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Europium and Ytterbium Complexes with the Redox Active Acenaphthene-1,2-Diimine Ligand

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Abstract—The oxidation of [(Dpp-Bian)Eu(Dme)$_2$] (**I**) (Dpp-Bian is the 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene dianion, Dme = 1,2-dimethoxyethane), prepared in situ, with 0.5 mol equiv. of iodine in Thf gives europium(II) dimer, [(Dpp-Bian)Eu(μ-I)(Thf)$_2$]$_2$ (**II**) (Thf = tetrahydrofuran), with the Dpp-Bian ligand as radical anion. The exchange reaction of **II** with potassium dithiocarbamate affords europium(II) dimer, [(Dpp-Bian)Eu[SC(S)NMe$_2$](Thf)]$_2$ (**III**), which also contains the Dpp-Bian radical anion. However, the oxidation of the ytterbium complex [(Dpp-Bian)Yb(Dme)$_2$] (**IV**) with 0.5 mol equiv. of [Me$_2$NC(S)S]$_2$ gives the monomeric product [(Dpp-Bian)Yb[SC(S)NMe$_2$](Dme)] (**V**), in which Dpp-Bian is still the dianion and the ytterbium atom is oxidized to the trivalent state. The reaction of **II** with potassium thiocyanate gives europium(II) isothiocyanate complex with the radical anion diimine ligand [(Dpp-Bian)Eu(NCS)(Dme)$_2$] (**VI**). The molecular structures of complexes **II**, **III**, **V**, and **VI** were determined by X-ray diffraction (CIF files CCDC 1576687–1576690, respectively).

Key words: europium, ytterbium, complexes, acenaphthene-1,2-diimines, molecular structure

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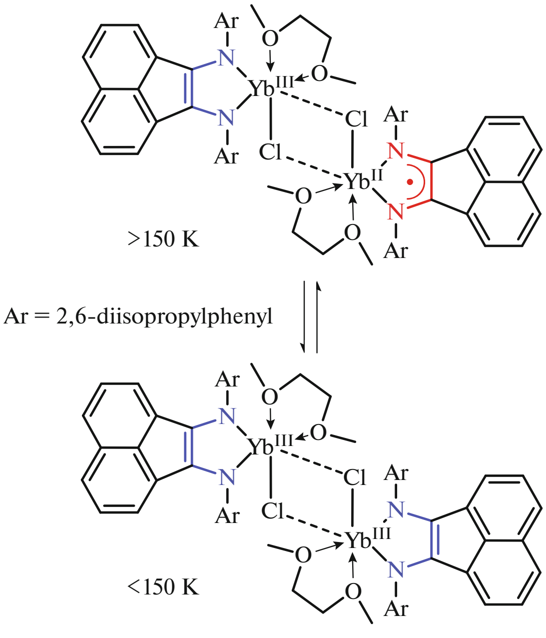
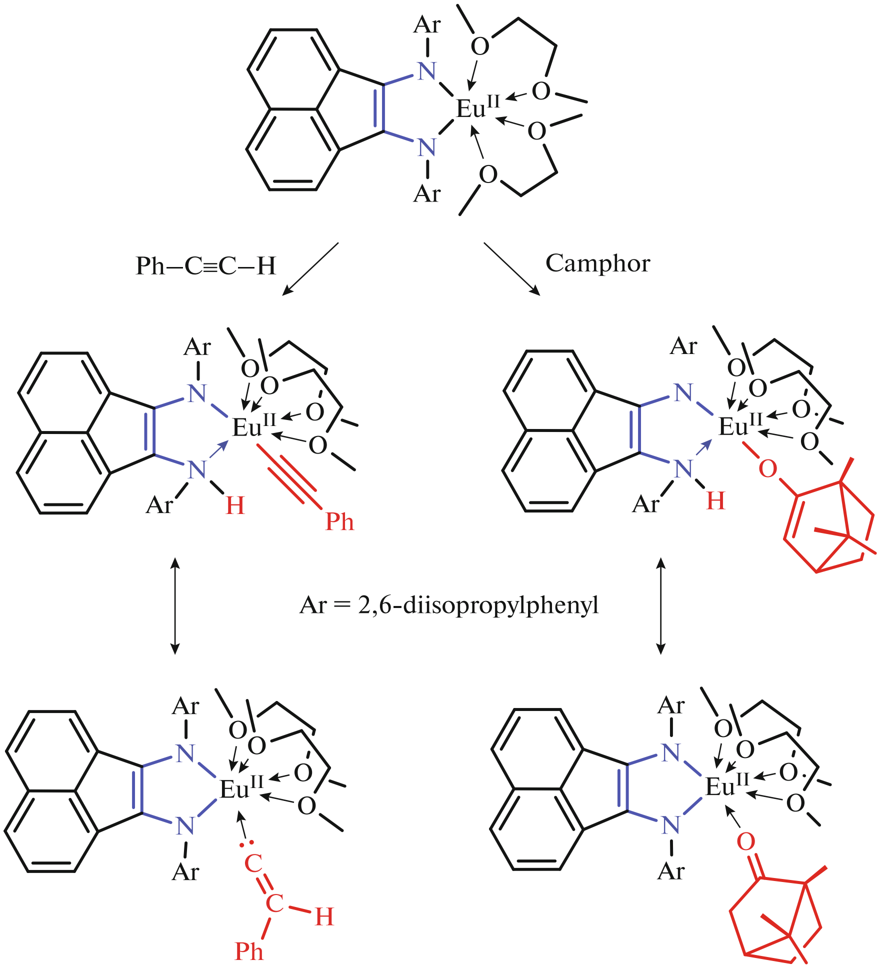
INTRODUCTION

