Synthesis and properties of homoleptic 2,2′-bipyridyl complexes of rare-earth elements. Crystal and molecular structures of the complexes $Ln(N_2C_{10}H_8)_4$ (Ln = Sm, Eu, Yb, or Lu) and the ionic complex $[Lu(N_2C_{10}H_8)_4][Li(THF)_4]$

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Homoleptic 2,2′-bipyridyl complexes of lanthanides (Ln), $Ln(bpy)_4$, were prepared by the reactions of iodides $LnI_2(THF)_2$ (Ln = Sm, Eu, Tm, or Yb), $LnI_3(THF)_3$ (Ln = La, Ce, Pr, Nd, Gd, or Tb), or bis(trimethylsilyl)amides $Ln[N(SiMe_3)_2]_3$ (Ln = Dy, Ho, Er, or Lu) with bipyridyllithium in tetrahydrofuran (THF) or 1,2-dimethoxyethane in the presence of free 2,2′-bipyridine. The IR and ESR spectral data, the magnetic susceptibilities, and the results of X-ray diffraction analysis indicate that the complexes of all elements of the lanthanide series, except for the europium complex, contain Ln^{+3} cations and anionic bpy ligands. According to the X-ray diffraction data, the coordination polyhedra about the Sm and Eu atoms are cubes, whereas the environment about the Yb atom is a distorted dodecahedron. In the ionic complex $[Lu(bpy)_4][Li(THF)_4]$, the geometry of the $[Lu(bpy)_4]^-$ anion is similar to that of the $Lu(bpy)_4$ complex. The possible modes of charge distributions over the ligands, *viz.*, $Ln(bpy^{2-})(bpy^{\cdot -})(bpy^0)_2$ and $Ln(bpy^{\cdot -})_3(bpy^0)$, are discussed.

Key words: rare-earth elements, 2,2′-bipyridine, complexes, structure, magnetic properties.

Recently, we have initiated a series of studies aimed at the synthesis of complexes of rare-earth elements with the chelating 2,2′-bipyridyl (bpy) ligand. This ligand possesses both σ-donor (four-electron *N*-donor) and π-acceptor properties. Successive reduction of the ligand allows one to prepare its mono- and dianionic forms. Bipyridyl complexes of many metals are known. In the case of d-block elements, the ligand acts to a greater extent as an n-donor and the LUMO of the ligand remains unoccupied, whereas electropositive metals can form complexes both with mono- and dianions. Previously, we have prepared various complexes of rare-earth elements with $bpy^{\cdot -}$ radical anions. Among them, three types can be distinguished: (a) the mixed bpy-DAD complex of samarium $[Sm^{+3}(DAD^{2-})(DAD^{\cdot -})(bpy^0)]$ (DAD = $Bu^tNCHCHNBu^t$);[1] (b) the anionic complexes $[Li(THF)_4]^+[Ln(bpy)_n]^-$ (Ln = Sm, Tb, Tm, Yb, or Lu, *n* = 3 or 4), which were synthesized by the reactions of iodides with Li(bpy) in THF;[2] and (c) the mixed iodine-bpy complexes of ytterbium(II), *viz.*, $YbI(bpy)(DME)_2$,[3] and lanthanum(III), *viz.*, $LaI_2(bpy)(DME)_2$ and $LaI_2(bpy)_2(DME)$,[4] which were formed in the reactions of the corresponding iodine-naphthalene complexes $[YbI(DME)_2]_2(\mu\text{-}C_{10}H_8)$ or $[LaI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$ with one or two equivalents of bpy. Recently,[5] we have reported the synthesis and X-ray diffraction study of the first complex of lanthanide with the bipyridyl dianion, $[Yb(bpy)(THF)_2]_3$ (the second metal complex of this type known to date), which was prepared by reduction of 2,2′-bipyridine (biPy) with an excess of $C_{10}H_8Yb(THF)_2$ in THF. When we started this work, only contradictory data on the synthesis of tetrakis(bipyridyl) complexes of composition $Ln(bpy)_4$ (Ln = Eu or Yb;[6] Ln = Nd or Ce [7]) were available in the literature. The $Ln(bpy)_4$ complexes (Ln = Eu or Yb) were prepared[6] by the reactions of solutions of the corresponding metals in liquid ammonia with free 2,2′-bipyridine. Based on the results of magnetic measurements, it was suggested[6] that these complexes contain the Eu^{+2} or Yb^{+2} cations and the $bpy^{\cdot -}$ radical anions. The complexes of neodymium and cerium were synthesized by the reactions of the dilithium salt of 2,2′-bipyridine with metal trichlorides in THF in the presence of 2,2′-bipyridine and were interpreted[7] as complexes of zero-valent lanthanides. With the aim of elucidating the nature of $Ln(bpy)_4$ and completing systematic studies of bipyridyl complexes of rare-earth elements, we synthesized the $Ln(bpy)_4$ complexes of elements of the overall series and studied them by IR and ESR spectroscopy, X-ray diffraction analysis, and magnetochemistry.

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Results and Discussion

The Ln(bpy)$_4$ complexes were prepared by the reactions of the corresponding lanthanide iodides or tris[bis(trimethylsilyl)amide]lanthanides with three equivalents of bipyridyllithium in the presence of free 2,2´-bipyridine in THF or DME. The Sm, Eu, Yb, and Tm complexes were synthesized with the use of diiodides LnI$_2$(B)$_n$ (Ln = Sm, Eu, or Yb, B = THF, n = 2; or Ln = Tm, B = DME, n = 3) as the starting reagents. Previously,[2] it has been found that the reaction of four equivalents of Li(bpy) with lutetium trichloride afforded the ate-complex [Li(THF)$_4$][Lu(bpy)$_4$]. The reactions with the use of triiodides of heavy lanthanides instead of amides in the synthesis of Ln(bpy)$_4$ gave rise to noncrystalline insoluble products, which we failed to identify. Apparently, the fact that the reactions of triiodides of light and heavy lanthanides afforded different products is associated with the difference in the structure of these triiodides. The triiodides of all elements of the series were prepared by the reactions of an excess of the corresponding metal with iodine in THF. However, X-ray diffraction study performed previously[8] demonstrated that iodides of the first elements of the lanthanide series are molecular compounds of composition LnI$_3$(THF)$_n$ (n = 3 or 4), whereas both molecular iodides and ionic complexes, *viz.*, [LnI$_2$(THF)$_5$]$^+$[LnI$_4$(THF)$_2$]$^-$, are known for the last members of the series.[9]

$$\mathrm{LnX_3(THF)}_n + 3\ \mathrm{Li(bpy)} + 2\ \mathrm{biPy} \xrightarrow{\mathrm{THF}} \mathrm{Ln(bpy)_4} + \mathrm{biPy},$$

