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# Crystal Structure of Organolanthanide Complexes $[Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Ln\cdot THF$ (Ln = La, Nd)

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## Abstract

The crystal and molecular structures of the title compounds have been determined from single crystal X-ray diffraction. The two complexes crystallize in the orthorhombic space group $Pna2_1$ with $Z = 4$. Lattice parameters are: $a = 10.504(2)$ [10.522(2)],* $b = 16.816(4)$ [16.927(3)] and $c = 18.931(4)$ [18.969(3)] Å. The two crystals are isomorphous. The structures were solved by Patterson and Fourier techniques and refined by least-squares techniques to $R = 0.0430$ for 1508 reflections. The $Nd^{3+}$ ion is eight-coordinate, being bonded to five carbons of the cyclopentadiene ring, to four chloride atoms and to the one oxygen atom of the THF ring. The Nd–C distances are in the range 2.67–2.85 Å (average: 2.77 Å) and Nd–Cl distances are in the range 2.76–2.80 Å (average: 2.78 Å). The Nd–O distance is 2.52 Å. The $Li^+$ ion is four-coordinate, being bonded to the two chloride atoms and to the two oxygen atoms of the two THF rings. The other $Li^+$ ion is the same as the above. The Li–Cl distances are in the range 2.17–2.55 Å (average: 2.35 Å) and Li–O distances are in the range 1.89–1.98 Å (average: 1.91 Å). The Nd atom and the two Li atoms are bridged asymmetrically by the chloride ions, respectively.

## Introduction

Manastyrsky [1] first reported the synthesis of cyclopentadienyl heavier lanthanide dichlorides, $C_5H_5LnCl_2$ (Ln = Sm–Lu). However, attempts to prepare similar complexes with light rare earth elements have failed and have been ascribed to the lanthanide contraction [1]. Recently, Chen *et al.* reported $C_5H_5LnCl_2$ (Ln = Pr, Ce, Nd) [2] and their crystal structure [3]. We now wish to report the new complexes of cyclopentadienyllanthanide dichloride $[Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Ln\cdot THF$ (Ln = La, Nd) and their crystal and molecular structures. The complexes prepared by treating $LnCl_3\cdot nLiCl\cdot nTHF$ [4] with one equivalent of $C_5H_5Na$ in THF (eqn. 1):

$$LnCl_3\cdot nLiCl\cdot nTHF + C_5H_5Na \longrightarrow [Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Ln\cdot THF \quad (1)$$

(yield: 45–57%)

(Ln = La, Nd)

The new compounds are not only easy to prepare and recrystallize, but they can also be used as an intermediate to synthesize a series of new organolanthanide derivatives [5]. The detailed synthesis of the new compounds will be reported in another paper [6].

## Experimental

Both the crystals $[Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Ln\cdot THF$ (Ln = La and Nd) are very unstable in moisture and air, so they were protected by dry nitrogen gas at −100 °C during data collection. The unit cell parameters were determined and X-ray intensity data with $2\theta$ values below 45° were collected on a Nicolet R3M/E four-circle diffractometer, using graphite-monochromated Mo K$\alpha$ radiation. The $\omega$ scanning mode was utilized during data collection with scan speeds from 3.91° to 19.53° $min^{-1}$ and a scan range of 1.1°. The intensities were corrected for Lorentz and polarization factors, but not for absorption. Crystal data are listed in Table I. The structures of the two compounds are isomorphous, so the neodymium compound structure only was determined.

TABLE I. Crystallographic Data

| | La | Nd |
|---|---|---|
| $a$ (Å) | 10.522(2) | 10.504(2) |
| $b$ (Å) | 16.927(3) | 16.816(4) |
| $c$ (Å) | 18.969(3) | 18.931(4) |
| $V$ (Å$^3$) | 3378.5 | 3343.8 |
| $Z$ | 4 | 4 |
| $D_c$ (g/cm$^3$) | 1.42 | 1.44 |
| $F$(000) | 1464 | 1476 |
| No. of reflections | | 1508 ($I/\sigma(I) > 2.0$) |

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*Data in parentheses are of the lanthanum compound.