A combination of a redox active ligand and redox active metal in the lanthanide chemistry may give rise to molecular systems exhibiting unusual spectral, magnetic, and chemical properties. For example, we accomplished for the first time a redox isomerization in the crystals of lanthanide complexes, namely, the ytterbium complex, [(Dpp-Bian)Yb(μ-Cl)(Dme)]2, containing the redox active bis(imino)acenaphthene ligand (Dpp-Bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and the 1,2-dimethoxyethane (Dme) ligand [1]. The obtained dimer exists in the crystalline state at room temperature as the [Yb(III)][Yb(II)] isomer, which is reversibly converted to the [Yb(III)][Yb(III)] isomer at ~150 K. The thermally induced intramolecular metal-to-ligand electron transfer in [(Dpp-Bian)Yb(μ-Cl)(Dme)]2 is shown in Scheme 1.



Scheme 1.

Recently, we prepared a series of 1,2-bis(imino)acenaphthene europium derivatives based on Dpp-Bian: [(Dpp-Bian)Eu(Dme)$_2$] (**I**), [(Dpp-Bian)Eu(μ-X)(Dme)]$_2$ (X = Cl, Br) [2], [(Dpp-Bian)Eu(Bipy)$_2$] (Bipy = bipyridine), [(Dpp-Bian)Eu(Mes-Dad)(Dme)] (Mes-Dad = *N*,*N*'-bis[2,4,6-trimethylphenyl]-1,4-diaza-1,3-butadiene), and [(Dpp-Bian)Eu(OC$_6$H$_2$-3,6-^{t}Bu$_2$-2-OEt)(Dme)] [3]. The molecular structure of these products in the crystals was determined and magnetic properties were measured over a wide temperature range. Unlike the ytterbium complex [(Dpp-Bian)Yb(μ-Cl)(Dme)]$_2$, the obtained europium complexes do not show redox isomerism. However, in the products of reaction of **I** with phenylacetylene and camphor (Camp), [H(Dpp-Bian)]Eu(C≡CPh)(Dme)$_2$] and [H(Dpp-Bian)]Eu(Camp)(Dme)$_2$], respectively, we observed for the first time the ligand-to-substrate proton transfer in the lanthanide coordination sphere [4]. The tautomeric transformations of phenylacetylene and camphor in the europium coordination sphere are shown in Scheme 2.



Scheme 2.

This communication describes the synthesis, structure, and properties of new europium and ytterbium derivatives based on the redox active Dpp-Bian ligand: [(Dpp-Bian)Eu(μ-I)(Thf)$_2$]$_2$ (**II**), [(Dpp-Bian)Eu[SC(S)NMe$_2$](Thf)]$_2$ (**III**), [(Dpp-Bian)-Yb[SC(S)NMe$_2$](Dme)] (**V**), and [(Dpp-Bian)-Eu(NCS)(Dme)$_2$] (**VI**).

EXPERIMENTAL

The initial compounds **I** and [(Dpp-Bian)Yb(Dme)$_2$] (**IV**) and the newly prepared complexes **II**, **III**, **V**, and **VI** are sensitive to oxygen and atmospheric moisture; therefore, all synthesis, isolation, and identification operations were carried out in vacuum using the Schlenk technique. 1,2-Dimethoxyethane, tetrahydrofuran, diethyl ether, and toluene were dried and stored with sodium benzophenone and withdrawn by condensation immediately prior to use.

For recording the IR spectra, mineral oil mulls of the compounds were prepared. The IR spectra were measured on an FSM-1201 FT IR spectrometer. The melting points of complexes **II**, **III**, **V**, and **VI** were determined in sealed capillaries. Dpp-Bian was synthesized by a known procedure [5]. The product yields were calculated in relation to Dpp-Bian taken for the synthesis (0.50 g, 1.0 mmol). The initial compounds **I** and **IV** were obtained by refluxing a Dpp-Bian suspension in Dme with an excess of activated metal under anaerobic conditions, as described in [2] and [6], respectively.

Synthesis of $[(\text{Dpp-Bian})\text{Eu}(\mu\text{-I})(\text{Thf})_2]_2 \cdot \text{Et}_2\text{O}$ (II · Et_2O). From a solution of compound **I** prepared in situ by refluxing a suspension of Dpp-Bian (0.5 g, 1 mmol) in Dme (25 mL) with excess europium metal, Dme was removed, and then Thf (30 mL) was added to the solution via evaporation–condensation. After that, iodine (0.127 g, 0.5 mmol) was added. The color of the reaction mixture instantaneously changed from brown to bright cherry. Crystallization from diethyl ether gave rhombic red crystals. The yield was 0.58 g (60%). T_m = 243°C.

