

JOM 23559

Synthesis and X-ray crystal structure of the cyclopentadienyl nitrito complex of ytterbium(III), $(C_5H_5)_2Yb(NO_2) \cdot THF$

Zhongzhi Wu, Zheng Xu, Xiaozeng You and Huaqing Wang

Coordination Chemistry Institute and the National Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210008, Jiangsu (China)

Xigen Zhou, Furen Sheng and Jiping Hu

Institute of Organic Chemistry, Anhui Normal University, Wuhu 241000, Anhui (China)

(Received October 23, 1992; in revised form January 22, 1993)

Abstract

$Cp_2Yb(NO_2) \cdot THF$ (1) ($Cp = C_5H_5$) was synthesized by the reaction of Cp_2YbCl and $NaNO_2$ (1:1 molar ratio) in THF at room temperature. It crystallizes in space group *Prma* with unit cell dimensions $a = 13.5530(3)$, $b = 11.8150(2)$, $c = 9.2790(2)$ Å, $Z = 4$, $V = 1485.8$ Å³ and $D_x = 1.883$ g cm⁻³. Least-squares refinement based on 1010 unique reflections with $I \geq 3\sigma(I)$ converged to a final R value of 0.023. The ytterbium atom was connected to two η^3 -bonded cyclopentadienyls and three oxygen atoms (one from the coordinated THF molecule and other two from the chelate nitrite ligands) in a distorted hexahedral arrangement. The average Yb–C(Cp) distance is 2.64(2) Å, Yb–O(THF) and Yb–O(NO₂) distances are 2.310(7) and 2.388(9) Å, respectively. The title complex loses the coordinated THF molecule readily on heating under vacuum to give dimeric complex $[Cp_2Yb(NO_2)]_2$ (2). Two new complexes have been characterized by elemental analysis and by IR spectroscopy and mass spectrometry.

1. Introduction

The nitrite ion is an unusual ligand because of the large number of different ways in which it can bind to a metal ion. Much has been published on the syntheses and structures of d-transition metal complexes involving nitrite ligands [1], and this has shown that monodentate nitro groups are quite common. To our knowledge, however, synthesis and structural studies on organolanthanide nitrite complexes have not so far been reported. In order to investigate the bonding mode of the NO_2^- ligand in organolanthanide complexes, we report here the synthesis and X-ray crystal structure of dicyclopentadienyl nitrito ytterbium complex $Cp_2Yb(NO_2) \cdot THF$.

2. Experimental section

All manipulations were performed under purified argon with rigorous exclusion of air and moisture by

using Schlenk and glovebox techniques. THF was refluxed and distilled over sodium benzophenone immediately before use. Dichloromethane and n-hexane were distilled over finely divided $LiAlH_4$. Anhydrous $YbCl_3$ [2] and Cp_2YbCl [3] were prepared according to the literature methods. Elemental analyses were carried out on a Perkin-Elmer 240C analyzer. Metal analyses for ytterbium were accomplished using the literature procedure [4]. Infrared spectra were obtained on a Perkin-Elmer 983G spectrometer with samples prepared as Nujol and Fluoroluble mulls between CsI plates. Mass spectra were recorded on a VG ZAB-HS mass spectrometer operating in EI mode. The crystal sample of the title complex was protected under argon and introduced by the direct inlet techniques with a source temperature 150°C and sample evaporation temperature in the range 25–300°C. The values of m/e are referred to the isotopes ¹²C, ¹H, ¹⁴N, ¹⁶O and ¹⁷⁴Yb.

2.1. Preparation of $Cp_2Yb(NO_2) \cdot THF$ (1)

A solution of $NaNO_2$ (0.103 g, 1.5 mmol) in 20 ml THF was added at room temperature to 30 ml of a

Correspondence to: Dr. Z. Wu.

