## Europium complexes with 1,2-bis(arylimino)acenaphthenes: a search for redox isomers

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Reduction of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian, 1) with metallic europium in 1,2-dimethoxyethane (dme) under anaerobic conditions gave a europium(II) complex with the acenaphthene-1,2-diimine dianion, (dpp-bian)Eu(dme)<sub>2</sub> (4), in high yield. Oxidation of complex 4 with triphenyltin chloride or 1,2-dibromostilbene afforded the corresponding halogen derivatives [(dpp-bian)Eu( $\mu$ -Cl)(dme)]<sub>2</sub> (5) and [(dpp-bian)Eu( $\mu$ -Br)(dme)]<sub>2</sub> (6). The molecular structures of complexes 4–6 were determined by X-ray diffraction. The magnetic moments of complexes 5 and 6 remain constant over a temperature range from 25 to 295 K; they are indicative of the presence of the europium(II) ion and the dpp-bian radical anion in both the complexes.

Key words: europium, diimines, molecular structure, magnetic properties.

Recently, we have observed for the first time redox isomerism for rare earth elements with acenaphthene-1,2-diimine derivatives of ytterbium as examples. Redox isomerism in metal complexes is impossible unless they contain two redox-active centers: a redox-active metal ion and a redox-active ligand (e.g., ortho-benzoquinone or 1,2-diimine). The phenomenon of redox isomerism is reversible intramolecular electron transfer metal-ligand under the action of external factors like a temperature change. This phenomenon has been often observed in organic derivatives of transition metals.<sup>1</sup> The thermally induced electron transfer in a rare-earth metal complex in solution, viz., in an ytterbium complex with 1,2-bis[(2,6diisopropylphenyl)imino]acenaphthene (dpp-bian, 1) and 1,2-dimethoxyethane (dme), [(dpp-bian)Yb(µ-Br)- $(dme)|_{2}$  (2), was first reported in 2009.<sup>2</sup> The interconversions of the isomers occurred between 278 and 368 K. In 2012,<sup>3</sup> we were the first to observe a true redox isomerization in the crystalline complex [(dpp-bian)Yb(µ-Cl)- $(dme)]_{2}$  (3) (Scheme 1, Fig. 1).

In the latter case, the redox isomerization is accompanied by simultaneous changes in several characteristics of complex 3: magnetic moment (Fig. 1), metal—ligand bond lengths, unit cell parameters, and heat capacity. Up to now,  $[(dpp-bian)Yb(\mu-Cl)(dme)]_2$  has been the only example of a rare-earth metal complex showing redox isomerism. Continuing a search for novel redox isomeric systems among lanthanide complexes, we studied another



lanthanide, *viz.*, europium, which also has two stable oxidation states (+2 and +3). Here we describe the synthesis, structures, and properties of new diimine derivatives

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Scheme 1



**Fig. 1.** Effective magnetic moment as a function of temperature (200-100 K) for complex **3** in the crystalline state:<sup>3</sup> (*1*) first cycle, (*2*) second cycle, and (*3*) third cycle.

of europium:  $(dpp-bian)Eu(dme)_2$  (4),  $[(dpp-bian)Eu(\mu-Cl)-(dme)]_2$  (5), and  $[(dpp-bian)Eu(\mu-Br)(dme)]_2$  (6).

## **Results and Discussion**

Reduction of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian, 1) with excess europium metal (small lumps) in 1,2-dimethoxyethane by heating under anaerobic conditions gave the complex (dpp-bian)- $Eu(dme)_2$  (4) in high yield (Scheme 2). During the reaction, the original bright orange solution turned brown, which corresponds to the dpp-bian dianion coordinated with a divalent metal ion. Air-unstable complex 4 was isolated from toluene as dark red orthorhombic crystals in 76% yield. With the aim of obtaining europium analogs of ytterbium complexes 2 and 3, we oxidized complex 4 with triphenyltin chloride and dibromostilbene (see Scheme 2). In both reactions, the brown solution of 4 in dme turned bright cherry-colored immediately upon the addition of