X = I, Ln = La, Ce, Pr, Nd, Gd, Tb, n = 3;
X = N(SiMe$_2$)$_2$, Ln = Dy, Ho, Er, Lu, n = 0

$$\mathrm{LnI_2(B)}_n + 2\ \mathrm{Li(bpy)} + 2\ \mathrm{biPy} \longrightarrow \mathrm{Ln(bpy)_4},$$

Ln = Sm, Eu, Yb; B = THF; n = 2
Ln = Tm; B = DME; n = 3

$$\mathrm{LnX_2(THF)_2} + 4\ \mathrm{Li(bpy)} \xrightarrow{\mathrm{THF}} \mathrm{Li(THF)_4][Lu(bpy)_4]},$$

X = Cl, I

All products were obtained in high yields as air-unstable black crystals (for Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) or finely crystalline powders (for La, Ce, Pr, Nd, Eu, and Sm). The complexes decomposed without melting upon heating above 160—180 °C. The complexes of light lanthanides, *viz.*, of La—Sm, are insoluble in organic solvents (THF, DME, diethyl ether, toluene, or hexane), the Eu, Gd, and Tb complexes are moderately soluble in THF and insoluble in other organic solvents, whereas the Dy, Ho, Er, Tm, Yb, and Lu complexes are readily soluble in THF and DME. The differences in the properties of the Ln(bpy)$_4$ complexes of the first and last members of the lanthanide series are manifested in their IR spectra (Fig. 1). The IR spectra of the La, Ce, Pr, Nd, Sm, Gd, and Tb complexes are virtually identical and differ from the spectra of the Dy, Ho, Er, Tm, Yb, and Lu complexes. The IR spectrum of the europium compound Eu(bpy)$_4$ differs from the spectra of all other complexes of the lanthanide series.

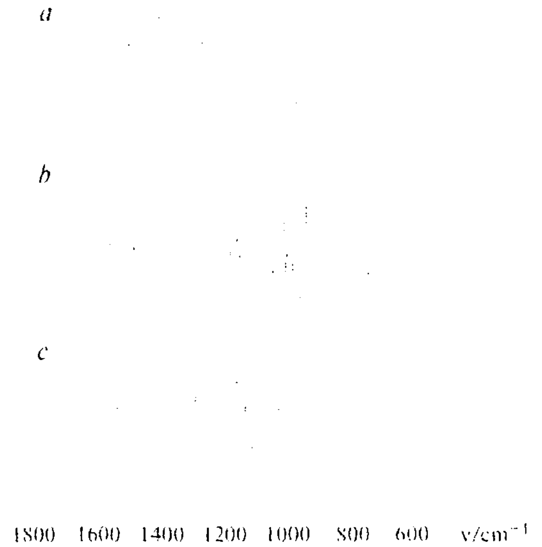

Fig. 1. IR spectra of the Ln(bpy)$_4$ complexes: (*a*) Ln = La, Ce, Pr, Nd, Sm, Gd, or Tb; (*b*) Ln = Eu; and (*c*) Ln = Dy, Ho, Er, Tm, Yb, or Lu.

The resulting complexes are paramagnetic. Their magnetic moments measured at room temperature are given in Table 1. The μ_{eff} values for most of the complexes differ noticeably from the values calculated for the [Ln^{+3}(bpy$^{\cdot-}$)$_3$(bpy^0)] systems on the assumptions that spin-spin coupling in the complexes is absent and that the magnetic moments of the individual magnetic centers (Ln^{+3}, 4f^{n}5d^{0}6s^0, n = 1—14 and three bpy$^{\cdot-}$ radical anions) are additive. The observed magnetic moments agree more closely with those calculated for the Ln^{+3}(bpy^{2-})(bpy$^{\cdot-}$)(bpy^0)$_2$] systems. Previously, we have observed an analogous electron nonequivalence of the ligands in the mixed bpy-DAD complex of samarium [Sm^{+3}(DAD^{2-})(DAD$^{\cdot-}$)(bpy^0)] (DAD = Bu^{t}NCHCHNBu^t).[1] It should be noted that the experimental μ_{eff} values allow also the third form of the complexes in which the metal atom exists in the oxidation state 0, *viz.*, [Ln^0(bpy^0)$_4$]. In this case, only the lanthanide atom can be responsible for the presence of the magnetic moment. For example, in the case of lutetium(0) possessing the electron configuration 4f^{14}5d^{1}6s^2, the magnetic moment is equal approximately to 1.73 μB. This value is close to that observed[11] for the zero-valent bisarene complex Lu(1,3,5-Bu$^t_3$C$_6$H$_3$)$_2$ (1.69 μB) and to the magnetic moment measured by us for Lu(bpy)$_4$ (1.88 μB). The temperature dependences of the magnetic moments for the La, Ce, Pr, and Nd complexes obey the Curie—Weiss law. In the temperature range of 80—290 K, the magnetic moments of the complexes remain virtually constant. A decrease in the temperature leads to a decrease in the magnetic moments, which is indicative of the effective antiferromagnetic interaction.

