

Synthesis and structural investigation of $\{\text{CpPr}[\text{CH}(\text{COOC}_2\text{H}_5)_2][\mu\text{-CH}(\text{COOC}_2\text{H}_5)_2]\}_2$

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Abstract

The reaction of a 1:2 molar ratio of Cp_3Pr with diethyl malonate in n-hexane results in the formation of $\{\text{CpPr}[\text{CH}(\text{COOC}_2\text{H}_5)_2][\mu\text{-CH}(\text{COOC}_2\text{H}_5)_2]\}_2$. X-ray analysis demonstrates that the complex is a dimer, the two praseodymium atoms are bridged by two oxygen atoms of two independent diethyl malonate ligands. The bridging ligands coordinate with the praseodymium atom in a tridentate mode, the other two diethyl malonate ligands coordinate with praseodymium in a bidentate mode. The complex crystallizes in the monoclinic system, space group $\text{P}2_1/a$ with unit cell constants $a = 9.675(4)$, $b = 18.134(3)$, $c = 12.795(3)$ Å, $\beta = 92.53(3)^\circ$, $D_c = 1.55$ g cm⁻³, $M_r = 1048.65$, $V = 2243(2)$ Å³, for $Z = 2$, $\mu = 22.01$ cm⁻¹ and $F(000) = 1056$. The structure was solved by heavy atom methods (DIRDIF) and full-matrix least-squares refinement to the final $R = 0.040$, $R_w = 0.048$.

Keywords: Praseodymium; Cyclopentadienyl; Diethyl malonate; Crystal structure

1. Introduction

In the past few decades, the chemistry of organolanthanide complexes has become one of the most active fields of organometallic chemistry. With respect to organolanthanide complexes involving both cyclopentadienyl and β -diketonato chelate ligands, several works have focused on thermal stability and mass spectra [1–4]. In addition, only two organolanthanide complexes involving both cyclopentadienyl and diethyl malonate have been prepared [1]. Moreover, up to now only a few structures of this type of complex are known [5–8], and neither the synthesis nor the structural characterization of a diethyl malonate chelating ligand of the early organolanthanide complexes has been reported. For the above reasons, we have synthesized and carried out structural investigations of the complex $\{\text{CpPr}[\text{CH}(\text{COOC}_2\text{H}_5)_2][\mu\text{-CH}(\text{COOC}_2\text{H}_5)_2]\}_2$.

2. Experimental

All reactions and operations were carried out using Schlenk techniques under an atmosphere of ultrapure argon. THF and n-hexane were dried over sodium and distilled under argon from sodium benzophenone ketyl immediately before use. Cp_3Pr was prepared by the published procedure [9]. Diethyl malonate was dried over anhydrous MgSO_4 and freshly distilled under argon before use. Elemental analysis data were obtained with a Yanaco MT-2 analyzer, the analysis for Pr was obtained by the published method [10]. IR spectra were recorded on a Perkin-Elmer 983 (G) spectrometer. MS signals were recorded on a ZAS-HS MS spectrometer. Melting points were determined in sealed argon-filled capillaries without correction.

2.1. Preparation of $\{\text{CpPr}[\text{CH}(\text{COOC}_2\text{H}_5)_2][\mu\text{-CH}(\text{COOC}_2\text{H}_5)_2]\}_2$

A mixture of Cp_3Pr and diethyl malonate in a molar ratio of 1:2 was stirred in n-hexane at room temperature for 2 days. Then n-hexane was removed in vacuum from the reaction mixture. The resulting solid was

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Table 1
MS signals

Compound	T (°C)	Signals
CpPrL ₂	150	524 (CpPrL ₂ ⁺), 430 (Cp ₂ PrL ⁺), 365 (CpPrL ⁺), 271 (Cp ₂ Pr ⁺), 206 (CpPr ⁺), 141 (Pr ⁺), 66 (HCp ⁺)
	> 200	618 (PrL ₃ ⁺), 524 (CpPrL ₂ ⁺), 459 (PrL ₂ ⁺), 430 (Cp ₂ PrL ⁺), 365 (CpPrL ⁺), 336 (Cp ₃ Pr ⁺), 271 (Cp ₂ Pr ⁺), 206 (CpPr ⁺), 141 (Pr ⁺), 66 (HCp ⁺)

L indicates diethyl malonate.

recrystallized twice from THF/n-hexane. Pale yellow crystals (yield 34.7% based on Cp₃Pr) were obtained upon cooling the solution at -10°C for several days. Anal. Found: Pr, 26.76; C, 42.98; H, 5.35. Calc: Pr, 26.87; C, 43.52; H, 5.19%. IR: 3080, 1750, 1566, 1548, 1530, 1440, 1175, 1080, 1000, 780, 250 cm⁻¹. Melting point 160°C (comp.). The complex is unstable to air and moisture both in solution and as a solid. The mass spectra signals of the title complex are listed in Table 1.

