

Synthesis and ESR-characterization of radical anion complexes of lanthanum. X-ray crystal structure of the mixed bipy, bipy⁻¹ complex of lanthanum(III) [LaI₂(bipy)(bipy)(DME)]: evidence for an inter-ligand charge transfer¹

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Abstract

The reaction of [LaI₂(THF)₃][C₁₀H₈] with excess of 2,2'-bipyridine (bipy) in DME or THF results in the formation of mixed radical anion ligand/neutral ligand complexes [LaI₂(bipy(0))(bipy(-1))(L)_n] with (L)_n = (DME) (1) and (THF)₂ (2), whereas a reactant ratio of 1:2 generates the mono-bipy complex [LaI₂(bipy)(DME)₂] (3). ESR and IR spectroscopic data show a fast shuttle electron transfer (SIET) between the neutral and the radical anion of bipy in 1 and 2. The X-ray structure shows 1 to be monoclinic, space group *P*2/*c*, *Z* = 2, with *a* = 10.0320(12), *b* = 9.7510(11), *c* = 16.296(8) Å, β = 90.43(2)°. The structure was refined to *R* = 0.0360 for 2562 observed reflections (*I* > 2σ(*I*)). It shows the lanthanum atom eight-coordinated by two iodine, two oxygen and four nitrogen atoms.

Keywords: Lanthanum; 2,2'-Bipyridyl complexes; X-ray structure; ESR spectra

1. Introduction

Various complexes of transition and non-transition metals with radical anions as ligands have been synthesized and studied before now [2,3], but only very few of them are known for the lanthanoid elements. Herzog et al. [4] and some years later Feistel and Mathai [5] reported the first homoleptic 2,2'-bipyridyl complexes, in which the presence of the [bipy]⁻¹ anion as a ligand was established on the basis of magnetic measurements. Later on, complexes containing radical anions of *ortho*-benzoquinone [6], diazabutadiene (dad) [7], bipyridine [8], anthracene [9], and the metal-centred radical anion [(C₅H₅)V(C₁₀H₈)]⁻ [10] have been obtained.

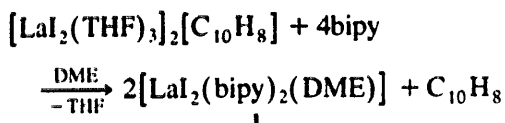
Our interest in the synthesis and investigation of radical anion complexes of the lanthanides was motivated specifically by the formerly observed unusual magnetic behaviour of some of the compounds cited above. For example, it could be shown that the homoleptic complexes [Eu(bipy)₄] [5] and Yb(dad)₃ [7d] showed decreasing values of the magnetic moment at low temperature. In the first case the authors attributed the low magnetic moment of the europium complex to an antiferromagnetic exchange coupling between the 4f electrons of Eu²⁺ and two unpaired electrons on the ligands. In the second case the spin balance has been rationalized in terms of [Yb(dad)₃] existing as a Yb(III) complex [Yb³⁺(dad⁻)₃] above 100 K and as a Yb(II) complex [Yb²⁺(dad⁻)₂(dad)] below this temperature. The calculated magnetic moments of 5.5 and 2.45 BM respectively, are in agreement with the observed magnitude. This paper reports the synthesis and ESR spectroscopic studies of three lanthanum(III) complexes containing the 2,2'-bipyridyl radical anion as ligand as well as the X-ray crystal structure analysis of one of them.

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2. Formation and properties

The binuclear lanthanum(III) complex $[\text{LaI}_2(\text{THF})_3]_2[\text{C}_{10}\text{H}_8]$ [11] containing a bridging naphthalene dianion reacts with an excess of 2,2'-bipyridine (bipy) in dimethoxyethane (DME) with formation of black $[\text{LaI}_2(\text{bipy})_2(\text{DME})]$ (**1**), which is insoluble in DME, diethyl ether, toluene and aliphatic hydrocarbons but slightly soluble in THF under exchange of the DME and formation of $[\text{LaI}_2(\text{bipy})_2(\text{THF})_2]$ (**2**). Both compounds lose DME or THF, respectively, on heating to 150°C for 3 h.