For $C_{92}H_{122}N_4O_5I_2Eu_2$

Anal. calcd., %	C, 57.47	H, 6.35
Found, %	C, 55.87	H, 6.24

IR (ν, cm^{-1}): 1590 m, 1516 m, 1412 w, 1248 m, 1215 m, 1182 m, 1111 m, 1063 m, 1040 m, 1011 m, 937 w, 928 w, 860 m, 840 w, 816 m, 800 w, 787 w, 771 m, 756 m, 677 s, 652 w, 536 m.

Synthesis of $[(\text{Dpp-Bian})\text{Eu}[\text{SC(S)NMe}_2](\text{Thf})]_2 \cdot$ 3Thf (III · 3Thf). A solution of $[\text{K(SC(S)NMe}_2)]$ in Thf (20 mL) synthesized in situ by the reaction of $[\text{Me}_2\text{NC(S)S}]_2$ (0.120 g, 0.5 mmol) with potassium metal (0.039 g, 1 mmol) was added to a solution of compound **II** in Thf (30 mL) obtained in situ, as described above, from Dpp-Bian (0.50 g, 1 mmol). The color of the solution changed from bright cherry to brown. The colorless precipitate of KI thus formed was separated filtered off. The subsequent concentration of the solution in Thf gave rhombic brown crystals. The yield was 0.67 g (70%). T_m = 194°C.

For $C_{98}H_{132}N_6O_5SEu_2$

Anal. calcd., %	C, 61.69	H, 6.92
Found, %	C, 60.74	H, 6.49

IR (ν, cm^{-1}): 1644 w, 1592 w, 1518 vs, 1428 m, 1416 w, 1350 w, 1339 w, 1320 s, 1248 m, 1215 w, 1182 s, 1128 w, 1105 w, 1071 s, 1036 s, 976 s, 939 w, 926 w, 912 m, 883 m, 843 m, 816 m, 797 s, 789 s, 771 s, 758 s, 667 w, 601 w, 571 w, 538 w.

Synthesis of $[(\text{Dpp-Bian})\text{Yb}[\text{SC(S)NMe}_2](\text{Dme})]$ (V). $[\text{Me}_2\text{NC(S)S}]_2$ (0.072 g, 0.3 mmol) was added to a solution of compound **IV** prepared in situ by refluxing a suspension of Dpp-Bian (0.3 g, 0.6 mmol) in Dme (40 mL) with excess ytterbium metal. The color of the reaction mixture instantaneously changed from red-brown to blue. The solvent was evaporated in vacuum and the residue was dissolved in tetrahydrofuran (30 mL). Then the solvent was again replaced by Dme (20 mL). Crystallization from Dme gave compound **V**. The yield of the green crystals was 0.16 g (30%). T_m > 190°C (decomp.).

For $C_{43}H_{56}N_3O_2S_2Yb$

Anal. calcd., %	C, 58.42	H, 6.38
Found, %	C, 60.38	H, 6.37

IR (ν, cm^{-1}): 1960 w, 1922 w, 1851 w, 1786 w, 1609 m, 1584 m, 1510 w, 1431 s, 1358 w, 1343 w, 1316 s, 1284 w, 1253 s, 1216 w, 1206 w, 1179 w, 1153 w, 1139 w, 1123 w, 1102 m, 1088 s, 1054 w, 1040 s, 1012 w, 996 w, 980 s, 934 w, 916 s, 886 w, 856 s, 813 s, 801 s, 768 s, 760 s, 701 w, 682 w, 668 w, 636 w, 623 m, 595 w, 574 w, 540 w, 515 w, 494 w. UV (293 K, Dme): λ = 691 nm; UV (293 K, toluene): λ = 672 nm.

Synthesis of $[(\text{Dpp-Bian})\text{Eu(NCS)}(\text{Dme})_2] \cdot$ Dme (VI · Dme). KSCN (0.110 g, 1.1 mmol) was added to a solution of compound **II** (prepared in situ from Dpp-Bian diimine (0.5 g, 1.0 mmol)) in Dme (30 mL). The reaction mixture was stirred at 110°C for 6 h and filtered to remove the potassium iodide formed. Concentrating the reaction mixture (20 mL) afforded red needle crystals. The yield was 0.74 g (75%). T_m = 174°C.