The ESR spectra of crystalline samples of the La, Ce, Pr, Nd, Eu, Gd, and Lu complexes have rather narrow signals (singlets) in the temperature range of 150—290 K

Table 1. Magnetic moments and the data of ESR spectroscopy for the Ln(bpy)$_4$ complexes

Ln	$\mu_{eff}/\mu B$[a] at 293 K (at 4 K)			ESR		
	Experiment	Calculation		g factor	$\Delta H_{1/2}$ /mT[d]	Dependence of the integral intensity of the signal on T
		I[b]	II[c]			
La	1.7 (0.85)	3.0	1.74	2.0007	5	Independent
Ce	2.5 (0.7)	3.94	2.65	2.0035	2	Increases with cooling
Pr	3.7 (1.3)	4.70	3.73	2.0035	1	Increases with cooling
Nd	3.9 (1.2)	4.75	3.73	2.0035	1	Increases with cooling
Sm	3.0 (0.6)	3.46	2.43[e]	—	—	Signal is absent
Eu	7.8	5.01	4.36[f]	~2.00	200	Decreases with cooling
Gd	8.2	8.59	8.19	2.0140	35	Increases with cooling
Tb	9.6	10.2	9.66	2.0030	2	Increases with cooling
Dy	10.2	11.0	10.74	—	—	Signal is absent
Ho	11.0	11.0	10.54	—	—	Signal is absent
Er	10.2	10.1	9.77	—	—	Signal is absent
Tm	8.3	8.2	7.50	—	—	Signal is absent
Yb	4.3	5.41	4.63[g]	—	—	Signal is absent
Lu	1.88	3.0	1.74	2.0014	8 (290 K)	Independent

[a] The average magnetic moments of Ln^{3+} typical of organic complexes[10] were used in calculations.

[b] For the [Ln^{+3}(bpy$^{\cdot-}$)$_3$(bpy^0)] system.

[c] For the [Ln^{+3}(bpy^{2-})(bpy$^{\cdot-}$)(bpy^0)$_2$] system.

[d] The relative width of the signal.

[e] [Sm^{+2}(bpy$^{\cdot-}$)$_2$(bpy^0)$_2$] μ_{eff} = 4.36 μB; [Sm^{+2}(bpy^{2-})(bpy^0)$_3$] μ_{eff} = 3.6 μB.

[f] [Eu^{+2}(bpy$^{\cdot-}$)$_2$(bpy^0)$_2$] μ_{eff} = 8.49 μB; [Eu(bpy^{2-})(bpy^0)$_3$] μ_{eff} = 7.8 μB.

[g] [Yb^{+2}(bpy$^{\cdot-}$)$_2$(bpy^0)$_2$] μ_{eff} = 2.46 μB; [Yb^{+2}(bpy^{2-})(bpy^0)$_3$] is the diamagnetic complex.

(Table 1). The terbium derivative gives a poorly resolved signal in one-half of the region. The absence of noticeable temperature dependences of the ESR signals for the complexes with the diamagnetic La^{III} and Lu^{III} cations is consistent with the assumption that the ligands of the molecules contain only one unpaired electron. The integral intensities of the ESR signals for the Ce, Pr, Nd, Gd, and Tb complexes increase by a factor of 10 as the temperature decreases from 290 to 150 K. In the case of Eu(bpy)$_4$, the broad singlet line observed at room temperature broadens as the temperature decreases and the signal virtually disappears at 150 K. Analogous ESR signals observed previously for the EuX$_2$ and REuX complexes (X = Cl, Br, or I; R = Et or Ph) were assigned to europium(II).[12] The fact that the g factors of the ESR signals for the crystalline complex Lu(bpy)$_4$ and its solution in tetrahydrofuran have similar values indicates that the molecular parameters of the complex in solutions are identical to those observed in the crystal, *i.e.*, all four ligands remain to be coordinated to the lutetium atom. The Sm, Dy, Ho, Er, and Yb complexes both in the crystals and solutions give no ESR signals.

Crystal and molecular structures of the Ln(bpy)$_4$ complexes. According to the X-ray diffraction data, eight nitrogen atoms of four bpy ligands in the isostructural samarium and europium complexes are coordinated to the metal atom to form a slightly distorted cube (Figs. 2 and 3, respectively). The average Ln—N distance (Table 2) in the europium complex is 0.158 Å larger than the

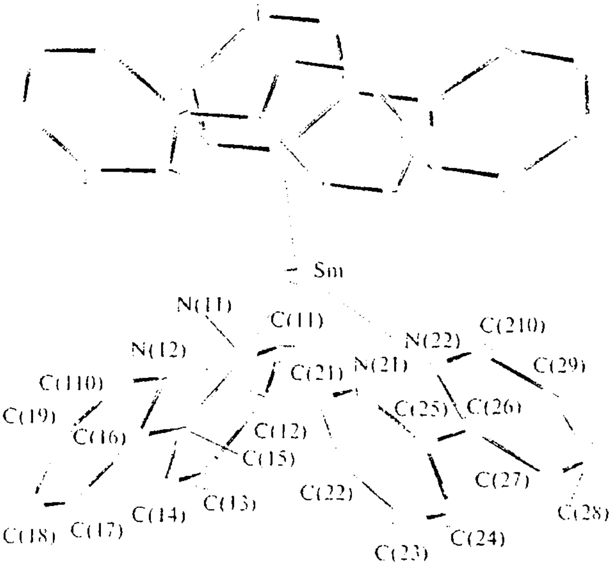

Fig. 2. Molecular structure (ORTEP[20]) of the Sm(bpy)$_4$ complex (thermal ellipsoids with the 40% probability). The hydrogen atoms are omitted.

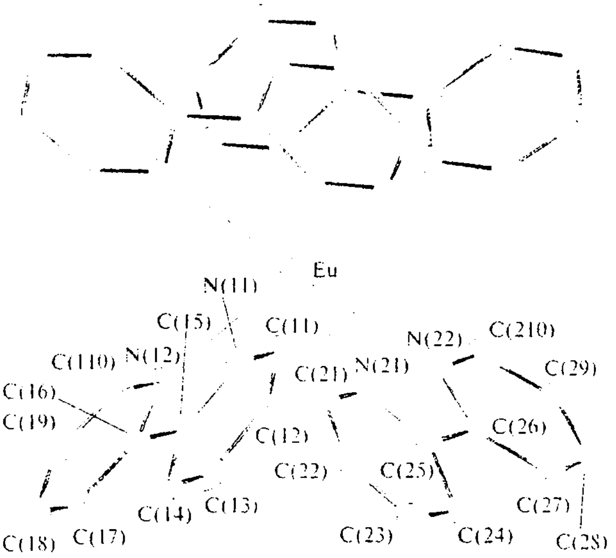

Fig. 3. Molecular structure (ORTEP[20]) of the Eu(bpy)$_4$ complex (thermal ellipsoids with the 40% probability). The hydrogen atoms are omitted.

