Synthesis and molecular structure of the complex YbI(bipy)(DME)$_2$

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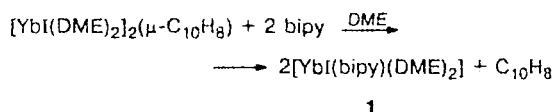*Fax: +7 (095) 954 1279. E-mail: snef@ionchran.msk.ru*

The reaction of the naphthalene complex of ytterbium, [Yb(DME)$_2$]$_2$(μ-C$_{10}$H$_8$), with 2,2'-bipyridine in 1,2-dimethoxyethane afforded the Yb^{II} complex containing the 2,2'-bipyridine radical anion. The resulting complex YbI(bipy)(DME)$_2$ was characterized by IR and ESR spectroscopy, X-ray diffraction analysis, and magnetochemistry.

Key words: ytterbium, complexes, bipyridine, structure.

Previously, the mixed bipyridine-iodine complexes of lanthanides, LaI$_2$(bipy)(DME)$_2$, LaI$_2$(bipy)$_2$(L)$_n$[1] (L = DME or THF), and (C$_5$Me$_5$)$_2$Sm(bipy)[2], were synthesized. These complexes each contain one bipyridine radical-anionic ligand. The first two complexes show well-resolved ESR signals of the 2,2'-bipyridine radical anion. The data on analogous compounds with divalent diamagnetic lanthanide atoms, whose bipy radical anions are well detected by magnetic methods, are unavailable in the literature. In this work, we synthesized such complex using the ytterbium(II) complex [YbI(DME)$_2$]$_2$(μ-C$_{10}$H$_8$)[3] as the initial compound.

Results and Discussion

Reduction of neutral 2,2'-bipyridine with the complex [YbI(DME)$_2$]$_2$(μ-C$_{10}$H$_8$) in 1,2-dimethoxyethane (DME) afforded the complex YbI(bipy)(DME)$_2$ (1) in high yield as black-red crystals, which are very air-unstable and readily soluble in THF, DME, and diethyl ether.

$$\text{[YbI(DME)}_2\text{]}_2(\mu\text{-C}_{10}\text{H}_8) + 2 \text{ bipy} \xrightarrow{\text{DME}}$$

$$\longrightarrow 2\text{[YbI(bipy)(DME)}_2\text{]} + \text{C}_{10}\text{H}_8$$

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A solution of complex **1** in DME gives a well-resolved ESR signal (Fig. 1) at 233 K. The observed value of the g factor (2.001) indicates that the unpaired electron is localized on the orbital of the bipyridine ligand. However, it is difficult to perform the complete interpretation of the spectrum because of a large number of individual components that appear due to the splitting of the unpaired electron on the ^{1}H, ^{14}N, ^{171}Yb, and ^{173}Yb nuclei.

The IR spectrum of compound **1** has an intense band at 950 cm^{-1}, which is typical of the bipyridine radical anion,[1,2] and absorption bands at 1050 and 860 cm^{-1}, which indicate that the complex contains coordinated DME molecules. The absorption bands at 755 and 1600 cm^{-1}, which are generally observed in the case of neutral bipyridine, and the band at 1520 cm^{-1}, which is typical of the bipyridine dianion, are absent in the IR spectrum of complex **1**.

The value of the magnetic moment μ_{eff} of complex **1** at 293 K (1.55 μB) is close to the value observed for the complex LaI$_2$(bipy)$_2$(DME) (1.6 μB),[1] which is apparently indicative of the presence of one unpaired electron in the molecule. The slight decrease in the value of μ_{eff} compared to the purely spin value (1.73 μB) may be associated with weak antiferromagnetic spin-spin exchange. Therefore, taking into account the presence of the Yb^{II} atom in complex **1**, the charge distribution can be formally described as follows: Yb^{+2}I$^-$(bipy$^-$)(DME)$_2$.