For $C_{49}H_{70}N_3O_6SEu$

Anal. calcd., %	C, 59.80	H, 7.11
Found, %	C, 59.99	H, 7.19

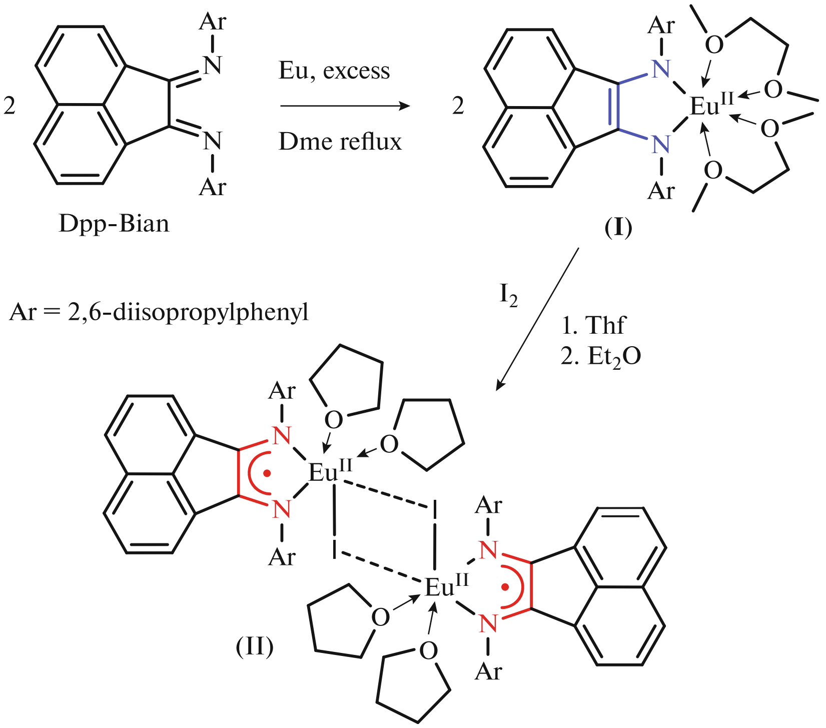
IR (ν, cm^{-1}): 2060 vs, 1516 s, 1430 s, 1416 s, 1360 m, 1341 m, 1330 m, 1320 m, 1277 w, 1248 s, 1185 s, 1111 s, 1070 s, 1059 s, 1018 w, 980 w, 940 w, 860 s, 850 s, 840 s, 820 s, 804 w, 800 w, 788 w, 766 m, 750 m, 667 w, 617 w, 602 w, 538 w.

X-ray diffraction study of **II**, **III**, **V**, and **VI** was carried out on Agilent Xcalibur (**II**, **V**) and Bruker D8 Quest (**III**, **VI**) diffractometers (ω-scan mode, MoK_α-radiation, λ = 0.71073 Å). The experimental sets of reflection intensities were integrated using CrysAlis Pro [7] (**II**, **V**) and SAINT [8] (**III**, **VI**) software. The structures were solved by the direct method and refined by the least squares method on F^2_{hkl} in the anisotropic approximation for all nonhydrogen atoms. The hydrogen atoms were placed into the geometrically calculated positions and refined isotropically in the riding model. The calculations were carried out using the SHELXTL software [9–11]. The absorption corrections were applied using the SADABS [12] (**II**, **V**) and ABSPACK (CrysAlis Pro) [13] (**III**, **VI**) programs. In complex **V**, one *iso*-Pr group of the acenaphthene-1,2-diimine ligand is disordered over two positions. The Et_2O (**II**), THF (**III**), and DME (**VI**) solvate molecules were found in the crystals of complexes.

The atom coordinates and other structure parameters are deposited with the Cambridge Crystallographic Data Centre (CCDC 1576687 (**II**), 1576688 (**III**), 1576689 (**V**), 1576690 (**VI**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The oxidation of [(Dpp-Bian)Eu$(Dme)_2$] (**I**), obtained in situ by refluxing a solution of Dpp-Bian in 1,2-dimethoxyethane (Dme) with excess europium metal, with one half mole equivalent of iodine in Thf leads to instantaneous change in the solution color from brown, which characterizes the Dpp-Bian dianion, to bright cherry color, indicating the presence of the Dpp-Bian radical anion in the mixture. The replacement of tetrahydrofuran solvent by diethyl ether resulted in the isolation of red rhombic crystals of compound **II**, suitable for X-ray diffraction, in 60% yield (Scheme 3).