the halogen-containing reagent. This color change indicates the presence of the dpp-bian radical anion in the mixture. The target complexes [(dpp-bian)Eu(µ-Cl)- $(dme)]_2$  (5) and  $[(dpp-bian)Eu(\mu-Br)(dme)]_2$  (6) were isolated from benzene as red crystals. Since both the complexes are paramagnetic, <sup>1</sup>H NMR spectroscopy cannot be used to obtain analytical information on these derivatives. Nor can ESR spectroscopy be employed for detecting the dpp-bian radical anion in complexes 5 and 6 because both contain paramagnetic Eu ions. The different reduction states of the diimine ligand in complex 4 and, on the other hand, in complexes 5 and 6 emerge from their IR spectra. The stretching vibrations of the single C–N bond in the dpp-bian dianion of complex 4 are manifested as a band at 1300 cm<sup>-1</sup>, while the C–N bond with half  $\pi$ -bonding between these atoms (hence, the bond order is 1.5) in the dpp-bian radical anion of complexes 5 and 6 absorbs at 1520 and 1515  $cm^{-1}$ , respectively.

The transition of the dpp-bian radical anion into the dianion in complexes **2** and **3** upon cooling below 0 °C is accompanied by a color change from cherry-colored to blue. The latter color is characteristic of the dpp-bian dianion coordinated by a trivalent metal ion. As for complexes **5** and **6**, their solutions do not change color even upon cooling to a liquid nitrogen temperature. A DSC study of the crystals of **5** in a range from 300 to 100 K (Fig. 2) also revealed no abnormalities that could be attributed to a redox isomerization accompanied by a phase transition. The weak endothermic peak at 150-160 K is probably associated with vanishing rotation of the Me groups of the isopropyl substituents. The same effect is observed in free dpp-bian.

In the case of redox isomerization, the transition  $Eu^{2+}\rightarrow Eu^{3+}$  should be accompanied by a drop in the magnetic moment from 11.24 to 4.95  $\mu_B$  (with respect to two Eu ions) because the  $\mu_{eff}$  values of  $Eu^{2+}$  and  $Eu^{3+}$  are 7.95 and 3.5  $\mu_B$ , respectively.<sup>4</sup> It can be seen in Fig. 3 that the

Scheme 2



*i*. Eu, DME (excess), reflux.

$$\begin{split} X = Cl~(\textbf{5}),~Br~(\textbf{6});~Ox = Ph_3SnCl~(\textbf{5}),~Ph(Br)CHCH(Br)Ph~(\textbf{6})\\ Ar~is~2,6-diisopropylphenyl. \end{split}$$



Fig. 2. DSC curves (heating) for dpp-bian (1) and complex 5 (2).

magnetic moments of complexes **5** and **6** provide unambiguous evidence for the presence of Eu<sup>2+</sup> ions over a wide temperature range (295–2 K): at room temperature,  $\mu_{eff} = 11.36$  (**5**) and  $11.28 \,\mu_B$  (**6**); these are very close to the value calculated for a molecule containing two Eu<sup>2+</sup> ions (11.24  $\mu_B$ ). Some decrease in the magnetic moments below 25 K is probably due to weak intermolecular antiferromagnetic exchange. The contribution of the unpaired electrons localized on the dpp-bian ligands to the total magnetic moments of dimeric complexes **5** and **6** is small: the magnetic moment calculated for the dimer containing two Eu<sup>2+</sup> ions and two dpp-bian radical anions is  $11.51 \,\mu_B$ .

To evaluate the isotropic exchange between the europium ions in complexes 5 and 6, we modeled the experi-



**Fig. 3.** Plots of  $\mu_{\text{eff}}$  (with respect to the dimers) *vs.* the temperature for  $[(dpp-bian)EuCl(dme)]_2$  (**5**) and  $[(dpp-bian)EuBr-(dme)]_2$  (**6**): the circles and the curves refer to the experimental and calculated data, respectively.

mental data using the Heisenberg—Dirac—van Vleck approximation with allowance for the Zeeman splitting:

$$\hat{H} = -2J\hat{S}_{\text{Eu1}}\hat{S}_{\text{Eu2}} + g\mu_{\text{B}}\vec{B}\sum_{i=1}^{4}\vec{S}_{i},$$

where J is the intramolecular Eu—Eu exchange coupling constant.

