Mediating Oxidation States in Decamethyleuropocene Complexes. The Role of the Diazabutadiene Fragment

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Summary: The Eu diazabutadiene complexes ($(C_5Me_5)_2Eu$(DADBu-t) and $(C_5Me_5)_2Eu(DADC_6F_5)$ (DADBu-t = t-BuNC(H)C(H)NBu-t; $DADC_6F_5 = C_6F_5NC(Me)C(Me)NC_6F_5$) have been prepared, and on the basis of characterization by X-ray crystallography, magnetic susceptibility, and ^1H NMR and IR spectroscopy, it is concluded that the Eu oxidation states in these complexes are +2 and +3, respectively. In the case of $(C_5Me_5)_2Eu(DADC_6F_5)$, the internal redox process is solvent sensitive.

Diazabutadiene ligands are used extensively in d- and p-block chemistry by virtue of their diversity of coordination modes and interesting redox properties. Significantly less information is available for diazabutadiene (DAD) complexes of the lanthanide elements, however. In the context of lanthanocene DAD complexes, structurally authenticated examples comprise $(C_5H_5)_2$Yb(DADBu-*t*) (**1**),[1] $(C_5Me_5)_2$Yb(DADBu-*t*) (**2**),[2] and $(C_5Me_5)_2$Sm(DADBu-*t*) (**3**)[3] (DADBu-*t* = *t*-BuNC(H)C(H)NBu-*t*). For each of these compounds, structural and spectroscopic data indicate that internal redox chemistry takes place, and the electronic structures of these complexes are best represented as $(C_5R_5)_2M^{III}$(DADBu-*t*)$^{\bullet-}$. Bis-indenyl complexes of ytterbium have also been structurally characterized and display similar behavior.[4] In a study of 2,2′-bipyridyl and 1,10-phenanthrolene complexes of substituted ytterbocenes, it has been shown that the Yb oxidation state depends on the nature of the substituents on the cyclopentadienide rings.[5] However, in the case of $(C_5Me_5)_2$Eu(bipy) the bipyridyl ligand was not reduced.

In the present communication, we report (i) the first structurally characterized DAD complexes of europium,[6] (ii) the isolation and structural characterization of Eu^{2+} and Eu^{3+} DAD complexes, and (iii) a reversible solvent-mediated Eu^{2+}/Eu^{3+} redox reaction.

Treatment of $(C_5Me_5)_2Eu\cdot OEt_2$[7] with equimolar quantities of DADBu-*t* and $DADC_6F_5$ ($DADC_6F_5 = C_6F_5NC(Me)C(Me)NC_6F_5$)[8] in toluene solution, followed by workup and recrystallization, resulted in the isolation of purple $(C_5Me_5)_2$Eu(DADBu-*t*) (**4**) and green $(C_5Me_5)_2Eu(DADC_6F_5)$ (**5**) in yields of 89% and 92%, respectively (Scheme 1).

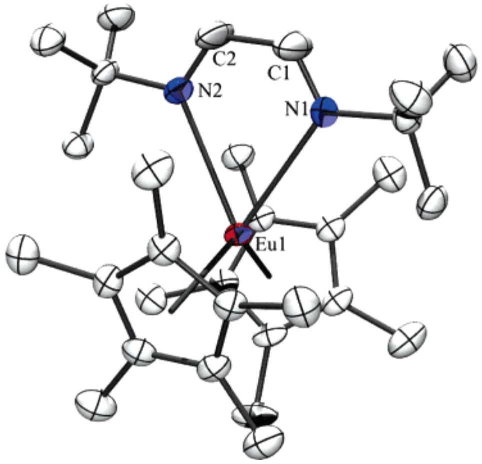

Figure 1. Molecular structure of **4** with thermal ellipsoids at the 50% probability level (hydrogen atoms omitted for clarity).

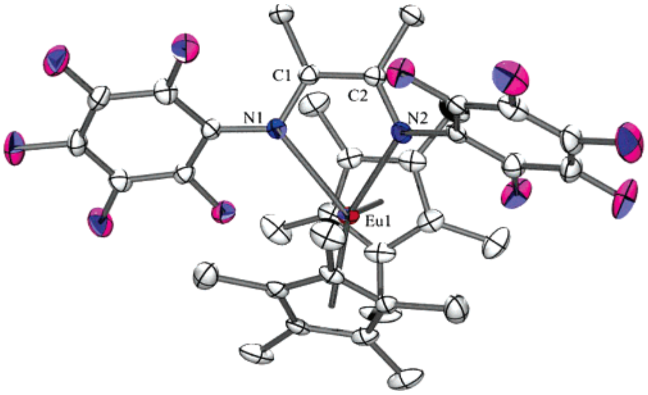

Figure 2. Molecular structure of **5** with thermal ellipsoids at the 50% probability level (hydrogen atoms omitted for clarity).

Single-crystal X-ray diffraction studies[9] reveal that **4** crystallizes in the orthorhombic space group *Pccn* with $Z = 8$, while **5** crystallizes in the monoclinic space group $C2/c$ with $Z = 4$. Neither structure features any close contacts between individual molecules, depictions of which appear in Figures 1 and 2.

