

Structural Investigations of the Isomorphous Propionitrile-tris(η^5 -cyclopentadienyl) Lanthanoid(III) (Ln = La, Pr, Yb) Complexes and of the Corresponding 1:2 Adducts*

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1:1 adducts $(C_5H_5)_3Ln(NCCH_2CH_3)$ (Ln = La, Pr, Yb) of the strongly Lewis acidic organolanthanoid complexes $(C_5H_5)_3Ln$ with the aliphatic nitrile CH_2CH_3CN have been prepared and characterized by three-dimensional X-ray diffraction data. Their crystal and molecular structures are presented here. The crystal structure of the 1:2 adduct, $(C_5H_5)_3La(NCCH_2CH_3)_2$, has also been investigated and is compared with that of the 1:1 adducts.

Experimental

$Cp_3Ln(NCCH_2CH_3)$ complexes (Cp = C_5H_5) with Ln = La, Pr, Yb were obtained by stoichiometric reaction between Cp_3Ln and CH_2CH_3CN in n-pentane. Extraction followed by recrystallization in n-pentane yielded single crystals suitable for X-ray analysis. A reaction between Cp_3La and excess CH_3CH_2CN followed by recrystallization from this solvent afforded the 1:2 adduct $Cp_3La(NCCH_2CH_3)_2$. The 1:1 adducts, $Cp_3Ln(NCCH_2CH_3)$ (Ln = La, Pr, Yb) are isomorphous, crystallizing in the triclinic space group $P\bar{1}$, with two molecules in the unit cell. Cell dimensions are shown in Table I.

The 1:2 adduct, $Cp_3La(NCCH_2CH_3)_2$ is monoclinic, space group $C2/c$, with cell dimensions $a = 14.988(5)$, $b = 8.448(3)$, $c = 31.893(6)$ Å, $\beta = 94.25(4)^\circ$, $V = 4027(4)$ Å³. There are eight molecules in the unit cell.

A complete structural analysis has been performed for the 1:1 adducts of La and Yb and for the 1:2 adduct of La. Three-dimensional X-ray intensity data

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TABLE I. Cell Dimensions of $Cp_3Ln(NCCH_2CH_3)$

	Ln = La	Ln = Pr	Ln = Yb
a (Å)	8.542(3)	8.468(6)	8.254(7)
b (Å)	9.388(3)	9.366(4)	9.306(5)
c (Å)	11.253(4)	11.221(4)	11.035(4)
α (°)	113.71(2)	113.71(2)	113.27(3)
β (°)	93.80(5)	93.76(5)	94.64(4)
γ (°)	90.25(4)	90.40(5)	90.68(5)
V (Å ³)	824(1)	813(1)	775(1)

were collected with an Enraf-Nonius four circle diffractometer using Mo $K\alpha$ radiation. Cell dimensions were established and refined by least-squares analysis of angle data for 25 reflections. The structures were solved by direct methods, Fourier techniques and full-matrix refinement. The conventional agreement factors are: $(C_5H_5)_3LaNCCH_2CH_3$, $R = 0.022$, $R_w = 0.042$ with 2122 independent reflections for which $I > 3\sigma(I)$, used in refinement; $(C_5H_5)_3YbNCCH_2CH_3$, $R = 0.028$, $R_w = 0.041$ with 2701 independent reflections for which $I > 3\sigma(I)$; $(C_5H_5)_3La(NCCH_2CH_3)_2$, $R = 0.40$, $R_w = 0.055$ with 1775 reflections for which $I > 3\sigma(I)$. Atomic coordinates and thermal parameters have been deposited as Supplementary Material.

Results and Discussion

The molecular structure of the isomorphous $Cp_3LnNCCH_2CH_3$ complexes is illustrated by Fig. 1.

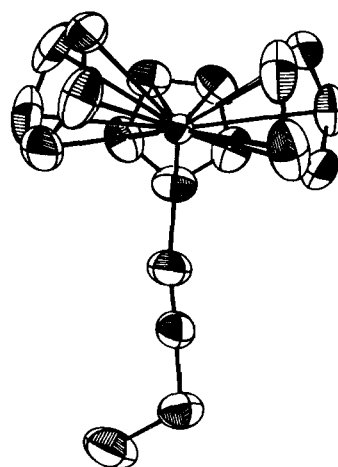


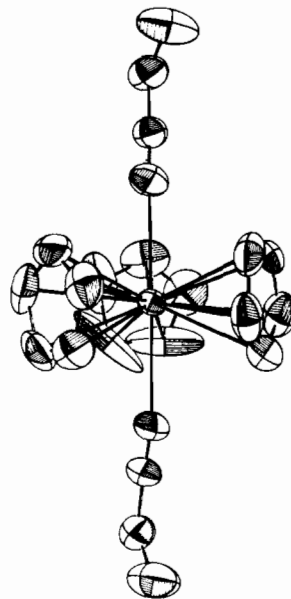
Fig. 1. Molecular structure of $Cp_3LaNCCH_2CH_3$.