Table 2. The Ln—N bond lengths (Å) in the Ln(bpy)$_4$ complexes

Atom	Sm(bpy)$_4$	Eu(bpy)$_4$	Yb(bpy)$_4$	Lu(bpy)$_4$	[Li(THF)$_4$] · [Lu(bpy)$_4$]
N(11)	2.560(3)	2.703(4)	2.423(6)	2.424(6)	2.413(4)
N(12)	2.537(4)	2.670(4)	2.414(6)	2.367(7)	2.462(4)
N(21)	2.605(4)	2.769(4)	2.403(6)	2.372(7)	2.448(4)
N(22)	2.600(4)	2.795(5)	2.440(7)	2.376(7)	2.424(4)
N(31)			2.517(7)	2.427(7)	
N(32)			2.559(6)	2.415(7)	
N(41)			2.416(6)	2.530(7)	
N(42)			2.434(6)	2.559(7)	
Average value	2.576	2.734	2.451	2.434	2.438

corresponding distance in the samarium analog, which corresponds to the difference between the ionic radii of Eu^{II} and Sm^{III}.[13] The twofold rotation axis generates two pairs of symmetrically equivalent bpy ligands, which is consistent with the scheme of the charge distribution in the europium complex [Eu^{2+}(bpy$^{\cdot-}$)$_2$(bpy^0)$_2$], but cannot be true for the samarium complex. In the latter complex, two combinations are possible, *viz.*, [Sm^{3+}(bpy$^{\cdot-}$)$_3$(bpy^0)] or [Sm^{3+}(bpy^{2-})(bpy$^{\cdot-}$)(bpy^0)$_2$], none of which can occur in the presence of the twofold rotation axis. The deviations from the expected symmetry in Sm(bpy)$_4$ may be associated with the molecular packing in the crystal (Fig. 4). In the crystals, the Ln(bpy)$_4$ molecules (Ln = Sm or Eu) are linked in one-dimensional quasi-polymer chains through short contacts between the bpy ligands. Two bpy ligands of two adjacent molecules are virtually parallel to each other and are arranged one above the other. In Sm(bpy)$_4$, the C(24)...C(26′) and C(26)...C(24′) distances are 3.25 Å; the corresponding distances in Eu(bpy)$_4$ are 3.31 Å (Table 3). It should be noted that these distances are substantially shorter than the distances between the layers in graphite (3.35 Å). Probably this molecular packing in the crystal is attributable to a some degree of electron density delocalization over the bpy

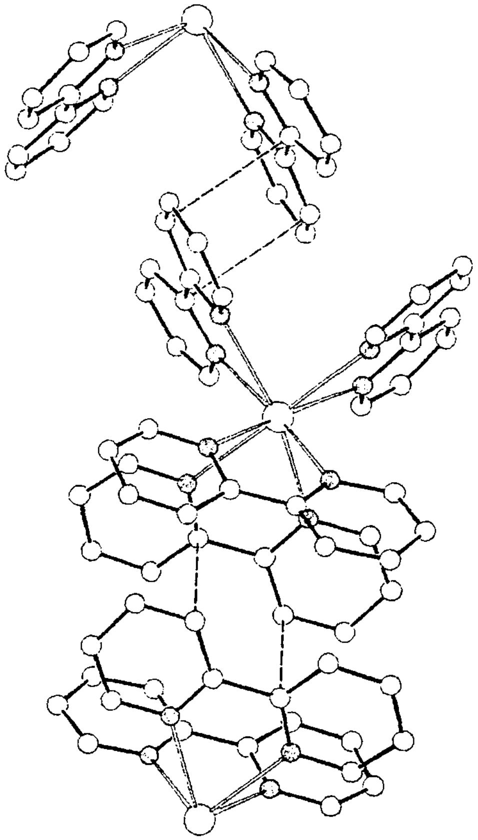

Fig. 4. One-dimensional polymer chain in the crystal of Sm(bpy)$_4$ formed by contacts between the bpy ligands.

Table 3. Intermolecular contacts (*d*) in the crystals of the Ln(bpy)$_4$ complexes (Ln = Sm, Eu, Yb, or Lu) and in the [Li(THF)$_4$][Lu(bpy)$_4$] complex

Complex	Distance	*d*/Å	Molecular packing in the crystal
Sm(bpy)$_4$	C(24)...C(26′)	3.247	Polymer chains
	C(26)...C(24′)	3.247	
Eu(bpy)$_4$	C(24)...C(26′)	3.312	Polymer chains
	C(26)...C(24′)	3.312	
Yb(bpy)$_4$	C(28)...C(36′)	3.302	Polymer chains
	C(29)...C(38′)	3.241	
Lu(bpy)$_4$	C(14)...C(18′)	3.326	Pairs
	C(18)...C(14′)	3.326	
	C(17)...C(17′)	3.155	
[Li(THF)$_4$][Lu(bpy)$_4$]	—	—	Isolated molecules

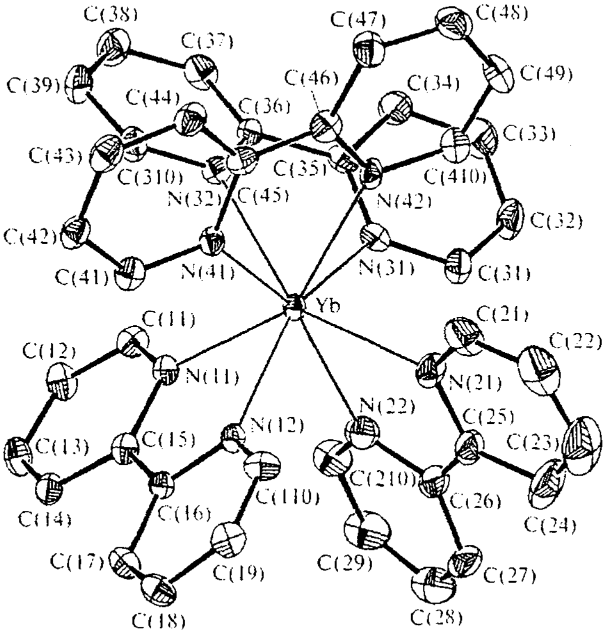

Fig. 5. Molecular structure (ORTEP[20]) of the Yb(bpy)$_4$ complex (thermal ellipsoids with the 40% probability). The hydrogen atoms are omitted.

