Inorganic Chemistry 2017 vol.56 N16, pages 9825-9833

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

Fedushkin I., Yambulatov D., Skatova A., Baranov E., Demeshko S., Bogomyakov A., Ovcharenko V., Zueva E.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

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 -). (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,--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-ethoxy-yclohexa-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 6 H 2 -3,6-tBu 2 -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.

http://dx.doi.org/10.1021/acs.inorgchem.7b01344

References

[1] Grützmacher, H. Cooperating Ligands in Catalysis Angew. Chem., Int. Ed. 2008, 47, 1814-1818 10.1002/anie.200704654

[2] Kaim, W.; Schwederski, B. Non-innocent ligands in bioinorganic chemistry: An overview Coord. Chem. Rev. 2010, 254, 1580-1588 10.1016/j.ccr.2010.01.009

[3] Dzik, W. I.; van der Vlugt, J. I.; Reek, J. N. H.; de Bruin, B. Ligands that Store and Release Electrons during Catalysis Angew. Chem., Int. Ed. 2011, 50, 3356-3358 10.1002/anie.201006778

[4] Chirik, P. J. Preface: Forum on Redox-Active Ligands Inorg. Chem. 2011, 50, 9737-9740 10.1021/ic201881k

[5] van der Vlugt, J. I. Cooperative Catalysis with First-Row Late Transition Metals Eur. J. Inorg. Chem. 2012, 2012, 363-375 10.1002/ejic.201100752

[6] Lyaskovskyy, V.; de Bruin, B. Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions ACS Catal. 2012, 2, 270-279 10.1021/cs200660v

[7] Broere, D. L. J.; Plessius, R.; van der Vlugt, J. I. New avenues for ligand-mediated processes-expanding metal reactivity by the use of redox-active catechol, o-aminophenol and o-phenylenediamine ligands Chem. Soc. Rev. 2015, 44, 6886-6915 10.1039/C5CS00161G

[8] Fedushkin, I. L.; Morozov, A. G.; Rassadin, O. V.; Fukin, G. K. Addition of Nitriles to Alkaline Earth Metal Complexes of 1,2-Bis[(phenyl)imino]acenaphthenes Chem.-Eur. J. 2005, 11, 5749-5757 10.1002/chem.200500330

[9] Fedushkin, I. L.; Morozov, A. G.; Chudakova, V. A.; Fukin, G. K.; Cherkasov, V. K. Magnesium(II) Complexes of the dpp-BIAN Radical-Anion: Synthesis, Molecular Structure, and Catalytic Activity in Lactide Polymerization Eur. J. Inorg. Chem. 2009, 2009, 4995-5003 10.1002/ejic.200900710

[10] Fedushkin, I. L.; Nikipelov, A. S.; Skatova, A. A.; Maslova, O. V.; Lukoyanov, A. N.; Fukin, G. K.; Cherkasov, A. V. Reduction of Disulfides with Magnesium(II) and Gallium(II) Complexes of a Redox-Active Diimine Ligand Eur. J. Inorg. Chem. 2009, 2009, 3742-3749 10.1002/ejic.200900456

[11] Fedushkin, I. L.; Skatova, A. A.; Lukoyanov, A. N.; Chudakova, V. A.; Dechert, S.; Hummert, M.; Schumann, H. Reactions of (dpp-BIAN)Mg(thf) complex (dpp-BIAN is 1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene) with halogen-containing reagents Russ. Chem. Bull. 2004, 53, 2751-2762 10.1007/s11172-005-0186-7

[12] Fedushkin, I. L.; Skatova, A. A.; Cherkasov, V. K.; Chudakova, V. A.; Dechert, S.; Hummert, M.; Schumann, H. Reduction of Benzophenone and 9(10H)-Anthracenone with the Magnesium Complex [(2,6-PrCH-Bian)Mg(thf)] Chem.-Eur. J. 2003, 9, 5778-5783 10.1002/chem.200305235

[13] Fedushkin, I. L.; Skatova, A. A.; Hummert, M.; Schumann, H. Reductive Isopropyl Radical Elimination from (dpp-Bian)Mg-iPr(EtO) Eur. J. Inorg. Chem. 2005, 2005, 1601-1608 10.1002/ejic.200400973