The mass spectra of the title compound at two different temperatures show that the compound is unstable while being heated and partially disproportionates into Cp₂PrL and PrL₃. Cp₂PrL can disproportionate into Cp₃Pr and PrL₃. The reaction may be described as follows:

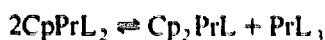


Table 2

Atomic coordinates and isotropic thermal parameters

Atom	x	y	z	B _{eq} (Å ²)
Pr	0.07640(4)	0.04587(2)	0.14433(3)	3.58(2)
O(1)	0.1927(5)	-0.0684(2)	0.1837(4)	5.0(2)
O(2)	0.2714(5)	0.0716(2)	0.2600(4)	4.9(2)
O(3)	0.3261(6)	-0.1597(3)	0.2508(5)	7.1(3)
O(4)	0.4726(6)	0.0694(3)	0.3530(4)	6.6(3)
O(5)	-0.0779(5)	-0.0114(3)	0.2647(4)	5.4(3)
O(6)	-0.1090(4)	-0.0226(2)	0.0461(3)	3.8(2)
O(7)	-0.2497(7)	-0.0679(4)	0.3446(5)	8.6(4)
O(8)	-0.2869(5)	-0.0792(3)	-0.0194(4)	5.0(2)
C(1)	-0.1313(9)	0.1487(5)	0.1703(8)	6.5(5)
C(2)	-0.0995(9)	0.1562(4)	0.0678(8)	6.1(5)
C(3)	0.030(1)	0.1866(5)	0.064(1)	7.6(6)
C(4)	0.079(1)	0.1982(5)	0.167(1)	8.0(6)
C(5)	-0.022(1)	0.1743(5)	0.2316(9)	8.3(6)
C(6)	0.3882(7)	-0.0401(4)	0.2937(6)	5.1(4)
C(7)	0.2964(7)	-0.0871(4)	0.2395(6)	4.5(3)
C(8)	0.3706(8)	0.0343(4)	0.2968(5)	4.5(3)
C(9)	0.226(1)	-0.2140(5)	0.215(1)	8.5(6)
C(10)	0.463(1)	0.1479(5)	0.3631(8)	9.0(6)
C(11)	0.128(2)	-0.2272(8)	0.294(1)	13(1)
C(12)	0.582(2)	0.1723(6)	0.433(1)	12.4(8)
C(13)	-0.2622(7)	-0.0704(4)	0.1667(6)	5.1(4)
C(14)	-0.1893(9)	-0.0468(5)	0.2583(6)	5.6(4)
C(15)	-0.2173(7)	-0.0564(3)	0.0703(6)	4.1(3)
C(16)	-0.201(1)	-0.032(1)	0.447(1)	13(1)
C(17)	-0.399(1)	-0.1334(5)	-0.0199(8)	7.9(5)
C(18)	-0.0121(2)	-0.086(1)	0.482(1)	16(1)
C(19)	-0.527(1)	-0.1032(6)	-0.029(1)	11.7(8)
Cent ^a	-0.02785	0.1727	0.1400	

^a Cent indicates the centroid of C(1) to C(5).

2.2. X-ray crystallography of {CpPr[CH(COOC₂H₅)₂]-μ-CH(COOC₂H₅)₂]₂

A single crystal of the title complex with dimensions 0.38 × 0.20 × 0.16 mm³ was selected and sealed in a thin-walled glass capillary under argon and used in the data collection. The intensity data and unit cell parameters were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα (graphite monochromated, λ = 0.71069 Å) in the range 2θ < 50°. The data were collected at a temperature of 296 K using the ω/2θ scanning technique. The scan rate is less than 5.49° min⁻¹. A total of 4358 unique reflections were collected, 2899 reflections with I > 3σ(I₀) of 4110 independent reflections were observed and used in the structure determination.