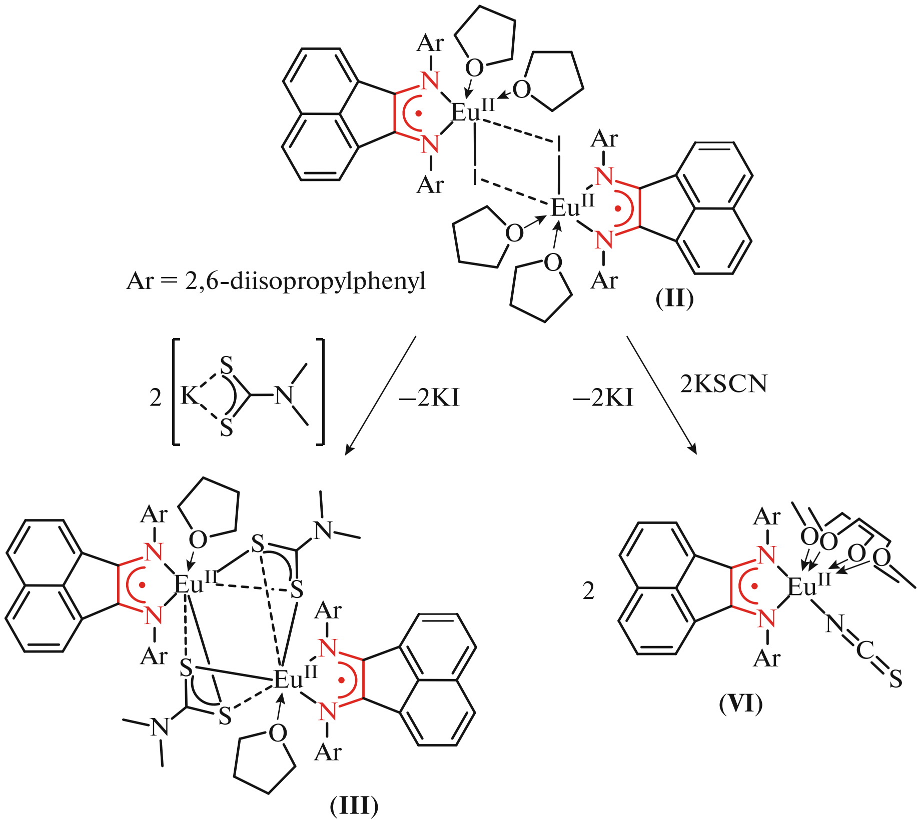


Scheme 3.

Since compound **II** is paramagnetic due to the Dpp-Bian radical anion, the ^1H NMR spectroscopy cannot be used for gaining analytical information about its structure. ESR spectroscopy is not applicable either for proving the presence of the Dpp-Bian radical anion in **II**, because of the presence of paramagnetic europium ion. The information about the structure of the complex was derived from IR spectroscopy and X-ray diffraction data. The IR spectrum of **II** does not show the characteristic stretching bands at 1671, 1652, and 1642 cm^{-1} for the C=N double bond of neutral Dpp-Bian diimine [5] or at 1310 cm^{-1} for the C–N bond of the dianionic ligand [2]. The one-and-a-half C–N bond of the Dpp-Bian radical anion is manifested in the IR spectrum of compound **II** at 1516 cm^{-1}.

In 2009, we observed for the first time the thermally induced electron transfer in a solution of a lanthanide complex, namely, the ytterbium complex [(Dpp-Bian)Yb(μ-Br)(Dme)$]_2$ [6]. The interconversion of the isomers took place in solvating solvents in the 278–368 K temperature range and was accompanied by a change in the solution color, with the red color observed on heating (Yb(II) complex with the Dpp-Bian radical anion) being changed to blue on cooling (Yb(III) complex with the Dpp-Bian dianion). The solution of europium iodide complex **II** we obtained in Thf or Dme does not change color on heating or on cooling, which is indicative of the absence of the thermally induced metal-to-ligand electron transfer in the solution of compound **II**.

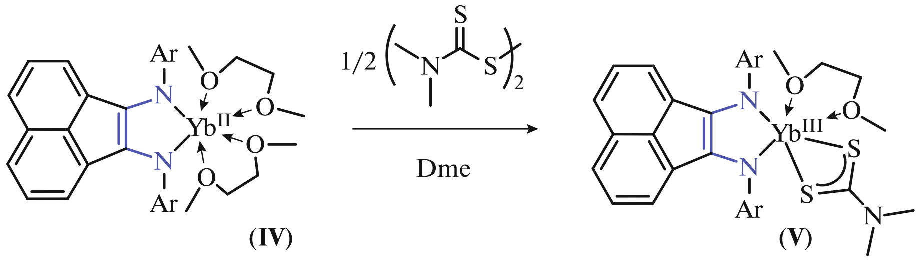
The addition of solution $K(SC(S)NMe_2)$ in Thf to a solution of compound **II** in situ induces a change in the color of the reaction mixture from bright cherry to brown. Concentrating the solution after separation of the KI precipitate gives rise to brown rhombic crystals of **III** in 70% yield (Scheme 4).



Scheme 4.

The structure of compound **III** was established by IR spectroscopy and X-ray diffraction. The search of the CCDC for lanthanide derivatives containing dithiocarbamate ligands results in ~20 monomeric Ce, Pr, Nd, Tb, Yb, and Dy dithiocarbamate salts containing a neutral diimine ligand (bipyridine and phenanthroline) [14–16]. The only dithiocarbamate derivative of a lanthanide, in particular samarium, $[(\text{Dpp-Bian})^{\cdot-}\text{Sm}^{3+}\text{I}^{-}\text{SC(S)NMe}_2)^{-}(\text{Dme})]$, containing the reduced Dpp-Bian diimine ligand was obtained by our research team [17] via oxidation of $[(\text{Dpp-Bian})^{2-}\text{Sm}^{3+}(\mu\text{-I})(\text{Dme})]_2$ with 0.5 mol equiv of $[Me_2NC(S)S]_2$. Europium derivative **III** also contains an acenaphthene-1,2-diimine ligand Dpp-Bian as radical anion, as indicated by the IR and X-ray diffraction data. In the IR spectrum of compound **III**, the stretching modes of the one-and-a-half C–N bond of the Dpp-Bian radical anion gives rise to an intense absorption band at 1518 cm^{-1} [2]. It is noteworthy that compound **III** we obtained is the only example of dimeric lanthanide dithiocarbamate derivative containing bridging dithiocarbamate ligands. The acenaphthene-1,2-diimine dithiocarbamate complexes of main group metals, $[(\text{Dpp-Bian})\text{Ga}(\text{SC(S)NMe}_2)]$ and $[(\text{Dpp-Bian})\text{Mg}(\text{SC(S)NMe}_2)(\text{Thf})]$ [18], and known lanthanide dithiocarbamate complexes are monomeric.