[14] Fedushkin, I. L.; Khvoinova, N. M.; Skatova, A. A.; Fukin, G. K. Oxidative addition of phenylacetylene through C-H bond cleavage to form the Mg-dpp-Bian Complex: Molecular structure of [Mg{dpp-Bian(H)}(C°CPh)(thf)] and its diphenylketone insertion product [Mg(dpp-Bian){OC(Ph)C°CPh}(thf)] Angew. Chem., Int. Ed. 2003, 42, 5223-5226 10.1002/anie.200352200

[15] Fedushkin, I. L.; Skatova, A. A.; Fukin, G. K.; Hummert, M.; Schumann, H. Addition of Enolisable Ketones to (dpp-Bian)Mg(THF) [dpp-Bian = 1,2-Bis{(2,6-diisopropylphenyl)imino}acenaphthene] Eur. J. Inorg. Chem. 2005, 2005, 2332-2338 10.1002/ejic.200400948

[16] Fedushkin, I. L.; Makarov, V. M.; Rosenthal, E. C. E.; Fukin, G. K. Single-Electron-Transfer Reactions of α-Diimine dpp-BIAN and Its Magnesium Complex (dpp-BIAN)Mg(THF) Eur. J. Inorg. Chem. 2006, 2006, 827-832 10.1002/ejic.200500860

[17] Razborov, D. A.; Lukoyanov, A. N.; Baranov, E. V.; Fedushkin, I. L. Addition of phenylacetylene to a magnesium complex of monoiminoacenaphtheneone (dpp-mian) Dalton Trans. 2015, 44, 20532-20541 10.1039/C5DT03174E

[18] Dodonov, V. A.; Skatova, A. A.; Cherkasov, A. V.; Fedushkin, I. L. Synthesis and structure of bischelate gallium complexes (dpp-Bian)Ga(acac) and (dpp-Bian)Ga(2,2′-bipy) (dpp-Bian is 1,2-bis[(2,--diisopropylphenyl)imino]acenaphthene Russ. Chem. Bull. 2016, 65, 1171-1177 10.1007/s11172-016-1433-9

[19] Fedushkin, I. L.; Skatova, A. A.; Dodonov, V. A.; Chudakova, V. A.; Bazyakina, N. L.; Piskunov, A. V.; Demeshko, S.; Fukin, G. K. Digallane with Redox-Active Diimine Ligand: Dualism of Electron-Transfer Reactions Inorg. Chem. 2014, 53, 5159-5170 10.1021/ic500259k

[20] Fedushkin, I. L.; Skatova, A. A.; Dodonov, V. A.; Yang, X.-J.; Chudakova, V. A.; Piskunov, A. V.; Demeshko, S.; Baranov, E. V. Ligand "Brackets" for Ga-Ga Bond Inorg. Chem. 2016, 55, 9047-9056 10.1021/acs.inorgchem.6b01514

[21] Fedushkin, I. L.; Maslova, O. V.; Hummert, M.; Schumann, H. One- and Two-Electron-Transfer Reactions of (dpp-Bian)Sm(dme) Inorg. Chem. 2010, 49, 2901-2910 10.1021/ic902439x

[22] Fedushkin, I. L.; Skatova, A. A.; Yambulatov, D. S.; Cherkasov, A. V.; Demeshko, S. V. Europium complexes with 1,2-bis(arylimino)acenaphthenes: a search for redox isomers Russ. Chem. Bull. 2015, 64, 38-43 10.1007/s11172-015-0817-6

[23] Fedushkin, I. L.; Maslova, O. V.; Baranov, E. V.; Shavyrin, A. S. Redox Isomerism in the Lanthanide Complex [(dpp-Bian)Yb(DME)(μ-Br)] (dpp-Bian = 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene Inorg. Chem. 2009, 48, 2355-2537 10.1021/ic900022s

[24] Fedushkin, I. L.; Maslova, O. V. et al., unpublished results.