TABLE II. Selected Bond Distances (Å) and Angles (°) in $(C_5H_5)_3Ln(NCH_2CH_3)$ (Ln = La, Yb)^a

	Ln = La	Ln = Yb
Intramolecular bond distances and angles		
Ln-C(1)	2.842(5)	2.696(6)
Ln-C(2)	2.830(5)	2.660(6)
Ln-C(3)	2.809(5)	2.654(7)
Ln-C(4)	2.813(5)	2.620(6)
Ln-C(5)	2.812(5)	2.629(6)
Ln-C(6)	2.809(5)	2.685(7)
Ln-C(7)	2.835(5)	2.697(7)
Ln-C(8)	2.865(6)	2.729(7)
Ln-C(9)	2.835(6)	2.690(7)
Ln-C(10)	2.810(5)	2.663(6)
Ln-C(11)	2.799(5)	2.624(7)
Ln-C(12)	2.856(5)	2.698(6)
Ln-C(13)	2.878(5)	2.768(6)
Ln-C(14)	2.851(5)	2.694(7)
Ln-C(15)	2.799(5)	2.654(6)
Ln-N	2.657(5)	2.414(5)
N-Ln-Rc1 ^b	97.2(2)	97.0(3)
N-Ln-Rc2 ^b	98.4(2)	97.5(3)
N-Ln-Rc3 ^b	99.7(2)	99.5(3)
Rc1-Ln-Rc2	118.7(2)	119.4(3)
Rc1-Ln-Rc3	118.2(2)	118.1(3)
Rc2-Ln-Rc3	116.8(2)	116.8(3)
Ln-N≡C(16)	168.3(4)	171.0(5)
N≡C(16)-C(17)	177.4(6)	179.3(6)
Short intra- or intermolecular contacts (<3.7 Å) ^c		
C(1)---C(11)	3.343(9)	3.07(1)
C(1)---C(17) ⁱ	3.601(8)	3.600(9)
C(3)---C(17) ⁱ	3.698(9)	(3.71(1))
C(4)---C(16) ⁱ	3.695(8)	(3.770(9))
C(4)---C(17) ⁱ	3.483(8)	3.486(9)
C(5)---C(16) ⁱ	3.593(7)	3.625(9)
C(5)---C(17) ⁱ	3.448(8)	3.428(9)
C(11)---C(16) ⁱⁱ	3.548(7)	3.475(9)
C(11)---C(17) ⁱⁱ	3.505(8)	3.42(1)
C(12)---C(16) ⁱⁱ	(3.779(7))	3.600(8)

^aStandard deviations are given in parentheses. ^bRc1 denotes centroid of ring 1 (C1, C2, C3, C4, C5); Rc2 denotes centroid of ring 2 (C6, C7, C8, C9, C10); Rc3 denotes centroid of ring 3 (C11, C12, C13, C14, C15). ^cSymmetry code: (i) $-x, -y + 1, -z$; (ii) $-x, -y, -z$.

Relevant bond distances and angles are reported in Table II. The Ln ion is penta-hapto covalently bonded to three cyclopentadienyl moieties and to a propionitrile nitrogen atom. The coordination geometry is a flattened tetrahedron, the site symmetry about the trivalent lanthanide ion being approximately C_{3v} . This arrangement is typical of most MCp_3X derivatives with ring centroid-metal-ring centroid angles in the range 112 to 119° [1]. The Ln^{3+} ion is assumed to be ten-coordinated, each η^5 -Cp ligand being considered as a donor of three electron pairs. The averaged Ln-C distances of 2.830(5) Å for Ln = La

Fig. 2. Molecular structure of $Cp_3La(NCCH_2CH_3)_2$.

and of 2.677(6) Å for Ln = Yb compare favorably with the distances previously reported for several cyclopentadienyl complexes [2, 3]. The Ln-N bond length is of 2.657(5) and 2.414(5) Å respectively for the La and the Yb complexes. The variations in bond distances observed between the La and the Yb complexes are in agreement with the variation of crystal radii along the lanthanoid series. Bond lengths can therefore be easily predicted for intermediate lanthanoid complexes in the whole isomorphous series. A significant feature observed in these complexes is the deviation from linearity of the Ln-N≡C-CH₂CH₃ arrangement, as shown by the Ln-N≡C angles reported in Table II.

