Anionic bipyridyl complexes of lanthanides. Structure of $[Yb(bipy)_3][Li(THF)_4]$

M. N. Bochkarev,[a]* B. I. Petrov,[a] I. L. Fedyushkin,[a] T. V. Petrovskaya,[a] V. I. Nevodchikov,[a] N. B. Patrikeeva,[a] L. N. Zakharov,[a] and Yu. T. Struchkov[b]†

[a]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: 007 (831 2) 66 1497. E-mail: imoc@infotel.msk.su
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085

Reactions of Sm^{II}, Tb^{III}, Tm^{II}, Yb^{II}, and Lu^{III} iodides with 2,2′-bipyridyllithium in THF afford $[Li(THF)_4][Ln(bipy)_n]$ complexes (n = 3 or 4) containing trivalent lanthanides. X-ray structural analysis demonstrated that in the crystalline state, the Yb derivative has the ionic structure, $[Li(THF)_4]^+[Yb(bipy)_3]^-$. In THF solutions, the reversible ligand exchange between metal atoms occurs to yield neutral compounds $[Ln(bipy)_{n-1}(THF)_x]$ and $[Li(bipy)(THF)_y]$. A decrease in the temperature shifts the equilibrium to ionic pairs.

Key words: lanthanides, complexes; bipyridyl, structure; ligand exchange.

As part of our continuing studies of bipyridyl complexes of rare-earth elements,[1] we studied reactions of samarium(II), thulium(II), and ytterbium(II) iodides with 2,2′-bipyridyllithium in THF taken in the ratio of 1 : 3. In all cases, ionic complexes of composition $\{[Li(THF)_4]^+[Ln(bipy)_n]^-\}$ are formed. The complexes of Tm (**1**) and Yb (**2**) contain three bipy ligands. In the samarium complex (**3**), n = 4. All products were isolated as black crystals, which are unstable in air and moderately soluble in THF. The ESR spectra of solutions of the compounds obtained show a well resolved ESR signal of $Li^+(bipy)^{\cdot -}$ (g = 2.0030). In the solid state, the complexes give no ESR signals. The electronic spectra of these compounds in THF solutions contain several maxima observed in the spectrum of bipyridyllithium (λ = 375, 384, 513, and 549 nm). The magnetic moments of the complexes at 293 K (6.4, 3.5, and 2.7 μ_B for **1**, **2**, and **3**, respectively) differ somewhat from those of the corresponding cations Tm^{III} (7.1—7.5 μ_B), Yb^{III} (3.8—4.9 μ_B), and Sm^{III} (1.36—1.9 μ_B) in organic derivatives.[2] Apparently, the difference in the μ_{eff} values is determined by impurities of divalent lanthanides in the compounds obtained (for Tm^{II}, μ_{eff} is 4.5 μ_B;* Yb^{II} is diamagnetic; and for Sm^{II}, μ_{eff} is 3.5—3.8 μ_B[2]). Previously, we have observed an analogous decrease in the magnetic moment of the diazabutadienyl complex of ytterbium, $(Bu^tNCHCHNBu^t)_3Yb$, due to the fact that Ln^{III} and Ln^{II} occur simultaneously.[3] The rather low values of the magnetic moments are indicative of the absence of the spin contribution of the ligands. This is attributable to either the antiferromagnetic interaction between the $bipy^{\cdot -}$ radical anions in the molecule of the complex or the formal charge distribution according to the following scheme: $[(bipy)^{2-}]_2(bipy)^0$ (for the Tm and Yb derivatives) or $[(bipy)^{2-}]_2[(bipy)^0]_2$ (for the Sm derivatives). The results of X-ray structural analysis of complex **2** agree with the former suggestion and, therefore, the formula of **2** may be written as $[Li(THF)_4][Yb(bipy)^{2-}(bipy)^{\cdot -}(bipy)^{\cdot -}]$.