ligands of the adjacent molecules resulting in the equalization of the geometric parameters of these molecules and, as a consequence, in the appearance of the twofold rotation axis on which the metal atom is located. Previously,[4] we have observed delocalization of one electron over two bpy ligands in the $LaI_3(bpy)_2(DME)$ complex. Apparently, it is these strong intermolecular interactions that are responsible for the low solubility of the La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb complexes.

In the compound $Yb(bpy)_4 \cdot 0.5THF$, the nitrogen atoms of the ligands form a distorted dodecahedron about the metal atom (Fig. 5). The Yb—N distances in four ligands (Table 2), though they lie in the range typical of trivalent ytterbium compounds, have different values. In three of the ligands, these distances have close values, but they are almost 0.1 Å shorter than this distance in the fourth ligand (Table 2). In addition, the torsion angle in the latter ligand is unusually large (20°) compared to the other three angles (from 1 to 9°). This molecular geometry corresponds more closely to the charge distribution described by the formula $[Yb^{3+}(bpy^{\cdot-})_3(bpy^0)]$. Two short C—C contacts exist between the bpy ligands of the adjacent molecules (C(29)...C(38′) is 3.24 Å and C(28)...C(36′) is 3.30 Å (Table 3), resulting in the formation of polymer chains in the crystal (Fig. 6). However, the mutual arrangement of the bpy ligands of the adjacent molecules in this case differs from those observed in the samarium and europium complexes and, apparently, does not provide electron delocalization in the chain formed. Probably, the observed mutual arrangement of the molecules in the crystal of $Yb(bpy)_4$ results exclusively from the requirement for the minimization of the energy of the crystal lattice. The fact that the intermolecular contacts in $Yb(bpy)_4$ are weak is also supported by the high solubility of the complex.

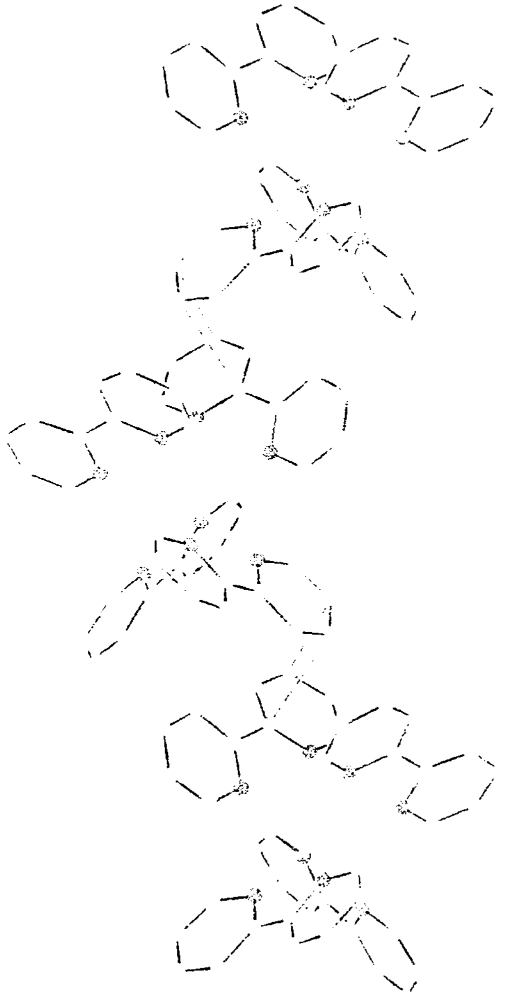

Fig. 6. One-dimensional polymer chain in the crystal of $Yb(bpy)_4$ formed by contacts between the bpy ligands.

According to the X-ray diffraction data, the coordination environment about the lutetium atom in the $Lu(bpy)_4 \cdot 2THF$ complex (Fig. 7) is a distorted dodecahedron formed by eight nitrogen atoms of four bpy ligands. In the crystal, there are short intermolecular C...C contacts (C(14)...C(18′) and C(18)...C(14′) are 3.33 Å and C(17)...C(17′) is 3.16 Å; Fig. 8) through which the molecules are linked in discrete pairs unlike the polymer chains observed in the Sm, Eu, and Yb complexes (Table 3). It should be noted that the average

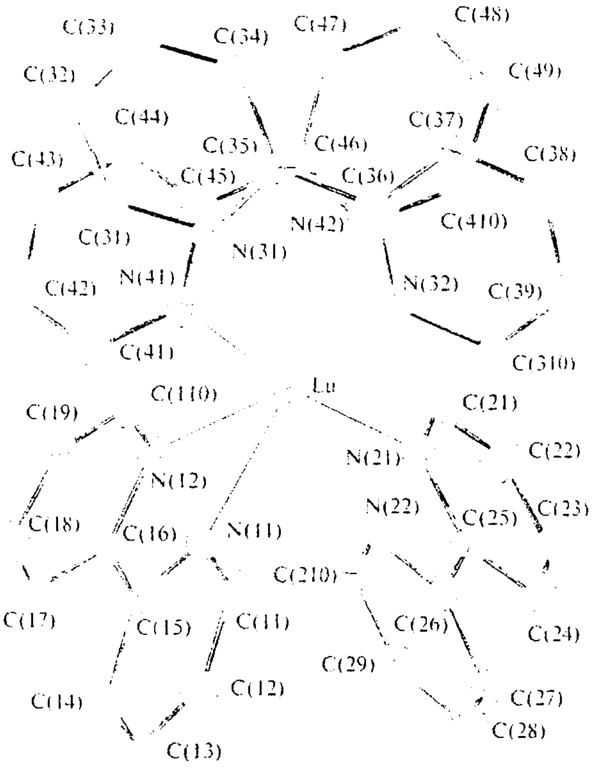

Fig. 7. Molecular structure (ORTEP[20]) of the $Lu(bpy)_4$ complex (thermal ellipsoids with the 40% probability). The hydrogen atoms are omitted.