It is evident from Table 1 that the metrical parameters for **4** and **5** are significantly different. In particular, it is worthy of note that the average N−C bond distance in **4** (1.252(6) Å) is

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[1] Trifonov, A. A.; Kirillov, E. N.; Bochkarev, M. N.; Schumann, H.; Muehle, S. *Russ. Chem. Bull., Int. Ed.* **1999**, *48*, 382.

[2] Trifonov, A. A.; Kurskii, Yu. A.; Bochkarev, M. N.; Muehle, S.; Dechert, S.; Schumann, H. *Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 601.

[3] Recknagel, A.; Noltemeyer, M.; Edelman, F. T. *J. Organomet. Chem.* **1991**, *410*, 53.

[4] (a) Trifonov, A. A.; Fedorova, E. E.; Ikorskii, V. N.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Eur. J. Inorg. Chem*. **2005**, 2812. (b) Trifonov, A. A.; Fedorova, E. E.; Fukin, G. K.; Ikorskii, V. N.; Kurskii, Yu. A.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Russ. Chem. Bull., Int. Ed.* **2004**, *53*, 2736.

[5] Schultz, M.; Boncella, J. M.; Berg, D. J.; Tilley, T. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 460.

[6] For mixed-ligand β-diketiminate DAD complexes of Eu^{3+} characterized by elemental analysis, TGA, and spectroscopy, see: Fernandes, J. A.; Sá Ferreira, R. A.; Pillinger, M.; Carlos, L. D.; Gonçalves I. S.; Ribeiro-Claro, P. J. A. *Eur. J. Inorg. Chem.* **2004**, 3913.

[7] Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865.

[8] Gordon, J. C.; Shukla, P.; Cowley, A. H.; Jones, J. N.; Scott, B. L. *Chem. Commun.* **2002**, 2710.

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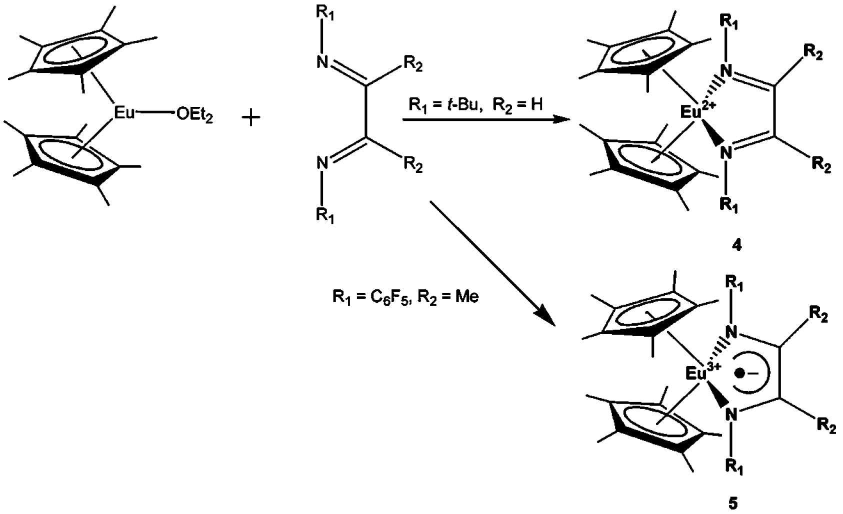
Table 1. Summary of Bond Distance Data for DAD Complexes

compound	N(1)−C(1)	N(2)−C(2)	C(1)−C(2)	M−N(1)	M−N(2)	Cp−M	Cp−M	ref
$(C_5Me_5)_2Eu(DADBu\text{-}t)$ (**4**)	1.249(5)	1.256(6)	1.482(6)	2.745(3)	2.741(3)	2.6180(7)	2.6210(7)	this work
$(C_5Me_5)_2Eu(DADC_6F_5)$ (**5**)	1.354(6)	1.346(6)	1.437(6)	2.496(4)	2.521(4)	2.4423(13)	2.4619(5)	this work
$(C_5Me_5)_2Yb(DADBu\text{-}t)$ (**2**)	1.339(4)	1.326(5)	1.398(5)	2.385(3)	2.394(3)			2
$(C_5Me_5)_2Sm(DADBu\text{-}t)$ (**3**)	1.326(9)	1.320(8)	1.386(10)	2.480(5)	2.489(2)			3
uncoordinated DADBu-*t* ligand	1.269(2)	1.269(2)	1.477(2)					10
$(C_5Me_5)_2Eu{\cdot}OEt_2$						2.5344(6)	2.5250(7)	this work

Scheme 1. Transformation of $(C_5Me_5)_2Eu{\cdot}OEt_2$ into Complexes 4 and 5 upon Treatment with DADBu-*t* and $DADC_6F_5$, Respectively



considerably shorter than that in **5** (1.350(6) Å). Furthermore, the C−C bond distance in **4** (1.482(6) Å) is longer than that in **5** (1.437(6) Å) and close to the value of 1.477(2) Å reported for the free DADBu-*t* ligand.[10]