Both complexes have to be formulated as $[\text{La}^{3+}(\text{I}^-)_2(\text{bipy}^-)(\text{bipy})(\text{L})_n]$ containing one neutral and one radical anionic bipy ligand each. This is proved by the IR spectrum of **1** (Fig. 1), which contains the bands of both the neutral (1595, 1570, 1420, 1260, 1090, 765, 625 cm^{-1}) and the anionic bipy ligand (1545, 1515, 1500, 1440, 1295, 1280, 1225, 1195, 1150, 1120, 770, 745, 685, 640, 610 cm^{-1}) together with bands at 1030 and 840 cm^{-1} for the coordinated DME. The IR spectrum of **2** is almost the same except that the DME bands are exchanged for bands at 1010 and 880 cm^{-1} for THF. The magnetic moment of 1.6 BM for both complexes is very close to the free spin-only value and unambiguously indicates that the unpaired electron

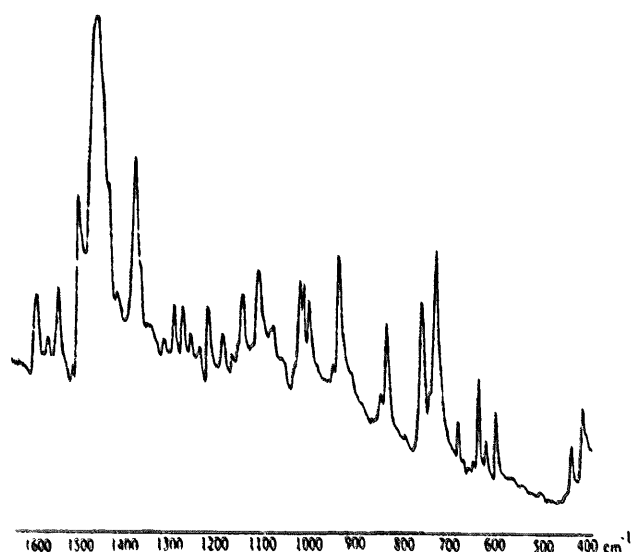
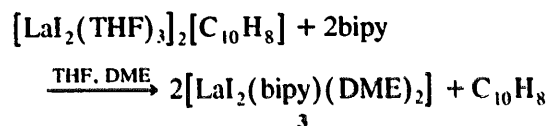


Fig. 1. IR spectrum of $[\text{LaI}_2(\text{bipy})_2(\text{DME})]$ between 1600 and 400 cm^{-1} .

is in a ligand-localized orbital. This is in accord with the commonly accepted opinion that La(II) complexes are not stable due to their high reduction potential (below -2.5 V). The UV-vis spectrum of **2**, diluted in THF, shows two strong absorptions at 392 and 490 nm.

The reaction of $[\text{LaI}_2(\text{THF})_3]_2[\text{C}_{10}\text{H}_8]$ in THF with only the 1.5 molar amount of bipy in DME gave dark red crystals of $[\text{LaI}_2(\text{bipy})(\text{DME})_2]$, which show the intense IR absorption bands of the anionic bipy ligand at 1500, 1440, 1200, 1020, 770, 740 and 650 cm^{-1} besides the DME bands at 1050 and 860 cm^{-1} .



The complexes **1–3** reveal the high reducing character due to the presence of $[\text{bipy}^{-1}]$ ($\text{bipy}/\text{bipy}^{-1} - 2.0$ V) [2]. When the reaction of **2** with 3,6-di-*tert*-butyl-*o*-benzoquinone was monitored by ESR spectroscopy at 20°C, we found that **2** was immediately converted to the 3,6-di-*tert*-butyl-*o*-benzosemiquinone (SQ) complex $[\text{LaI}_2(\text{SQ})(\text{THF})_3]$ (**4**), which could be identified by its ESR spectrum; this shows ten lines ($A_{\text{La}} = A_{\text{H}} = 0.36$ mT). **4** was isolated in crystalline form and its characterization will be published elsewhere. To investigate the reactivity of **2** towards metallocenes, **2** was allowed to react with $(\text{C}_5\text{H}_5)_2\text{V}$ in THF. The initial ESR signals for **2** and $(\text{C}_5\text{H}_5)_2\text{V}$ rapidly disappeared and a new signal for $[\text{V}(\text{bipy})_2]$ (octet, $A_{\text{V}} = 8.35$ mT) [12] was observed. **1**, **2** and **3** are immediately hydrolyzed with formation of lanthanum hydroxide and bipy. It is interesting to observe that hydrolysis of **1**, **2** and **3** does not cause hydrogenization of bipy, but results in the formation of the free ligand. In contrast, naphthalene complexes of the lanthanoids containing C_{10}H_8 dianions give, under the same conditions, a mixture of 1,2- and 1,4-dihydronaphthalene in quantitative yields [11], but the reaction of lanthanoid(0) arene complexes with substrates containing acidic hydrogens did not cause the hydrogenization of the arene ligands [13].