Fig. 8. Intermolecular contacts in the crystal of $Lu(bpy)_4$.

Lu—N distance (2.434 Å) agrees well (taking into account the difference in the ionic radii of Sm^{III}, Eu^{II}, and Lu^{III}) with the Sm—N and Eu—N distances. The observed change in the Lu—N bond lengths (2.376 and 2.372 Å for the first ligand, 2.367 and 2.425 Å for the second ligand, 2.429 and 2.414 Å for the third ligand, and 2.529 and 2.559 Å for the fourths bpy ligand) is in better agreement with the scheme $[Lu^{3+}(bpy^{\cdot -})_3(bpy^0)]$ than with the scheme $[Lu^{3+}(bpy^{2-})(bpy^{\cdot -})(bpy^0)]$ containing the dianionic ligand. However, it should be noted that the molecular packing in the crystals of homoleptic compounds analogous to those under consideration can substantially affect the geometric parameters, thus hindering their interpretation.

Similar Lu—N bond lengths (the average value is 2.437 Å) are observed in the ionic complex $[Li(THF)_4][Lu(bpy)_4]$ (Fig. 9). This compound was prepared from $LuCl_3$ and Li(bpy) according to a procedure reported previously.[2] The lutetium atom is coordinated by eight nitrogen atoms, which form a virtually ideal (unlike $Lu(bpy)_4$) dodecahedron. The Lu—N distances are in the range of 2.413—2.462 Å (Table 2). Since all four bpy ligands bear identical charges, no noticeable differences in their geometry are observed. The lithium cation is coordinated by four THF molecules. In the crystal of $[Lu(bpy)_4][Li(THF)_4]$, significant intermolecular contacts are absent.

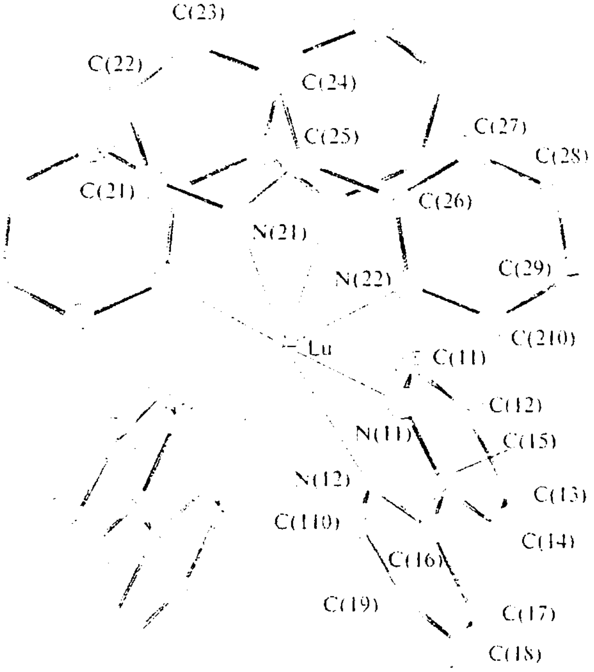

Fig. 9. Molecular structure (ORTEP[20]) of the $[Lu(bpy)_4]^-$ anion (thermal ellipsoids with the 40% probability). The hydrogen atoms are omitted.

Therefore, the results of IR and ESR spectroscopy, magnetic measurements, and X-ray diffraction study suggest that the bipyridyl complexes of rare-earth elements of the $Ln(bpy)_4$ series can exist in two major forms, *viz.*, as $[Ln^{3+}(bpy^{2-})(bpy^{\cdot -})(bpy^0)]$ (**A**) and $[Ln^{3+}(bpy^{\cdot -})_3(bpy^0)]$ (**B**). The europium complex contains the divalent metal atom, *viz.*, $[Eu^{2+}(bpy^{\cdot -})_2(bpy^0)_2]$. The simultaneous presence of the dianion and the neutral ligand in the molecule (form **A**) is attributable to a considerable gain in the energy in the case of formation of the $[XLn^{2+}][B^{2-}]$ moiety. In the crystalline state, most of the complexes are characterized by intermolecular electron interactions.

Experimental

All syntheses of the compounds and subsequent operations were carried out *in vacuo* with the use of Schlenk tubes. The triiodides $LnI_3(THF)_3$ (Ln = La, Ce, Pr, or Nd) were prepared by the reactions of the corresponding metals with iodine or CH_2I_2 in THF; Gd and Tb triiodides were prepared by the reactions of the corresponding metals with iodine in DME and recrystallized from THF. Tris[bis(trimethylsilyl)amides] of Dy, Ho, Er, Yb, and

Lu were synthesized according to a procedure reported previously[14] and purified by sublimation *in vacuo*. The diiodides of Sm, Eu, and Yb were prepared according to a known procedure;[15] $TmI_2(DMF)_3$ was synthesized according to a procedure reported previously.[16] Tetrahydrofuran and 1,2-dimethoxyethane were dried and kept over sodium benzophenone ketyl and were taken for the reactions by condensation *in vacuo* immediately before use. The IR spectra were recorded on a Specord-M80 spectrometer. The samples were prepared as Nujol mulls and placed as films between KBr glasses. The ESR spectra were measured on a Bruker ESR 200D-SCR instrument (9.35 GHz).