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TABLE II. Atomic Coordinates ($\times 10^4$) and Equivalent Temperature Factors $U$ ($\times 10^3$ Å$^2$)

| | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| Nd | 2220(1) | 5405(1) | 5000 | 50(1) |
| Cl(3) | 2954(7) | 4482(6) | 3311(9) | 67(4) |
| Cl(4) | 2950(8) | 4506(7) | 6767(12) | 80(5) |
| Cl(2) | 1111(7) | 5848(6) | 6779(9) | 62(4) |
| Cl(1) | 1084(3) | 5868(2) | 3303(4) | 76(2) |
| O(1) | 1256(5) | 4386(4) | 4998(23) | 72(4) |
| C(11) | 965(24) | 4036(19) | 6102(24) | 76(15) |
| C(12) | 709(24) | 3317(16) | 5689(43) | 194(27) |
| C(13) | 506(19) | 3438(17) | 4292(31) | 105(12) |
| C(14) | 931(20) | 4069(20) | 3821(32) | 124(16) |
| O(2) | 257(5) | 7235(4) | 4894(34) | 81(5) |
| C(21) | 336(11) | 7721(8) | 3992(14) | 87(8) |
| C(22) | 771(30) | 8398(21) | 4322(40) | 126(18) |
| C(23) | 821(8) | 8222(7) | 5712(12) | 63(6) |
| C(24) | 306(10) | 7663(7) | 6186(18) | 89(8) |
| O(3) | 9241(5) | 5934(4) | 4803(31) | 70(6) |
| C(31) | 8993(7) | 5230(6) | 5247(34) | 55(8) |
| C(32) | 8117(7) | 5219(7) | 5090(69) | 106(8) |
| C(33) | 7859(8) | 5983(8) | 4862(46) | 90(8) |
| C(34) | 8572(8) | 6379(8) | 5335(23) | 80(10) |
| O(4) | 3246(8) | 2933(6) | 4845(29) | 112(7) |
| C(41) | 3237(15) | 2507(10) | 6009(20) | 141(12) |
| C(42) | 2584(18) | 1939(17) | 5647(44) | 123(14) |
| C(43) | 2923(17) | 1733(11) | 4404(18) | 165(16) |
| C(44) | 2953(14) | 2505(11) | 3916(16) | 134(12) |
| O(5) | 5343(7) | 6034(7) | 103(33) | 101(5) |
| C(51) | 4837(14) | 5805(15) | 1106(20) | 87(11) |
| C(52) | 4115(9) | 5529(10) | 626(16) | 113(9) |
| C(53) | 4374(10) | 5395(10) | −753(16) | 114(9) |
| C(54) | 4964(14) | 5999(12) | −1065(27) | 209(17) |
| Li(1) | 308(12) | 6240(12) | 4845(81) | 63(15) |
| Li(2) | 3494(15) | 3893(14) | 4854(77) | 67(11) |
| C(1) | 2708(10) | 6783(8) | 5717(29) | 136(19) |
| C(2) | 2814 | 6700 | 4384 | 66(10) |
| C(3) | 3430 | 6199 | 4187 | 96(13) |
| C(4) | 3705 | 5972 | 5398 | 108(14) |
| C(5) | 3259 | 6333 | 6343 | 88(11) |

Systematic absences $0kl$, $k + l = 2n$, $h0l$, $h = 2n$ indicate the space group $Pna2_1$.

The heavy atom was located by Patterson techniques and the light atoms were then found on successive Fourier syntheses. The initial model of the crystal structure was determined as: $[Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Nd\cdot THF$. Hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors, $B = 5.0$ Å, and were not refined. All positional parameters and temperature factors for non-hydrogen atoms were refined anisotropically. The final $R$ index is 0.043. The computational work was carried out on an Eclipse S/140 minicomputer. Final atomic coordinates are given in Table II and selected bond lengths and angles in Table III.