3. ESR spectra

In general the ESR spectra of the complexes **1–3** give highly symmetric signals at room temperature. In solution, all three complexes show coupling of the unpaired electron to the lanthanum nucleus and no broadened signals with shifted g -values could be observed in the solid samples.

Because **1** is insoluble in DME its ESR spectrum was instantly recorded after treating of the starting materials before the complex could crystallize. The resulting ESR spectrum of **1** at room temperature exhibits hyperfine

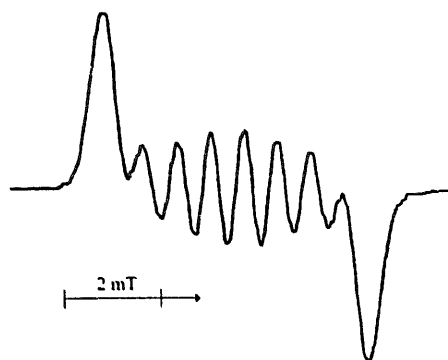


Fig. 2. ESR spectrum of $[\text{LaI}_2(\text{bipy})(\text{bipy}^-)(\text{DME})]$ in DME solution at 293 K.

splitting (eight lines) due to coupling of the unpaired $e_{\text{t}}^{\text{electron}}$ to the lanthanum atom ^{139}La ($A_{\text{La}} = 0.74$ mT, $g = 2.0031$) (Fig. 2). A hyperfine coupling to ^1H and ^{14}N was not observed due to the broadening of the signal. Crystalline **1** gives a spectrum with a narrow line ($\Delta H = 1$ mT, $g = 2.0030$), which is typical of a system with ligand-orbital electron localization. No broad line with a shifted g -value was observed. Recently, we found a distinctly different ESR behaviour for the tetra-decker complex $[\text{CpV}(\text{C}_{10}\text{H}_8)_2\text{Eu}(\text{THF})(\text{DME})]$ [10]. In solution this complex shows an ESR signal for the vanadium-centred radical anion $[\text{CpV}(\text{C}_{10}\text{H}_8)]^-$ ($A_{\text{V}} = 4.5$ mT, $g = 2.0$). Solid $[\text{CpV}(\text{C}_{10}\text{H}_8)_2\text{Eu}(\text{THF})(\text{DME})]$ gives a spectrum with a clearly stated anisotropy and substantial shift of the g -value ($g_{\perp} = 1.6$, $g_{\parallel} = 3.19$, $g_{\text{eff}} = 2.65$). Therefore a redox isomerization was suggested for this complex, which exists in solution as ions $[\text{Eu}]^{2+}$ and $[\text{CpV}(\text{C}_{10}\text{H}_8)]^-$, whereas in the solid state it can be considered as a complex of neutral $[\text{CpV}(\text{C}_{10}\text{H}_8)]$ ligands with formally zero-valent europium. A similar approach has been used earlier for the explanation of the ESR data of some diimine complexes of ruthenium(II) [14].

$[\text{LaI}_2(\text{bipy})_2(\text{THF})_2]$ (**2**) shows, in THF solution at 293 K, an ESR signal with hyperfine structure because of coupling to ^{139}La , ^1H and ^{14}N ($A_{\text{La}} = 0.59$ mT, $A_{\text{H}} = 0.13$ mT (four equal protons) and $A_{\text{N}} = 0.13$ mT (four equal ^{14}N), $g = 2.0009$) (Fig. 3(a)). Considering the stoichiometry of this complex the unpaired electron must be delocalized between two bipy ligands, either with occupation of the overall molecular orbital of both bipy ligands, which should be completely equal in their electronic and geometric structure, or by a fast transfer between the HOMO of the radical anion $(\text{bipy})^-$ and the LUMO of the neutral ligand (bipy). The first model of delocalization of this unpaired electron is not in agreement with the IR data, because the IR spectra of **1** and **2** show absorptions for both the radical anion as well as the neutral bipy ligand. Therefore the most reasonable explanation of the ESR and IR spectroscopic data of **1** and **2** is a fast (in the ESR time scale) shuttle