The crystal of compound **2** consists of $[Yb(bipy)_3]^-$ anions and $[Li(THF)_4]^+$ cations (Fig. 1). The Yb and Li atoms are located on twofold axes. The coordination about the Yb atom of the $[Yb(bipy)_3]^-$ anion is an irregular six-coordinate polyhedron (Table 1). The dihedral angles between the mean planes of the bipy ligands A and A' and between A and B are 76.2° and 52.6°, respectively. The bipy ligands are slightly twisted about the central C—C bond: the N(1)—C(5)—C(6)—N(2) and N(3)—C(15)—C(15a)—N(3a) torsion angles are 2.8 and −5.9°, respectively. The Yb atom is in the mean plane of the bipy ligand B and deviates from the mean plane of the ligand A by 0.44 Å. The Yb—N(1) and Yb—N(2) distances in the bipy ligand A (2.345(10) and 2.371(9) Å, respectively) are substantially larger than the Yb—N(3) distance (2.289(9) Å) in the bipy

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† Deceased.

* Calculated according to the following formula: $\mu_{eff} = g[J(J+1)]^{1/2}$. For $TmI_2(DME)_3$, it was found that μ_{eff} = 4.5 μ_B (293 K).

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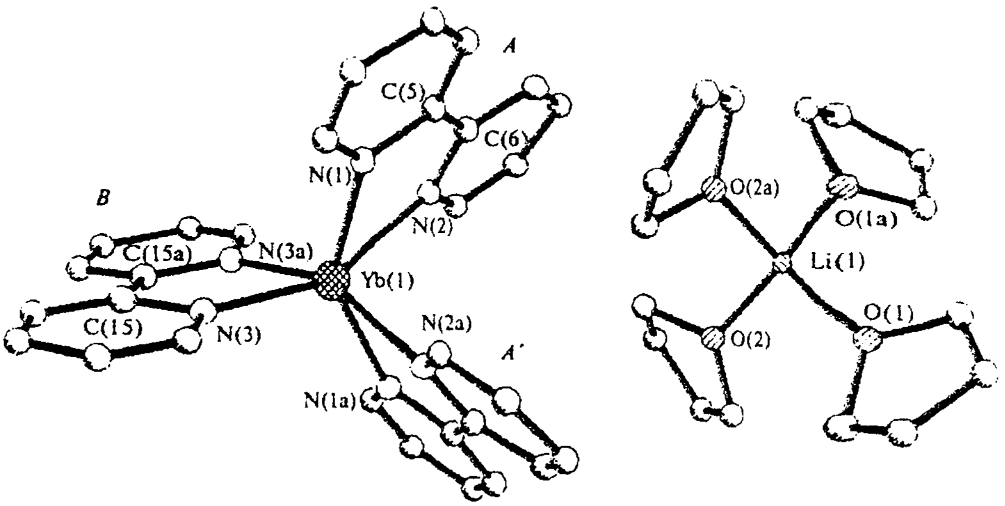

Fig. 1. Structure of compound 2.

ligand *B*. In the $[Li(THF)_4]^+$ cation, the coordination about the Li atom is a distorted tetrahedron. The Li—O(1) and Li—O(2) distances are 1.90(2) and 1.92(2) Å, respectively. The O—Li—O angles are in the range of 103.9(4)—115.5(4)° (the average value is 109.5(6)°).

On the one hand, the fact that in the solid state compound 2 consists of homoleptic ions $[Li(THF)_4]^+$ and $[Yb(bipy)_3]^-$, and on the other hand, the appearance of an intense ESR signal of the lithium salt of bipyridyl in solution are indicative of the reversible exchange of the bipy and THF ligands between the cations of a rare-earth metal and lithium, which occurs upon dissolution of the complex in THF.

$$[Yb(bipy)_3]^-[Li(THF)_4]^+ \xrightarrow{THF}$$

$$\rightleftharpoons [Yb(bipy)_2(THF)_x] + [Li(bipy)(THF)_y]$$

Cooling the solution from 300 to 200 K resulted in a reversible change in the ESR spectrum: the signal narrowed, and its intensity increased somewhat. We did not observe a change in the number of THF ligands at the Li atom and the attachment of one or several ligands to the Yb atom. However, taking into account the coordination numbers typical of Li and Yb, the coordination spheres about these atoms with $x = 3$ and $y = 2$, respectively, are, apparently, most probable.

