

# Synthesis and molecular structure of $\text{Na}(\{1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}\text{Yb}^{\text{II}})_2(\mu\text{-I})$

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Received 12 March 1997

## Abstract

The reaction of  $\text{YbI}_2$  with 2 equiv. of  $\text{Cp}^*\text{Na}$  ( $\text{Cp}^* = 1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ ) in boiling toluene gives  $\text{Na}(\text{Cp}^*_2\text{Yb})_2(\mu\text{-I})$  in 71% yield. On the evidence of X-ray diffraction analysis of this Yb(II) complex ( $P2_1/n$ ,  $a = 13.5582(2)$ ,  $b = 17.4047(2)$ ,  $c = 26.9829(1)$  Å,  $\beta = 97.562(1)^\circ$ ,  $Z = 4$ ,  $d_{\text{calc}} = 1.404 \text{ g cm}^{-3}$ ,  $R_1 = 0.0521$  and  $wR_2 = 0.1107$ ), the crystal unit cell contains crystallographically independent anion complex  $[\text{Cp}^*_2\text{Yb}-\text{I}-\text{YbCp}^*_2]$  ( $\text{Yb}-\text{I}$  3.1115(6), 3.0855(6) Å) and  $\text{Na}^+$  cation. No additional neutral ligands were found at the metal atoms. © 1997 Elsevier Science S.A.

**Keywords:** Ytterbium; Silicon

## 1. Introduction

Unsolvated bis(cyclopentadienyl)lanthanides(II) are of importance as convenient precursors for the synthesis of well-designed ytterbium, samarium and europium complexes [1]. Several unsolvated bis(cyclopentadienyl)lanthanides have been recently prepared from the corresponding solvates  $\text{Cp}^*_2\text{Ln}(\text{L})_2$ , where  $(\text{L})_2 = (\text{THF})_2$ ,  $(\text{Et}_2\text{O})_2$ , DME etc. This procedure is rather difficult, gives  $\text{Cp}^*_2\text{Ln}$  in a low yield and moreover, has failed for some compounds [1]. Here we attempted to prepare in a single-step manner the unsolvated complex,  $[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Yb}$ , starting from  $\text{YbI}_2$  and  $\text{Na}[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]$  in toluene. We succeeded in the preparation of the coordination polymer,  $[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Yb} \cdot \text{NaI}$ , which was characterized by X-ray crystal structure analysis. This synthetic procedure looks like a general method for the preparation of unsolvated ate-complexes of bis(cyclopentadienyl)lanthanides(II) (see also the synthesis of  $\text{Na}(\text{Yb}^{\text{II}}[\text{N}(\text{SiMe}_3)_2])_2$  [2]).

## 2. Results and discussion

The reaction of  $\text{YbI}_2$  with 2 equiv. of  $\text{Cp}^*\text{Na}$  in boiling toluene for 4 h gives perfectly black reaction mixture. The solution was filtered off; black crystals of the  $\text{Na}(\text{Cp}^*_2\text{Yb})_2(\mu\text{-I})$  coordination polymer were isolated in 71% yield after the crystallization.



The structure of this Yb(II) complex was determined by X-ray diffraction analysis. The crystal unit cell contains crystallographically independent anion complex  $[\text{Cp}^*_2\text{Yb}-\text{I}-\text{YbCp}^*_2]$  and  $\text{Na}^+$  cation. No additional neutral ligands were found at the metal atoms. In the anion (Fig. 1), the I bridge between the Yb(II) atoms is a linear one (angle is  $176.11(3)^\circ$  and  $\text{Yb}-\text{I}$  bond lengths are 3.1115(6) and 3.0855(6) Å, Table 1). The similar linear I bridges have been earlier observed for the Ni (angle  $180^\circ$ ) [3], Co (angle  $180^\circ$ ) [4], Au (angle  $161^\circ$ ) [5], and Hg (angle  $180^\circ$ ) [6] complexes. The  $\text{Cp}^*_2\text{Yb}-\text{F}-\text{YbCp}^*_2$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) complex with the linear F bridge is also known [7].