Tetrakis(2,2´-bipyridyl)samarium. A solution of bipyridyllithium (which was prepared *in situ* from lithium (11.4 mg, 1.64 mmol) and 2,2´-bipyridine (0.64 g, 4.1 mmol)) in THF (30 mL) was added to a solution of $SmI_2(THF)_2$ (0.45 g, 0.821 mmol) in THF (20 mL). The reaction mixture was stirred for 10 min with slight heating (~50 °C) and then the finely crystalline precipitate of $Sm(bpy)_4$ that formed was filtered off. The precipitate was washed with THF (2×10 mL) and dried *in vacuo* to obtain $Sm(bpy)_4$ as a black finely crystalline powder in a yield of 0.53 g (83.3%). Found (%): Sm, 19.47. $C_{40}H_{32}N_8Sm$. Calculated (%): Sm, 19.40. IR (KBr, Nujol mulls): 1590 w, 1570 w, 1550 w, 1540 m, 1515 v.s, 1500 v.s, 1470 v.s, 1410 s, 1345 s, 1310 w, 1290 w, 1275 m, 1255 m, 1220 w, 1205 s, 1160 m, 1150 s, 1080 m, 1030 w, 1020 w, 990 w, 970 v.s, 940 sh, 760 m, 740 s, 720 s, 690 w, 640 m, 605 w, 450 w, 440 w. The magnetic susceptibility $\chi(293\ K) = 3931 \cdot 10^{-6}\ cm^3\ mol^{-1}$, $\mu_{eff} = 3.0\ \mu B$. The La, Ce, Pr, Nd, Gd, and Tb complexes were prepared analogously from the corresponding triiodides. Their IR spectra are identical. Since the samarium complex formed in the reaction occurred as an insoluble finely crystalline powder, sufficiently large single crystals of $Sm(bpy)_4$ suitable for X-ray diffraction analysis were prepared according to the following procedure. A lithium wire (27.1 mg, 3.898 mmol), which was made to sink to the bottom of a tube with the use of a glass sinker, $SmI_2(THF)_2$ (1.05 g, 1.915 mmol), and 2,2´-bipyridine (1.55 g, 9.93 mmol) were placed into Schlenk tube. Then THF (40 mL) was added and the mixture was kept without stirring for two weeks. Large needle-like crystals were isolated after repeated decantation from the finely crystalline powder.

Tetrakis(2,2´-bipyridyl)europium. A solution of bipyridyllithium (which was prepared *in situ* from lithium (14 mg, 2.02 mmol) and 2,2´-bipyridine (1.05 g, 6.73 mmol)) in THF (30 mL) was added to a solution of $EuI_2(THF)_2$ (0.55 g, 1.0 mmol) in THF (25 mL). The reaction mixture was stirred for 10 min and the black powder that formed was filtered off and dried *in vacuo* to obtain $Eu(bpy)_4$ as black microcrystals in a yield of 0.72 g (92%). Found (%): Eu, 19.72. $C_{40}H_{32}N_8Eu$. Calculated (%): Eu, 19.56. IR (KBr, Nujol mulls): 1600 m, 1570 m, 1540 w, 1510 w, 1490 v.s, 1480 s, 1420 s, 1320 w, 1275 s, 1265 s, 1200 m, 1170 w, 1160 m, 1150 s, 1110 w, 1085 w, 1050 w, 1020 m, 1010 m, 990 w, 950 s, 900 w, 765 s, 750 m, 720 s, 690 m, 640 w, 605 w, 450 w, 430 m, 420 w. The magnetic susceptibility $\chi(293\ K) = 26211 \cdot 10^{-6}\ cm^3\ mol^{-1}$, $\mu_{eff} = 7.84\ \mu B$. Single crystals of $Eu(bpy)_4$ suitable for X-ray diffraction study were prepared as described above for $Sm(bpy)_4$.

Tetrakis(2,2´-bipyridyl)thulium. A solution of bipyridyllithium (which was prepared *in situ* from lithium (13.1 mg, 1.87 mmol) and 2,2´-bipyridine (0.58 g, 3.72 mmol)) in DME (30 mL) was added to a solution of $TmI_2(DME)_3$ (0.64 g, 0.932 mmol) in DME (20 mL). At the instant the reagents were mixed, the mixture turned brown-red. After 1 h, the solution was decanted from the black crystals of $Tm(bpy)_4$ (0.4 g, 74%) that formed. The crystals were washed with cold DME (3×7 mL). Found (%): Tm, 21.27. $C_{40}H_{32}N_8Tm$. Calculated (%): Tm, 21.28. IR (KBr, Nujol mulls): 1600 w, 1555 w, 1545 m, 1480 v.s, 1435 s, 1415 m, 1310 w, 1295 s, 1275 s, 1260 s, 1210 s, 1170 m, 1150 s, 1120 m, 1085 m, 1060 w, 1020 m, 1000 m, 950 v.s, 760 w, 750 w, 725 v.s, 680 m, 640 m, 600 w, 455 m, 425 m. The magnetic susceptibility $\chi(293\ K) = 29444 \cdot 10^{-6}\ cm^3\ mol^{-1}$, $\mu_{eff} = 8.34\ \mu B$. Oxidation of $Tm(bpy)_4$ with atmospheric oxygen (24 h) afforded 2,2´-bipyridine (89%), which was identified by ^1H NMR spectroscopy.

Tetrakis(2,2´-bipyridyl)ytterbium. A solution of bipyridyllithium (which was prepared *in situ* from lithium (55.2 mg, 7.95 mmol) and 2,2´-bipyridine (2.458 g, 15.76 mmol)) in THF (30 mL) was added to a solution of $YbI_2(THF)_2$ (2.25 g, 3.94 mmol) in THF (40 mL) after which the mixture turned dark-brown. After 24 h, the solution was decanted from the crystals of the $Yb(bpy)_4$ complex that formed (1.78 g, 57%). The crystals were washed with cold DME (3×7 mL). The remaining solution was concentrated to obtain additionally 0.67 g of the complex. The total yield was 78%. Found (%): Yb, 20.69. $C_{40}H_{32}N_8Yb \cdot 0.5THF$. Calculated (%): Yb, 20.75. IR (KBr, Nujol mulls): 1600 w, 1555 w, 1545 m, 1480 v.s, 1435 s, 1415 m, 1310 w, 1295 s, 1275 s, 1260 s, 1210 s, 1170 m, 1150 s, 1120 m, 1085 m, 1060 w, 1020 m, 1000 m, 950 v.s, 760 w, 750 w, 725 v.s, 680 m, 640 m, 600 w, 455 m, 425 m. The magnetic susceptibility $\chi(293\ K) = 9211 \cdot 10^{-6}\ cm^3\ mol^{-1}$, $\mu_{eff} = 4.64\ \mu B$.

