

Synthesis and structures of 1,2-bis(imino)acenaphthene (BIAN) lanthanide complexes that involve the transfer of zero, one, or two electrons

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The syntheses and X-ray crystal structures of the first 1,2-bis(imino)acenaphthene (BIAN) complexes of the lanthanides are described.

Interest in the 1,2-bis(arylimino)acenaphthene (aryl-BIAN) ligand class stems from the ability of these ligands to function as both electron and proton sponges. In turn, this desirable combination of properties is attributable to the presence of both a naphthalene ring and a 1,4-diaza-1,3-butadiene moiety. The d-block chemistry of aryl-BIAN ligands is now well established and many transition complexes have been employed as catalysts.¹ In view of the foregoing, it is surprising that no lanthanide BIAN complexes have been reported previously. In the present communication, we report (i) the syntheses and X-ray crystal structures of four lanthanide BIAN complexes, and (ii) control of zero, one, or two metal \rightarrow BIAN electron transfers by the choice of metal, ligand tuning, or ligand bulk.

Treatment of $(C_5Me_5)_2M\cdot OEt_2$ ($M = Sm, Eu$) with an equimolar quantity of the appropriate R-BIAN ligand ($R = mesityl$,² *tert*-butyl,³ *p*-methoxyphenyl⁴) in toluene solution at ambient temperature, followed by work-up of the reaction mixtures, resulted in 85–90% yields of $(C_5Me_5)_2Sm(mes-BIAN)$ (**1**) $(C_5Me_5)_2Eu(t-Bu-BIAN)$ (**2**) and $(C_5Me_5)_2Eu(p-MeO-BIAN)$ (**3**), each of which was characterized by single-crystal X-ray diffraction.⁵ In each complex, a metal($\eta^5-C_5Me_5$)₂ unit is attached to the two nitrogen atoms of the BIAN ligand, thus forming a five-membered MNCCN ring. A summary of pertinent metrical parameters is presented in Table 1. Since main group fragments such as AlR_2 ⁶ and GaI_2 ⁷ are known to transfer an electron from the metal to a low-lying π^* orbital of the BIAN ligand system, it was reasonable to anticipate that a similar process might occur in the case of the new lanthanide complexes. As depicted in structure **A**, such a one-electron lanthanide \rightarrow ligand back transfer process would be evident from metrical parameters of the C_2N_2M ring by

(i) lengthening of the C–N bonds and (ii) decreases in the C–C and N–M bond distances. Furthermore, the M^{2+} to M^{3+} oxidation state change would result in shortening of the metal– C_5Me_5 ring centroid distance. On the other hand, if metal \rightarrow ligand back transfer did not occur, the structure would be that of a bis(diimine) complex as depicted in structure **B**.⁸ The C(1)–C(12) bond distances in *t*-Bu-BIAN,³ mes-BIAN,⁹ and *p*-MeO-BIAN⁴ are 1.551(4), 1.528(2), and 1.530(2) Å, respectively. Reference to Table 1 reveals that for complexes **1** and **3** the C(1)–C(12) bond distances are shorter than those for the free ligands, thus implying that electron transfer has taken place and that structure **A** is adopted in both cases. On the other hand, the C(1)–C(12) separation in **2** (Fig. 1) is identical to that reported for *t*-Bu-BIAN,³ within experimental error, thus indicating the presence of a single bond at this location and conformity with structure **B**. Note also that the nitrogen–carbon bond distances for complexes **1** and **3** are longer than those for **2**, which is consistent with the presence of C–N double bonding in the latter and single bonding

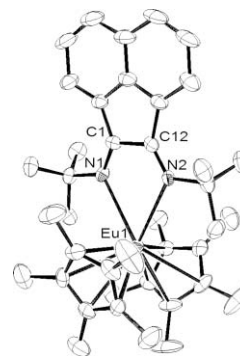


Fig. 1 View of Eu(II) complex $(C_5Me_5)_2Eu(t-Bu-BIAN)$ (**2**) showing the atom numbering scheme and thermal ellipsoids at 50% probability (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles ($^\circ$): Eu(1)–N(1) 2.794(3), Eu(1)–N(2) 2.768(3), C(1)–N(1) 1.295(5), C(12)–N(2) 1.278(5), C(1)–C(12) 1.548(6), N(1)–Eu(1)–N(2) 59.84(10), Eu(1)–N(1)–C(1) 120.8(3), N(1)–C(1)–C(12) 117.7(4), C(1)–C(12)–N(2) 119.2(4), C(12)–N(2)–Eu(1) 121.8(3).