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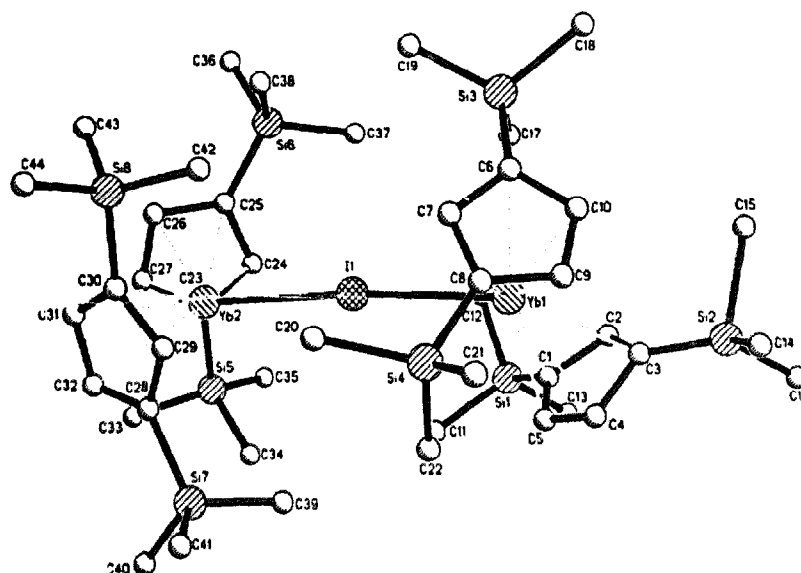


Fig. 1. Structure of  $[\text{Cp}^*_2\text{Yb-I-YbCp}^*_2]^-$  ( $\text{Cp}^* = 1,3\text{-(Me}_2\text{Si)}_2\text{C}_5\text{H}_3$ ) anion; for simplicity, all disordered  $\text{SiMe}_3$  groups are drawn as ordered ones.

Two  $\text{Cp}^*_2\text{Yb}$  fragment are rotated with respect to one another around the  $\text{Yb-I-Yb}$  fragment. Such a peculiarity was also found in the above-mentioned F-bridged Yb complex [7]. The dihedral angle between the  $\text{Yb(1)AB}$  and  $\text{YbCD}$  planes (A, B, C, D are centroids of the Cp rings at the corresponding Yb atoms) is equal to  $59.9^\circ$ . The lines  $\text{Yb(1)=A}$  and  $\text{Yb(1)=B}$  as well as  $\text{Yb(2)=C}$  and  $\text{Yb(2)=D}$  form the angles of  $132.5^\circ$  and  $134.1^\circ$  which in fact coincide with the angles between the normals to the corresponding Cp rings,  $132.0$  and  $133.1$ , respectively. These values lie within the range found for the other  $\text{Cp}^*_2\text{Ln}$  complexes:  $130.2^\circ$  for Pr [8],  $126.0^\circ$  and  $126.3^\circ$  for Nd [9,10],  $129.5^\circ$  for Sm [11],  $129.5\text{--}138.1^\circ$  for Yb [11–13], and  $128.2\text{--}139.0^\circ$  for Lu [14–16] complexes.

It is of interest that no additional neutral ligands at Yb atoms were found in this coordinatively unsaturated structure. It probably results from the efficient screening the metals with bulky  $\text{Cp}^*$  ligands, although weak agostic bonds with Me groups can also stabilize the structure. The distance from  $\text{Yb(1)}$  to the nearest Me ( $\text{C(17)}$ ) is of  $3.33 \text{ \AA}$ ; all distances from  $\text{Yb(2)}$  to the nearest Me groups are longer than  $4 \text{ \AA}$ . Moreover,  $\text{C(17)}$  methyl group is oriented towards the open space of the  $\text{Cp}^*_2\text{Yb(1)}$  fragment. It is likely that one H atom at this Me group is oriented towards the  $\text{Yb(2)}$  atom to form agostic bond. This suggestion is supported by the longer  $\text{Yb(1)-I}$  bond distance than the  $\text{Yb(2)-I}$  one.