The structure was solved by the heavy atom method. The positions of all non-hydrogen atoms were revealed

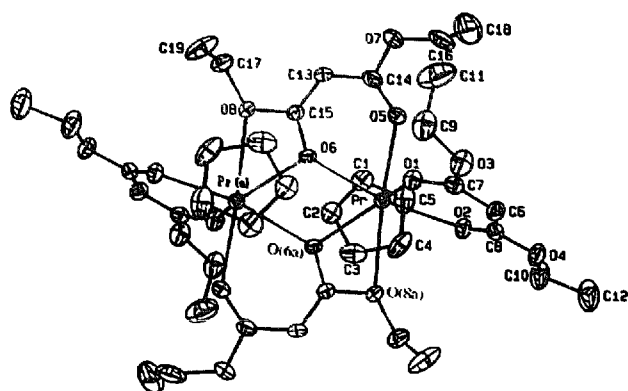


Fig. 1. The structure of $(\text{CpPr}[\text{CH}(\text{COOC}_2\text{H}_5)_2][\mu\text{-CH}(\text{COOC}_2\text{H}_5)_2]_2)$.

by successive Fourier synthesis. Hydrogen atoms were introduced in calculated positions. All positions and thermal parameters for non-hydrogen atoms were refined anisotropically with full-matrix least-squares methods and converged to final $R = 0.040$, $R_w = 0.048$ [$w = 1/\sigma^2(F)$, $s = 1.13$ and $(\Delta/\sigma)_{\text{max}} = 0.03$]; the final difference Fourier map of the complex showed no peak higher than $0.75 \text{ e } \text{\AA}^{-3}$ or less than $-0.59 \text{ e } \text{\AA}^{-3}$. All calculations were performed on a Micro VaxII computer with the TEXSAN V2.1 package.

3. Results and discussion

Atomic coordinates and isotropic thermal parameters, selected bond distances and bond angles of all non-hydrogen atoms are listed in Tables 2–4 respectively. Figs. 1 and 2 give the structure of the molecule and the unit cell package of the molecule respectively.

Table 3
Selected bond distances (Å)

Pr–O(2)	2.392(5)	O(6)–C(15)	1.264(8)
Pr–O(1)	2.400(5)	O(7)–C(14)	1.33(1)
Pr–O(5)	2.426(5)	O(7)–C(16)	1.52(2)
Pr–O(6)	2.478(4)	O(8)–C(15)	1.369(8)
Pr–O(6a)	2.507(4)	O(8)–C(17)	1.464(9)
Pr–O(8a)	2.712(5)	C(1)–C(2)	1.37(1)
Pr–C(5)	2.770(9)	C(1)–C(5)	1.37(1)
Pr–C(1)	2.772(8)	C(2)–C(3)	1.37(1)
Pr–C(2)	2.777(7)	C(3)–C(4)	1.40(1)
Pr–C(4)	2.778(8)	C(4)–C(5)	1.38(1)
Pr–C(3)	2.781(8)	C(6)–C(8)	1.36(1)
O(1)–C(7)	1.253(8)	C(6)–C(7)	1.39(1)
O(2)–C(8)	1.249(8)	C(9)–C(11)	1.43(2)
O(3)–C(7)	1.353(8)	C(10)–C(12)	1.50(1)
O(3)–C(9)	1.44(1)	C(13)–C(15)	1.35(1)
O(4)–C(8)	1.355(8)	C(13)–C(14)	1.41(1)
O(4)–C(10)	1.43(1)	C(16)–C(18)	1.32(2)
O(5)–C(14)	1.254(9)	C(17)–C(19)	1.36(1)
Pr–Cent ^a	2.511(5)		

^a Cent indicates the centroid of C(1) to C(5).

Fig. 2 shows that there are two molecules in each unit cell.

X-ray structural analysis indicates that the title complex is a dimer and the molecule has a crystallographic symmetric center. From Fig. 1, we can see that the diethyl malonate coordinates with the praseodymium ion in two ways, one with the center ion in bidentate mode, the other with the ion in tridentate mode in a bridging fashion. Each praseodymium ion is surrounded by six oxygen atoms of the diethyl malonate ligands and one cyclopentadienyl ligand coordinated with the center ion in η^5 -fashion. So, the coordination number of each praseodymium ion is 9 and the geometry around the praseodymium ion can be described as a pentagonal bipyramid, the atoms O(6), O(2), O(5), O(6a) and O(8a) (the plane formed by which has mean deviation only 0.0551 \AA) situated at equatorial positions and the center of the cyclopentadienyl ring and the atom O(1) situated at axial positions.

