Organometallic Chemistry

Synthesis and crystal structure of the $Sm(Bu^tNCHCHNBu^t)_2(bpy)$ complex

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Reaction of $Sm(bpy)_4$ (bpy is 2,2′-bipyridyl) with di-*tert*-butyldiazabutadiene (dad) in tetrahydrofuran (THF) affords the mixed-ligand complex $Sm(dad)_2(bpy)$ (**1**). Complex **1** was isolated as black paramagnetic crystals readily soluble in THF, 1,2-dimethoxyethane (DME), toluene, and ether. Compound **1** was characterized by IR and ESR spectroscopy, X-ray diffraction analysis, and by the results of magnetic measurements. Based on the difference between the Sm—N bond lengths and on the data of IR spectroscopy, the following formal charge distribution in the molecule of complex **1** was proposed: $Sm^{3+}(dad)^{2-}(dad)^{1-}(bpy)^0$.

Key words: samarium, ytterbium, complexes; bipyridyl, diazabutadiene, structure.

Recently we have prepared homoleptic bipyridyl complexes of the composition $Ln(bpy)_4$ for the whole series of rare earth metals.[1] The fact that these complexes contain bipyridyl ligands of the radical-anion nature accounts for their interesting physicochemical properties. Taking into account the reducing character of the bipyridyl radical anion, one may expect that these compounds would be highly reactive. Previously we have shown that the lanthanide complexes containing a naphthalene dianion are highly reactive toward various inorganic, organic, and organometallic substrates.[2] In order to study the chemical properties of the $Ln(bpy)_4$ complexes, we studied the reaction of $Sm(bpy)_4$ with diazabutadiene (dad) and the reaction of $Yb(bpy)_4$ with vanadocene.

The reaction of $Sm(bpy)_4$ with excess diazabutadiene is completed over a period of several minutes (THF, 80 °C).

$$Sm(bpy)_4 + dad \xrightarrow[80\ ^\circ C]{THF} \underset{\mathbf{1}}{Sm(dad)_2(bpy)}$$

Contrary to expectations, this reaction does not lead to the tris(diazabutadiene) complex of samarium (which was formed in the reaction with naphthaleneytterbium[3]); instead, it stops at the step of the formation of the mixed complex, $Sm(dad)_2(bpy)$ (**1**). Compound **1** was isolated, after recrystallization from ether, as black crystals unstable in air (yield 75%). Unlike the initial $Sm(bpy)_4$, compound **1** is readily soluble in THF, DME, toluene, and ether. In the solid state, the complex exhibits no ESR signal. The magnetic moment of compound **1** at 293 K is 1.6 μ_B, which falls within the range of magnetic moments typical of organic derivatives of Sm^{III} (1.36—1.9 μ_B [4]). The IR spectrum of compound **1** exhibits absorption bands at 1580 and 1600 cm^{-1}, char-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1860—1862, October, 1997.

1066-5285/97/4610-1766 $18.00 © 1997 Plenum Publishing Corporation

Table 1. Some bond lengths (*d*) in the Sm(dad)$_2$(bpy) complex

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
Sm—N(11)	2.590(7)	N(11)—C(11)	1.341(12)	C(15)—C(16)	1.458(13)	N(22)—C(27)	1.485(12)
Sm—N(12)	2.692(7)	N(11)—C(15)	1.356(12)	C(16)—C(17)	1.391(13)	C(25)—C(26)	1.398(13)
Sm—N(21)	2.452(8)	N(12)—C(16)	1.363(12)	C(17)—C(18)	1.36(2)	N(31)—C(31)	1.473(11)
Sm—N(22)	2.541(8)	N(12)—C(110)	1.312(12)	C(18)—C(19)	1.36(2)	N(31)—C(35)	1.371(12)
Sm—N(31)	2.257(7)	C(11)—C(12)	1.392(14)	C(19)—C(110)	1.369(14)	N(32)—C(36)	1.401(12)
Sm—N(32)	2.299(7)	C(12)—C(13)	1.36(2)	N(21)—C(21)	1.496(11)	N(32)—C(37)	1.473(12)
Sm—C(35)	2.780(10)	C(13)—C(14)	1.37(2)	N(21)—C(25)	1.335(12)	C(35)—C(36)	1.374(12)
Sm—C(36)	2.795(10)	C(14)—C(15)	1.385(13)	N(22)—C(26)	1.327(12)		

acteristic of the neutral bpy ligand. The intense band at 950 cm^{-1}, which is normally present in the IR spectra of complexes with the bipyridyl radical anion,[1,5] is not manifested in the spectrum of complex **1**. This makes it possible to suggest that the bpy ligand in compound **1** is neutral.

