)	0.1983(9)	0.4145(6)	6.8(3)	1.000
C503	−0.6749(7)	0.1091(9)	0.3223(6)	6.3(2)	1.000
O1	−0.3798(5)	0.3634(4)	0.2798(3)	5.3(1)	1.000
C2	−0.3389(8)	0.4567(7)	0.3843(5)	6.3(2)	1.000

(continued)

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

0020-1693/87/$3.50

TABLE I. *(continued)*

Atom	x	y	z	B_{eq}	Mult.
C3	−0.2260(7)	0.5772(7)	0.3761(6)	6.2(2)	1.000
O4	−0.2481(4)	0.6482(4)	0.3172(4)	5.3(1)	1.000
C5	−0.2903(8)	0.5545(7)	0.2123(6)	5.9(2)	1.000
C6	−0.4029(7)	0.4370(8)	0.2217(6)	6.2(2)	1.000
O7	−0.2837(4)	−0.1037(5)	0.2838(4)	5.7(1)	1.000
C8	−0.4003(6)	−0.1614(8)	0.2370(7)	6.6(2)	1.000
C9	−0.4646(6)	−0.0655(7)	0.2913(7)	5.9(2)	1.000
O10	−0.3916(4)	0.0708(4)	0.2834(4)	5.5(1)	1.000
C11	−0.2780(7)	0.1269(7)	0.3320(7)	6.4(2)	1.000
C12	−0.2117(7)	0.0324(8)	0.2761(7)	7.3(2)	1.000
O13	−0.5004(4)	0.0813(5)	0.1052(4)	5.6(1)	1.000
C14	−0.6116(6)	−0.0214(9)	0.0520(7)	6.6(2)	1.000
C18	0.410(1)	0.869(1)	0.972(1)	5.8(4)	0.604
C18*	0.605(1)	0.033(2)	0.050(1)	5.8(5)	0.396
O19	−0.1013(4)	−0.0472(5)	0.4405(4)	5.1(1)	1.000
C20	0.0097(6)	−0.0570(8)	0.3897(6)	5.5(2)	1.000
C24	−0.0773(6)	0.0707(7)	0.5353(6)	5.1(2)	1.000

[a] Double starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Single starred atoms and those with the same numbers were disordered.

TABLE II. Bond Distances (A) with their e.s.d.s in Parentheses

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ce	C101	2.858(7)	C302	C303	1.369(10)
Ce	C102	2.811(7)	C401	C402	1.26(2)
Ce	C103	2.726(8)	C5	C6	1.479(8)
Ce	C201	2.835(8)	O7	C8	1.451(7)
Ce	C202	2.808(10)	O7	C12	1.445(7)
Ce	C203	2.810(9)	C8	C9	1.516(8)
Ce	C301	2.839(9)	C9	O10	1.449(7)
Ce	C302	2.806(8)	O10	C11	1.433(7)
Ce	C303	2.712(8)	C11	C12	1.525(10)
Ce	C401	2.81(2)	O13	C14	1.457(6)
Ce	C402	2.82(2)	O13	C18	1.465(10)
C401*	C402*	1.44(2)	C402	C403	1.53(2)
C402*	C403*	1.37(2)	Li1	C502	2.511(10)
C501	C502	1.400(10)	Li1	C503	2.252(11)
C502	C503	1.341(9)	Li1	O1	1.981(9)
O1	C2	1.448(6)	Li1	O10	2.006(10)
O1	C6	1.469(7)	Li1	O13	1.957(9)
C2	C3	1.495(8)	Li2	C501	2.200(11)
C3	O4	1.447(7)	Li2	O4	1.993(10)
O4	C5	1.456(7)	Li2	O7	1.981(10)
Ce	C403	2.81(2)	Li2	O19	1.946(9)
Ce	C401*	2.854(12)	O13	C18*	1.586(15)
Ce	C402*	2.789(14)	C14	C18	1.406(11)
Ce	C403*	2.744(14)	C14	C18*	1.336(14)
C101	C102	1.367(9)	C18	C18*	1.34(2)
C102	C103	1.351(10)	O19	C20	1.448(6)
C201	C202	1.381(11)	O19	C24	1.441(6)
C202	C203	1.351(11)	C20	C24	1.509(8)
C301	C302	1.369(11)			