THF solution of Cp_2YbCl (0.508 g, 1.5 mmol). The reaction mixture was stirred overnight, then centrifuged to remove the $NaCl$ precipitate. The resulting solution was concentrated under reduced pressure to ca. 10 ml and n-hexane (40 ml) was added. An orange solid was precipitated, which was recrystallized from THF/n-hexane to afford the product (0.43 g, 68.5%). X-ray quality crystals were grown from a concentrated solution of THF at about $-30^\circ C$. Anal. Found: C, 39.65; H, 4.23; N, 3.46; Yb, 41.13. $C_{14}H_{18}NO_3Yb$ calc.; C, 39.91; H, 4.31; N, 3.32; Yb, 41.07%. IR (cm^{-1}): 3078m, 1442s, 1307s, 1226m, 1045s, 1011s, 896s, 842m, 778s, 482m, 248w. MS (e.t. = $120^\circ C$): $m/e = 422$ [M, 1.4%], 350 [M - THF, 3.0%], 285 [M - THF - Cp, 14.0%], 220 [M - THF - 2Cp, 1.4%], 190 [YbO, 0.9%], 174 [Yb, 0.6%], 72 [THF, 64.8%], 66 [HCp, 100.0%], 65 [Cp, 21.5%], MS (e.t. = $220^\circ C$): $m/e = 700$ [M', 0.3%], 635 [M' - Cp, 7.4%], 570 [M' - 2Cp, 15.7%], 540 [M' - 2Cp - NO, 11.5%], 510 [M' - 2Cp - 2NO, 8.9%], 494 [M' - 2Cp - NO₂ - NO, 0.7%], 445 [M' - 3Cp - 2NO, 7.2%], 380 [M' - 4Cp - 2NO, 2.6%], 350 [M'', 2.1%], 304 [M'' - NO₂, 25.8%], 239 [M'' - Cp - NO₂, 17.5%], 220 [M'' - 2Cp, 8.4%], 190 [YbO, 2.2%], 174 [Yb, 3.0%], 66 [HCp, 100.0%], 65 [Cp, 77.2%]. {e.t. = evaporation temperature; M = $Cp_2Yb(NO_2) \cdot THF$; M' = $[Cp_2Yb(NO_2)]_2$; M'' = $Cp_2Yb(NO_2)$ }.

2.2. Preparation of $[Cp_2Yb(NO_2)]_2$ (2)

To a suspension of Cp_2YbCl (0.41 g, 1.2 mmol) in CH_2Cl_2 (40 ml) was added a sample of $NaNO_2$ (0.08 g, 1.2 mmol). After stirring for 48 h at room temperature, the reaction mixture was centrifuged to remove the $NaCl$ precipitate. Then, the resulting solution was concentrated by reducing pressure to ca. 10 ml. Upon addition of 30 ml n-hexane, an orange solid precipitated, which was recrystallized from CH_2Cl_2 /n-hexane and dried *in vacuo* to afford the product (0.28 g, 67.3%). Anal. Found: C, 33.85; H, 2.76; N, 4.12; Yb, 49.63. $C_{20}H_{20}N_2O_4Yb_2$ calc.: C, 34.39; H, 2.89; N, 4.01; Yb, 49.55%. IR (cm^{-1}): 3081m, 1445s, 1312s, 1215m, 1012s, 845m, 782s, 485s, 250w. MS (e.t. = $200^\circ C$): $m/e = 700$ [M', 0.5%], 635 [M' - Cp, 18.3%], 570 [M' - 2Cp, 36.4%], 540 [M' - 2Cp - NO, 10.2%], 510 [M' - 2Cp - 2NO, 10.6%], 494 [M' - 2Cp - NO₂ - NO, 3.8%], 445 [M' - 3Cp - 2NO, 13.5%], 380 [M' - 4Cp - 2NO, 2.8%], 350 [M'', 3.6%], 304 [M'' - NO₂, 28.3%], 285 [M'' - Cp, 12.6%], 239 [M'' - Cp - NO₂, 15.4%], 220 [M'' - 2Cp, 4.7%], 190 [YbO, 1.3%], 174 [Yb, 6.8%], 66 [HCp, 100.0%], 65 [Cp, 56.3%].