The  $\chi$  values were corrected for temperature-independent paramagnetism (TIP) by using the equation  $\chi_{calc} = \chi + TIP$ . Theoretical curves are fitted best to the experimental data for the following equation parameters:  $g_{dpp-bian} = 2.00, g_{Eu} = 1.95, J_{Eu-Eu} = -0.05 \text{ cm}^{-1}$ , and TIP = 1480  $\cdot 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for 5 and  $g_{dpp-bian} = 2.00$ ,  $g_{Eu} = 1.94, J_{Eu-Eu} = -0.04 \text{ cm}^{-1}$ , and TIP = 1000  $\cdot 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for 6.

Molecular structures of complexes 4-6. Structures 4-6were determined by X-ray diffraction and are shown in Figs 4-6, respectively. Since intramolecular electron transfers in crystalline samples are accompanied by changes in the molecular bond lengths and, consequently, in the crystal lattice parameters, we carried out X-ray diffraction experiments at different temperatures to detect redox isomerism in complexes 5 and 6: at 120 and 298 K for 5 and at 120 and 170 K for 6. We found that both the unit cell and molecular parameters of complexes 5 and 6 are temperature-independent. Structure 4 was determined at 100 K. Crystallographic parameters and the data collection and refinement statistics at low temperatures are summarized in Table 1; selected bond lengths and bond angles are listed in Table 2.

In structure 4 (Fig. 4), the six-coordinate environment of the Eu atom is made up of four O atoms of two dme molecules and two N atoms of the dpp-bian ligand. The Eu atom is appreciably out of the plane of the diimine fragment: the dihedral angle between the



Fig. 4. Molecular structure 4 with atomic displacement ellipsoids (p = 50%). The hydrogen atoms are omitted.

Parameter	$\mathbf{4 \cdot C_7 H_8}$	5 • 2C <sub>6</sub> H <sub>6</sub>	<b>6</b> • 2C <sub>6</sub> H <sub>6</sub>
Molecular formula	$C_{51}H_{68}EuN_2O_4$	$C_{92}H_{112}Cl_2Eu_2N_4O_4$	$C_{92}H_{112}Br_2Eu_2N_4O_4$
М	925.03	1712.67	1801.60
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	Pbca	$P\overline{1}$	$P\overline{1}$
T/K	100(2)	120(2)	120(2)
a/Å	21.7278(7)	12.1878(2)	12.1266(10)
b/Å	18.1487(6)	14.0814(3)	14.1253(12)
c/Å	24.1760(8)	14.8548(3)	14.8549(13)
α/deg	90	63.0289(18)	64.0510(10)
β/deg	90	83.0457(15)	83.462(2)
γ/deg	90	71.3756(16)	71.344(2)
$V/Å^3$	9533.4(5)	2152.28(8)	2166.8(3)
Z	8	1	1
$\rho/g  \mathrm{cm}^{-3}$	1.289	1.321	1.381
$\mu/mm^{-1}$	1.359	1.556	2.406
F(000)	3864	884	920
Crystal dimensions/mm	0.30×0.15× 0.15	$0.30 \times 0.30 \times 0.20$	$0.38 \times 0.28 \times 0.09$
$\theta$ scan range/deg	1.93-26.00	2.96-27.00	1.77 - 28.00
Ranges of $h, k, l$	$-26 \le h \le 26$	$-15 \le h \le 15$	$-16 \le h \le 15$
	$-22 \le k \le 22$	$-17 \le k \le 17$	$-18 \le k \le 18$
	$-29 \le l \le 29$	$-18 \le l \le 18$	$-19 \le l \le 19$
Number of measured reflections	78822	36742	21494
Number of unique reflections	9351	9373	10317
R <sub>int</sub>	0.0382	0.0261	0.0135
Absorption correction (max/min) (SADABS)	0.8221/0.6859	1.0000/0.8218	0.8126/0.4616
$GOOF(F^2)$	1.020	1.055	1.046
$R_1/wR_2 (I \ge 2\sigma(I))$	0.0402/0.0967	0.0194/0.0472	0.0257/0.0638
$R_1/wR_2$ (for all reflections)	0.0524/0.1025	0.0231/0.0486	0.0305/0.0653
Residual electron density (max/min), e $Å^{-3}$	1.345/-0.936	0.633/-0.397	1.802/-0.498