$\text{Na}^+$  cation is packed between two almost parallel (dihedral angle  $8.1^\circ$ ) Cp rings of the two adjacent anions related by twofold screw axis. The  $\text{Na-C(Cp)}$  distances vary within  $2.66\text{--}2.74 \text{ \AA}$  (Table 1). Such a coordination of  $\text{Na}^+$  has been earlier observed by others [11,17] where  $\text{Na-C}$  distances range between  $2.73\text{--}2.83$  and  $2.60\text{--}2.64 \text{ \AA}$ , respectively. In the crystal, such  $\text{Cp} \cdots \text{Na} \cdots \text{Cp}$  interactions combine anions and cations in the infinite zig-zag-like chains running along the  $b$ -axis (Fig. 2).

Considerable broadening of lines in  $^1\text{H-NMR}$  spectra of  $\text{Na(Cp}^*_2\text{Yb)}_2(\mu\text{-I)}$  in  $\text{C}_6\text{D}_6$  may be regarded as the evidence in favor of fluxional behavior of this compound. This can be accounted for the fast ion-pair exchange involving  $[\text{Na(C}_6\text{D}_6)_n][\text{Cp}^*_2\text{YbI}]$  and related compounds and/or the exchange of unequivalent  $\text{Cp}^*$  ligands, i.e.



Table 1  
Selected bond lengths,  $\text{\AA}$

$\text{Yb(1)-I(1)}$	3.1115(6)	$\text{Yb(2)-I(1)}$	3.0855(6)
$\text{Yb(1)-C(1)}$	2.690(9)	$\text{Yb(2)-C(23)}$	2.655(9)
$\text{Yb(1)-C(2)}$	2.70(1)	$\text{Yb(2)-C(24)}$	2.663(8)
$\text{Yb(1)-C(3)}$	2.72(1)	$\text{Yb(2)-C(25)}$	2.704(7)
$\text{Yb(1)-C(4)}$	2.658(9)	$\text{Yb(2)-C(26)}$	2.708(7)
$\text{Yb(1)-C(5)}$	2.668(9)	$\text{Yb(2)-C(27)}$	2.669(8)
$\text{Yb(1)-C(6)}$	2.701(7)	$\text{Yb(2)-C(28)}$	2.780(7)
$\text{Yb(1)-C(7)}$	2.732(8)	$\text{Yb(2)-C(29)}$	2.742(7)
$\text{Yb(1)-C(8)}$	2.774(8)	$\text{Yb(2)-C(30)}$	2.702(8)
$\text{Yb(1)-C(9)}$	2.720(8)	$\text{Yb(2)-C(31)}$	2.692(8)
$\text{Yb(1)-C(10)}$	2.679(7)	$\text{Yb(2)-C(32)}$	2.742(7)
$\text{Na(1)-C(28)}$	2.718(8)	$\text{Na(1)-C(6)\#1}$	2.743(9)
$\text{Na(1)-C(29)}$	2.662(8)	$\text{Na(1)-C(7)\#1}$	2.699(8)
$\text{Na(1)-C(30)}$	2.692(8)	$\text{Na(1)-C(8)\#1}$	2.689(8)
$\text{Na(1)-C(31)}$	2.739(9)	$\text{Na(1)-C(9)\#1}$	2.658(8)
$\text{Na(1)-C(32)}$	2.741(9)	$\text{Na(1)-C(10)\#1}$	2.692(9)

Symmetry transformations used to generate equivalent atoms: #1  
 $= x + 1/2, y - 1/2, z + 1/2$ .

