Synthesis, properties, and the crystal structure of the complex $Cp_2Yb(DAD)$

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The diazadiene complex of trivalent ytterbium, $Cp_2Yb(DAD)$ (1) (DAD = $Bu^t{-}N{=}CH{-}CH{=}N{-}Bu^t$) was prepared according to three different procedures, namely, by oxidation of $Cp_2Yb(THF)_2$ with diazadiene in THF, by the reaction of Cp_2YbCl with $DAD^{2-}Na^+{}_2$ taken in a ratio of 2 : 1, and by the reaction of $Cp_2YbCl(THF)$ with $DAD^{\cdot-}K^+$ taken in a ratio of 1 : 1. Complex **1** was characterized by microanalysis, IR spectroscopy, magnetochemistry, and X-ray diffraction analysis.

Key words: ytterbium, diazabutadiene; X-ray diffraction analysis.

Due to the presence of lone electron pairs of the nitrogen atoms and π-electrons of the C=N bonds, the molecule $Bu^t{-}N{=}CH{-}CH{=}N{-}Bu^t$ (DAD) can act simultaneously as an n- and π-donor supplying from two to eight electrons for complex formation. On the other hand, the DAD molecule can oxidize positively charged metal ions, for example, lanthanide ions, being reduced to the radical anion or dianion. The known diazadiene derivatives of organolanthanides can be classed into two types depending on the degree of reduction of the DAD ligand. In the first class of these derivatives, the DAD molecule exists as a radical anion, while in the second group, it occurs as the DAD^{2-} dianion. The homoligand Yb^{III} complex with three equivalent radical anions of diazadiene, $Yb(DAD)_3$,[1] (**2**), and the Y and Sm heteroligand complexes, *viz*., $(C_5Me_5)Y[(C_6H_4{-}4{-}Me)N{=}C(Ph)C(Ph){=}N(C_6H_4{-}4{-}Me)]$ [2] and $(C_5Me_5)_2Sm(DAD)$,[3] belong to the first group. The binuclear Ln^{III} complexes with the bridging DAD^{2-} dianions, *viz*., $(DAD)Li(DME)$, $Cp_2Yb(DAD)K(THF)_2$,[4] $\{Ln(DAD)_2Cl\}Li_2(THF)(OEt_2)$ (Ln = Y or Lu), and $\{Ln(DAD)_2Li_2(THF)_2X_2\}Li(THF)_2$ (Ln = La or Sm; X = Cl or I),[5] can be placed into the second group. Recently, the samarium complex with the $Sm^{III}(DAD^{\cdot-})(DAD^{2-})$(bpy) (bpy — 2,2-dipyridyl) formal charge distribution was prepared by the reaction of $Sm(bpy)_4$ with di-*tert*-butyldiazadiene.[6] Compounds of this class attract interest because it is known that compound **2** exhibits unusual magnetic properties at low temperature[1] and diazadiene derivatives of organolanthanides can manifest catalytic properties in polymerization of the simplest alkenes. The aim of this work is to synthesize and study the properties of a mixed-ligand diazadiene ytterbium complex.

Results and Discussion

The reaction of $Cp_2Yb(THF)_2$ with an equimolar amount of DAD proceeded at room temperature with oxidation of ytterbium to the trivalent state to form the complex $Cp_2Yb(DAD)$.

$$Cp_2Yb(THF)_2 + DAD \xrightarrow{THF} \underset{\mathbf{1}}{Cp_2Yb(DAD)}$$

In a mixture with $Cp_2Yb(THF)_2$, complex **1** was formed according to the following reaction:

$$2\,Cp_2YbCl(THF) + DAD^{2-}Na^+{}_2 \xrightarrow{THF} Cp_2Yb(DAD) + Cp_2Yb(THF)_2 + 2\,NaCl.$$

Compound **1** can also be prepared by the reaction of equimolar amounts of $Cp_2YbCl(THF)$ and $DAD^{\cdot-}K^+$.

$$Cp_2YbCl(THF) + DAD^{\cdot-}K^+ \xrightarrow{THF} Cp_2Yb(DAD) + KCl$$

Recrystallization of compound **1** from toluene afforded dark-brown crystals. Complex **1** is soluble in THF and ether and insoluble in hexane. At >190 °C, complex **1** decomposes. The magnetic moment of **1** at room temperature is 4.8 μ_B. The increased value of μ_{eff} compared to the average value observed for Yb^{III} derivatives (4.3—4.5 μ_B)[7] can be explained taking into account the radical-anionic character of the DAD fragment and its contribution to the total magnetic moment of the molecule. The calculated magnetic moment for complex **1** (4.8 μ_B) agrees with the experimental value.

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However, the ESR spectra of a solid sample of **1** and of its solution in THF or toluene at room temperature have no signals of the radical anion $DAD^{\cdot -}$. This is attributable to a substantial broadening of the signal of the radical anion $DAD^{\cdot -}$ in the field of the paramagnetic ytterbium atom. The IR spectrum of **1** has absorption bands of the C=N and C—N bonds at 1635 and 1210 cm^{-1}, respectively, and bands of the Cp rings at 1020 and 770 cm^{-1}.