2.3. Transformation of 1 into 2

Crystals of 1 were pulverized and heated to ca. $120^\circ C$ under vacuum for 4 h, giving an orange powder

TABLE 1. Crystal and data collection parameters

Molecular weight	421.34
Crystal size (mm)	$0.30 \times 0.30 \times 0.40$
Space group	<i>Pnma</i>
Cell constants	
<i>a</i> (Å)	13.5530(3)
<i>b</i> (Å)	11.8150(2)
<i>c</i> (Å)	9.2790(2)
<i>V</i> (Å ³)	1485.8
<i>D_c</i> (g cm ⁻³)	1.883
<i>Z</i>	4
μ_c (cm ⁻¹)	62.78
Scan mode	$\omega - 2\theta$
Range of transmission factors	0.61–1.00
2θ range (deg)	1–50
No. of reflections measured	2022
No. of reflections observed $I \geq 3\sigma(I)$	1010
<i>F</i> (000)	812
GOF	1.69
$R = \sum(F_o - F_c) / \sum F_o $	0.023
$R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$	0.026
Residual electron density (eÅ ⁻³)	0.80
<i>p</i> in weight scheme	0.04

that elemental analysis, IR and MS showed to be identical with the product 2 described above.

2.4. X-ray crystallography of $Cp_2Yb(NO_2) \cdot THF$

A single crystal ($0.3 \times 0.3 \times 0.4$ mm) of 1 was sealed in an argon atmosphere in a thin-walled glass capillary. The unit cell parameters were obtained from least-squares fit for 25 centered reflections with $20^\circ \leq 2\theta \leq 30^\circ$. Data were collected on an Enraf-Nonius CAD4 four-circle diffractometer at room temperature

TABLE 2. Atomic coordinates ($\times 10^3$) and equivalent thermal parameters

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²) ^a
Yb	399.50(3)	250	684.57(5)	3.959(7)
O1	512.5(8)	250	486(1)	7.2(3)
O2	575.3(6)	250	677(1)	7.4(3)
O3	298.8(5)	250	483.7(7)	6.4(2)
N	575.0(7)	250	553.4(9)	5.8(2)
C11	328(2)	250	335(3)	7.9(6) ^{*b}
C12	234(1)	250	245(2)	8.1(3) [*]
C13	151(1)	250	355(2)	9.3(4) [*]
C14	194(1)	294(1)	487(2)	5.7(3) [*]
C21	302(1)	393(1)	843(1)	4.5(3) [*]
C22	410(1)	393(1)	899(1)	4.4(3) [*]
C23	466(1)	445(1)	780(2)	5.8(3) [*]
C24	399(1)	471(1)	669(2)	5.7(3) [*]
C25	301(1)	439(1)	708(2)	5.4(3) [*]

^a Anisotropically atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot (a^2 \cdot B_{1,1} + b^2 \cdot B_{2,2} + c^2 \cdot B_{3,3} + ab(\cos \gamma) \cdot B_{1,2} + ac(\cos \beta) \cdot B_{1,3} + bc(\cos \alpha) \cdot B_{2,3})$.

^b Starred atoms were refined isotropically.

using graphite monochromated Mo $K\alpha$ (0.71073 Å) radiation. A total of 2022 intensities was obtained within the range of $1^\circ \leq 2\theta \leq 50^\circ$, of which 1010 unique reflections with $I \geq 3\sigma$ were considered observable. There was no obvious change in check reflection intensities indicating that the crystal remained stable during data collection. The intensities were corrected for Lorentz-polarization factors. For the absorption correction a ψ scan was applied. A summary of data collection parameters is given in Table 1.

The structure was solved by the direct method. Successive Fourier syntheses gave the coordinates of all non-hydrogen atoms refined by the full-matrix least-squares method (Table 2). The hydrogen atom positions were obtained from a difference Fourier map, and their parameters were not refined. Further refinement led to final convergence at $R = 0.023$. All calculations were performed on a PDP 11/44 computer using SDP programs.