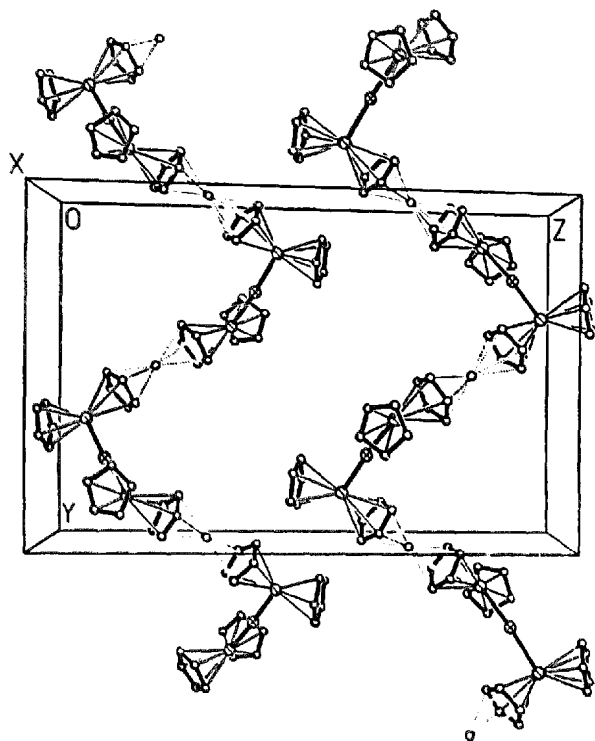


Fig. 2. Packing of ions in the unit cell; all  $\text{SiMe}_3$  groups are rejected for simplicity.

The observed broadening of the resonance lines cannot result from the presence of any paramagnetic species in the solution, since the resonances of the solvent and all impurities are rather narrow.

### 3. Experimental details

All manipulations have been done either on the high-vacuum line in all-glass apparatus equipped with PTFE stopcocks or in the atmosphere of thoroughly purified argon using standard Schlenk technique. Toluene for synthesis and benzene- $d_6$  for NMR investigation were distilled and stored over  $\text{CaH}_2 \cdot \text{YbI}_2$  [18] and  $\text{Cp}^*\text{Na}$  [19] were prepared by the published methods.  $^1\text{H}$  spectra were recorded with Bruker AM 360. Electron probe X-ray analysis were done with a scanning electron microscope SEM-505 (Phillips) equipped with a unit for X-ray energy dispersive analysis (Edax).

#### 3.1. $\text{Na}[\{1,3-(\text{Me}_3\text{Si})_2\text{C}_2\text{H}_4\}_2\text{Yb}\}_2(\mu-1)$

A mixture of 2.05 g (4.8 mmol) of  $\text{YbI}_2$  with 2.33 g (10.0 mmol) of  $\text{Cp}^*\text{Na}$  in 50 ml of toluene was stirred at  $110^\circ\text{C}$  for 4 h. Black solution was filtered off and evaporated to ca. 15 ml. Black crystals precipitated for 1 week at room temperature were separated, washed with minimal amount of cold toluene and dried in vacuo. Yield 1.56 g (71%). Anal. Calcd. for  $\text{C}_{22}\text{H}_{42}\text{IN-}$

$\text{aSi}_4\text{Yb}_2$ : C 28.88; H 4.60. Found: C 29.01; H 4.70. Electron probe microanalysis:  $\text{Yb/Si/I/Na} = 2:4:1:1$ .  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta$  0.49 (s,  $\Delta\nu_{1/2} = 15.9$  Hz, 36H,  $\text{Me}_3\text{Si}$ ), 6.74 (s,  $\Delta\nu_{1/2} = 18.7$  Hz, 12H,  $\text{C}_5\text{H}_5$ ).