TABLE III. Bond Angles (°) with their e.s.d.s in Parentheses

Atom	Angle	Atom	Angle
C101–Ce–C102	27.9(2)	C202–Ce–C401	99.0(4)
C101–Ce–C103	52.1(2)	C202–Ce–C402	97.9(4)
C101–Ce–C201	170.7(2)	C202–Ce–C403	118.1(4)
C101–Ce–C202	160.8(2)	C202–Ce–C401*	92.4(3)
C101–Ce–C203	134.8(2)	C202–Ce–C402*	112.6(4)
C101–Ce–C301	96.3(2)	C202–Ce–C403*	108.6(4)
C101–Ce–C302	81.5(2)	C203–Ce–C301	90.2(3)
C101–Ce–C303	87.2(2)	C203–Ce–C302	117.5(3)
C101–Ce–C401	86.8(4)	C203–Ce–C303	129.9(3)
C101–Ce–C402	95.2(4)	C203–Ce–C401	91.2(4)
C101–Ce–C403	79.9(4)	C203–Ce–C402	102.3(4)
C101–Ce–C401*	89.3(3)	C203–Ce–C403	131.6(4)
C101–Ce–C402*	77.0(3)	C203–Ce–C401*	80.1(3)
C101–Ce–C403*	87.8(3)	C203–Ce–C402*	107.9(4)
C102–Ce–C103	28.2(2)	C203–Ce–C403*	118.4(4)
C102–Ce–C201	158.6(2)	C301–Ce–C302	28.1(2)
C102–Ce–C202	134.2(3)	C301–Ce–C303	52.8(3)
C102–Ce–C203	107.0(3)	C301–Ce–C401	173.9(4)
C102–Ce–C301	102.0(2)	C301–Ce–C402	148.2(4)
C102–Ce–C302	98.7(2)	C301–Ce–C403	123.2(4)
C102–Ce–C303	112.5(2)	C301–Ce–C401*	170.2(3)
C102–Ce–C401	83.3(4)	C301–Ce–C402*	160.1(4)
C102–Ce–C402	102.0(4)	C301–Ce–C403*	134.1(4)
C102–Ce–C403	99.4(4)	C302–Ce–C303	28.7(2)
C102–Ce–C401*	79.4(3)	C302–Ce–C401	148.7(4)
C102–Ce–C402*	81.0(3)	C302–Ce–C402	126.8(4)
C102–Ce–C403*	102.4(3)	C302–Ce–C403	97.1(4)
C103–Ce–C201	136.8(2)	C302–Ce–C401*	161.7(3)
C103–Ce–C202	108.7(3)	C302–Ce–C402*	132.3(4)
C103–Ce–C203	83.9(3)	C302–Ce–C403*	109.7(4)
C103–Ce–C301	86.3(3)	C303–Ce–C401	122.3(4)
C103–Ce–C302	95.7(2)	C303–Ce–C402	98.4(4)
C103–Ce–C303	120.1(2)	C303–Ce–C403	70.4(4)
C103–Ce–C401	99.8(4)	C303–Ce–C401*	135.8(3)
C103–Ce–C402	123.7(4)	C303–Ce–C402*	107.6(4)
C103–Ce–C403	127.5(4)	C303–Ce–C403*	81.9(4)
C103–Ce–C401*	90.9(3)	C401–Ce–C402	25.8(5)
C103–Ce–C402*	103.5(3)	C401–Ce–C403	52.1(5)
C103–Ce–C403*	128.8(3)	C401–Ce–C401*	13.5(4)
C201–Ce–C202	28.3(2)	C401–Ce–C402*	16.8(4)
C201–Ce–C203	53.3(2)	C401–Ce–C403*	40.5(5)
C201–Ce–C301	87.6(2)	C402–Ce–C403	31.5(5)
C401*–C402*–C403*	129.0(1)	C402–Ce–C401*	38.1(4)
C201–Ce–C302	98.6(2)	C402–Ce–C402*	21.0(4)
C201–Ce–C303	88.6(2)	C402–Ce–C403*	17.8(4)
C201–Ce–C401	88.5(4)	C403–Ce–C401*	65.6(5)
C201–Ce–C402	77.2(4)	C403–Ce–C402*	37.6(5)
C201–Ce–C403	90.9(4)	C403–Ce–C403*	13.9(4)
C201–Ce–C401*	88.0(3)	C401*–Ce–C402*	29.5(4)
C201–Ce–C402*	96.4(3)	C401*–Ce–C403*	53.9(4)
C201–Ce–C403*	83.5(3)	C402*–Ce–C403*	28.6(4)
C202–Ce–C203	27.8(2)	C101–C102–C103	129.2(7)
C202–Ce–C301	79.6(3)	C201–C202–C203	135.8(9)
C202–Ce–C302	101.5(3)	C301–C302–C303	129.1(9)
C202–Ce–C303	104.6(3)	C401–C402–C403	124.0(2)
C501–C502–C503	132.2(8)	C503–Li1–O1	118.9(5)
O10–C11–C12	109.1(6)	C503–Li1–O10	116.2(5)
O13–C18*–C14	108.0(1)	C503–Li1–O13	104.4(4)