3. Results and discussion

3.1. X-ray crystal structure of 1

The molecular structure of $Cp_2Yb(NO_2) \cdot THF$ is shown in Fig. 1, which is a typical bent sandwich metallocene. The molecule crystallizes in a monomeric unit. The ytterbium ion is coordinated by two cyclopentadienyl ring centroids, two oxygen atoms of NO_2^- ligand and one oxygen atom of the coordinated THF molecule, forming a distorted tetragonal bipyramid with the Cp ring centroids in axial directions, and O1, O2, O3 and Yb atoms on the equatorial plane. Selected bond lengths and angles are listed in Tables 3 and 4. The Yb–C(Cp) distances range from 2.63(2) to 2.66(2)

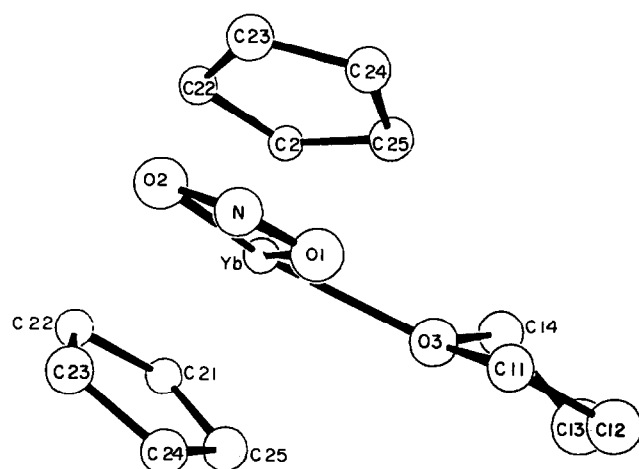


Fig. 1. The structure of $Cp_2Yb(NO_2) \cdot THF$ with the hydrogen atoms omitted for clarity.

TABLE 3. Important bond lengths (Å)

Yb–O1	2.394(9)	N–O1	1.052(13)
Yb–O2	2.383(8)	N–O2	1.151(14)
Yb–O3	2.310(7)	O3–C11	1.430(2)
Yb–N	2.672(9)	O3–C14	1.520(2)
Yb–C21	2.593(13)	C11–C12	1.53(3)
Yb–C22	2.615(13)	C12–C13	1.52(2)
Yb–C23	2.625(15)	C13–C14	1.45(2)
Yb–C24	2.614(15)	C21–C22	1.54(2)
Yb–C25	2.611(14)	C22–C23	1.47(2)
Yb–Cent ^a	2.305(13)	C23–C24	1.41(2)
Yb–C(Cp)av.	2.612(14)	C24–C25	1.42(2)
C25–C21	1.37(2)		

^a Cent represents the centroid of the cyclopentadienyl ring.

Å and average 2.64(2) Å, which is normal compared to these found in related compounds $Cp_2Yb(OC_9H_7) \cdot THF$ [5], 2.60(2) Å; $Cp_2YbCH_3 \cdot THF$ [6], 2.60(2) Å; $Cp_2Yb(acac)$ [7], 2.611 Å; $[Cp_2Yb(\mu-OCH_2CH_2CH_3)]_2$ [8], 2.60(2) Å; $[Cp_2Yb(\mu-OCH_2CH=CH_2)]_2$ [9], 2.60(2) Å. The Yb–O(THF) distance of 2.310(7) Å is similar to those found in some related complexes $Cp_2YbCH_3 \cdot THF$ [6], 2.31(1) Å and $Cp_2Yb(OC_9H_7) \cdot THF$ [5], 2.31(2) Å. The Yb–O(NO_2^-) distances [2.394(9) and 2.383(8) Å] are comparable with those found in related d-block transition metal bidentate chelating nitrite complexes [1], when taking the difference of metal ionic radii into account. It is to be noted that the Yb–O1 distance [2.394(9) Å] is similar to the Yb–O2 distance [2.383(8) Å]. This indicates that the NO_2^- ligand chelates symmetrically to the metal.