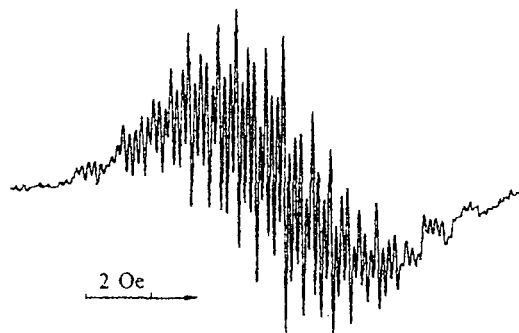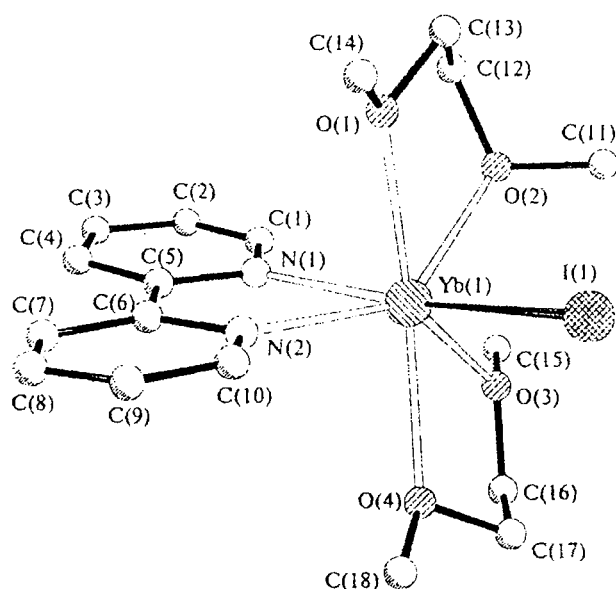According to the data of X-ray diffraction analysis, the ytterbium atom in complex **1** is bonded to the iodine

Fig. 1. ESR spectrum of the complex YbI(bipy)(DME)$_2$ (**1**) in a solution in DME at 233 K.

Table 1. Bond lengths d in complex 1

Bond	d/Å	Bond	d/Å	Bond	d/Å
Yb(1)—I(1)	3.120(1)	Yb(1)—O(1)	2.559(5)	Yb(1)—O(2)	2.525(7)
Yb(1)—O(3)	2.552(6)	Yb(1)—O(4)	2.538(6)	Yb(1)—N(1)	2.454(10)
Yb(1)—N(2)	2.439(9)	O(1)—C(13)	1.423(14)	O(3)—C(16)	1.428(11)
O(4)—C(17)	1.415(14)	N(1)—C(1)	1.352(15)	N(1)—C(5)	1.395(15)
N(2)—C(6)	1.378(15)	N(2)—C(10)	1.360(14)	C(1)—C(2)	1.344(21)
C(2)—C(3)	1.397(22)	C(3)—C(4)	1.353(19)	C(4)—C(5)	1.438(19)
C(5)—C(6)	1.419(14)	C(6)—C(7)	1.408(16)	C(7)—C(8)	1.360(20)
C(8)—C(9)	1.356(24)	C(9)—C(10)	1.357(19)	C(12)—C(13)	1.498(16)
C(16)—C(17)	1.493(17)				

Fig. 2. Structure of the complex YbI(bipy)(DME)₂ (1).

Table 2. Bond angles (ω) in complex 1

Angle	ω/deg	Angle	ω/deg
I(1)—Yb(1)—O(1)	82.2(2)	I(1)—Yb(1)—O(2)	96.3(2)
O(1)—Yb(1)—O(2)	65.5(2)	I(1)—Yb(1)—O(3)	103.0(2)
O(1)—Yb(1)—O(3)	138.5(2)	O(2)—Yb(1)—O(3)	73.0(2)
I(1)—Yb(1)—O(4)	82.3(2)	O(1)—Yb(1)—O(4)	154.7(2)
O(2)—Yb(1)—O(4)	136.2(2)	O(3)—Yb(1)—O(4)	64.9(2)
I(1)—Yb(1)—N(1)	162.9(2)	O(1)—Yb(1)—N(1)	85.8(2)
O(2)—Yb(1)—N(1)	89.7(3)	O(3)—Yb(1)—N(1)	94.0(2)
O(4)—Yb(1)—N(1)	104.3(3)	I(1)—Yb(1)—N(2)	98.6(2)
O(1)—Yb(1)—N(2)	80.0(2)	O(2)—Yb(1)—N(2)	140.0(2)
O(3)—Yb(1)—N(2)	137.6(2)	O(4)—Yb(1)—N(2)	82.7(2)
N(1)—Yb(1)—N(2)	67.3(3)	Yb(1)—O(1)—C(13)	117.6(5)
Yb(1)—O(3)—C(16)	116.8(6)	Yb(1)—O(4)—C(17)	110.5(6)
Yb(1)—N(1)—C(1)	125.2(8)	Yb(1)—N(1)—C(5)	118.1(7)
C(1)—N(1)—C(5)	116.5(10)	Yb(1)—N(2)—C(6)	119.1(6)
Yb(1)—N(2)—C(10)	124.2(8)	C(6)—N(2)—C(10)	116.6(10)
N(1)—C(1)—C(2)	127.2(13)	C(1)—C(2)—C(3)	117.1(13)
C(2)—C(3)—C(4)	119.5(14)	C(3)—C(4)—C(5)	121.4(13)
N(1)—C(5)—C(4)	118.2(10)	N(1)—C(5)—C(6)	117.6(10)
C(4)—C(5)—C(6)	124.2(11)	N(2)—C(6)—C(5)	117.9(10)
N(2)—C(6)—C(7)	120.5(9)	C(5)—C(6)—C(7)	121.7(11)
C(6)—C(7)—C(8)	118.6(13)	C(7)—C(8)—C(9)	122.0(14)
C(8)—C(9)—C(10)	117.4(13)	N(2)—C(10)—C(9)	124.7(13)
O(1)—C(13)—C(12)	106.8(8)	O(3)—C(16)—C(17)	108.8(7)
O(4)—C(17)—C(16)	108.1(10)		