(continued)

TABLE III. *(continued)*

Atom	Angle	Atom	Angle
C3–O4–C5	110.4(4)	O1–Li1–O10	110.2(5)
C20–O19–C24	110.8(4)	O1–Li1–O13	104.7(4)
O19–C20–C24	109.3(5)	O10–Li1–O13	99.6(4)
O19–C24–C20	109.3(5)	C501–Li2–O4	115.0(5)
C8–C9–O10	110.1(5)	C501–Li2–O7	107.4(5)
C9–O10–C11	110.6(4)	C501–Li2–O19	119.6(5)
O1–C2–C3	109.9(5)	O4–Li2–O7	107.9(5)
C2–C3–O4	109.6(5)	O4–Li2–O19	103.0(5)
C14–O13–C18*	108.0(7)	O7–Li2–O19	103.0(4)
O1–C6–C5	109.3(5)	O13–C18–C14	111.6(8)
C8–O7–C12	111.2(5)	C2–O1–C6	109.3(4)
O7–C8–C9	109.4(5)	O7–C12–C11	109.4(5)
C502–Li1–C503	32.1(3)	C14–O13–C18	109.6(5)
C502–Li1–O1	98.1(4)	O4–C5–C6	109.5(5)
C502–Li1–O10	107.3(4)	O13–C14–C18	110.4(6)
C502–Li1–O13	135.9(5)	O13–C14–C18*	111.5(9)

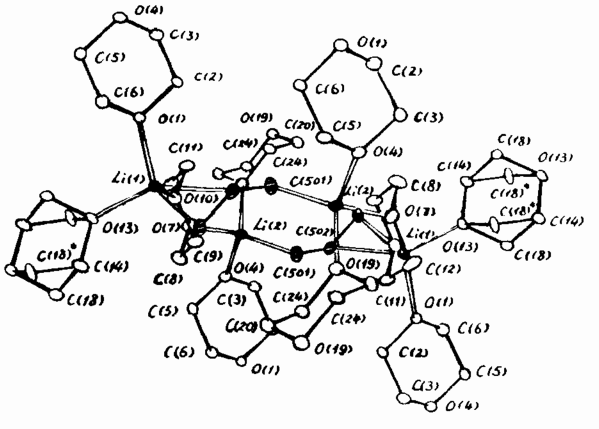

Fig. 1. A view of the cation framework.