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Table 1 Summary of bond distance (Å) and angle ($^\circ$) data for lanthanide BIAN complexes **1–4**

Compound	C(1)–C(12)	M–N(1)	M–N(2)	N(1)–C(1)	N(2)–C(12)	C_5Me_5 –M	$\Sigma MNCCN$
$(C_5Me_5)_2Sm(mes-BIAN)$ (1)	1.444(6)	2.530(3)	2.501(3)	1.352(5)	1.338(5)	2.489(2)	518.1(3)
$(C_5Me_5)_2Eu(t-Bu-BIAN)$ (2)	1.548(6)	2.794(3)	2.768(3)	1.295(5)	1.278(5)	2.670(2)	539.3(3)
$(C_5Me_5)_2Eu(p-MeO-BIAN)$ (3)	1.442(8)	2.454(4)	2.456(4)	1.345(6)	1.334(7)	2.485(2)	536.1(5)
$(C_5Me_5)Sm(dpp-BIAN)(thf)$ (4)	1.414(6)	2.269(3)	2.232(4)	1.387(5)	1.405(5)	2.420(1)	516.7(6)

in the former. The observation that the metal–nitrogen bond distances for **2** are ~ 0.3 Å longer than those for **1** and **3** is consistent with the retention of the +2 oxidation state in **2**. As reflected by the sums of bond angles for the MNCCN rings, these metallacycles are close to planar for **2** and **3**. The significant folding along the N–N vector in the case of **1** is attributable to the steric demands of the mesityl substituents.

The proposed structures for **1–3** are also in accord with IR, ^1H NMR, and magnetic moment data. Thus, only **2** exhibits an IR peak at 1636 cm^{-1} , which falls in the region reported for the C=N stretching mode,¹⁰ therefore indicating that metal \rightarrow ligand electron transfer has not occurred in this case. Moreover, the detection of a ^1H NMR resonance for **3** at $\delta -21.30$ supports the assignment of the +3 oxidation state in this complex since Evans *et al.*¹¹ reported a peak with a similar chemical shift ($\delta -19.7$) for the Me_5C_5 protons of the Eu (+3) complex, $[(\text{C}_5\text{Me}_5)_2\text{Eu}(\text{OCMe}_3)_2(\mu\text{-OCMe}_3)]_2$. The magnetic moment values (Evans method) of 1.82, 6.98, and 3.55 BM for **1**, **2** and **3**, respectively, also support the oxidation state assignments proposed above.

The reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm}\cdot\text{OEt}_2$ with one equivalent of the sterically encumbered ligand, dpp-BIAN¹² (dpp = 2,6-diisopropylphenyl) in THF solution at ambient temperature resulted in loss of a C_5Me_5 group and formation of $(\text{C}_5\text{Me}_5)\text{Sm}(\text{dpp-BIAN})(\text{thf})$ (**4**) in 85% yield. Akin to **1** and **3**, compound **4** features a five-membered MNCCN ring. However, a single-crystal X-ray analysis⁵ revealed that the ring structure of **4** differs significantly from those of **1–3** (Fig. 2). Thus, the C(1)–C(12) separation in **4** is ~ 0.03 Å less than those in **1** and **3**. Furthermore, there are short contacts of 2.692(4) and 2.707(4) Å between these carbon atoms and the Sm center, and the N–C bond distances are ~ 0.05 Å longer than those in **1** and **3**. The Sm– C_5Me_5 ring centroid distance of 2.420(1) Å is similar to that of **1** and therefore indicative of a Sm(III) center in **4**. Moreover, the N–C and C–C bond distances in **4** are very similar to those of the dianionic dpp-BIAN ligand in magnesium and calcium complexes.¹³ Overall, the metrical parameters for **4** imply that two-electron reduction of the dpp-BIAN ligand has taken place and that the bonding

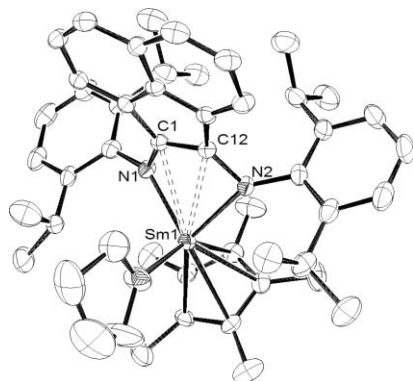
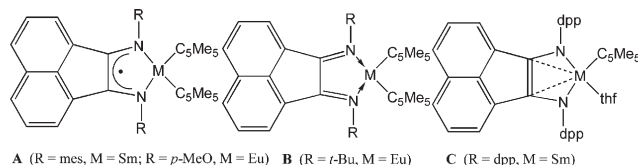


Fig. 2 View of the Sm(III) complex $(\text{C}_5\text{Me}_5)\text{Sm}(\text{dpp-BIAN})(\text{thf})$ (**4**) showing the atom numbering scheme and thermal ellipsoids at 50% probability (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles ($^\circ$): Sm(1)–N(1) 2.269(3), Sm(1)–N(2) 2.232(4), Sm(1)–C(1) 2.704(4), Sm(1)–C(12) 2.692(4), C(1)–N(1) 1.387(5), C(12)–N(2) 1.405(5), C(1)–C(12) 1.414(6), N(1)–Sm(1)–N(2) 83.1(1), Sm(1)–N(1)–C(1) 92.4(2), N(1)–C(1)–C(12) 119.3(3), C(1)–C(12)–N(2) 124.4(4), C(12)–N(2)–Sm(1) 92.6(2).



