

# Ytterbium and Europium Complexes of Redox-Active Ligands: Searching for Redox Isomerism

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## Abstract

© 2017 American Chemical Society. The reaction of (dpp-Bian)Eu II (dme) 2 (3) (dpp-Bian is dianion of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene; dme is 1,2-dimethoxyethane) with 2,2'-bipyridine (bipy) in toluene proceeds with replacement of the coordinated solvent molecules with neutral bipy ligands and affords europium(II) complex (dpp-Bian)Eu II (bipy) 2 (9). In contrast the reaction of related ytterbium complex (dpp-Bian)Yb II (dme) 2 (4) with bipy in dme proceeds with the electron transfer from the metal to bipy and results in (dpp-Bian)Yb III (bipy)(bipy<sup>-</sup>) (10) - ytterbium(III) derivative containing both neutral and radical-anionic bipy ligands. Noteworthy, in both cases dianionic dpp-Bian ligands retain its reduction state. The ligand-centered redox-process occurs when complex 3 reacts with N,N'-bis[2,4,6-trimethylphenyl]-1,4-diaza-1,3-butadiene (mes-dad). The reaction product (dpp-Bian)Eu II (mes-dad)(dme) (11) consists of two different redox-active ligands both in the radical-anionic state. The reduction of 3,6-di-tert-butyl-4-(3,6-di-tert-butyl-2-ethoxyphenoxy)-2-ethoxycyclohexa-2,5-dienone (the dimer of 2-ethoxy-3,6-di-tert-butylphenoxy radical) with (dpp-Bian)Eu II (dme) 2 (3) caused oxidation of the dpp-Bian ligand to radical-anion to afford (dpp-Bian)(ArO)Eu II (dme) (ArO = OC<sub>6</sub>H<sub>2</sub>-3,6-tBu<sub>2</sub>-2-OEt) (12). The molecular structures of complexes 9-12 have been established by the single crystal X-ray analysis. The magnetic behavior of newly prepared compounds has been investigated by the SQUID technique in the range 2-310 K. The isotropic exchange model has been adopted to describe quantitatively the magnetic properties of the exchange-coupled europium(II) complexes (11 and 12). The best-fit isotropic exchange parameters are in good agreement with their density functional theory-computed counterparts.

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