[25] Fedushkin, I. L.; Maslova, O. V.; Morozov, A. G.; Dechert, S.; Demeshko, S.; Meyer, F. Genuine Redox Isomerism in a Rare-Earth-Metal Complex Angew. Chem., Int. Ed. 2012, 51, 10584-10587 10.1002/anie.201204452

[26] Tezgerevska, T.; Alley, K. G.; Boskovic, C. Valence tautomerism in metal complexes: Stimulated and reversible intramolecular electron transfer between metal centers and organic ligands Coord. Chem. Rev. 2014, 268, 23-40 10.1016/j.ccr.2014.01.014

[27] Sato, O. Dynamic molecular crystals with switchable physical properties Nat. Chem. 2016, 8, 644-656 10.1038/nchem.2547

[28] Trifonov, A. A. Reactions of Ytterbocenes with Diimines: Steric Manipulation of Reductive Reactivity Eur. J. Inorg. Chem. 2007, 2007, 3151-3167 10.1002/ejic.200601209

[29] Petrovskaya, T. V.; Fedyushkin, I. L.; Bochkarev, M. N.; Shumann, G.; Veimann, R. Synthesis and crystal structure of the Sm(BuNCHCHNBu)(bpy) complex Russ. Chem. Bull. 1997, 46, 1766-1768 10.1007/BF02495133

[30] Bunzli, J.-C. G. Benefiting from the Unique Properties of Lanthanide Ions Acc. Chem. Res. 2006, 39, 53-61 10.1021/ar0400894

[31] Mikheev, N. B.; Auerman, L. N.; Rumer, I. A.; Kamenskaya, A. N.; Kazakevich, M. Z. The anomalous stabilisation of the oxidation state 2+ of lanthanides and actinides Russ. Chem. Rev. 1992, 61, 990-998 10.1070/RC1992v061n10ABEH001011

[32] Yamagata, M.; Katayama, Y.; Miura, T. J. Electrochemical behavior of samarium, europium, and ytterbium in hydrophobic room-temperature molten salt systems J. Electrochem. Soc. 2006, 153, E5-E9 10.1149/1.2136088

[33] Schultz, M.; Boncella, J. M.; Berg, D. J.; Tilley, T. D.; Andersen, R. A. Coordination of 2,2′-Bipyridyl and 1,10-Phenanthroline to Substituted Ytterbocenes: An Experimental Investigation of Spin Coupling in Lanthanide Complexes Organometallics 2002, 21, 460-472 10.1021/om010661k

[34] Budnikova, Y. G. et al., unpublished results (for details see Supporting Information).

[35] Bochkarev, M. N.; Fedushkin, I. L.; Nevodchikov, V. I.; Cherkasov, V. K.; Schumann, H.; Hemling, H.; Weimann, R. Synthesis and ESR-characterization of radical anion complexes of lanthanum. X-ray crystal structure of the mixed bipy, bipy complex of lanthanum(III) [LaI(bipy)(bipy)(DME)]: evidence for an inter-ligand charge transfer J. Organomet. Chem. 1996, 524, 125-131 10.1016/S0022-328X(96)06425-X

[36] Abakumov, G. A.; Cherkasov, V. K.; Nevodchikov, V. I.; Druzhkov, N. O.; Fukin, G. K.; Kursky, Y. A.; Piskunov, A. V. The oxidation of 2-alkoxy-3,6-di-tert-butylphenols. The reversible dimerization of 2-alkoxy-3,6-di--ert-butylphenoxy radicals Tetrahedron Lett. 2005, 46, 4095-4097 10.1016/j.tetlet.2005.04.012

[37] Abakumov, G. A.; Cherkasov, V. K.; Piskunov, A. V.; Lado, A. V.; Fukin, G. K.; Abakumova, L. G. New lead(II) catecholate and o-semiquinone complexes Russ. Chem. Bull. 2006, 55, 1146-1154 10.1007/s11172-006-0391-z

[38] Piskunov, A. V.; Aivaz'yan, I. A.; Cherkasov, V. K.; Abakumov, G. A. New paramagnetic N-heterocyclic stannylenes: An EPR study J. Organomet. Chem. 2006, 691, 1531-1534 10.1016/j.jorganchem.2005.11.064

[39] Chegerev, M. G.; Piskunov, A. V.; Maleeva, A. V.; Fukin, G. K.; Abakumov, G. A. Multiple Reactivity of Sn Complexes Bearing Catecholate and o-Amidophenolate Ligands Eur. J. Inorg. Chem. 2016, 2016, 3813-3821 10.1002/ejic.201600501

[40] Vasudevan, K. V.; Cowley, A. H. Synthesis and structures of 1,2-bis(imino)acenaphthene (BIAN) lanthanide complexes that involve the transfer of zero, one, or two electrons Chem. Commun. 2007, 3464-3466 10.1039/b708758f