As expected, the pseudo-tetrahedral $Ln(C_5H_5)_3NCCH_2CH_3$ system is able to accommodate an additional propionitrile molecule to give the 1:2 adducts: $Ln(C_5H_5)_3(NCCH_2CH_3)_2$. The molecular structure of the La derivative of this series is represented by Fig. 2. Relevant bond distances and angles are reported in Table III. In this complex the coordination geometry of the Ln atom is trigonal bipyramidal with a pseudo-symmetry of D_{3h} for the Ln atom site. The three η^5 -covalently bonded cyclopentadienyl rings occupy the equatorial plane and the propionitrile ligands the *trans* diaxial positions. The average ring centroid-La-ring centroid angle is 120.0° and the ring centroid-La-N angle is 90.0°. The La³⁺ ion in this complex appears to be eleven-coordinated.

No significant differences in La-C bond lengths are observed between the 1:2 adduct (average distance 2.86(1) Å) and the 1:1 adduct (average distance 2.830(5) Å). On the other hand, La-N bonds in $(C_5H_5)_3La(NCCH_2CH_3)_2$ are significantly weaker than

TABLE III. Selected Bond Distances (Å) and Angles (°) in $(C_5H_5)_3La(NCCH_2CH_3)_2^a$

Intramolecular bond distances and angles			
La-C(1)	2.858(9)	N(1)-La-Rc1 ^b	91.4(2)
La-C(2)	2.829(9)	N(1)-La-Rc2 ^b	89.1(2)
La-C(3)	2.860(9)	N(1)-La-Rc3 ^b	89.7(2)
La-C(4)	2.89(1)	N(2)-La-Rc1	90.5(2)
La-C(5)	2.88(1)	N(2)-La-Rc2	91.3(2)
La-C(6)	2.86(1)	N(2)-La-Rc3	88.0(2)
La-C(7)	2.867(9)	Rc1-La-Rc2	119.3(4)
La-C(8)	2.86(1)	Rc1-La-Rc3	117.9(4)
La-C(9)	2.846(9)	Rc2-La-Rc3	122.9(4)
La-C(10)	2.84(1)		
La-C(11)	2.83(1)	La-N(1)-C(16)	165.4(9)
La-C(12)	2.89(1)	La-N(2)-C(19)	167.4(8)
La-C(13)	2.88(1)		
La-C(14)	2.85(1)	N(1)≡C(16)-C(17)	177(1)
La-C(15)	2.83(1)	N(2)≡C(19)-C(20)	177(1)
La-N(1)	2.759(9)		
La-N(2)	2.756(9)		
Short intra- or intermolecular contacts (<3.7 Å) ^c			
C(3)---C(17) ⁱ	3.63(1)		
C(4)---C(17) ⁱ	3.69(1)		
C(5)---C(18) ⁱⁱ	3.64(2)		
C(7)---C(20) ⁱⁱⁱ	3.55(1)		
C(10)---C(19) ^{iv}	3.66(1)		
C(20)---C(20) ^v	3.56(3)		

^aStandard deviations are given in parentheses. ^bRc1 denotes centroid of ring 1 (C1, C2, C3, C4, C5); Rc2 denotes centroid of ring 2 (C6, C7, C8, C9, C10); Rc3 denotes centroid of ring 3 (C11, C12, C13, C14, C15). ^cSymmetry code (i) 0.5 + x, 0.5 + y, z; (ii) 1 - x, y + 1, 0.5 - z; (iii) x, y - 1, z; (iv) 1 - x, -y, -z; (v) 1 - x, 1 - y, -z.

in the 1:1 adduct. They compare favorably with the distance of 2.785(8) Å reported for the corresponding acetonitrile complex $(C_5H_5)_3La(NCCH_3)_2$ [3]. As for the 1:1 adduct, the propionitrile ligands are not co-linear with the La-N bond (Table III). Here a bending of about 10° is observed for the two axial ligands toward one cyclopentadienyl ring. Since there are some short ($d < 4.0$ Å) intermolecular distances between neighboring molecules (Table III) these bendings may be due to steric hindrance. Nevertheless it should be noted that similar bendings have been reported for the acetonitrile derivative $(C_5H_5)_3La(NCCH_3)_2$ [3], too, while a nearly linear Pr-C≡N-R arrangement has been observed in one isocyanide complex [4].

Supplementary Material

Tables of positional and thermal parameters are available from the authors on request.

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