It is interesting to note that the N–O bond distances [1.151(14) and 1.052(13) Å] in the title complex are significantly shorter than that in $NaNO_2$ [1.24 Å] [10]. This deviation may be due to the chelating coordination of the nitrite ligand to the ytterbium atom, the π -antibonding orbital electronic density of NO_2^- ligand partially transferring to the central metal, thus leading to the shortening of the N–O bonds. This trend can be indicated by comparing the N–O bonds in NO_2^- [1.24 Å] [10], NO_2 [1.188 Å] [11] and $[NO_2]^+$ [1.154 Å] [11]. The N–O₂ distance [1.151(14) Å] is 0.099 Å larger than

TABLE 4. Selected bond angles (deg)

O1–Yb–O2	48.6(4)	C11–O3–C14	106.0(1)
O1–Yb–O3	76.0(3)	O3–C11–C12	107.0(2)
O2–Yb–O3	124.6(3)	C11–C12–C13	105.0(1)
Yb–O1–N	93.4(7)	O3–C14–C13	104.0(1)
Yb–O2–N	91.4(7)	C12–C13–C14	105.0(1)
O1–N–O2	127.0(1)	C21–C22–C23	103.0(1)
Cent–Yb–Cent	131.4(3)	C22–C23–C24	108.0(1)
Cent–Yb–O1	112.8(3)	C23–C24–C25	111.0(1)
Cent–Yb–O2	98.8(2)	C25–C21–C22	109.0(1)
Cent–Yb–O3	103.19(3)	C24–C25–C21	109.0(1)

the N–O1 distance [1.052(13) Å]. This distortion has been observed in some d-block element nitrite complexes [1,12,13] and arises from an unresolvable disorder of this ligand.

The Cent–Yb–Cent angle [131.4(3)°] is similar to that found in the analogous complex $Cp_2Yb(OC_9H_7) \cdot THF$ [131.2°] [5]. The angle of O1–N–O2 [127.0(1)°] is significantly larger than that of $NaNO_2$ [114.9(5)°] [10]. This result is in contrast to that reported for d-transition metal complexes [14,15] and can be ascribed to the larger ionic radii of f-block elements relative to the d-block elements. The two Cp rings are planar and form a dihedral angle of 50.4°. The Yb, O1, O2, O3, N, C11, C12 and C13 atoms lie on a crystallographic mirror plane at $y = 1/4$, and thus the C14 atom of the THF molecule occupies two positions related by a mirror symmetry with each half occupancy and the two Cp rings are located on either side of the plane at the same distance. In view of the stereochemistry, the above structure has a suitable geometrical arrangement.

3.2. Spectroscopic characterization of $Cp_2Yb(NO_2) \cdot THF$ (1) and $[Cp_2Yb(NO_2)]_2$ (2)

The two compounds have been characterized by elemental analysis, IR spectroscopy and mass spectrometry. The IR spectra of 1 and 2 contain bands which are interpretable primarily in terms of coordinated Cp group at about 3100, 1440, 1010, 780 and 250 cm^{-1} [16,17]. In addition, the IR spectra also exhibit the characteristic absorption peaks for coordinated THF at 1045 and 896 cm^{-1} in 1, which are absent from 2.

It is well known that the nitrite IR frequencies can be a useful guide to the nature of its coordination [1,18,19]. The behaviour of the two NO stretching frequencies ν_s and ν_{as} generally provides the best indication of the manner of nitrite coordination in a complex. M.A. Hitchman *et al.* [15] have pointed out that in a symmetrically chelated nitrite group (with two similar M–O distances), the difference between ν_s and ν_{as} is similar to that in the free ion NO_2^- (ca. 70 cm^{-1}), while for asymmetrically chelated groups, the splitting is observed to lie between these two extremes. This difference in the complex 1 is 83 cm^{-1} , which is close to that of the free ion NO_2^- . This suggests the nitrite group in 1 chelates approximately symmetrically to the metal. The crystal structure supports this conclusion.

The mass spectra of 1 and 2 were recorded at different evaporation temperatures. It is interesting to note that when the evaporation temperature of a crystal sample of complex 1 reaches 120°C, the mass spectra show only the molecular ion peak and certain fragments, such as $[THF]^+$ and $[Cp]^+$ ions. In the

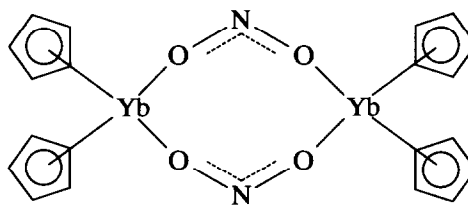


Fig. 2. The proposed structure for $[Cp_2Yb(NO_2)]_2$.