According to X-ray diffraction data, the Sm atom in complex **1** has a distorted octahedral coordination: the six N atoms of the two dad ligands and one bpy ligand are located at the vertices of an octahedron. The structure of the molecule is shown in Fig. 1, and the main bond lengths and angles are listed in Tables 1 and 2. The Sm—N(21) and Sm—N(22) bonds in one dad ligand (**A**) (2.452 and 2.541 Å, respectively) are much longer than the Sm—N(31) and Sm—N(32) distances in the other dad ligand (**B**) (2.257 and 2.299 Å, respectively). With allowance for the difference between the effective ion radii of Sm^{III} (0.958 Å) and Yb^{III} (0.868 Å),[6] the lengths of the Sm—N(21) and Sm—N(22) bonds are close to the Yb—N bond lengths in the (Bu^{t}NCHCHNBu^t)$_3$Yb complex[3] in which the average Yb—N distance is equal to 2.411 Å. The C(25)—C(26) distance in complex **1** (1.398 Å) is very close to the length of the corresponding bond in the complex of ytterbium (1.39 Å) and is somewhat longer than the C(35)—C(36) distance (1.374 Å) in complex **1**. The Sm—N(bpy) bond lengths in complex **1** (2.590 and 2.692 Å; 2.641 Å, on the average) are much greater than the Sm—N bond lengths in the Sm(bpy)$_4$ complex (2.577 Å, on the average),[1] taking into account the difference between the effective ion radii of Sm^{III} with a coordination number of 6 (0.958 Å) and Sm^{III} with a coordination number of 8 (1.079 Å).[6]

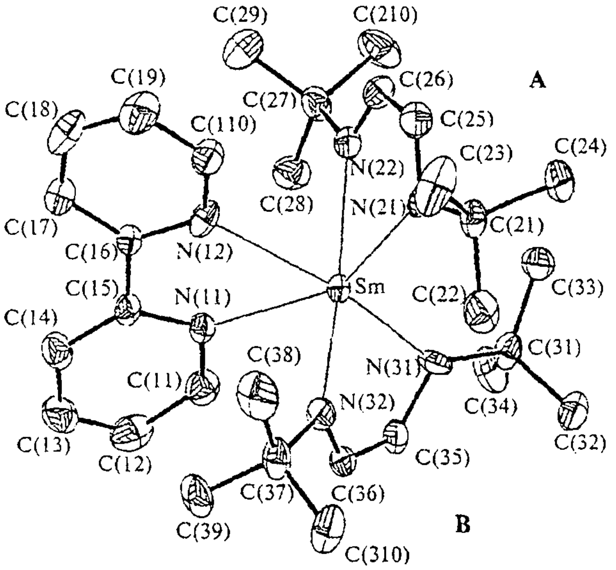

Fig. 1. Molecular structure of the Sm(dad)$_2$(bpy) complex.

Table 2. Some bond angles in the Sm(dad)$_2$(bpy) complex

Angle	ω/deg
N(11)—Sm—N(12)	61.9(2)
N(21)—Sm—N(22)	69.4(3)
N(31)—Sm—N(32)	80.3(3)
C(25)—N(21)—C(21)	115.2(8)
N(21)—C(25)—C(26)	122.5(9)
N(22)—C(26)—C(25)	123.3(9)
C(26)—N(22)—C(27)	116.2(8)
C(35)—N(31)—C(31)	119.2(8)
N(31)—C(35)—C(36)	124.1(9)
C(35)—C(36)—N(32)	124.5(9)
C(36)—N(32)—C(37)	114.8(8)

The bond lengths in the bpy ligand in complex **1** are close to the corresponding bond lengths in free 2,2′-bipyridyl.[7—10] For example, the C(15)—C(16), C(15)—N(11), C(15)—C(14), C(16)—N(12), and C(16)—C(17) distances in the bpy ligand in complex **1** are 1.458, 1.356, 1.385, 1.363, and 1.391 Å, respectively, whereas the lengths of the corresponding bonds in free 2,2′-bipyridyl are 1.490, 1.346, 1.394, 1.346, and 1.394 Å. This indicates that the geometry of the bpy ligand in complex **1** differs only slightly from that of neutral $C_{10}H_8N_2$. Thus, it can be assumed that the mixed samarium complex incorporates a radical anion (ligand **A**) and dianion (ligand **B**) derived from diazabutadiene, together with a neutral bpy ligand, and that the formal charge distribution can be represented by the following scheme: Sm^{+3}(dad$^-$)(dad^{2-})(bpy^0). This assumption is in line with the difference between the reduction potentials of 2,2′-bipyridyl (−2.18 V)[11] and diazabutadiene (−1.822 V)[12].