Collectively, the structural data imply that only the $DADC_6F_5$ ligand of **5** has undergone reduction and consequently that the oxidation states of europium in **4** and **5** are +2 and +3, respectively, as represented in Scheme 1. Such a view is consistent with the fact that the average Eu−N bond distance in **4** (2.743(3) Å) is longer than that in **5** (2.508(4) Å) on account of the ionic radius trend $Eu^{2+} > Eu^{3+}$. As expected, the average ring centroid−europium distances for **4**, **5**, and $(C_5Me_5)_2Eu{\cdot}OEt_2$ follow the same trend. Note also that the C−C and N−C bond distances in **5** are very similar to those in **2** and **3**, complexes that have been shown to have undergone intramolecular electron transfer.[2,3]

The structural assignments presented in Scheme 1 for **4** and **5** are also supported by magnetic susceptibility data. Thus the magnetic moment values for crystalline **4** and **5** (298 K) are 6.6 and 3.7 μ_B, respectively. Typical values of 7.6−8.0 μ_B and 3.7−4.2 μ_B have been reported for other Eu^{2+} and Eu^{3+} complexes,[11] respectively. The proposed structures are also in accord with IR and ^1H NMR spectroscopic data. Thus, **4** exhibits a characteristic C═N stretching frequency (1620 cm^{-1}),[12] while the absence of this vibration in the IR spectrum of **5** supports the proposal that electron transfer into the N−C−C−N fragment has taken place. No ^1H NMR signal could be detected for the Eu^{2+} complex **4**; however, in the case of **5**, a singlet was detected at δ −24.2 ppm (C_6D_6) and is attributable to the Me_5C_5 groups. This value is similar to the value of δ −19.7 ppm reported for the Me_5C_5 protons of the europium(III) complex $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$ by Evans et al.[11]

The internal redox reaction that takes place in the formation of **5** is solvent sensitive and can be made reversible. Thus, removal of the solvent from a C_6D_6 solution of **5** under reduced pressure, followed by redissolution of the green solid in THF-d_8, results in the formation of a red solution. Monitoring of this process by ^1H NMR spectroscopy revealed the disappearance of the C_5Me_5 peak of **5** at δ −24.2 ppm and the appearance of the spectrum characteristic of the free $DADC_6F_5$ ligand.[10] A very broad resonance at δ ~2.0 was also apparent and attributable to the methyl protons of a THF-solvated $(C_5Me_5)_2$-Eu fragment. The foregoing spectroscopic data imply that the displacement of the $DADC_6F_5$ ligand of **5** by THF-d_8 solvent molecules is accompanied by electron transfer from the radical anion $[DADC_6F_5]^{\bullet -}$ back to the Eu(III) center. Stripping of the THF-d_8 solvent in vacuo, followed by redissolution of the residue in C_6D_6, restores the original spectrum of **5**.

The foregoing observations serve to highlight the weak electron-donating characteristics of the $DADC_6F_5$ ligand toward the Eu(III) center of solvated **5** and the degree to which the Coulombic interaction between the Eu(III) cation and the $DADC_6F_5$ radical anion can be overcome by formation of two Eu−O bonds in the complex $(C_5Me_5)_2Eu(THF)_2$. Similar solvent-mediated redox transformations have been reported for DADBu-*t* and DADDIPP complexes of ytterbium supported by C_5Me_5 and indenyl ligation (DADDIP = $(2,6\text{-}i\text{-}Pr_2C_6H_3)NC(H)C(H)N(2,6\text{-}i\text{-}Pr_2C_6H_2))$).[2,4]

Systems that undergo reversible and facile changes of oxidation state via intramolecular electron transfer are of

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[9] *Crystal data for* **4**: $C_{30}H_{50}EuN_2$, orthorhombic, space group *Pccn*, a = 16.841(5) Å, b = 22.372(5) Å, c = 15.725(5) Å, V = 5925(3) $Å^3$, Z = 8, D_c = 1.324 g cm^{-3}, μ(Mo Kα) = 2.136 mm^{-1}, R_1 = 0.0367, wR_2 = 0.0784, GOF = 1.028. For **5**: $C_{80}H_{80}Eu_2F_{20}N_4$, monoclinic, space group *C2/c*, a = 36.315(5) Å, b = 9.444(5) Å, c = 22.422(5) Å, β = 107.777(5)°, Z = 4, D_c = 1.616 g cm^{-3}, μ(Mo Kα) = 1.796 mm^{-1}, R_1 = 0.0413, wR_2 = 0.1185, GOF = 1.095.

[10] Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolt, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714.

[11] Evans, W. J.; Shreeve, J. L.; Ziller, J. W. *Organometallics* **1994**, *13*, 731.

[12] Kliegman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555.

potential interest for the construction of molecular switches. We are continuing to investigate the magnetic, electrochemical, and spectroscopic behavior of these and related systems in this context.

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Supporting Information Available: Experimental details, spectroscopic data for **4** and **5**, and X-ray crystallographic data (CIF) for $(C_5Me_5)_2Eu{\cdot}OEt_2$, **4**, and **5**. CCDC numbers 281946, 281944, and 281945, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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