To prepare ytterbium dithiocarbamate derivative, we carried out the reaction of ytterbium(II) complex **IV** containing the Dpp-Bian dianion, which was obtained in situ by reduction of the Dpp-Bian diimine with excess ytterbium metal in Dme, with 0.5 mol equiv of $[Me_2NC(S)S]_2$. The reaction was accompanied by metal oxidation to give ytterbium(III) complex **V**, which was isolated from Dme as green crystals in 30% yield (Scheme 5). The transition of ytterbium from the divalent to trivalent state is confirmed by characteristic change of the solution color from red-brown to blue during the reaction. According to X-ray diffraction data, complex **V**, unlike similar europium dithiocarbamate complex **III**, is monomeric. This is caused by large ionic radius of Eu(II) (1.17 Å) as compared with the Yb(III) ionic radius (0.868 Å) [19].



Ar = 2,6-diisopropylphenyl

Scheme 5.

The electron distribution in molecule **V** is confirmed by spectral and diffraction methods. Thus the IR spectrum of compound **V** does not exhibit intense stretching bands for the double and one-and-a-half carbon–nitrogen bonds, which are characteristic of neutral Dpp-Bian ligands (1671, 1652, and 1642 cm^{-1}) [5] or the Dpp-Bian radical anions (1500–1550 cm^{-1}), respectively [2], but contains instead an intense band for the single C–N bonds in the Dpp-Bian dianion (1316 cm^{-1}). Due to the presence of paramagnetic ytterbium(III), compound **V** cannot be identified by NMR. Thus, X-ray diffraction and IR spectroscopy are the key methods for determination of the electronic structure of compound **V**. It is noteworthy that the addition of 1 mol equiv of [Me$_2$NC(S)S]$_2$ to **IV** leads to destruction of the complex to give free Dpp-Bian and europium(II) bis(dithiocarbamate).

The exchange reaction between europium iodide derivative **II** with KSCN in Dme is not accompanied by a color change of the reaction mixture, because no change in the redox state of the ligand or the oxidation state of the metal takes place, and affords monomeric europium(II) complex **VI** (75%) containing Dpp-Bian radical anion and the isothiocyanate ligand (Scheme 4). The SCN group can exist as two isomeric forms, –S–C≡N (thiocyanate) ↔ –N=C=S (isothiocyanate), which are clearly discriminable in the IR spectrum. The IR spectrum of compound **VI** exhibits a very strong ν(C=N) band at 2060 cm^{-1} and a strong ν(C=S) band at 820 cm^{-1}, which is indicative of the isothiocyanate mode of ligand-to-metal coordination via nitrogen. In the case of alternative coordination mode (via sulfur), the C≡N vibrations would be manifested as intense bands at 2100–2120 cm^{-1}, while the C–S vibrations would occur at 780–790 cm^{-1} [20–23]. The IR spectrum of **VI** also exhibits a ν(C–N) band for the Dpp-Bian radical anion (1516 cm^{-1}), but no bands for neutral diimine or the Dpp-Bian dianion. The structure of **VI** was also confirmed by X-ray diffraction. Solutions of compounds **III**, **V**, and **VI** in Dme or Thf do not change color on changing the temperature, which indirectly attests to the absence of thermally induced metal-to-ligand electron transfer in the europium coordination sphere.

The structures of compounds **II**, **III**, **V**, and **VI** in the crystalline state were established by X-ray diffraction and shown in Fig. 1. The crystal data and experiment details are summarized in Table 1 and selected bond lengths and bond angles are in Table 2.

The crystals of europium iodide derivative **II** suitable for X-ray diffraction were obtained from diethyl ether. The compound is a centrosymmetric dimer (the inversion center is in the midpoint of the line segment connecting the metal atoms). The coordination polyhedron of europium is a distorted octahedron with the N(2) and I(1') atoms in the apical positions and the O(1), O(2), I(1), and N(1) atoms in the equatorial plane (Fig. 1a). The bond lengths of the diimine moiety in **II** (C(1)–N(1), C(2)–N(2), and C(1)–C(2): 1.331(4), 1.325(4), and 1.449(5) Å) correspond to those in the known chloride analogue [(Dpp-Bian)Eu(μ-Cl)(Dme)]$_2$ (C(1)–N(1), C(2)–N(2), and C(1)–C(2): 1.340(1), 1.330(1), and 1.448(2) Å) [2] and bromide complex [(Dpp-Bian)Eu(μ-Br)(Dme)]$_2$ (C(1)–N(1), C(2)–N(2), and C(1)–C(2): 1.329(2), 1.326(2), and 1.455(2) Å) [2], which is indicative of the radical anion state of Dpp-Bian. The C–N distances in **II** (1.331(4), 1.325(4) Å) are shorter than those in the initial compound **I** (average, 1.387 Å), which contains Dpp-Bian as the dianion. Thus, treatment of compound **I** containing two reaction centers, the Dpp-Bian dianion and europium(II), with iodine leads to oxidation of the diimine ligand to the radical anion, but not to oxidation of the metal atom to the trivalent state.