Table 1. Selected bond lengths (d) and bond angles (ω) in 2

Bond	d/Å	Bond	d/Å
Yb(1)—N(1)	2.35(1)	Yb(1)—N(2)	2.371(9)
Yb(1)—N(3)	2.289(9)	Li(1)—O(1)	1.90(2)
Li(1)—O(2)	1.92(2)	N(1)—C(5)	1.40(2)
N(2)—C(6)	1.41(2)	N(3)—C(15)	1.43(1)
C(5)—C(6)	1.41(2)	C(15)—C(15a)	1.41(2)
Angle	ω/deg	Angle	ω/deg
N(1)—Yb(1)—N(2)	68.8(3)	N(1)—Yb(1)—N(3)	94.2(3)
N(2)—Yb(1)—N(3)	154.6(3)	N(1)—Yb(1)—N(1a)	143.3(4)
N(2)—Yb(1)—N(1a)	87.4(3)	N(3)—Yb(1)—N(1a)	116.0(3)
N(2)—Yb(1)—N(2a)	99.3(4)	N(3)—Yb(1)—N(2a)	98.5(3)
N(3)—Yb(1)—N(3a)	71.3(5)	O(1)—Li(1)—O(2)	103.9(4)
O(1)—Li(1)—O(1a)	112.4(14)	O(2)—Li(1)—O(1a)	115.5(4)
O(2)—Li(1)—O(2a)	105.8(14)		

The degree of dissociation of the $[Yb(bipy)_3]^-[Li(THF)_4]^+$ complex was determined from the ratio of intensities of the ESR signals of the bipy$^{\cdot -}$ radical anion, which were observed in solutions of complex 2 and individual Li(bipy) at approximately equal concentrations ($\sim 2.1 \cdot 10^{-2}$ mol L^{-1}) at room temperature. The data obtained suggest that the degree of dissociation is not greater than 90%. The individual Li(bipy) gives the ESR signal both in the solid state and in solution. The intensity of this signal does not change with temperature, *i.e.*, the ESR spectra of solutions of the complexes obtained is unaffected by the presence of impurities of the initial bipyridyllithium.

The formation of $[LnR_4][Li]$ ate-complexes in reactions of LnR_3 with LiR (R is alkyl, aryl, cyclopentadienyl, *etc.*) is well known in the organolanthanide chemistry.[3] However, to our knowledge, the reverse process, namely, redistribution of the charged ligands in heterobimetallic complexes to form neutral compounds, was observed for the first time.

The $[Ln(bipy)_4][Li(THF)_4]$ complexes of trivalent lanthanides of terbium (4) and lutetium (5) were synthesized analogously to the Sm, Yb, and Tm derivatives by reactions of $TbI_3(THF)_3$ and $LuCl_3$ with bipyridyllithium in the presence of free bipyridine. Their properties, including the ESR and IR spectra, are analogous to the properties of compounds **1**—**3**. However, their magnetic moments (10.1 and 2.57 μ_B for **4** and **5**, respectively) are larger than the expected values (for Tb^{III}, μ_{eff} is 9.5 μ_B; and Lu^{III} is diamagnetic[2]). This indicates that unlike complexes 1—3, unpaired electrons of the ligands contribute to the overall magnetic moments of complexes **4** and **5**.

Experimental

Because all the products obtained are highly sensitive with respect to oxygen and moisture, all operations associated with the syntheses and isolation of the compounds were carried out using the standard Schlenk technique under conditions precluding exposure to the atmosphere. The IR spectra (Nujol mulls) were recorded on a Perkin—Elmer 577 instrument. The UV spectra were measured on a Specord-M40 instrument. The ESR spectra were recorded on a Bruker-ER 200D-1SRC instrument.