atom (Yb—I, 3.120(1) Å), four oxygen atoms of two coordinated DME molecules (Yb—O, 2.525(7)—2.559(5) Å), and two nitrogen atoms of the bipyridine molecule. As a result, the coordination number of ytterbium is 7 (Fig. 2, Tables 1 and 2). The Yb—N bonds in complex 1 (2.454(9) and 2.439(9) Å) are substantially shorter than the metal—nitrogen bonds in the complexes of divalent ytterbium with coordination numbers of 7 and 8 (in Yb(py)₅(TePh)₂, Yb—N are 2.606—2.628 Å;[4] in (Me₅C₅)₂Yb(py)₂, Yb—N are 2.544 and 2.586 Å,[5] and in the Yb[III] complex, Yb(acac)₃bipy, Yb—N are 2.518 and 2.522 Å[6]). The above-mentioned bonds are somewhat longer than the analogous Yb—N(bipy⁻) distances in the Yb(bipy)₃⁻ anion (Yb—N, 2.371(9) and 2.35(1) Å)[7] and are noticeably elongated compared to the Yb—N(bipy⁻²) bonds in the same anion (Yb—N, 2.289(9) Å). Apparently, these differences are determined not only by the difference in the charges of the bipy⁻ⁿ radical anions (n = 1 or 2) but also by the steric factors, which lead to the elongation of the M—N bonds in complex 1 because of the larger coordination number of the metallocenter.

Experimental

Compound 1 was synthesized in vacuo under conditions precluding exposure to atmospheric oxygen and moisture using the standard Schlenk technique. Diethyl ether, THF, and 1,2-dimethoxyethane 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-SRC instrument. The content of the rare-earth metal in the reaction products was determined chelatometrically. The content of 2,2′-bipyridine was determined by the weight method after oxidation by atmospheric oxygen.

Synthesis of the complex YbI(bipy)(DME)₂. 2,2′-Bipyridine (0.61 g, 3.91 mmol) and DME (40 mL) were added to the mixed naphthalene-iodine complex [YbI(DME)₂]₂(μ-C₁₀H₈) (2.1 g, 1.93 mol). The precipitate of the initial complex was rapidly dissolved with intense stirring to give a red-orange solution. The solvent was slowly removed in vacuo at ~20 °C to yield black-red single crystals of complex 1. The single

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($B_{eq} \times 10^2 / \text{Å}^2$) for complex 1