## Results and Discussion

Figure 1 is the perspective view of the structure. The neodymium(III) ion is eight-coordinate, being bonded to four chloride ions, to one oxygen of the THF ring and to five carbon atoms of the cyclo-

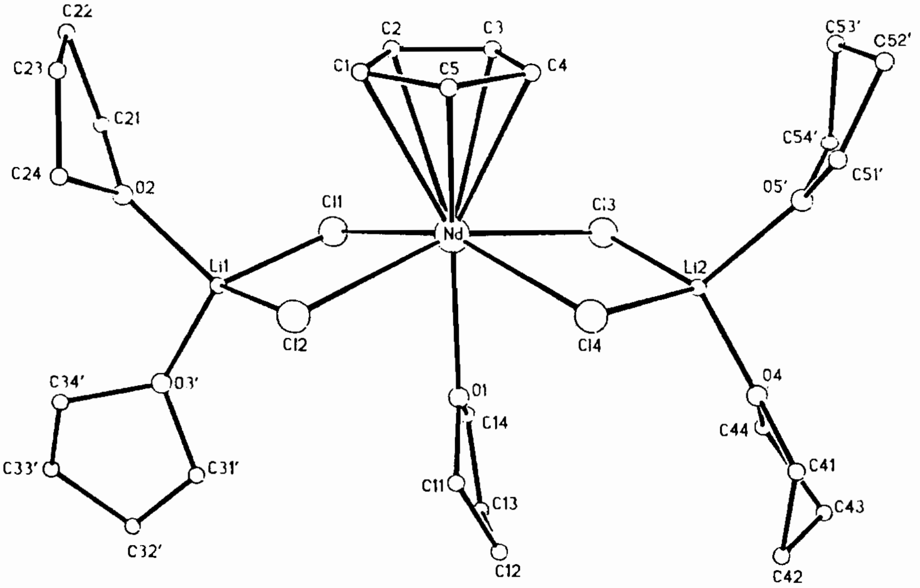

Fig. 1. Perspective view of $[Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Nd\cdot THF$.

TABLE III. Selected Bond Lengths (Å) and Bond Angles (°)

| | | | |
|---|---|---|---|
| Nd–Cl(1) | 2.757(4) | Nd–Cl(2) | 2.771(11) |
| Nd–Cl(3) | 2.778(11) | Nd–Cl(4) | 2.800(13) |
| Nd–O(1) | 2.519(8) | Nd–C(1) | 2.837(17) |
| Nd–C(2) | 2.725(17) | Nd–C(3) | 2.669(18) |
| Nd–C(4) | 2.750(17) | Nd–C(5) | 2.852(21) |
| Li(1)–Cl(1) | 2.197(64) | Li(1)–Cl(2) | 2.550(71) |
| Li(1)–O(2) | 1.885(24) | Li(1)–O(3) | 1.885(22) |
| Li(2)–Cl(3) | 2.168(63) | Li(2)–Cl(4) | 2.494(68) |
| Li(2)–O(4) | 1.864(28) | Li(2)–O(5) | 1.978(31) |
| Cl(1)–Nd–Cl(2) | 82.7(2) | Cl(1)–Nd–Cl(3) | 95.4(2) |
| Cl(1)–Nd–Cl(4) | 157.7(3) | Cl(1)–Nd–C(2) | 79.3(5) |
| Cl(2)–Nd–Cl(3) | 157.0(3) | Cl(2)–Nd–Cl(4) | 91.8(3) |
| Cl(2)–Nd–C(1) | 74.7(5) | Cl(3)–Nd–Cl(4) | 81.2(3) |
| Cl(3)–Nd–C(3) | 79.1(5) | Cl(4)–Nd–C(4) | 74.9(6) |
| O(1)–Nd–Cl(1) | 78.3(4) | O(1)–Nd–Cl(2) | 78.4(5) |
| O(1)–Nd–Cl(3) | 78.7(5) | O(1)–Nd–Cl(4) | 79.5(5) |
| O(1)–Nd–C(5) | 150.0(8) | | |
| Cl(1)–Li(1)–Cl(2) | 100.3(9) | Cl(1)–Li(1)–O(2) | 111.6(28) |
| Cl(1)–Li(1)–O(3′) | 116.6(32) | Cl(2)–Li(1)–O(2) | 107.1(30) |
| Cl(2)–Li(1)–O(3′) | 115.7(32) | O(2)–Li(1)–O(3′) | 105.3(11) |
| Cl(3)–Li(2)–Cl(4) | 102.1(11) | Cl(3)–Li(2)–O(4) | 113.8(30) |
| Cl(3)–Li(2)–O(5′) | 118.5(27) | Cl(4)–Li(2)–O(4) | 112.1(30) |
| Cl(4)–Li(2)–O(5′) | 102.9(28) | O(4)–Li(2)–O(5′) | 106.9(15) |