#### 3.2. X-ray diffraction study

Crystallographic parameters and details of the X-ray experiment are given in Table 2. The most of  $\text{SiMe}_3$  groups manifest high thermal rotational motion or disorder. Only one  $\text{SiMe}_3$  group at Si(8) is strictly ordered. Two different sets of methyl groups were distinctly

Table 2

Crystal data, data collection, structure solution and refinement parameters

Empirical formula	$\text{C}_{44}\text{H}_{84}\text{INaSi}_8\text{Yb}_2$
Formula weight	1333.80
Colour, habit	Black-brown, plate
Crystal size, mm	$0.08 \times 0.20 \times 0.44$
Crystal system	Monocline
Space group	$\text{P}2_1/\text{n}$
Unit cell dimensions:	
$a$ , Å	13.5582(2)
$b$ , Å	17.4047(2)
$c$ , Å	26.9829(1)
$\alpha$ , deg	90
$\beta$ , deg	97.562(1)
$\gamma$ , deg	90
Volume, Å <sup>3</sup>	6312.0(1)
$Z$	4
Density (calculated), g/cm <sup>3</sup>	1.404
Absorption coefficient, mm <sup>-1</sup>	3.618
$F(000)$	2656
Diffractometer	Siemens SMART
Temperature, K	150.0(2)
Radiation, ( $\lambda$ , Å)	Graphite monochromatized Mo K $\alpha$ (0.71073)
Scan mode	$\omega$
Scan step (in omega), deg	0.3
Time per step, s	30
Theta range, deg	1.40 to 27.00 deg
Index ranges	$-19 \leq h \leq 19$ , $-24 \leq k \leq 24$ , $-38 \leq l \leq 34$
Reflections collected	44177
Independent reflections	13774 [ $R(\text{int}) = 0.0690$ ]
Data reduction	Siemens SAINT (Siemens Analytical X-ray Instruments, 1995)
Absorption corrections	Empirical (SHELXTL-Plus)
Min. and max. transmission	0.20294 and 0.32322
Solution method	Direct methods (SHELX-86)
Refinement method	Full-matrix least-squares on $F^2$ (SHELX-93)
Hydrogen treatment	None
Data/restraints/parameters	12158/0/607
Goodness-of-fit on $F^2$	1.053
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0521$ , $wR_2 = 0.1107$
$R$ indices (all data)	$R_1 = 0.0889$ , $wR_2 = 0.1452$
Extinction coefficient	0.00011(3)
Largest diff. peak and hole, eÅ <sup>-3</sup>	1.371 and $-1.588$

found for one of them (at Si(4) atom) and a number of weak peaks in the difference Fourier synthesis which can be related to a number of Me group sets were found in the vicinity of other SiMe<sub>3</sub> groups. Two silicon atoms, Si(2) and Si(5), were found to occupy two positions with their own sets of Me groups each. These silicon atoms have different site occupation factors (0.64 and 0.36 for Si(2) and Si(2A) and 0.52 and 0.47 for Si(5) and Si(SA)). The distances between Si(2) and Si(2A) as well as between Si(5) and Si(SA) are close to 1 Å and the bond angles at the corresponding parent C(Cp) atom were found to be significantly irregular. Attempts to restrain each of these pairs of the silicon atoms in single geometrically regular positions even with a soft tolerances resulted in (1) increase in *R* index (*R*<sub>1</sub> = 0.0666, *wR*<sub>2</sub> = 0.2263), goodness-of-fit (1.525) and mean square atomic displacements (*U*) for Si(2) and Si(5); (2) instability of least-squares refinement for other carbon atoms; and (3) appearance of high residual peaks of electron density in the positions corresponding to previous positions of these Si atoms (Si(2) and Si(2A) as well as Si(5) and Si(SA)). Similar but less significant distortion of the Si–C–C angles at C(Cp) was also observed in dimeric Sm and Yb complexes where each lanthanide atom bears two bis SiMe<sub>3</sub>-substituted Cp ligands [11]. Apparently, we have here an example of structural non-rigidity which was earlier observed for Hg(II) and Au(I) compounds [20–22].

Least-squares refinement was carried out in the anisotropic approximation for all atoms except Me groups at disordered Si atoms. Because of high thermal motion of the most of Me groups, hydrogen atoms were not accounted in the final refinement. All peaks of residual electron density are located in the vicinity of disordered Me group and heavy atoms.