Scheme 1

arrangement is best represented by structure **C** (Scheme 1). The angle between the N(1)–Sm–N(2) and N(1)–C(1)–C(12)–N(2) planes (47.54°) is larger than that in **1** (42.80°) due to the concerted effects of increased substituent bulk and optimization of the interaction between Sm and the C(1)–C(12) double bond. It is likely that the reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm}\cdot\text{OEt}_2$ with dpp-BIAN proceeds *via* initial displacement of Et_2O to form $(\text{C}_5\text{Me}_5)_2\text{Sm}^{\text{II}}(\text{dpp-BIAN})$, followed by intramolecular electron transfer to generate $(\text{C}_5\text{Me}_5)_2\text{Sm}^{\text{III}}(\text{dpp-BIAN}^-)$, which eliminates $[\text{C}_5\text{Me}_5]^-$. In turn, $[\text{C}_5\text{Me}_5]^-$ transfers the second electron to the singly-reduced BIAN ligand.¹⁴ Support for this idea stems from the detection of the oxidized product, $[\text{C}_5\text{Me}_5]_2$, in the reaction mixture by ^1H NMR spectroscopy. This type of process has been elegantly investigated by Evans and Davis¹⁵ and dubbed “sterically induced reduction.”

In summary, we have prepared the first lanthanide 1,2-bis(imino)acenaphthene complexes and demonstrated that the metal \rightarrow BIAN charge transfer process can be controlled by (a) the choice of metal, (b) tuning of the BIAN ligand substituents, or (c) use of a bulky BIAN ligand.

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- All X-ray data were collected at 153 K on a Nonius-Kappa CCD diffractometer. *Crystal data* for **1**: $\text{C}_{64}\text{H}_{74}\text{N}_2\text{Sm}$, $M_r = 1021.60$, triclinic, space group $P\bar{1}$, $a = 12.319(5)$, $b = 14.294(5)$, $c = 16.910(5)$ Å, $\alpha = 70.589(5)$, $\beta = 82.726(5)$, $\gamma = 69.084(5)^\circ$, $V = 2623.2(16)$ Å³, $Z = 2$, $T = 153(2)$ K, $\mu = 1.161\text{ mm}^{-1}$, reflections collected/independent = 17880/11973 ($R_{\text{int}} = 0.0373$), $R_1(I > 2\sigma(I)) = 0.1107$. For **2**: $\text{C}_{47}\text{H}_{62}\text{EuN}_2$, $M_r = 806.95$, monoclinic, space group $P2_1/n$, $a = 10.250(5)$, $b = 18.436(5)$, $c = 23.258(5)$ Å, $\beta = 94.739(5)^\circ$, $V = 4380(3)$ Å³, $Z = 4$, $T = 153(2)$ K, $\mu = 1.463\text{ mm}^{-1}$, reflections collected/independent = 16952/10032 ($R_{\text{int}} = 0.0358$), $R_1(I > 2\sigma(I)) = 0.0443$ and $wR_2(I > 2\sigma(I)) = 0.1103$. For **3**: $\text{C}_{46}\text{H}_{50}\text{EuN}_2\text{O}_2$, $M_r = 814.88$, triclinic, space group $P\bar{1}$, $a = 9.5567(19)$, $b = 10.286(2)$, $c = 20.283(4)$ Å, $\alpha = 101.15(3)$, $\beta = 94.09(3)$, $\gamma = 104.01(3)^\circ$, $V = 1883.4(7)$ Å³, $Z = 2$, $T = 153(2)$ K, $\mu = 1.706\text{ mm}^{-1}$, reflections collected/independent = 12045/8520 ($R_{\text{int}} = 0.0398$), $R_1(I > 2\sigma(I)) = 0.0476$.

and $wR_2 (I > 2\sigma(I)) = 0.0989$. For **4**: $C_{40}H_{54}N_2Sm$, $M_r = 713.20$, monoclinic, space group $P2_1/c$, $a = 18.640(4)$, $b = 10.563(2)$, $c = 17.493(4)$ Å, $\beta = 97.49(3)^\circ$, $V = 3414.8(12)$ Å³, $Z = 4$, $T = 153(2)$ K, $\mu = 1.749$ mm⁻¹, reflections collected/independent = 12820/7785 ($R_{int} = 0.0517$), $R_1 (I > 2\sigma(I)) = 0.0576$ and $wR_2 = 0.1431 (I > 2\sigma(I))$. Crystals of **1**, **2**, **3**, and **4** were covered with a mineral oil prior to mounting on the goniometer of a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream liquid nitrogen cooling system. The four data sets were corrected for absorption: CCDC 650007 (**1**), 650008 (**2**), 650009 (**3**) and 650010 (**4**). For crystallographic data in CIF format see DOI: 10.1039/b708758f.

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