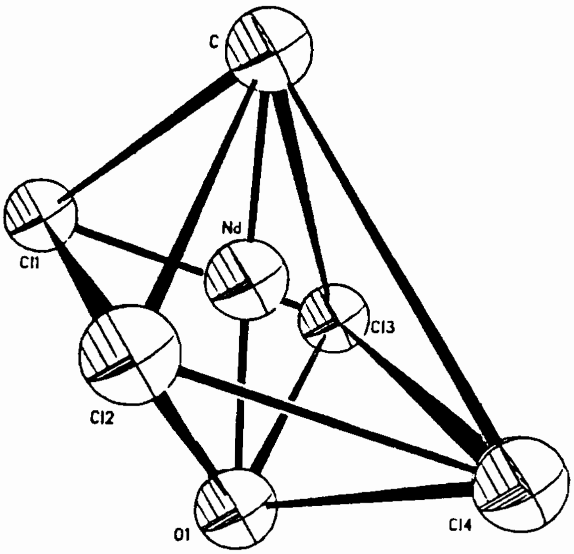

Fig. 2. Coordination polyhedron of $[Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Nd\cdot THF$.

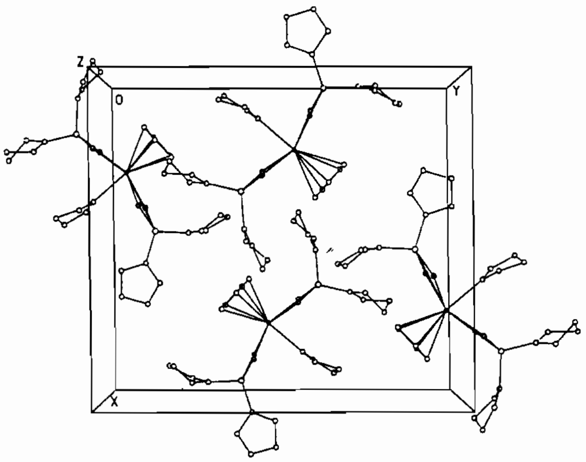

Fig. 3. Stereoscopic packing diagram of $[Li(THF)_2]_2(\mu\text{-}Cl)_4(\eta^5\text{-}C_5H_5)Nd\cdot THF$.

pentadiene ring system, in an octahedral array if the centroid of the ring is taken as one point (Fig. 2). The Nd–Cl distances are in the range 2.76–2.80 Å (average: 2.78 Å). The Nd–C distances are in the range 2.67–2.85 Å (average: 2.77 Å); Nd–O = 2.52 Å. The lengths of both the Nd–C and the Nd–O bonds accord with the corresponding values in $(\eta^5\text{-}C_5H_5)_3Nd\cdot THF$ [7]. The two lithium(I) ions are four-coordinate, being bonded to two chloride ions and to the two oxygens of the two THF rings, respectively, in tetrahedral array. The two Li atoms and Nd atom are bridged by the two chlorine atoms respectively. Figure 3 is a stereoscopic packing diagram of the molecule.

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