It was reported that a β -diketo ligand is bonded to the rare earth ions in the bidentate mode $\text{Ln} \begin{matrix} \text{O}-\text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{O}-\text{C} \end{matrix}$ [5–8]. In the present structure each rare earth ion is coordinated to one β -diketo ligand in the bidentate mode $\text{Pr} \begin{matrix} \text{O}_1-\text{C}_7 \\ \diagdown \\ \text{C}_6 \\ \diagup \\ \text{O}_2-\text{C}_8 \end{matrix}$ and to two β -diketo ligands in a

mixture coordinating way $\text{Pr} \begin{matrix} \text{O}_5-\text{C}_{14} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{O}_6-\text{C}_{15} \end{matrix}$ (both chelating mode and bridging mode). Based on the ways in which these atoms coordinate the center

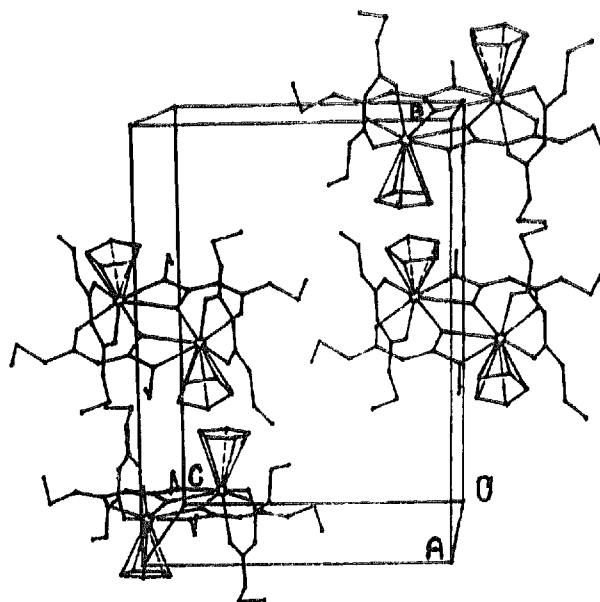


Fig. 2. The unit cell package of $(\text{CpPr}[\text{CH}(\text{COOC}_2\text{H}_5)_2][\mu\text{-CH}(\text{COOC}_2\text{H}_5)_2]_2)$.

praseodymium atom, the six oxygen atoms can be classified into three types, O(6) and O(6a) form the first, bridging type, O(5), O(1) and O(2) form the second chelating type, and O(8a) is the third, internal type.

From Table 3, the bond distances Pr–O(5) and Pr–O(6) are 2.426(5) and 2.478(4) Å respectively, both much longer than the average bond distances Pr–O(1) and Pr–O(2) (2.349 Å). This result may be due to the different coordination modes of the two diethyl mal-

onate ligands and the repulsive interaction of atoms around the two praseodymium ions. The bond distance Pr–O(8a) is 2.712 Å, which is much longer than that of any other Pr–O bonds in the molecule. This suggests that this internal coordination bond is quite weak.

From Table 3, the distance between the center of the cyclopentadienyl ring and the praseodymium atom is 2.511(5) Å, which is almost as long as that observed in Cp₃Pr [11] (average bond distance 2.507 Å not includ-

Table 4
Selected bond angles (°)