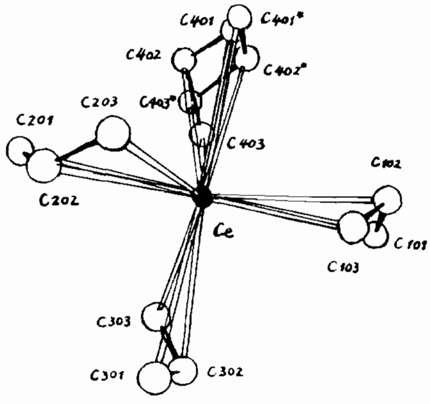

Fig. 2. A view of the anion.

Discussion

The structure of the compound consists of a three-dimensional developing cation framework and the anion $[Ce(C_3H_5)_4]^-$. The anion is of the pure allyl type and in it the cerium atom is symmetrically η^3-bonded to four allyl groups, all of which have quite high temperature factors. However, the fourth allyl group takes two arrangements around the central metal, which indicate the presence of two conformational isomers (shown in Fig. 2). The bond lengths found were: Ce–C(1), 2.81 to 2.86 Å; Ce–C(2), 2.79 to 2.82 Å; Ce–C(3), 2.71 to 2.81 Å. The angles of the η^3-allyl groups C(1)–C(2)–C(3) (124.0 to 135.8°) were bigger than the 120° generally found for allyl transition metal compounds. The dihedral angles between the planes defined by the three-carbon skeleton of the η^3-allyl groups and the planes defined by the metal atom and terminal carbon atoms of the η^3-allyl groups were 115.9, 118.9, 117.6, 111.1 and 113.8°.

It is very interesting that the anions occupy the channels of a three-dimensional cation framework. The dioxane molecules are linked to the lithium atoms by their two oxygen atoms. There exist four unique molecules of dioxane, named dioxane 1 (O1, C2, C3, O4, C5, C6), 2(O7, C8, C9, O10, C11, C12), 3(O13, C14, C18′, O13′, C14′, C18) and 4(O19, C20, C24′, O19′, C20′, C24) in the structure; dioxane 3 and 4 have centric symmetry, and they play different roles in forming the skeleton. Dioxane 1 is bonded to Li1 via O1, and to Li2 via O4; dioxane 2 is linked to Li1 via O10 and to Li2 via O7; however, dioxane 3 is linked only to Li1 via O13 or O13′, and dioxane 4 only to Li2 via O19 or O19′.

Four lithium atoms are bonded by two μ-allyl groups and two dioxane 2 and form a cyclic unit (radius about 2.7 Å) and the unit has a center at (0.5, 0, 0.5) and is extended by dioxane 1 along the *b* axis, and by dioxane 3 at (0, 0, 0.5) along the *a* axis, and by dioxane 4 at (0.5, 0, 0) along the *c* axis. Two anions are located at both sides of the ring (shown in Fig. 3).

Two of three atoms of the μ-bonded allyl group are bonded to the Li1, and the third to the Li2 atom; this type is the same as in compound $[Pt(C_3H_5)(C_5H_7O_2)]_2$ [5]. Compared to compound $[Pt(C_3H_5)(C_5H_7O_2)]_2$, the lengths C501–C502 of 1.40(1) Å and C502–C503 of 1.34(1) Å are a little shorter than the 1.37 to 1.49 Å of that compound and the angle C501–C502–C503 of 132.2(8)° is larger (121 to 123°).

Due to the three-dimensional structure of the cation, the size of the anion should be compatible with the dimensions of channel where the anions are located in the framework (shown in Fig. 4). It is assumed that if the cerium ion were replaced by other rare earth ions, such as Pr, Nd, Sm, Gd and Lu, the series of compounds mentioned above would be understood.