Table 1	۱. ۱	Crystallographic	parameters a	nd the	data coll	ection and	refinement	statistics	for com	plexes 4-	-6
			P								

N(1)C(1)C(2)N(2) and N(1)Eu(1)N(2) planes is 11.6°. The Eu–N bond lengths in complex 4 are close to each other (2.475(3) and 2.445(3) Å) but noticeably shorter than those in the complex Cp\*<sub>2</sub>Eu(Bu<sup>t</sup>-bian) (2.794(3) and 2.768(3)  $\text{\AA})^5$  containing neutral acenaphthene-1,2diimine. At the same time, the Eu-N bond lengths in structure 4 are similar to those in the complex  $Cp^*_2Eu(p-$ MeO-bian) (2.454(4) and 2.456(4) Å)<sup>5</sup> containing the acenaphthene-1,2-diimine radical anion. However, in the absence of other anionic ligands, dpp-bian cannot be present in complex 4 as a radical anion because the metal atom must be monovalent in this case, which is very unlikely. Each reduction state of the dpp-bian ligand is known to be characterized by its own structural "fingerprints". When moving from the neutral ligand through the radical anion to the dianion, the occupation of the LUMO of dpp-bian shortens the C(1)-C(2) bond and lengthens the C(1)-N(1) and C(2)-N(2) bonds. The bond lengths of the diimine fragment in complex 4 suggest its dianionic state. For instance, the C(1)-N(1) and C(2)-N(2) bonds (1.395(4) and 1.378(4) Å) are substantially longer than those in free dpp-bian  $(1.284(4) \text{ Å}, \text{both})^6$  as well as in the complexes  $Cp_2^*Eu(Bu^t-bian)$  (1.295(5) and 1.278(5) Å)<sup>5</sup> and  $Cp_2^*Eu(p-MeO-bian)$  (1.345(6) and 1.334(7) Å).<sup>5</sup> In addition, the C—N bond lengths in the dpp-bian ligand of complex **4** are comparable with those in (dpp-bian)-Yb(dme)<sub>2</sub> (1.392(3) and 1.379(3) Å).<sup>2</sup>

**Table 2.** Selected bond lengths *d* and bond angles  $\omega$  in complexes **4**–**6** 

Parameter	4	5	6
Bond		d∕Å	
C(1)—C(2)	1.404(5)	1.448(2)	1.455(2)
N(1) - C(1)	1.395(4)	1.340(1)	1.329(2)
N(2) - C(2)	1.378(4)	1.330(1)	1.326(2)
Eu(1) - N(1)	2.475(3)	2.5704(9)	2.566(1)
Eu(1) - N(2)	2.445(3)	2.5894(9)	2.568(1)
Eu(1) - X(1)	_	2.8704(3)	3.0485(3)
Eu(1)—X(1)'	—	2.8890(3)	3.0695(3)
Angle		ω/deg	
N(1)-Eu(1)-N(2)	72.68(9)	66.60(3)	66.92(4)