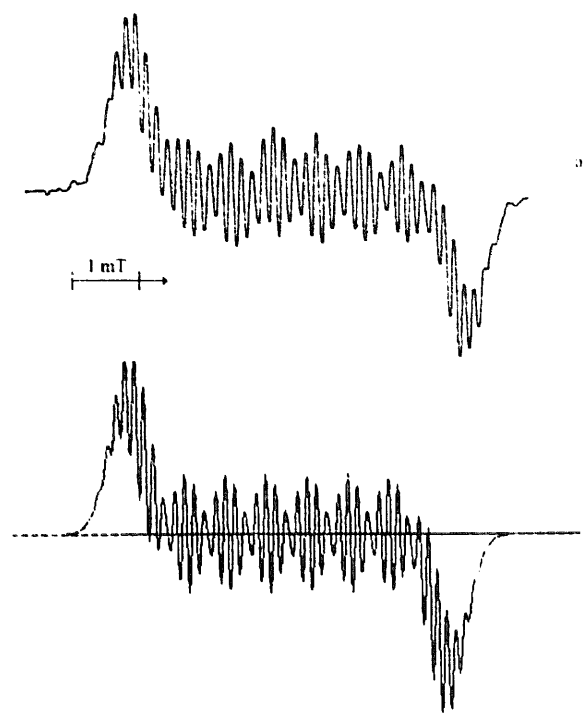


Fig. 3. (a) ESR spectrum of $[\text{LaI}_2(\text{bipy})(\text{bipy}^-)(\text{THF})_2]$ in THF solution at 293 K; (b) simulation of the ESR spectrum of $[\text{LaI}_2(\text{bipy})(\text{bipy}^-)(\text{THF})_2]$.

electron transfer (SIET) between the neutral (bipy) and the anion (bipy^-) . A similar ligand–ligand inter-valence charge transfer (IVCT) has been reported by Heath et al. [15]. They attribute a weak broad band near 4500 cm^{-1} in the IR spectrum of $[\text{Ru}(\text{II})(\text{bipy})_{3-n}(\text{bipy}^-)_n]^{2-n}$ ($n = 1$ or 2) to a bipy/bipy $^-$ IVCT transition. We found a weak band with a maximum at 6500 cm^{-1} in the near IR spectrum of a THF solution of **2**, which confirms the hypothesis of an SIET transition in this lanthanum bipy complex.

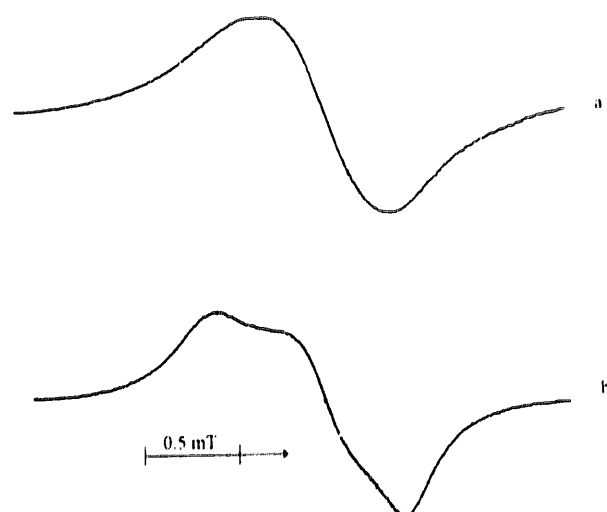


Fig. 4. ESR spectrum of $[\text{LaI}_2(\text{bipy})(\text{bipy}^-)(\text{THF})_2]$ in the solid state: (a) at 293 K; (b) after heating to 443 K for 3 h.

The crystalline **2** shows an ESR signal ($g = 2.0030$) similar to that of **1** (Fig. 4(a)). An ESR signal with a rhombic symmetry of the g -tensor ($g_1 = 2.0060$, $g_2 = 2.0028$, $g_3 = 2.004$, $g_{\text{eff}} = 2.0031$) (Fig. 4(b)) was observed after heating of **2** to 150°C for 3 h. When the heated sample is redissolved in THF, the initial ESR signal of **2** appears. Therefore, the coordination geometry of **2** does not change significantly at 150°C because the widths of the ESR signals and their g -factors are very similar before and after heating. The rhombic symmetry of the g -tensor in the ESR spectrum of the heated complex likely results from some deformation of the crystal structure.