Complex **III**, unlike the samarium complex [(Dpp-Bian)SmI(SC(S)NMe$_2$)(Dme)] obtained previously [24] and ytterbium complex **V**, is a centrosymmetric dimer in which the europium atoms are connected with dithiocarbamate bridges (Fig. 1b). The europium atom forms an irregular seven-coordination. As noted above, compound **III** is the only example of a bimetallic dithiocarbamate-bridged lanthanide dimer. Dithiocarbamate-bridged dimers of this type are typical of bismuth [25–27], chromium [28], copper [29, 30], tungsten [31], rhenium [32, 33], molybdenum [34], zinc [35], and thallium [36] compounds. In compound **III**, the Eu–S distance (average 3.10 Å) is 0.25 Å longer than that in europium(III) tris(morpholine-4-carbodithionato)-(1,10-phenanth-

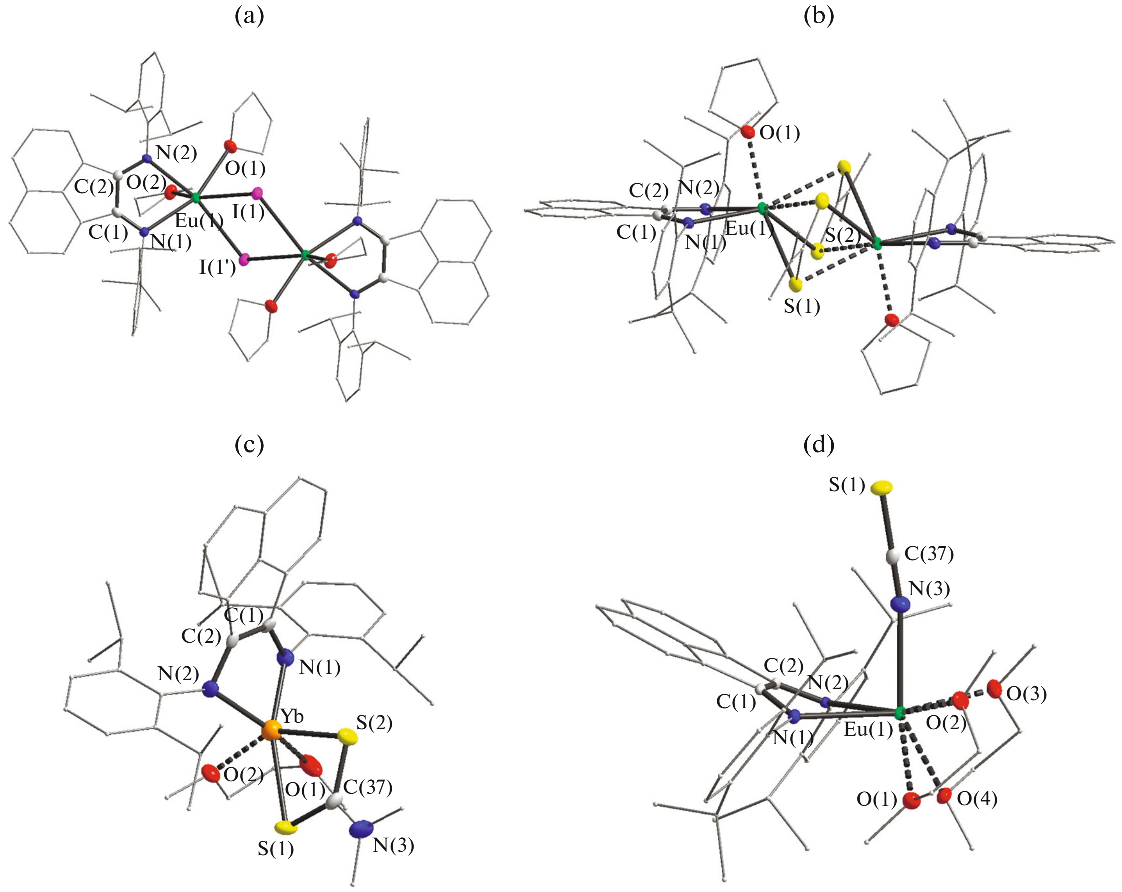


Fig. 1. Molecular structure of complexes (a) **II**, (b) **III**, (c) **V**, and (d) **VI**. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms are not shown.

roline) (average 2.85 Å) [15], because the greater ionic radius of Eu^{2+} (1.17 Å) in comparison with Eu^{3+} (0.95 Å) [19] allows dithiocarbamate groups to form bridges.