Atom	x	y	z	B_{eq}
Yb(1)	2366(1)	3956(1)	2466(1)	20(1)
I(1)	−160(1)	5397(1)	2414(1)	31(1)
O(1)	504(7)	2056(7)	575(5)	28(3)
O(2)	3054(7)	4307(8)	793(5)	30(3)
O(3)	4828(7)	6202(8)	3217(5)	33(3)
O(4)	3125(7)	5512(8)	4548(5)	30(3)
N(1)	3691(9)	2151(9)	2329(6)	28(3)
N(2)	1165(8)	1967(9)	3023(5)	24(3)
C(1)	4895(12)	2162(12)	1921(9)	35(5)
C(2)	5606(14)	1159(16)	1780(10)	50(6)
C(3)	5020(13)	−62(14)	2047(10)	47(5)
C(4)	3811(14)	−164(14)	2457(10)	40(5)
C(5)	3091(10)	943(11)	2602(7)	28(4)
C(6)	1790(10)	874(11)	2990(7)	25(4)
C(7)	1145(12)	−268(11)	3332(8)	32(4)
C(8)	−144(16)	−305(16)	3646(10)	45(6)
C(9)	−823(14)	717(14)	3633(9)	39(5)
C(10)	−144(12)	1817(13)	3322(8)	33(5)
C(11)	2988(16)	5611(16)	602(11)	45(6)
C(12)	2383(13)	2950(13)	−203(8)	36(5)
C(13)	700(13)	2299(14)	−399(8)	39(5)
C(14)	−1087(12)	1324(14)	404(9)	37(5)
C(15)	6130(13)	6337(14)	2784(10)	37(5)
C(16)	5303(12)	7096(13)	4387(8)	38(5)
C(17)	3924(13)	7022(13)	4782(8)	37(5)
C(18)	2100(14)	5400(18)	5215(8)	44(6)

Table 4. Crystallographic parameters of complex 1

Formula	$C_{18}H_{28}IN_2O_4Yb$
Space group	$P\bar{1}$
$a/\text{Å}$	9.509(3)
$b/\text{Å}$	10.106(3)
$c/\text{Å}$	13.225(4)
α/deg	108.82(2)
β/deg	100.71(3)
γ/deg	105.19(3)
$V/\text{Å}^3$	1108(6)
Z	2
$\rho_{calc}/\text{g cm}^{-3}$	1.906
Radiation	Mo-Kα ($\lambda = 0.71073$ Å)
$\theta/2\theta$-scanning range/deg	2—48
Number of measured reflections	3767
Number of reflections with $I > 4\sigma$	2761
Weighting scheme	$w^1 = \sigma^2(F) + 0.0008F^2$
R	0.041
R_w	0.046

The atomic coordinates are given in Table 3. The principal geometric characteristics of molecule 1 (the bond lengths and bond angles) are listed in Tables 1 and 2.

X-ray diffraction analysis was performed in the Center for X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

crystals were separated from the mother liquor by decantation, washed with cold DME (10 mL), and dried *in vacuo* at -20 °C. The yield was 1.67 g (68%). Found (%): Yb, 26.81; bipy 22.10. $C_{18}H_{28}IN_2O_4Yb$. Calculated (%): Yb 27.20; bipy 24.53. IR (Nujol mulls), ν/cm^{-1}: 1570 w, 1550 w, 1290 w, 1280 m, 1270 s, 1250 w, 1215 m, 1195 w, 1170 w, 1120 m, 1100 m, 1060 v.s, 1030 w, 1020 m, 1000 m, 985 m, 950 v.s, 860 v.s, 840 w, 825 w, 750 w, 720 v.s, 705 m, 685 m, 640 w, 605 w, 445 w, 425 w. The magnetic moment $\mu_{eff} = 1.55 \mu B$ (293 K).

X-ray diffraction study. A single crystal of complex 1 was glued to a glass needle using epoxy resin under a stream of argon and was rapidly transferred under a stream of liquid nitrogen evaporated. The X-ray intensity data ($\theta/2\theta$ scanning technique, λMo-Kα radiation, $\lambda = 0.71073$ Å) were collected on an automated four-circle Siemens P3/PC diffractometer at −112 °C. The unit cell parameters were determined and refined using 24 equivalent reflections with $2\theta < 24$—28°. Three intense standard reflections with $0 < \chi < 60°$ were monitored after each 100 reflections. The intensities of the standard reflections showed no decrease in the course of data collection, and therefore, the corresponding corrections were ignored. The crystallographic parameters of compound 1 and selected details of the refinement are given in Table 4.

The structure of the complex was solved by direct methods, which allowed us to reveal all nonhydrogen atoms. The nonhydrogen atoms were refined isotropically. At this stage, the absorption correction ($\mu = 5.632$ mm^{-1}) was applied with the use of the program reported in Ref. 8. The positions of all hydrogen atoms were located from difference Fourier syntheses and refined isotropically. All calculations were carried out using the SHELXTL PLUS program package (PC version).[9]

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