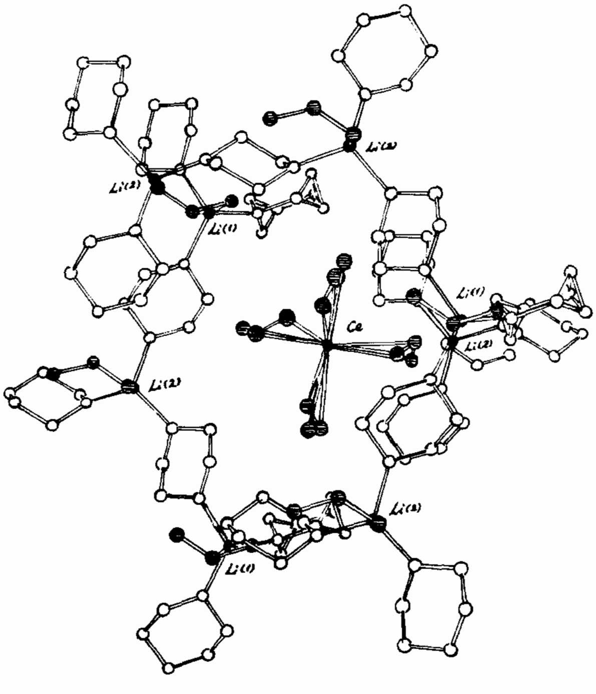

Fig. 3. Location of anions and cation unit: •, cerium atom; ⊜, carbon atom in allyl group; ○, carbon or oxygen atom in dioxane molecules.

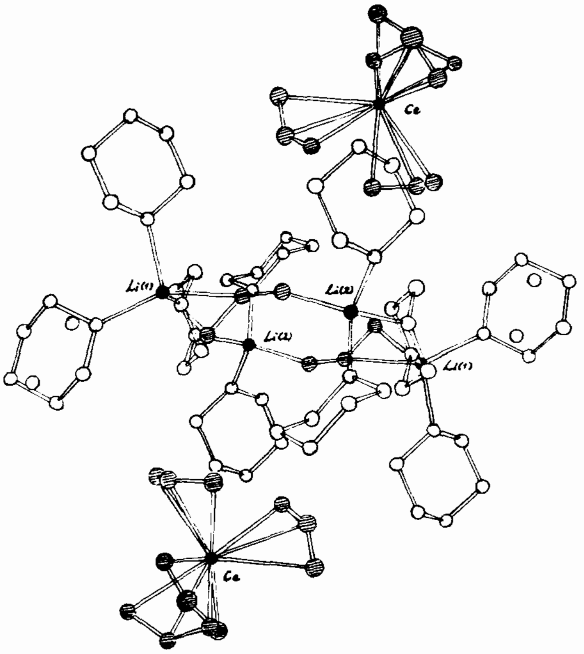

Fig. 4. The anion $[Ce(C_3H_5)_4]^-$ in the channel.

Acknowledgement

This research project was supported by the PRC National Science Foundation.

References

1 Zuen Huang, Wenjie Qiu, Ruifang Cai, Shanming Zhuang, Shihui He, Fan Li, Jingde Wei, Yueming Sheng and Wenling Wu, *Acta Chim. Sin., 44,* 817 (1986).
2 Wenjie Qiu, Zuen Huang, Shanming Zhuang and Wenling Wu, *J. Inorg. Chem. (China), 1,* 173 (1985).
3 M. Tsutsui and N. J. Ely, *J. Am. Chem. Soc., 97,* 3551 (1975).
4 A. Mazzei, in T. J. Marks and R. D. Fischer (eds.), 'Organometallics of the f-Elements', D. Reidel, Dordrecht, 1979, p. 379.
5 G. Raper and W. S. McDonald, *J. Chem. Soc., Dalton Trans.,* 265 (1972).