Inorganic Chemistry

Communication

Redox Isomerism in the Lanthanide Complex [(dpp-Bian)Yb(DME)(μ-Br)]₂ (dpp-Bian = 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene)[†]

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Ytterbium reacts with 1,2-bis[(2,6-diisopropylphenyl)imino]-acenaphthene (**1**, dpp-Bian) in 1,2-dimethoxyethane (DME) to give complex (dpp-Bian)Yb(DME)₂ (**2**). Oxidation of **2** with an 0.5 mol equivalent of dibromostilbene affords dimeric compound [(dpp-Bian)Yb(DME)(μ-Br)]₂ (**3**). Molecular structures of **2** and **3** were determined by single-crystal X-ray analysis. In complex **3** in a DME solution, a temperature-dependent reversible intramolecular electron transfer between the ligand and the metal takes place.

The redox isomerism phenomenon[1] is characterized by the existence of two electronic isomers with different charge distributions. It can take place in molecules with at least two redox-active centers, for instance, in transition-metal complexes. The interconversion between the different electronic isomers in such complexes may be induced thermally and is accomplished by an intramolecular electron transfer involving the metal ion and the redox-active ligand (for example, *o*-benzoquinones or diimines). Redox isomers have different molecular and electronic structures. Hence, their optical, electrical, and magnetic properties are not the same. Such complexes have been proposed as candidates for use in information storage and integrated molecular-sized devices.

In 1980, Pierpont and Buchanan reported for the first time the reversible metal-to-ligand electron transfer in an *o*-benzoquinonecobalt complex.[1a] Two years later a similar process has been observed by Abakumov et al. in a copper complex.[2] Until now, redox isomeric transformations, in the solid state and in solution, were known for the complexes of transition metals, e.g., Co,[3] Ru,[4] Cr,[5] Ni,[6] Mn,[7] Fe,[8] Rh,[1b,9] Cu,[10] and Ir.[11] The redox isomerism in the lanthanide complex was assumed first in 1995[12] and then in 2005.[13] In 2007, such a process was claimed for the lanthanide diimine
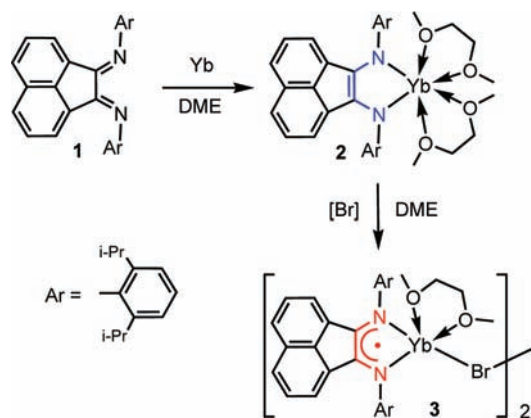

[†] Dedicated to Professor Mikhail N. Bochkarev on the occasion of his 70th birthday.

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Scheme 1

Figure 1. Crystal structure of **2**. The isopropyl groups are omitted for clarity. Selected bond lengths (Å): Yb(1)-N(1) 2.347(2), Yb(1)-N(2) 2.363(2), N(1)-C(1) 1.391(3), N(2)-C(2) 1.378(3), C(1)-C(2) 1.409(3), Yb-O(1) 2.418(1), Yb-O(2) 2.610(2), Yb-O(3) 2.510(2), Yb-O(4) 2.470(1). For details, see the Supporting Information.
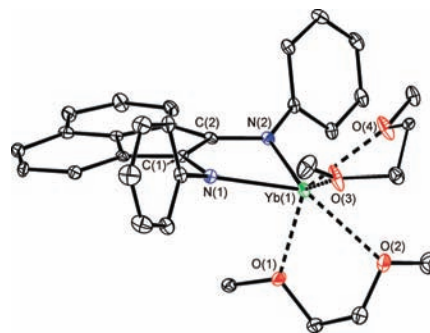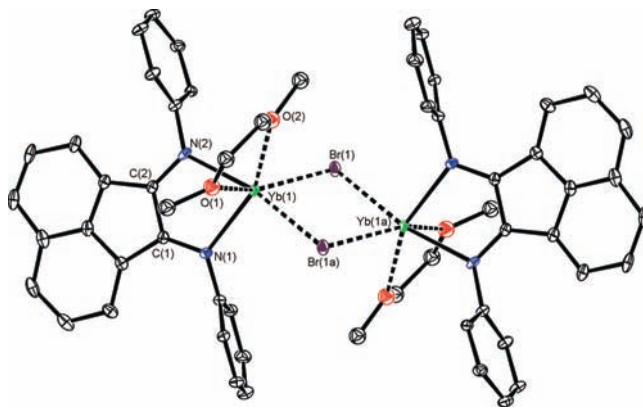