Tetrakis(2,2´-bipyridyl)erbium. A solution of bipyridyllithium (which was prepared *in situ* from lithium (53.8 mg, 7.75 mmol) and 2,2´-bipyridine (2.0 g, 12.76 mmol)) in THF (30 mL) was added to a solution of $[(Me_3Si)_2N]_3Er$ (1.66 g, 2.56 mmol) in THF (20 mL). After 4 h, the solution was decanted from the crystals of $Er(bpy)_4$ (0.4 g, 74%) that formed. Found (%): Er, 20.11. $C_{40}H_{32}N_8Er \cdot 0.5THF$. Calculated (%): Er, 20.19. IR (KBr, Nujol mulls): 1600 w, 1555 w, 1545 m, 1480 v.s, 1435 s, 1415 m, 1310 w, 1295 s, 1275 s, 1260 s, 1210 s, 1170 m, 1150 s, 1120 m, 1085 m, 1060 w, 1020 m, 1000 m, 950 v.s, 760 w, 750 w, 725 v.s, 680 m, 640 m, 600 w, 455 m, 425 m. The magnetic susceptibility $\chi(293\ K) = 44563 \cdot 10^{-6}\ cm^3\ mol^{-1}$, $\mu_{eff} = 10.22\ \mu B$. After hydrolysis of the complex and extraction of the products with diethyl ether, free 2,2´-bipyridine was isolated (in 94% yield), which was identified by ^1H NMR spectroscopy.

The Dy, Ho, and Lu complexes were prepared analogously from the corresponding bis(trimethylsilyl)amides. Unlike the Dy, Ho, Er, Tm, and Yb complexes, the crystals of the $Lu(bpy)_4$ complex contain two THF molecules of solvation per molecule of the complex. Found (%): Lu, 18.43. $C_{40}H_{32}N_8Lu \cdot 2THF$. Calculated (%): Lu, 18.54.

X-ray diffraction study of the $Ln(bpy)_4$ complexes. X-ray diffraction data sets for the single crystals of the $Sm(bpy)_4$, $Lu(bpy)_4$, $Eu(bpy)_4$, and $[Li(THF)_4][Lu(bpy)_4]$ complexes were collected on an Enraf-Nonius CAD 4 diffractometer (Mo-Kα radiation, graphite monochromator, ω-2θ scanning technique) at 163 K. The unit cell parameters were determined with the use of 25 reflections. In the course of X-ray diffraction data collection, no destruction of the crystals was observed. Absorption was ignored. The X-ray diffraction data for $Yb(bpy)_4$ were collected on a Siemens SMART CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω scanning technique) at 173 K. The unit cell parameters were determined using 7524 reflections. Absorption corrections were applied with the use of the SADABS program[17] (max/min transmission was 0.6999/0.4681). The structures were solved by direct methods with the use of the SHELXS86 program package.[18] The subsequent refinement was carried out by the full-matrix least-squares method based on F^2 using the SHELXL93 program package.[19] All nonhydrogen atoms (except for some disordered molecules of solvation in

Table 4. Crystallographic data and details of X-ray data collection and refinement for the Sm(bpy)$_4$, Eu(bpy)$_4$, Yb(bpy)$_4$ · (THF)$_{0.5}$, Lu(bpy)$_4$ · (THF)$_2$, and [Li(THF)$_4$][Lu(bpy)$_4$] complexes

Parameter	Sm(bpy)$_4$	Eu(bpy)$_4$	Yb(bpy)$_4$ · (THF)$_{0.5}$	Lu(bpy)$_4$ · (THF)$_2$	Lu(bpy)$_4$ (ionic)
Molecular formula	$C_{40}H_{32}N_8Sm$	$C_{40}H_{32}EuN_8$	$C_{42}H_{36}N_8O_{0.5}Yb$	$C_{48}H_{48}LuN_8O_2$	$C_{56}H_{64}LiLuN_8O_4$
Mol. weight	775.10	776.71	833.83	943.91	1095.06
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*C*2/*c* (No.15)	*C*2/*c* (No.15)	*Pcan* (No.60)	*P*21/*c* (No.14)	*C*2/*c* (No.15)
a/Å	13.326(2)	13.582(3)	18.139(4)	12.483(3)	19.878(5)
b/Å	13.557(3)	13.558(4)	19.097(3)	16.720(3)	17.620(2)
c/Å	17.209(8)	17.389(4)	20.351(3)	20.187(5)	16.671(3)
β/deg	96.30(2)	97.37(2)	90	101.56(2)	119.92(2)
V/Å^3	3090(2)	3175.5(13)	7050(2)	4128(2)	5061(2)
Z	4	4	8	4	4
d_{calc}/g cm^{-3}	1.666	1.625	1.571	1.519	1.437
μ/mm^{-1}	1.863	1.927	2.698	2.347	1.928
F(000)	1560	1552	3344	1904	2236
Crystal dimension/mm	0.27×0.19×0.15	0.25×0.10×0.08	0.32×0.16×0.12	0.35×0.30×0.06	0.25×0.15×0.10
Scan range/deg	$2.15 \le \theta \le 23.94$	$2.13 \le \theta \le 23.93$	$1.55 \le \theta \le 27.50$	$1.59 \le \theta \le 22.48$	$1.65 \le \theta \le 22.45$
Reflections measured/observed	2615/2405	2644/2474	49850/8096	5784/5375	3517/3285
GOOF (F^2)	1.047	1.017	1.029	1.071	1.052
R_1/wR_2 ($I > 2\sigma(I)$)	0.0310/0.0700	0.0342/0.0725	0.0558/0.1136	0.0422/0.0975	0.0344/0.0725
R_1/wR	0.0491/0.0838	0.0589/0.0824	0.1201/0.1443	0.0764/0.1326	0.0568/0.0817
Residual electron density /e · Å^{-3}, max/min	0.613/−0.608	0.807/−0.432	3.931/−2.251	1.270/−1.931	0.647/−0.564

Yb(bpy)$_4$) were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The crystallographic data and the details of X-ray diffraction study and refinement are summarized in Table 4. The complete tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

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