When a THF solution of **2** was cooled to 150 K the hyperfine structure of the ESR signal to ^1H and ^{14}N disappeared but the coupling to lanthanum became significantly larger: $A_{\text{La}} = 0.87$ mT, $g = 2.0030$. This approaching of the parameters of this spectrum to that of **1** in DME at 293 K is likely a result of the changing coordination environment of lanthanum in **2** in solution at different temperatures. We predict lanthanum to be seven-coordinated in **2** in THF solution at 280–320 K ($[\text{LaI}_2(\text{bipy})_2(\text{THF})]$) and eight-coordinated at low temperature ($[\text{LaI}_2(\text{bipy})_2(\text{THF})_2]$). Owing to the intricacy of the hyperfine structure of this ESR signal of **2**, thermodynamic and kinetic aspects of the behaviour of this complex in solution, as well as the SET process, have not been studied until now.

To prove our interpretation of the ESR spectra of the lanthanum complexes containing both (bipy) and $(\text{bipy})^-$ ligands in solution, we investigated the ESR spectrum of $[\text{LaI}_2(\text{bipy})(\text{DME})_2]$ (**3**) which contains the bipy ligand only as a radical anion. **3** shows, in THF solution, an ESR signal with $A_{\text{La}} = 0.7$ mT, $A_{\text{N}} = A_{\text{H}} = 0.26$ mT (for 2N and for 2H), $g = 2.0015$ (Fig. 5), demonstrating significant evidence for the shuttle electron transfer in the bipy ligand mixed complexes of lanthanum, because in the case of a fast (in the ESR time scale) SIET transition the coupling of the unpaired electron to the ^1H and ^{14}N nuclei must be only half (in

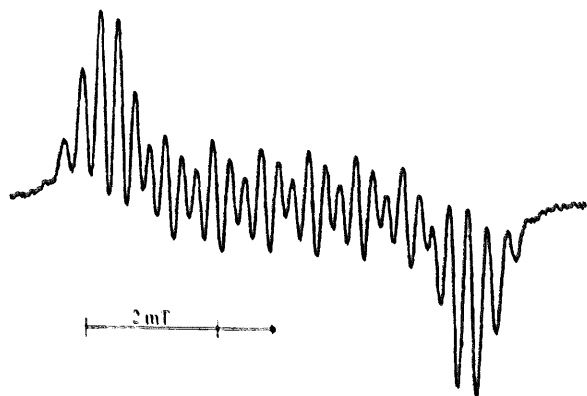


Fig. 5. ESR spectrum of $[\text{LaI}_2(\text{bipy})(\text{DME})_2]$ in THF solution.

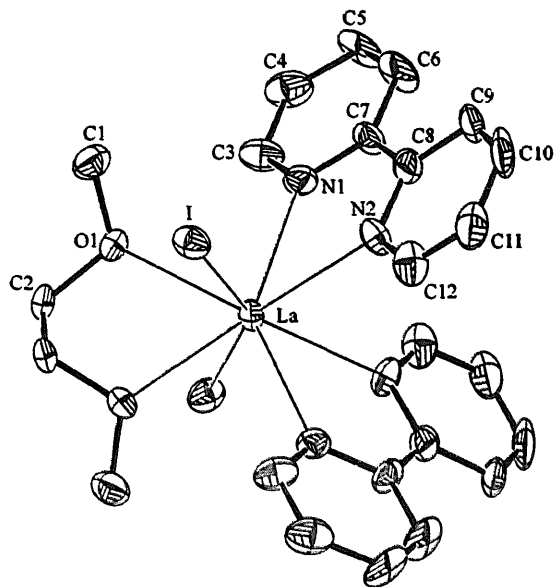


Fig. 6. ORTEP [21] projection of one molecule of $[\text{LaI}_2(\text{bipy})_2(\text{DME})]$ (**1**) (50% probability level) with numbering scheme. Hydrogen atoms are excluded for clarity.

size) than in the complex containing only $(\text{bipy})^-$ radical anions, which is exactly the case here.

4. Molecular structure of $[\text{LaI}_2(\text{bipy})_2(\text{DME})]$ (**1**)

In the solid state **1** crystallizes in discrete monomer units (Fig. 6). The La^{3+} cation is coordinated by two iodine anions, two oxygen atoms of the neutral DME ligand and four nitrogens of two bipy ligands, resulting in coordination number 8 for lanthanum in a distorted tetragonal antiprismatic environment with one bipy, one iodine and one oxygen atom on each side of the mirror plane (Fig. 7). Both bipy ligands are bonded in the same way to the lanthanum atom with equal $\text{La}-\text{N}$ distances of 2.591 ($\text{La}-\text{N}(1)$) and 2.599 Å ($\text{La}-\text{N}(2)$), which is in accordance with the IR and ESR spectroscopic results, indicating a shuttle electron transfer between lanthanum and two bipy ligands. These $\text{La}-\text{N}$ distances are comparable with the $\text{La}-\text{N}$ distances found in $[\text{La}(\text{bipy})_2]$ -