Complexes 5 (Fig. 5) and 6 (Fig. 6) are isostructural; both their crystallographic and molecular parameters are similar, except for the metal-halogen bond lengths. Both the complexes are centrosymmetric dimers with centers of inversion at the midpoints of the segments connecting the metal atoms. The coordination polyhedra of the Eu atoms are somewhat distorted octahedra. The Eu-N bonds in structures 5 (2.5704(9) and 2.5894(9) Å) and 6 (2.5658(12) and 2.5683(12) Å) are similar in length to each other, although being longer than those in complex 4 by more than 0.1 Å. This lengthening of the metal-nitrogen bonds in complexes 5 and 6 suggests that the europium cations interact with the dpp-bian radical anion in structures 5 and **6** more weakly than they interact with the dianion in complex 4. The bond lengths in the diimine fragments of the dpp-bian ligands in complexes 5 and 6 correspond to their radical anion character: the C–N bonds in 5(1.335 Å)and 6 (1.327 Å) are longer than those in the neutral bian ligand in Cp\*<sub>2</sub>Eu(Bu<sup>t</sup>-bian) (1.2870 Å),<sup>5</sup> are virtually equal to that in the bian radical anion in  $Cp_{2}Eu(p-MeO-bian)$  (1.340 Å),<sup>5</sup> but are shorter than the C—N bonds (1.387 Å) in structure **4** containing the dpp-bian dianion.

To sum up, when complex **4** containing two reactive sites (the dpp-bian dianion and the Eu<sup>2+</sup> ion) is treated with oxidants, the diimine ligand becomes transformed into the radical anion, while the divalent metal ion remains intact. The reverse reactivity was noted for a samarium analog of complex **4**, *viz.*, the complex (dpp-bian)-Sm(dme)<sub>2</sub>.<sup>7</sup> In the presence of oxidants, it is the metal that oxidizes first. In contrast to ytterbium complexes **2** and **3**, complexes **5** and **6** show no thermally induced electron transfer metal—ligand. Apparently, this is due to a large potential difference between Eu<sup>2+</sup>/Eu<sup>3+</sup> (-0.35 V) and (dpp-bian)<sup>2-</sup>/(dpp-bian)<sup>-</sup> (-1.1 V).

## **Experimental**

Complexes 4-6 are sensitive to oxygen and air moisture, so all manipulations dealing with the synthesis, isolation, and identification of these complexes were carried out *in vacuo* using the



Fig. 5. Molecular structure 5 with atomic displacement ellipsoids (p = 50%). The hydrogen atoms are omitted.



Fig. 6. Molecular structure 6 with atomic displacement ellipsoids (p = 50%). The hydrogen atoms are omitted.

Schlenk equipment. 1,2-Dimethoxyethane, toluene, and benzene were dried with and stored over sodium benzophenone ketyl and distilled from it immediately before use. IR spectra (Nujol) were recorded on an FSM-1201 FTIR spectrometer. The magnetic susceptibilities  $\chi$  of polycrystalline samples were measured on a MPMS-XL-5 SQUID magnetometer (Quantum Design) in a temperature range from 2 to 295 K (H = 5 kOe). The paramagnetic contribution to the magnetic susceptibility was determined with allowance for the diamagnetic contribution  $\chi$  of a sample estimated by the formula  $\chi = -0.5 \cdot M \cdot 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ , where M is the molar mass of the sample. Effective magnetic moments were calculated by the formula  $\mu_{eff} = [3k\chi T/(N_A\mu_B^2)]^{1/2}$ , where  $N_A$  is Avogadro's number,  $\mu_B$  is the Bohr magneton, and k is the Boltzmann constant. Magnetic exchange constants were calculated with the DAVE program.<sup>8</sup> The melting points of complexes 4-6 were determined in sealed capillaries. 1,2-Bis[(2,6diisopropylphenyl)imino]acenaphthene (dpp-bian) was prepared according to a known procedure.<sup>5</sup> The yields of the reaction products were calculated with respect to the amount of dpp-bian used (0.50 g, 1.0 mmol).