[41] Chisholm, M. N.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. Bis(2,2′-bipyridyl)diisopropoxymolybdenum(II). Structural and spectroscopic evidence for molybdenum-to-bipyridyl π∗ bonding J. Am. Chem. Soc. 1981, 103, 4945-4947 10.1021/ja00406a048

[42] Biju, S.; Ambili Raj, D. B.; Reddy, M. L. P.; Jayasankar, C. K.; Cowley, A. H.; Findlater, M. Dual emission from stoichiometrically mixed lanthanide complexes of 3-phenyl-4-benzoyl-5-isoxazolonate and 2,2′-bipyridine J. Mater. Chem. 2009, 19, 1425-1432 10.1039/b809563a

[43] Moore, J. A.; Cowley, A. H.; Gordon, J. C. Mediating Oxidation States in Decamethyleuropocene Complexes. The Role of the Diazabutadiene Fragment Organometallics 2006, 25, 5207-5209 10.1021/om060793j

[44] Panda, T. K.; Kaneko, H.; Pal, K.; Tsurugi, H.; Mashima, K. Salt Metathesis and Direct Reduction Reactions Leading to Group 3 Metal Complexes with a N,N-Bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene Ligand and Their Solid-State Structures Organometallics 2010, 29, 2610-2615 10.1021/om1003144

[45] Booth, C. H.; Walter, M. D.; Kazhdan, D.; Hu, Y.-J.; Lukens, W. W.; Bauer, E. D.; Maron, L.; Eisenstein, O.; Andersen, R. A. Decamethylytterbocene Complexes of Bipyridines and Diazabutadienes: Multiconfigurational Ground States and Open-Shell Singlet Formation J. Am. Chem. Soc. 2009, 131, 6480-6491 10.1021/ja809624w

[46] Lukens, W. W.; Magnani, N.; Booth, C. H. Application of the Hubbard Model to Cp∗Yb(bipy), a Model System for Strong Exchange Coupling in Lanthanide Systems Inorg. Chem. 2012, 51, 10105-10110 10.1021/ic300037q

[47] Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. PHI: A powerful new program for the analysis of anisotropic monomeric and exchange-coupled polynuclear d- and f-block complexes J. Comput. Chem. 2013, 34, 1164-1175 10.1002/jcc.23234

[48] Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. Imidazolylidenes, imidazolinylidenes and imidazolidines Tetrahedron 1999, 55, 14523-14534 10.1016/S0040-4020(99)00927-8

[49] Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy Phys. Chem. Chem. Phys. 2005, 7, 3297-3305 10.1039/b508541a

[50] Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn Phys. Chem. Chem. Phys. 2006, 8, 1057-1065 10.1039/b515623h

[51] Dolg, M.; Stoll, H.; Preuss, H. Energy adjusted abinitio pseudopotentials for the rare earth elements J. Chem. Phys. 1989, 90, 1730-1734 10.1063/1.456066

[52] Neese, F. The ORCA program system Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2012, 2, 73-78 10.1002/wcms.81

[53] Shoji, M.; Koizumi, K.; Kitagawa, Y.; Kawakami, T.; Yamanaka, S.; Okumura, M.; Yamaguchi, K. A general algorithm for calculation of Heisenberg exchange integrals J in multispin systems Chem. Phys. Lett. 2006, 432, 343-347 10.1016/j.cplett.2006.10.023

[54] Pantazis, D. A.; Neese, F. J. All-Electron Scalar Relativistic Basis Sets for the Lanthanides J. Chem. Theory Comput. 2009, 5, 2229-2238 10.1021/ct900090f

[55] CrysalisPro, Software Package Data Collection, Reduction, and Correction Program; Agilent Technologies, 2012.

[56] SAINT Plus, Data Reduction and Correction Progra m, v. 6.45a; Bruker AXS: Madison, WI, 2003.

[57] SAINT, Data Reduction and Correction Program, v. 8.34b; Bruker AXS: Madison, WI, 2014.

[58] Sheldrick, G. M. SHELXTL, Structure Determination Software Suite, v. 6.14; Bruker AXS: Madison, WI, 2003.

[59] SCALE3 ABSPACK, Empirical absorption correction, CrysalisPro-Software Package; Agilent Technologies: Yarnton, U.K, 2012.

[60] Sheldrick, G. M. SADABS, Bruker/Siemens Area Detector Absorption Correction Program, v. 2014/5; Bruker AXS: Madison, WI, 2014.