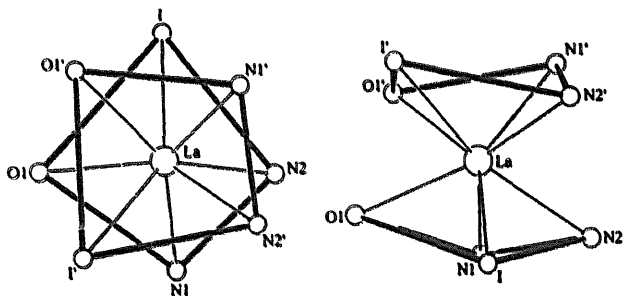


Fig. 7. The coordination sphere around La in $[\text{LaI}_2(\text{bipy})_2(\text{DME})]$ (**1**) showing the distorted tetragonal antiprismatic environment of the La^{3+} cation.

Table 1
Selected bond distances (Å) in **1** with estimated standard deviations in parentheses

Bond	Distance	Bond	Distance
La–N(1)	2.591(5)	C(5)–C(6)	1.360(13)
La–N(2)	2.599(5)	C(6)–C(7)	1.392(9)
La–I	3.2550(11)	C(7)–C(8)	1.457(10)
La–O(1)	2.612(4)	C(8)–C(9)	1.398(9)
N(1)–C(3)	1.332(9)	C(9)–C(10)	1.396(12)
N(1)–C(7)	1.368(8)	C(10)–C(11)	1.381(12)
N(2)–C(8)	1.363(8)	C(11)–C(12)	1.348(10)
N(2)–C(12)	1.354(9)	C(1)–O(1)	1.430(8)
C(3)–C(4)	1.391(10)	O(1)–C(2)	1.459(7)
C(4)–C(5)	1.393(14)	C(2)–C(2′)	1.496(13)

Symmetry transformations (′) used to generate equivalent atoms: $-x, y, 0.5-z$.

(NO₃)₃ (2.665 and 2.658 Å [16] and 2.68 and 2.47 Å [17]), but they are shorter than in lanthanoid complexes with one bipy ligand, like [Nd(OC^tBuCHC(O)^tBu)₃(bipy)] (2.723 and 2.744 Å [18], [Nd(OC(CF₃)CHC(O)C₄H₉S)₃(bipy)] (2.689 and 2.724 Å [19], and longer than in (C₅Me₅)₂Sm(bipy) (2.427 and 2.436 Å) [9] and [Yb(acac)₃(bipy)] (2.48 and 2.55 Å) [20].

The bipy ligands are planar with C–C distances in the range 1.348 to 1.398 Å, 1.457 Å for the distance between the connecting carbon atoms C(7) and C(8) and C–N distances between 1.332 and 1.368 Å, which is in accordance with the same distances in the other lanthanoid bipy complexes [9,16–20] but different from free bipyridine which has a significantly longer C–C distance of 1.49 Å for the connection of both pyridine rings [22], also an argument for a reduced bipy ligand with electron delocalization between the connected pyridine rings. The shortening of the distance C(7)–C(8) in **1** is only 0.033 Å compared with 0.058 Å in (C₅Me₅)₂Sm(bipy) [9], a Sm(III) complex which transfers one electron to only one bipy ligand.

The La–I distances (3.2550 Å) are 0.035 Å shorter than in [LaI₂(THF)₃]₂[C₁₀H₈] [11] and the La–O distances (2.612 Å) are in the expected range [10]. Selected

Table 2
Selected bond angles (°) in **1** with estimated standard deviations in parentheses

Atoms	Angle	Atoms	Angle
N(1)–La–N(2)	62.2(2)	I–La–O(1)	78.46(10)
N(1)–La–I	101.43(12)	I–La–I′	149.09(2)
N(2)–La–I	73.97(11)	I–La–O(1′)	75.54(10)
N(1)–La–O(1)	78.2(2)	O(1)–La–O(1′)	64.9(2)
N(2)–La–O(1)	124.8(2)	N(1)–La–I′	89.38(12)
N(1)–La–N(2′)	83.7(2)	N(2)–La–I′	135.51(11)
N(1)–La–N(1′)	138.8(2)	N(1)–La–O(1′)	142.9(2)
N(2)–La–N(2′)	69.7(2)	N(2)–La–O(1′)	144.49(14)

Symmetry transformations (′) used to generate equivalent atoms: $-x, y, 0.5-z$.

bond distances and angles for **1** are given in Tables 1 and 2.