(1,2-Bis{(2,6-diisopropylphenyl)imino}acenaphthene)bis-(1,2-dimethoxyethane)europium (4). Iodine (0.013 g, 0.05 mmol) was added to excess europium metal (18 g, 118 mmol) in dme. The resulting colorless solution of EuI<sub>2</sub> was poured off the metal by decantation. The metal was repeatedly washed with the solvent. Then a solution of dpp-bian (0.5 g, 1 mmol) in DME (25 mL) was added to activated europium. The reaction mixture was heated on a water bath (90 °C) and vigorously shaken from time to time. The originally orange reaction mixture turned redbrown. After 2 h, the resulting solution was poured off the excess metal by decantation, filtered, and concentrated in vacuo. The dark crystalline precipitate that formed was dissolved in hot toluene (20 mL). The resulting solution was concentrated under reduced pressure and left for crystallization at room temperature. The yield of complex 4 was 0.7 g (76%), dark red orthorhombic crystals, m.p. 293 °C. Found (%): C, 65.82; H, 6.89.  $C_{51}H_{68}EuN_2O_4$  (925.03 g mol<sup>-1</sup>). Calculated (%): C, 66.22; H, 7.41. IR (Nujol), v/cm<sup>-1</sup>: 1671 m, 1648 m, 1592 m, 1377 s, 1349 w, 1300 s, 1251 m, 1211 w, 1195 w, 1171 w, 1111 s, 1164 s, 1020 w, 982 w, 920 s, 854 s, 810 s, 753 vs, 725 w, 676 vs, 613 w, 594 w, 536 w, 512 w, 487 w.

**Bis**[1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene]dichlorobis(1,2-dimethoxyethane)dieuropium (5). Triphenyltin chloride (0.39 g, 1.0 mmol) was added to a solution of complex 4 (*in situ* prepared from diimine 1 (0.5 g, 1 mmol) in DME). The brown reaction mixture promptly turned bright cherry-colored. The solvent was replaced by benzene; the large colorless crystals of hexaphenyldistannane that formed were filtered off. The benzene solution was concentrated to give complex 5 (0.35 g, 41%) as red orthorhombic crystals, m.p. 280 °C. Found (%): C, 64.12; H, 6.31. C<sub>92</sub>H<sub>112</sub>Cl<sub>2</sub>Eu<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (1712.67 g mol<sup>-1</sup>). Calculated (%): C, 64.52; H, 6.59. IR (Nujol), v/cm<sup>-1</sup>: 1670 m, 1643 m, 1592 m, 1520 s, 1311 w, 1251 m, 1183 w, 1073 s, 1113 m, 1073 m, 1038 m, 924 s, 861 w, 835 w, 816 w, 788 m, 751 s, 723 s, 664 w, 601 w, 536 w.

**Bis**[1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene]dibromobis(1,2-dimethoxyethane)dieuropium (6). 1,2-Dibromostilbene (0.17 g, 0.5 mmol) was added to a solution of complex 4 (*in situ* prepared from diimine **1** (0.5 g, 1 mmol) in DME). The brown reaction mixture promptly turned bright cherry-colored. Crystallization from benzene gave complex **6** (0.49 g, 54%) as red crystals, m.p. 265 °C. Found (%): C, 61.12; H, 6.01.  $C_{92}H_{112}Br_2Eu_2N_4O_4$  (1801.60 g mol<sup>-1</sup>). Calculated (%): C, 61.34; H, 6.27. IR (Nujol), v/cm<sup>-1</sup>: 1671 m, 1643 m, 1590 m, 1515 s, 1311 w, 1251 m, 1185 s, 1073 s, 1031 s, 924 m, 877 m, 836 w, 821 w, 795 w, 777 w, 755 s, 720 w, 667 w, 601 w, 538 w.

X-ray diffraction study of complexes 4–6 was carried out on Bruker Smart Apex (4, 6) and Agilent Xcalibur E diffractometers (5) ( $\omega$  scan mode, Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, graphite monochromator). The structures were solved by direct methods and refined anisotropically (for all non-hydrogen atoms) by the least-squares method on  $F_{hkl}^2$ . The hydrogen atoms were located geometrically and refined isotropically using a riding model. The calculations were performed with the SHELXTL<sup>9</sup> and Crys-Alis Pro program packages.<sup>10</sup> Absorption corrections were applied with the SADABS<sup>11</sup> and ABSPACK (CrysAlis Pro) programs.<sup>10</sup> The structures have been deposited with the Cambridge Structural Database (CCDC Nos 1034227 (4), 1034228 (5), and 1034229 (6)) and can be retrieved from the website ccdc.cam.ac.uk/community/requestastructure/.

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