An attempt to reduce DAD to the dianion by a twofold excess of $Cp_2Yb(THF)_2$ in THF resulted in a mixture of complex **1** and unconsumed $Cp_2Yb(THF)_2$.

X-ray diffraction analysis of crystals of **1** (Fig. 1, Tables 1 and 2) demonstrated that the Yb atom is coordinated by two Cp rings and two nitrogen atoms, N(1) and N(2). The fragment YbN(2)C(6)C(1)N(1)-C(2)C(7) is nearly planar (the mean deviation of the atoms from the plane is 0.27 Å). The coordination environment about the ytterbium atom is a distorted tetrahedron. The coordination number of the metal atom is 8. The angle between the plane containing the centers of the Cp rings and the Yb atom and the plane of the YbN(2)C(6)C(1)N(1)C(2)C(7) fragment is 88.5°. The Cp—Yb—Cp angle is 128.1°. The N(1)—Yb—N(2) angle is 74.7°. The distances between the ytterbium atom and the centers of the Cp rings are 2.324 and 2.333 Å. The bond lengths in the diazadiene lanthanide complexes containing the radical-anionic and dianionic DAD ligands are given in Table 3 for comparison. The Yb—N(1) and Yb—N(2) distances are somewhat longer than the Yb—N distances in the complexes with the DAD dianion and are slightly shorter than the corresponding distances in complex **2**. The C(1)—N(1) and C(6)—N(2) bond lengths are smaller than the analogous C—N bond lengths in the DAD dianion and are close to the corresponding values observed in the radical-anionic DAD ligands in the heteroligand complexes of lanthanides. The C(1)—C(6) distance in the DAD ligand is noticeably longer than the C=C double bonds in the dianionic diazadiene fragments and differs only slightly from the C—C bond lengths in the diazadiene radical anions bonded to ytterbium atoms.

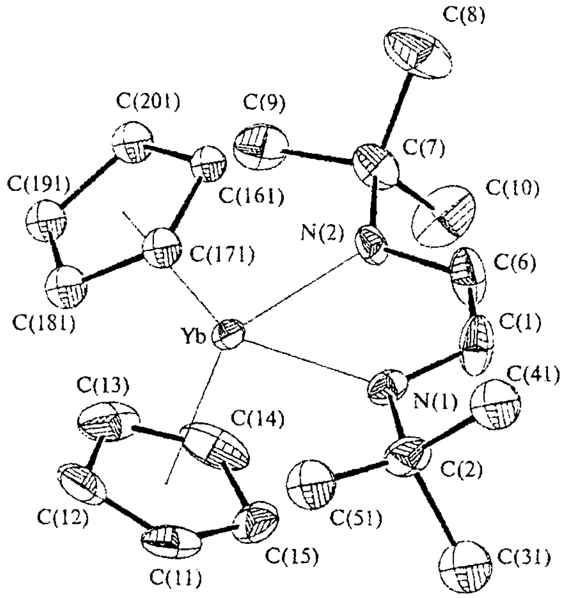

Fig. 1. Molecular structure of the complex $Cp_2Yb(DAD)$.

Table 1. Bond lengths (*d*) in complex **1**

Bond	*d*/Å	Bond	*d*/Å
Yb—N(1)	2.306(9)	N(2)—C(7)	1.51(2)
Yb—N(2)	2.309(9)	C(1)—C(6)	1.40(2)
Yb—Cp(1)*	2.324(7)	C(2)—C(51)	1.39(3)
Yb—Cp(21)*	2.334(4)	C(7)—C(10)	1.50(2)
N(1)—C(1)	1.31(2)	C(11)—C(12)	1.32(3)
N(1)—C(2)	1.50(2)	C(161)—C(171)	1.33(4)
N(2)—C(6)	1.30(2)		

* Cp(1) = Cp(C(11)—C(15)) and Cp(21) = Cp(C(161)—(201)).

Therefore, the results of magnetochemical measurements and a comparative analysis of the bond lengths in the diazadiene fragment of complex **1** suggest that the DAD ligand in this complex exists as a radical anion.

Experimental

Complex **1** was synthesized under conditions precluding exposure to atmospheric oxygen and moisture using the standard Schlenk technique. Hexane, toluene, THF, and ether were dried over sodium benzophenone ketyl and distilled into a reaction tube immediately before use. The IR spectra were recorded on a Specord M-80 instrument (as Nujol mulls). The ESR spectra were measured on a Bruker ER 200D-1SRC instrument. The content of ytterbium in the reaction products was determined chelatometrically. The magnetic measurements were carried out according to a known procedure.[8]