O(2)–Pr–O(1)	71.9(2)	O(5)–Pr–C(3)	122.3(2)
O(2)–Pr–O(5)	100.4(2)	O(6)–Pr–O(6a)	62.8(2)
O(2)–Pr–O(6)	160.9(1)	O(6)–Pr–O(8a)	111.0(1)
O(2)–Pr–O(6a)	120.3(2)	O(6)–Pr–C(5)	111.8(3)
O(2)–Pr–O(8a)	74.3(2)	O(6)–Pr–C(1)	83.4(2)
O(2)–Pr–C(5)	82.1(3)	O(6)–Pr–C(2)	76.3(2)
O(2)–Pr–C(1)	110.5(2)	O(6)–Pr–C(4)	123.7(2)
O(2)–Pr–C(2)	122.2(2)	O(6)–Pr–C(3)	99.8(3)
O(2)–Pr–C(4)	74.8(2)	O(6a)–Pr–O(8a)	48.3(1)
O(2)–Pr–C(3)	99.2(3)	O(6a)–Pr–C(5)	126.4(3)
O(1)–Pr–O(5)	78.1(2)	O(6a)–Pr–C(1)	110.7(2)
O(1)–Pr–O(6)	89.8(1)	O(6a)–Pr–C(2)	83.1(2)
O(1)–Pr–O(6a)	88.9(2)	O(6a)–Pr–C(4)	105.5(3)
O(1)–Pr–O(8a)	87.7(2)	O(6a)–Pr–C(3)	79.6(3)
O(1)–Pr–C(5)	143.8(3)	O(8a)–Pr–C(5)	109.3(3)
O(1)–Pr–C(1)	153.0(3)	O(8a)–Pr–C(1)	119.2(2)
O(1)–Pr–C(2)	166.0(2)	O(8a)–Pr–C(2)	95.5(2)
O(1)–Pr–C(4)	146.5(2)	O(8a)–Pr–C(4)	80.5(3)
O(1)–Pr–C(3)	159.4(3)	O(8a)–Pr–C(3)	71.9(2)
O(5)–Pr–O(6)	69.8(2)	C(5)–Pr–C(1)	28.6(3)
O(5)–Pr–O(6a)	130.8(2)	C(5)–Pr–C(2)	47.2(3)
O(5)–Pr–O(8a)	165.7(2)	C(5)–Pr–C(4)	28.8(3)
O(5)–Pr–C(5)	82.6(3)	C(5)–Pr–C(3)	47.6(3)
O(5)–Pr–C(1)	75.1(3)	C(1)–Pr–C(2)	28.5(2)
O(5)–Pr–C(2)	98.5(3)	C(1)–Pr–C(4)	47.4(3)
O(5)–Pr–C(4)	111.3(3)	C(1)–Pr–C(3)	47.3(3)
C(2)–Pr–C(4)	47.4(2)	C(3)–C(4)–Pr	75.5(5)
C(2)–Pr–C(3)	28.6(3)	C(1)–C(5)–C(4)	108(1)
C(4)–Pr–C(3)	29.2(3)	C(1)–C(5)–Pr	75.8(5)
C(7)–O(1)–Pr	135.2(4)	C(4)–C(5)–Pr	75.9(5)
C(8)–O(2)–Pr	134.4(4)	C(8)–C(6)–C(7)	122.9(7)
C(14)–O(5)–Pr	136.8(5)	O(1)–C(7)–O(3)	119.1(6)
O(1)–C(7)–C(6)	126.5(6)	O(3)–C(7)–C(6)	114.4(6)
C(15)–O(6)–Pr	135.1(4)	O(2)–C(8)–O(4)	118.4(6)
C(15a)–O(6a)–Pr	107.3(4)	O(2)–C(8)–C(6)	128.4(7)
C(15)–O(8)–C(17)	122.9(6)	C(15)–C(13)–C(14)	122.3(7)
C(15a)–O(8a)–Pr	94.2(4)	C(2)–C(3)–C(4)	107(1)
C(17a)–O(8a)–Pr	136.3(3)	O(5)–C(14)–O(7)	120.1(8)
C(2)–C(1)–C(5)	108(1)	O(5)–C(14)–C(13)	127.4(7)
C(2)–C(1)–Pr	75.9(5)	O(7)–C(14)–C(13)	112.4(7)
C(5)–C(1)–Pr	75.6(5)	O(6)–C(15)–C(13)	128.2(7)
C(1)–C(2)–C(3)	108.8(9)	O(6)–C(15)–O(8)	108.9(6)
C(1)–C(2)–Pr	75.5(5)	C(13)–C(15)–O(8)	122.9(6)
C(3)–C(2)–Pr	75.9(5)	C(5)–C(4)–C(3)	107.3(9)
C(2)–C(3)–Pr	75.5(5)	C(5)–C(4)–Pr	75.3(5)
C(4)–C(3)–Pr	75.3(5)	O(4)–C(8)–C(6)	113.1(7)
O(2)–Pr–Cent ^a	96.47	O(1)–Pr–Cent	167.4
O(5)–Pr–Cent	100.1	O(6)–Pr–Cent	101.34
O(6a)–Pr–Cent	101.35	O(8a)–Pr–Cent	93.7
Pr–O(6)–Pr(a)	117.2(2)	Pr–O(6a)–Pr(a)	117.2(2)

^a Cent indicates the centroid C(1) to C(5).

ing the bond formed by the bridging cyclopentadienyl) and much shorter than that in $\text{Cp}(\text{COT})\text{Pr}(\text{THF})_2$ [12] ($\text{COT} = \text{cyclooctatetraene dianion } \text{C}_8\text{H}_8^{2-}$) (2.805(5) Å). This result may presumably be due to the existence of the strong ligand of COT (stronger than diethyl malonate) weakening the Pr–Cp bond.

From Table 4, the bond angle O(1)–Pr–O(2) is 71.9° , which is 1.3° smaller than that of O(1)–Ho–O(2) (73.2°) in $\text{Cp}_2\text{Ho}(\text{C}_{10}\text{H}_7\text{COCHCOCF}_3)(\text{THF})$ and 6.1° smaller than that of O(1)–Yb–O(2) (78.0°) in $\text{Cp}_2\text{Yb}(\text{CH}_3\text{COCHCOCF}_3)$. These results may primarily be due to different geometric configurations around the center lanthanide ions. In a ytterbium complex, the geometry can be described as tetrahedral around the center ion. In a holmium complex, the geometry around the center ion has been described as a trigonal bipyramid. In contrast, in the title complex the geometry can be described as a pentagonal bipyramid.

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