To estimate the degree of dissociation, solutions of $[Yb(bipy)_3][Li(THF)_4]$ ($2.14 \cdot 10^{-2}$ mol L^{-1}) and Li(bipy) ($2.19 \cdot 10^{-2}$ mol L^{-1}) were prepared directly in tubes adapted to recording the ESR spectra. The ESR spectra were obtained at room temperature. At the concentrations used, the spectra are broadened singlets. Integrated intensities of the signals were estimated within the framework of the approximate formula $\Delta h^2 \cdot I$ (where Δh is the line width, and I is the intensity of the signal). The calculated concentration of Li(bipy) formed upon dissociation of complex **2** was $1.99 \cdot 10^{-2}$ mol L^{-1}.

Lithium[tetrakis(tetrahydrofuran)]tri(2,2-bipyridyl)thulium (1). A purple solution of bipyridyllithium [Li (0.0461 g, 6.64 mg-at.) and 2,2′-bipyridyl (1.0265 g, 7.07 mmol)] in THF (20 mL) was added to a green solution of $TmI_2(DME)_3$ (1.52 g, 2.19 mmol) in THF (40 mL). The reaction mixture developed a dark-purple color, and cubic crystals precipitated immediately. The solution was decanted from crystals. The crystals were washed with cold THF and dried *in vacuo*. Complex **1** was obtained in a yield of 1.0 g (49%). When heated to 150 °C, compound **1** lost THF molecules. Further increase in the temperature (to 260 °C) did not cause visible changes. Found (%): Li, 0.74; Tm, 17.72; bipy, 50.21. $C_{46}H_{56}N_6O_8LiTm$. Calculated (%): Li, 0.75; Tm, 18.13; bipy, 52.3. IR (Nujol mulls), ν/cm^{-1}: 1520, 1475, 1400, 1365, 1280, 1260, 1195, 1160, 1135, 1105, 1035, 1000, 935, 900, 880, 715, 690, 670, 630, 445, 405.

Complexes **2**, **3**, **4**, and **5** were obtained analogously in yields of 74, 38, 23, and 54%, respectively. The content of metal atoms and bipy ligands of these compounds agrees well with the calculated values. The IR spectra of the compounds are identical to the spectrum of the Tm analog mentioned above.

X-ray structural study of compound **2** was carried out on a Siemens P3/PC diffractometer at 153 K (Mo-Kα radiation, $2\theta/\theta$ scanning technique, $2 < 2\theta < 44°$, 6533 measured reflections, 1411 independent reflections with $F > 6\sigma(F)$). The unit cell parameters at 153 K are: a = 12.713(5) Å, b = 18.052(6) Å, c = 18.679(5) Å; V = 4287(4) $Å^3$, d_{calc} = 1.452 g cm^{-3}, μ(Mo-Kα) = 2.23 mm^{-1}, Z = 4 for $C_{46}H_{56}O_4N_6LiYb$, space group *Pbcn*. The structure was solved using the direct method and difference Fourier syntheses. All nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms were calculated from geometric considerations and refined within the framework of the rigid group model with fixed isotropic thermal parameters. The absorption correction was applied with the use of the DIFABS program.[4] The final values of the R factors were as follows: $R = 0.041$, $R_w = 0.047$, $S = 1.08$ for the observed reflections. The following weighting scheme was used: $w = 1/[\sigma^2(F) + 0.001F^2]$. The value of $(\Delta/\sigma)_{aver}$ in the final cycle of the refinement was 0.002. In the final difference electron density map, the highest peaks were — 0.79 and −0.85 ($e^- \cdot Å^{-3}$). All calculations were carried out with the use of the SHELXTL-PLUS program package.[5]

Concentrations of the rare-earth metals in the products were determined chelatometrically. The number of bipy ligands was determined by the weight method after oxidation of the complexes by atmospheric oxygen. The initial Sm^{II} and Yb^{II} iodides were synthesized according to the known procedure.[6] Tm^{II} iodide was prepared by a procedure similar to that reported previously.[7]

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