Table 2. Bond angles (ω) in complex **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
N(1)—Yb—N(2)	74.7(3)	C(2)—N(1)—Yb	132.8(8)	N(2)—C(6)—C(1)	122.3(1)
Cp(1)—Yb—N(1)	109.5(2)	C(6)—N(2)—C(7)	116.5(1)	N(2)—C(6)—Yb	46.0(6)
Cp(1)—Yb—N(2)	108.7(2)	C(6)—N(2)—Yb	110.2(9)	C(1)—C(6)—Yb	76.5(7)
Cp(21)—Yb—N(1)	109.6(3)	C(7)—N(2)—Yb	133.3(7)	C(10)—C(7)—N(2)	110.7(3)
Cp(21)—Yb—N(2)	113.5(3)	N(1)—C(1)—C(6)	122.8(1)	C(9)—C(7)—N(2)	109.8(1)
Cp(1)—Yb—Cp(21)	128.11(2)	N(1)—C(1)—Yb	46.0(5)	N(2)—C(7)—C(8)	108.1(1)
C(1)—N(1)—C(2)	117.5(1)	C(51)—C(2)—N(1)	114.0(2)	C(12)—C(11)—C(15)	111.0(2)
C(1)—N(1)—Yb	109.8(8)	C(41)—C(2)—C(31)	102.0(2)	C(171)—C(161)—C(201)	105.0(3)

Table 3. Bond lengths (*d*) in the diazadiene complexes of Yb and Sm

Bond	*d*/Å					
	$Cp_2Yb(DAD)$	$Yb(DAD)_3$ [1]	$Cp^*{}_2Sm(DAD)$ [3]	$Cp_2Yb(DAD)Li(DME)$ [4]	$Sm(DAD)_2(bpy)$ [6]	
					$DAD^{\cdot -}$	DAD^{2-}
Ln—N(1)	2.306(9)	2.40—2.43	2.480(5)	2.241(7)	2.452(8)	2.237(7)
Ln—N(2)	2.309(9)	2.40—2.43	2.489(5)	2.243(8)	2.541(8)	2.299(7)
C(1)—N(1)	1.31(2)	1.51—1.61	1.326(9)	1.39(1)	1.328(2)	1.402(2)
C(6)—N(2	1.30(2)	1.51—1.61	1.320(8)	1.40(1)	1.336(2)	1.372(2)
C(1)—C(6)	1.40(2)	1.39(3)	1.387(1)	1.36(2)	1.399(3)	1.375(2)

Synthesis of $Cp_2Yb(DAD)$. Method *A*. A solution of DAD (0.11 g, 0.68 mmol) in THF (5 mL) was added to $Cp_2Yb(THF)_2$ (0.303 g, 0.68 mmol). The color of the reaction mixture changed from red-violet to yellow-green. The solvent was removed under reduced pressure. The brown-green precipitate was dried for 30 min and then recrystallized from toluene. Compound **1** was isolated as brown crystals in a yield of 0.26 g (82%). Found (%): C, 50.97; H, 6.36; Yb, 36.71. $C_{20}H_{30}N_2Yb$. Calculated (%): C, 50.92; H, 6.29; Yb, 36.73. IR (Nujol mulls), ν/cm^{-1}: 1620 (C=N); 1210 (C—N); 1020, 770 (C—H vibrations of Cp rings).

Method *B*. A red solution of $DAD^{\cdot -}Na^+$, in THF, which was prepared from DAD (0.225 g, 1.34 mmol) and Na (0.068 g, 2.68 mmol), was added to an orange solution of $Cp_2YbCl(THF)$ (1.10 g, 2.68 mmol) in THF. The reaction mixture turned dark-violet. The solution was stirred for 16 h. Then NaCl that precipitated was separated, THF was removed, and the dry residue was extracted with toluene. Cooling of the concentrated toluene extract afforded $Cp_2Yb(DAD)$ in a yield of 0.44 g (70%). Recrystallization of the toluene-insoluble residue from a THF—hexane mixture gave $Cp_2Yb(THF)_2$ as dark-violet crystals in a yield of 0.46 g (78%).

Method *C*. A red solution of $DAD^{\cdot -}K^+$ in THF, which was prepared from K (0.12 g, 3.12 mmol) and DAD (0.52 g, 3.12 mmol), was added to an orange solution of $Cp_2YbCl(THF)$ (1.28 g, 3.12 mmol) in THF. The color of the solution changed to brown-green and a white precipitate of KCl was formed. The solution was separated from the precipitate and the solvent was removed *in vacuo*. The brown-green precipitate was washed with hexane and recrystallized from toluene. The yield of **1** was 1.02 g (70%).

X-ray diffraction study of crystals of 1 was performed on a four-circle Enraf-Nonius CAD4 diffractometer. The unit cell parameters and intensities of 2357 independent reflections were measured at 193(2) K, λ(Mo-Kα) = 0.71069 Å, and the scanning range was $4° \le 2\theta \le 53°$. The crystals are orthorhombic, $a = 8.5203(14)$ Å, $b = 15.008(4)$ Å, $c = 15.640(5)$ Å, $V = 2000.0(8)$ Å^3, $d_{calc} = 1.566$ g cm^{-3}, $Z = 4$; space group $P2_12_12_1$. The structure was solved by direct methods in combination with difference electron density syntheses (SHELXS 86 [9] and SHELXS 93 [10] program packages) and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms were placed in calculated positions (C—H 0.96 Å, $U_{iso} = 0.08$ Å^2). The final refinement with the use of 2198 independent reflections with $I > 2\sigma(I)$ converged to $R = 0.0571$, $R_w = 0.1328$, GOF = 1.126.

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