5. Experimental

The complexes described below are extremely sensitive to moisture and air. Therefore, both the synthesis and subsequent manipulations of these compounds were conducted in vacuum lines with rigorous exclusion of air and water using Schlenk techniques. THF and DME were distilled from sodium benzophenone ketyl. [LaI₂(THF)₃]₂[C₁₀H₈] was prepared by the published procedure [10]. IR spectra were recorded as Nujol mulls with a Specord M-80 spectrometer, the ESR spectra using a Bruker ER 200D-SCR spectrometer (9.35 GHz).

5.1. [LaI₂(bipy)(bipy⁻)(DME)] (**1**)

A solution of 2,2′-bipyridine (0.8 g, 5.12 mmol) in 20 ml of DME was added to a suspension of 1.55 g (1.15 mmol) of [LaI₂(THF)₃]₂[C₁₀H₈] in 25 ml of DME with vigorous stirring. The original La complex dissolved gradually with formation of a brown solution. After 5 to 10 min of stirring, dark crystals precipitate from the solution. After 2 h storage the solution was decanted and the resulting crystalline product was rinsed twice with cold DME (2 × 10 ml) and dried in vacuum, yielding 0.8 g (80%) of dark brown, almost black crystals of **1**, which contain another molecule DME per molecule **1** in the crystals; 160°C (decomp.). IR (CsI, cm⁻¹): 1595, 1570, 1548, 1505, 1420, 1320, 1296, 1280, 1260, 1225, 1190, 1150, 1120, 1085, 1030, 1020, 1010, 945, 840, 765, 735, 685, 645, 625, 610, 450, 420. Magnetic susceptibility: $\chi_M(293\text{ K}) = 1080 \times 10^{-6}$ cgsu, $\mu_{\text{eff}} = 1.6$ BM. Anal. Found: La, 15.8. C₂₈H₃₆I₂LaN₄O₄ (1 · DME) Calc.: La, 15.95%.

5.2. [LaI₂(bipy⁻)(DME)₂] (**3**)

A solution of 2,2′-bipyridine (0.5 g, 3.2 mmol) in 20 ml of THF was added to a suspension of 2.7 g (2.0 mmol) of [LaI₂(THF)₃]₂[C₁₀H₈] in 20 ml of THF with vigorous stirring. The reaction mixture rapidly changed colour to red–brown. THF was removed in vacuo and the residue was dissolved in 35 ml of DME. After concentration of this solution to 10 ml and cooling to –10°C for 15 h, dark red crystals of **3** precipitated from the solution. Yield: 0.31 g (27%). IR: (CsI, cm⁻¹): 1500, 1440, 1200, 1120, 1050, 1020, 860, 770, 740, 650, 625. Anal. Found: La, 18.58; I, 34.93; bipy, 19.06. C₁₈H₂₈I₂LaN₂O₄ (**3**) Calc.: La, 19.05; I, 34.81; bipy, 21.42%.

5.3. X-ray crystal structure determination of **1**

Crystal data and other details of the structure determination are collected in Table 3. The crystals were

selected using a modified device, similar to that of Veith and Bärninghausen [23]. The crystals were mounted on a glass fibre and transferred to an Enraf-Nonius CAD-4 four-circle diffractometer, controlled by a PC fitted with a low-temperature equipment. The cell parameters were obtained from a least-squares treatment of the SET4 setting angles of 25 reflections in the range $18^\circ < 2\theta < 30^\circ$. Data were collected at 165(2) K. Reflections were scanned with variable scan time, depending on the intensity, with 2/3 of the time used for scanning the peak and 1/6 for measuring both the left and the right background. The intensities of three check reflections monitored after 2 h showed only statistical fluctuations during the course of the data collection. The crystal orientation was checked every 200 intensity measurements by scanning three reflections. A new orientation matrix was automatically calculated from a list of 25 recentered reflections in case the angular change was greater than 0.1%. All raw data were corrected for Lorentz, polarisation, and absorption effects and for decay (min. 0.9902, max. 1.0480) [24]. Refine-