Figure 2. Crystal structure of **3**. The isopropyl groups are omitted for clarity. Selected bond lengths (Å): Yb(1)-N(1) 2.427(6), Yb(1)-N(2) 2.430(6), N(1)-C(1) 1.338(10), N(2)-C(2) 1.354(10), C(1)-C(2) 1.452(11), Yb-O(1) 2.479(6), Yb-O(2) 2.422(7). For details, see the Supporting Information.

complex (dpp-dad)YbCp*(THF) (THF = tetrahydrofuran).[14] According to the solid-state magnetic susceptibility data, this complex consists of ytterbium(II) and a dpp-dad radical anion at 2 K, (dpp-dad)$^-$Yb^{2+}Cp*(THF) (μ_{eff} = 2.03 μ_B), whereas at 300 K, it exists as a ytterbium(III) complex with a dpp-dad dianion, (dpp-dad)$^{2-}$Yb^{3+}Cp*(THF) (μ_{eff} = 4.41 μ_B). To our knowledge, these redox preferences are opposite to all of the earlier reported cases; i.e., the low-temperature form is always represented by species with a more oxidized metal ion M^{n+1}, and the high-temperature isomer consists of the reduced metal ion M^n. The decrease of the magnetic moment with a lowering of the temperature in the solid state has been observed in several ytterbium complexes with redox-active nitrogen ligands, and it is ascribed to the antiferromagnetic coupling between unpaired electrons of ytterbium and a ligand.[15]

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (**1**, dpp-Bian) is a redox-active ligand, whose main-group metal complexes have been reported during the last years.[16a] The reduction of **1** with sodium affords its mono-, di-, tri-, and tetraanions,[16b] while with group II metals, it stops with the formation of complexes with dianionic ligands.[16c] Recently, Cowley and Vasudevan reported that the choice of metal, ligand tuning, or ligand bulk allows the control of zero-, one-, or two-electron transfer from metallocenes Cp*$_2$Ln^{II} (Ln = Sm, Eu) to acenaphthene-1,2-diimines.[17]

We report here that activated metallic ytterbium readily reacts with **1** in 1,2-dimethoxyethane (DME) to produce (dpp-Bian)Yb(DME)$_2$ (**2**)[18] (Scheme 1). Oxidation of **2** with

bromine-containing reagents, e.g., α,α-dibromostilbene, gives dimeric complex [(dpp-Bian)Yb(DME)(μ-Br)]$_2$ (**3**).[19]

The molecular structures of **2** (Figure 1) and **3** (Figure 2) have been determined by single-crystal X-ray diffraction at 100 K. The difference in the reduction state of the dpp-Bian ligands in **2** and **3** is evident from the bond lengths in these complexes. The Yb−N bond lengths in **2** (av. 2.355 Å) are shorter than those in **3** (av. 2.428 Å). This indicates that in **2** the dpp-Bian acts as dianion, while in **3**, it is presented as a radical anion. The alteration of the C−N and C−C distances within the metallacycles in **2** and **3** also corresponds to the difference in the nature of the dpp-Bian ligands in **2**

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(18) α,α-Dibromostilbene (5 mg, 0.015 mmol) and **1** (0.5 g, 1 mmol) were added to the ytterbium metal (10.5 g, 60.7 mmol) in DME (30 mL). Within 30 min of reflux, the reaction mixture turned brown. The solvent was slowly evaporated from the decanted solution. Compound **2** was isolated (0.64 g, 75%) as deep-red prismatic crystals. Elem anal. Calcd for C$_{44}$H$_{60}$YbN$_2$O$_4$ (853.98): C, 61.88; H, 7.08. Found: C, 61.35; H, 7.93. ^{1}H NMR (THF-d_8, 200 MHz): δ 6.91 (d, 4 H, CH arom, ^3J = 7.53 Hz), 6.67 (t, 2 H, CH arom, ^3J = 7.53 Hz), 6.54 (d, 2 H, CH arom, ^3J = 8.03 Hz), 6.46 (dd, 2 H, CH arom, ^3J = 6.53 Hz, ^3J = 8.03 Hz), 5.64 (d, 2 H, CH arom, ^3J = 6.53 Hz), 3.94 (sept, 4 H, CH(CH$_3$)$_2$, ^3J = 6.78 Hz), 1.16 (d, 12 H, CH(CH$_3$)$_2$, ^3J = 6.78 Hz), 1.06 (d, 12 H, CH(CH$_3$)$_2$, ^3J = 6.78 Hz).