The reaction of $Yb(bpy)_4$ with vanadocene occurs in THF at room temperature over a period of several seconds. The resulting blue solution exhibits a strong ESR signal corresponding to tris(bipyridyl)vanadium (octet, $a(^{51}V) = 8.35$ mT).[13] The reaction products are not volatile and possess close solubilities, which hampers their separation. Repeated extraction of the reaction products with toluene made it possible to isolate only $V(bpy)_3$ in relatively low yield.

Unlike naphthalene complexes of lanthanides, the $Ln(bpy)_4$ complexes proved to be inert with respect to acetylene, tolan, stilbene, hydrogen, and other reagents, which points to their relatively low reactivity.

Experimental

The synthesis of compound **1** and its reactions were carried out *in vacuo* under conditions ruling out contact with air or moisture; this was done using the standard Schlenk technique. Ether, THF, DME, and toluene were dried with benzophenone sodium ketyl and distilled into the reaction tube immediately prior to use. IR spectra were recorded on a Specord M-80 instrument; the samples were prepared as suspensions in Vaseline oil. ESR spectra were obtained on a Bruker-ER 200D-1SRC instrument. The content of the lanthanide in the reaction products was found by complexometry.

Synthesis of $Sm(Bu^tNCHCHNBu^t)_2(C_{10}H_8N_2)$. A solution of diazabutadiene (0.7 g, 4.14 mmol) in THF (20 mL) was added to a suspension of $Sm(bpy)_4$ (0.6 g, 0.77 mmol) in 40 mL of THF. The mixture acquired a greenish-brown color. When the mixture was kept at 80 °C for 15 min, the initial complex of samarium dissolved to give a dark green solution. The solvent was evaporated *in vacuo*. The residue was recrystallized from ether and dried *in vacuo* to give 0.374 g (75%) of complex **1**. Found: Sm, 23.21%. $C_{30}H_{49}N_6Sm$. Calculated: Sm, 23.38%. IR, ν/cm^{-1}: 1640 w, 1600 s, 1580 m, 1570 m, 1545 w, 1520 w, 1470 vs, 1435 vs, 1395 s, 1380 vs, 1370 s, 1360 s, 1315 m, 1260 s, 1235 m, 1210 vs, 1150 m, 1125 s, 1080 w, 1060 w, 1040 m, 1010 m, 1000 m, 925 m, 900 m, 835 m, 790 m, 760 vs, 740 m, 725 s, 670 w, 640 w, 620 w, 525 m, 490 m, 465 m. Magnetic moment (293 K) $\mu_{eff} = 1.6\ \mu_B$.

The X-ray diffraction study of compound **1** was carried out on an Enraf-Nonius CAD 4 four-circle diffractometer. The unit cell parameters and the intensities of 4581 independent reflections were obtained at 240(2) K (λ(Mo-Kα) radiation of 0.71069 Å, scanning in the $0.5° < 2\theta < 45°$ range). The crystals of the complex are monoclinic, $a = 10.971(2)$ Å, $b = 16.042(5)$ Å, $c = 18.902(4)$ Å, $\beta = 102.01(2)°$, $V = 3253.7(14) \cdot 10^{-30}$ m^3; $d_{calc} = 1317$ kg m^{-3}, $Z = 4$; space group $P2_1/c$. The absorption in the crystal ($\mu = 1.752$ mm^{-1}) was taken into account using the DIFABS program. The structure was solved by a combination of the direct method and differential synthesis (SHELX-86 [14] and SHELX-93 [15] programs) and refined by the full-matrix least-squares method with anisotropic parameters of thermal vibrations for non-hydrogen atoms. Hydrogen atoms were placed to the calculated positions (C—H 0.96 Å, $U_{iso} = 0.08$ Å^2). The density of free electrons in the last F-map was 0.992 e Å^{-3} in the maximum and -1.272 e Å^{-3} in the minimum. The final refinement over 4229 independent reflections with $I > 2\sigma(I)$ gave $R = 0.0443$, $R_w = 0.1128$, GOF = 0.89.

This work was carried out with the financial support of Volkswagen-Stiftung.

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Received April 9, 1997;
in revised form June 6, 1997