Table 3
Crystal data and data collection parameters for 1

Formula	$C_{24}H_{26}I_2LaN_4O_2(C_4H_{10}O_2)$
Molecular weight ($g\ mol^{-1}$)	885.33
Crystal size (mm^3)	$0.1 \times 0.2 \times 0.2$
Temperature (K)	165(2)
Crystal system	monoclinic
Space group	$P2/c$ (No. 13)
Unit cell dimensions	
a (Å)	10.0320(12)
b (Å)	9.7510(11)
c (Å)	16.296(8)
β (°)	90.43(2)
V (Å ³)	1594.1(2)
Z	2
ρ_{calc} ($g\ cm^{-3}$)	1.844
μ_{calc} (mm^{-1})	3.314
$F(000)$	854
Diffractometer	Enraf-Nonius CAD-4
Radiation; wavelength (Å)	Mo K α , $\lambda = 0.71069$
Monochromator	graphite
Scan type, 2θ -range	ω , $4-50^\circ$
hkl range	$-11 \leq h \leq 11; 0 \leq k \leq 11;$ $0 \leq l \leq 19$
Measured reflections	2728
Unique reflections	2579 ($R_{int} = 0.0449$)
Data for refinement (n , after DIFABS)	2562
Refinement method	Full-matrix least-squares on F^2
Parameters refined (p)	175
Final R_1^a ($I > 2\sigma(I)$)	0.0360
Final wR_2^b	0.0994
Goodness-of-fit GOOF ^c	0.827
Largest difference peak and hole ($e\ \text{Å}^{-3}$)	0.995 and -0.846

$$^a R_1 = \frac{\sum (|F_o| - |F_c|) / \sum |F_o|}{\sum w |F_o|^2}^{1/2}; \quad ^b wR_2 = \frac{[\sum w (|F_o| - |F_c|)^2]}{\sum w |F_o|^2}^{1/2};$$

$$^c GOOF = [\sum w (|F_o| - |F_c|)^2 / (n - p)]^{1/2}.$$

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 1 with estimated standard deviations in parentheses.

Atom	x	y	z	U_{eq}^a
La	0	2283(1)	2500	23(1)
I	-2007(1)	1394(1)	1014(1)	33(1)
C(1)	1404(7)	-267(8)	1145(4)	40(2)
O(1)	1113(4)	23(4)	1985(3)	32(1)
C(2)	738(7)	-1206(6)	2439(4)	33(1)
N(1)	2022(5)	3217(6)	1693(3)	30(1)
C(3)	3192(6)	2581(8)	1765(4)	40(2)
C(4)	4374(7)	3076(11)	1436(5)	54(2)
C(5)	4290(8)	4323(11)	1022(5)	64(3)
C(6)	3105(8)	4985(10)	931(5)	54(2)
C(7)	1955(6)	4422(7)	1265(4)	32(1)
C(8)	651(7)	5068(7)	1183(4)	35(2)
N(2)	-353(5)	4470(5)	1613(3)	32(1)
C(9)	423(9)	5216(7)	687(4)	42(2)
C(10)	-869(10)	6736(7)	620(5)	54(2)
C(11)	-1873(8)	6151(8)	1078(4)	45(2)
C(12)	-1575(7)	5048(8)	1543(4)	41(2)
C(21)	5029(9)	8531(11)	703(6)	66(3)
O(2)	4712(11)	7871(14)	1424(7)	52(3)
C(22)	5326(19)	8683(22)	2086(11)	50(5)
O(2) ^b	5528(16)	8665(19)	3518(10)	81(4)
C(22) ^b	4807(23)	8140(27)	2843(12)	68(6)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b Defined disorder positions.

ments in the monoclinic space group $P2/c$ were successful. The position of the lanthanum atom was determined from a three-dimensional Patterson synthesis (SHELXS 86) [25]. The calculated difference Fourier map (SHELXL 93) [26] revealed all other missing non-hydrogen atoms. The asymmetric unit contains half an La complex and half an independent, disordered, DME solvent molecule. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated in idealized positions ($d_{CH} = 0.96$ Å, $U_{iso} = 0.08$ Å²). Scattering factors were taken from Refs. [27–29]. After all atoms had been added to the model of the structure, an empirical absorption correction was applied (DIFABS [30]; min. and max. correction factors 0.714, 1.409). Final residuals of least squares: $R = 3.6\%$. Data reduction was performed using the PC software package [24]. All other calculations were carried out using SHELXL 93 [26] and performed on an IBM Risk 6000 computer. The final atomic coordinates and equivalent isotropic displacement parameters are given in Table 4.

6. Supplementary material available

Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen,

Germany, on quoting the depository number CSD 404893, the names of the authors and the journal citation.

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