The structure was solved and refined using SHELXS86 [23] and SHELXL93 [24] software. Software SHELXTL-Plus was used for graphics and preparation of material for publication.

### Acknowledgements

This work was generously supported by the Russian Foundation for Basic Research (Grant No. 95-03-09658).

### References

- [1] M.N. Bochkarev, L.N. Zakharov, G.S. Kalinina, *Organoderivatives of Rare Earth Elements*, Kluwer, Dordrecht, 1995.
- [2] T.D. Tilley, R.A. Andersen, A. Zalkin, *Inorg. Chem.* 23 (1984) 2271.
- [3] L. Sacconi, P. Dapporto, P. Stoppioni, *Inorg. Chem.* 16 (1977) 224.
- [4] D. Baumann, H. Endres, H.J. Keller, B. Nuber, J. Weiss, *Acta Crystallog. B* 31 (1975) 40.
- [5] C. Jaw Huey-Rong, M.M. Savas, R.D. Rogers, W.R. Mason, *Inorg. Chem.* 28 (1989) 1028.
- [6] R.E. Cramer, M.J.J. Carrie, *Inorg. Chem.* 29 (1990) 3902.
- [7] C.J. Burns, R.A. Andersen, *J. Chem. Soc. Chem. Commun.* (1989) 136.
- [8] M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, *J. Chem. Soc. Chem. Commun.* (1981) 1190.
- [9] M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, *J. Chem. Soc. Chem. Commun.* (1981) 1191.
- [10] M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, H.-M. Zhang, *J. Chem. Soc. Chem. Commun.* (1983) 69.
- [11] P.B. Hitchcock, M.F. Lappert, S. Prashar, *J. Organomet. Chem.* 413 (1991) 79.
- [12] M.F. Lappert, P.I.W. Yarrow, J.L. Atwood, R. Shakir, J. Holton, *J. Chem. Soc. Chem. Commun.* (1980) 987.
- [13] P.B. Hitchcock, J.A.K. Howard, M.F. Lappert, S. Prashar, *J. Organomet. Chem.* 437 (1992) 177.
- [14] I.P. Beletskaya, A.Z. Voskoboynikov, E.B. Chuklanova, N.I. Kirillova, A.K. Shestakova, I.N. Parshina, A.I. Gusev, G.K.-I. Magomedov, *J. Am. Chem. Soc.* 115 (1993) 3156.
- [15] I.P. Beletskaya, A.Z. Voskoboynikov, N.I. Kirillova, A.I. Gusev, A.K. Shestakova, I.N. Parshina, *Izv. Akad. Nauk SSSR Ser. Khim.* (1993) 574.
- [16] B. Zhang, Zh. Jin, Yu. Wang, G. Wei, W. Chen, *Chem. Res. Chin. Univ.* 8 (1992) 15.
- [17] J. Wessel, E. Lork, R. Mews, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2376.
- [18] T.D. Tilley, J.M. Boncella, D.J. Berg, C. Burns, R.A. Andersen, G.A.I. Wiess, M.A. Edelman, M.F. Lappert, *Inorg. Synth.* 27 (1990) 146.
- [19] A.Z. Voskoboynikov, Thesis, GNIChTEOS, Moscow, 1989.
- [20] C.L. Raston, B.M. Skelton, A.H. White, *Aust. J. Chem.* 31 (1978) 537.
- [21] L.G. Kuz'mina, N.V. Dvortsova, M.A. Porai-Koshits, E.I. Smyslova, K.I. Grandberg, E.G. Perevalova, *Metalloorg. Khim.* 2 (1989) 1344.
- [22] Yu.T. Struchkov, Yu.L. Slovokhotov, D.N. Kravtsov, T.V. Baukova, E.G. Perevalova, K.I. Grandberg, *J. Organomet. Chem.* 338 (1988) 269.
- [23] G.M. Sheldrick, *Acta Crystallog. A* 46 (1990) 467.
- [24] G.M. Sheldrick, SHELXL93, Program for the refinement of Crystal Structures, University of Göttingen, Germany, 1993.