(19) The addition of 85 mg (0.25 mmol) of α,α-dibromostilbene to a solution of **2** (0.43 g, 0.5 mmol) in DME (40 mL) caused an immediate color change to brown. Slow evaporation of the solvent from this solution gave **3** (0.17 g, 40%) as deep-red crystals. Mp > 280 °C. Elem anal. Calcd for C$_{80}$H$_{100}$Yb$_2$N$_4$O$_4$Br$_2$·2C$_4$H$_{10}$O$_2$ (1867.78): C, 56.59; H, 6.48. Found: C, 56.28; H, 6.30.
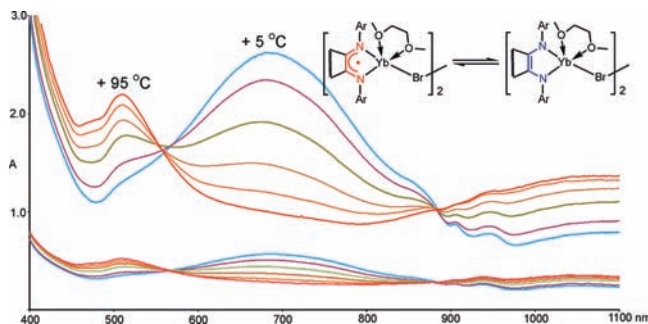
Figure 3. Temperature dependence of the absorption spectrum of **3** in DME. For clarity, the naphthalene part of the dpp-Bian ligand is omitted.

and **3**. The population of the lowest unoccupied molecular orbital going from neutral dpp-Bian to its radical anion and further to the dianion must result in a shortening of the central C(1)−C(2) bond and an elongation of the C(1)−N(1) and C(2)−N(2) distances. Thus, the C(1)−N(1) and C(2)−N(2) distances get longer in the sequence **1** (dpp-Bian⁰), **3** (dpp-Bian⁻), and **2** (dpp-Bian²⁻) [**1**, both 1.281(3) Å; **3**, 1.338(10) and 1.354(10) Å; **2**, 1.391(3) and 1.378(3) Å], while the C(1)−C(2) bonds become shorter [**1**, 1.534(6) Å; **3**, 1.452(11) Å; **2**, 1.409(3) Å].

For complex **3**, one can expect the existence of two redox isomers: (dpp-Bian)⁻Yb²⁺Br and (dpp-Bian)²⁻Yb³⁺Br. Both isomers as well as an interconversion between them have been observed in a DME solution in the range from +5 to +95 °C. The interconversion process has been examined by electron absorption spectroscopy (Figure 3).

At +5 °C, the spectrum of **3** exhibits absorption at 683 nm, which indicates the presence of a dpp-Bian dianion in solution. For comparison, the DME solution of the dimeric neodymium(III) complex [(dpp-Bian)NdCl(THF)₂]₂,[13] which also consists of the dpp-Bian dianion, has an absorption maximum at 671 nm. In the case of **3** raising the temperature leads to a decrease of absorption at 683 nm with a simultaneous increase of absorption at 510 nm. The later corresponds to the radical anion of dpp-Bian. Thus, in the calcium radical-anionic complex [(dpp-Bian)⁻Ca²⁺I(THF)₂]₂, which is also a dimer in the solid state, the respective band has a maximum in DME at 510 nm.[13] In order to identify whether the redox isomerization in solution is accompanied with dissociation of the dimer to a monomer, we have recorded the spectra of a solution of **3** with a lower concentration (ca. 6 times). Because the redox isomer equilibrium temperatures in both cases are quite close (30

°C in a more concentrated solution and 34 °C in a diluted solution), we conclude that the redox isomerization process is not accompanied with dissociation of the dimers to monomers.

The magnetic susceptibility data (Evans method) for complex **3** in solution are also consistent with those of the redox isomerization process. In the range between −40 and 0 °C, $1/\chi$ is linear with T and the magnetic moment is equal to 4.0 μ_B (per Yb ion). Although this value is somewhat lower than those observed in the ytterbium(III) complexes (4.3−4.9 μ_B),[20] it is well above the value expected for the dpp-Bian radical anion (1.73 μ_B), thus indicating the presence in solution of the isomer (dpp-Bian)²⁻Yb³⁺Br. Raising the temperature should lead to a linear decrease of the magnetic moment, which at T above +80 °C is expected to be close to 1.73 μ_B, the value for the organic radical with $S = {}^1/_2$, i.e., isomer (dpp-Bian)¹⁻Yb²⁺Br. In the redox isomerization interval at a given temperature, the resulting magnetic moment should be an additive value of the magnetic moments of two isomeric forms. This is exactly the case here. The magnetic moment of the sample at 60 °C (the concentration ratio [Yb²⁺]/[Yb³⁺] = 3) is 2.7 μ_B, and it agrees with the calculated value of 2.4 μ_B.

In conclusion, compound **3** is the first lanthanide complex in which the redox isomerism phenomenon takes place in solution. As in transition-metal complexes, the low-temperature redox isomer of **3** is presented by molecule with a dianionic ligand, whereas the high-temperature isomer consists of the radical anion. However, as shown by single-crystal X-ray analysis in the solid state at 100 K, complex **3** is best described as (dpp-Bian)⁻Yb²⁺Br. The temperature-dependent solid-state magnetochemistry for complex **3** will be carried out to see whether the redox isomerization process also takes place in the solid state. Because some other lanthanides, namely, Eu, Sm, Tm, Dy, and Nd, form compounds in the oxidation states 2+ and 3+, the redox isomerism phenomenon is expected in their complexes as well, when an appropriate redox-active ligand will be chosen.

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