spectra of 2, however, only the $[Cp]^+$ ion peak is observed at about 120°C. When the evaporation temperature exceeds 200°C, the spectra of both 1 and 2 exhibit the molecular ions and fragments corresponding to $[Cp_2Yb(NO_2)]_2$ (2). This shows that the monomeric solvated complex $Cp_2Yb(NO_2) \cdot THF$ (1) easily loses the coordinated THF molecule by heating under vacuum, which has been verified by experiments (see Experimental section). The MS spectra for 2 show the dimeric molecular ion peak and a series of fragments of oxygen bridging units, such as $[Cp_2Yb_2O_2]^+$, $[CpYb_2O_2]^+$ and $[Yb_2O_2]^+$ ions. The IR spectra of 2 revealed that the NO_2^- ligand probably chelates symmetrically to the ytterbium atom, because the difference of ν_s (1312 cm^{-1}) and ν_{as} (1215 cm^{-1}) of NO stretchings (97 cm^{-1}) is close to that of the free ion NO_2^- [15]. So, based on the elemental analytical and spectral results, it was suggested that the nitrite groups in 2 bridge symmetrically to the ytterbium atoms bidentately. Thus, the structure shown in Fig. 2 may be proposed for 2.

Acknowledgment

This work was supported through grants from the National Natural Science Foundation.

References

- 1 M.A. Hitchman and G.L. Rowbottom, *Coord. Chem. Rev.*, **42** (1982) 55 and references cited therein.
- 2 M.D. Taylor and C.P. Carter, *J. Inorg. Nucl. Chem.*, **24** (1962) 387.
- 3 R.E. Maginn, S. Manastyrskj and M. Dubeck, *J. Am. Chem. Soc.*, **85** (1963) 672.
- 4 C. Ye and Y. Li, *J. Org. Chem.*, (1981) 210 (in Chinese).
- 5 X.G. Zhou, Z.Z. Wu and Z.S. Jin, *J. Organomet. Chem.*, **431** (1992) 289.
- 6 W.J. Evans, R. Dominguez and T.P. Hanusa, *Organometallics*, **5** (1986) 263.
- 7 L. Shi, H. Ma, Y. Yu and Z. Ye, *J. Organomet. Chem.*, **339** (1988) 227.
- 8 Z.Z. Wu, Z. Xu, X.Z. You, X.G. Zhou and Z.S. Jin, *Polyhedron*, **11** (1992) 2673.

- 9 Z.Z. Wu, Z. Xu, X.Z. You, X.G. Zhou and Z.S. Jin, *Inorg. Chim. Acta.*, submitted for publication.
- 10 M.I. Kay and B.C. Frazer, *Acta Crystallogr.*, 14 (1961) 56.
- 11 H.J.A. Bowen, J. Donohue, D.G. Jenkin, O. Kennard, P.J. Whetley and D.H. Whiffen, *Chem. Soc. (London), spec. publ.* (1958), No. 11, p. 377.
- 12 J.K. Simondson and R.D. Feltham, *Inorg. Chim. Acta*, 71 (1983) 185.
- 13 A. Gleizes, A. Meyer, M.A. Hitchman and O. Kahn, *Inorg. Chem.*, 21 (1982) 2257.
- 14 I. Grenthe and E. Nordin, *Inorg. Chem.*, 18 (1979) 1109.
- 15 M.A. Hitchman and R. Thomas, *J. Chem. Soc., Dalton Trans.*, (1983) 2273.
- 16 N.M. Ely and M. Tsutsui, *Inorg. Chem.*, 14 (1975) 2680.
- 17 C. Qian, C. Yc, H. Lu, J. Zhou, Y. Ge and M. Tsutsui, *J. Organomet. Chem.*, 247 (1983) 161.
- 18 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 2nd edn., John Wiley, New York, 1972, pp. 89 and 160.
- 19 A.J. Finney, M.A. Hitchman, C.L. Raston, G.L. Rowbottom and A.H. White, *Aust. J. Chem.*, 34 (1981) 2159.