The coordination polyhedron of ytterbium in complex **V** is a distorted octahedron formed by two nitrogen atoms N(1) and N(2) of the Dpp-Bian ligand, two sulfur atoms S(1) and S(2) of the dithiocarbamate ligand, and two oxygen atoms O(1) and O(2) of the coordinated 1,2-dimethoxyethane (Fig. 1c). The ytterbium atom deviates from the N(1)–C(1)–C(2)–N(2) plane by 0.953 Å, which is twice greater than this value in the initial complex **IV** (0.426 Å) [6]. The dihedral angle between the N(1)–C(1)–C(2)–N(2) and N(1)–Yb(1)–N(2) planes is also greater in **V** (35.88°) than in **IV** (13.29°). These changes in the structure of complex **V** are indicative of its increasing steric crowding compared with **IV**. The Yb–S(1) and Yb–S(2) distances in **V** (2.7758(13) and 2.6933(13) Å) are close to those in $[(Me_5C_5)_2Yb(SC(S)NEt_2)]$ (both 2.70(1) Å) [37]. In free tetramethylthiuram disulfide [38], the C(1)–S(1) double bond (1.647 Å) is shorter than the C(1)–S(2) single bond (1.805 Å). Meanwhile, the C(37)–S(1) and C(37)–S(2) distances in the dithiocarbamate anion of **V** differ little (1.719(5) and 1.728(5) Å). These data indicate that the negative charge is delocalized between the $[SC(S)NMe_2]^-$ sulfur atoms of the complex. In addition, the C(37)–N(3) bond is somewhat shorter in **V** (1.315(6) Å) than in free tetramethylthiuram disulfide (1.329(3) Å) [38], which attests to possible double bonding between the C(37) and N(3) atoms in the zwitterion $[S^-{-}C(S^-){=}N^+Me_2]^-$ as a resonance structure of the dithiocarbamate anion.

In complex **VI** (Fig. 1d), the Eu coordination number is 7. The coordination polyhedron is formed by four oxygen atoms of 1,2-dimethoxyethane molecules, two nitrogen atoms of Dpp-Bian, and the isothiocyanate nitrogen atom. The bond lengths of the diimine moiety of the ligand attest to its radical anion state. The C–N distance in **VI** (average 1.336 Å) correlates with analogous distances in the europium and ytterbium complexes, in which the Dpp-Bian ligand is also in the radical anion state: $[(Dpp\text{-}Bian)Eu(\mu\text{-}Cl)(Dme)]_2$ (1.3348 Å) [2], $[(Dpp\text{-}Bian)Yb(\mu\text{-}Cl)(Dme)]_2$ (1.3322 Å) [1]. The C(1)–C(2) distance (1.443(9) Å) in **VI** is intermediate between those in free Dpp-Bian (1.534 Å) [39] and the Dpp-Bian dianion of **I** (1.404(5) Å) [2]. The Eu(1)–N(3) bond length

Table 1. Crystallographic data, X-ray experiment details, and structure refinement parameters for compounds **II**, **III**, **V**, and **VI**

Compound	**II** · Et_2O	**III** · 3Thf	**V**	**VI** · Dme
Molecular formula	$C_{92}H_{122}N_4O_5I_2Eu_2$	$C_{98}H_{132}N_6O_5S_4Eu_2$	$C_{43}H_{56}N_3O_2S_2Yb$	$C_{49}H_{70}N_3O_6SEu$
M	1921.65	1906.25	884.07	981.10
System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$Pca2_1$
Temperature, K	100(2)	100(2)	100(2)	100(2)
a, Å	12.0593(2)	17.0556(5)	18.9123(3)	23.5165(18)
b, Å	18.4238(2)	13.5739(4)	23.4398(3)	12.5527(10)
c, Å	21.5360(3)	20.4234(7)	20.0120(3)	16.3764(13)
β, deg	99.399(1)	103.6392(15)	108.856(2)	90
V, Å^3	4720.59(12)	4594.9(2)	8395.2(2)	4834.2(7)
Z	2	2	8	4
ρ(calcd.), g/cm^3	1.352	1.378	1.399	1.348
μ, mm^{-1}	2.018	1.498	2.365	1.390
F(000)	1948	1984	3624	2048
Crystal size, mm	0.50 × 0.50 × 0.10	0.39 × 0.29 × 0.05	0.27 × 0.10 × 0.03	0.37 × 0.21 × 0.05
Range of θ, deg	2.984–25.999	2.326–28.000	3.06–30.00	2.220–25.998
Ranges of indices	$-14 \le h \le 14$, $-22 \le k \le 22$, $-26 \le l \le 26$	$-22 \le h \le 22$, $-17 \le k \le 17$, $-26 \le l \le 26$	$-26 \le h \le 26$, $-32 \le k \le 32$, $-28 \le l \le 26$	$-29 \le h \le 29$, $-15 \le k \le 15$, $-20 \le l \le 20$
Observed reflections	71685	91697	95499	44163
Unique reflections (R_{int})	9190 (0.0379)	11058 (0.0688)	24457 (0.0901)	9468 (0.0670)
Absorption correction	SADABS (max/min 1.0000/0.3948)	SADABS (max/min 0.7678/0.5484)	SADABS (max/min 0.9324/0.5677)	SADABS (max/min 0.8017/0.6223)
Data/restraints/parameters	9190/38/506	11058/3/526	24457/0/973	9468/19/556
GOOF (F^2)	1.068	1.033	0.974	1.056
R_1, wR_2 ($I > 2\sigma(I)$)	0.0320, 0.0774	0.0301, 0.0669	0.0598/0.0679	0.0422/0.0914
R_1, wR_2 (for all parameters)	0.0386/0.0809	0.0437/0.0706	0.1283/ 0.0798	0.0505/0.0940
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	1.586/–1.008	1.419/–0.560	2.920/–2.210	2.498/–1.175

(2.545(7) Å) in complex **VI** is comparable with a similar bond length in the Eu(II) isothiocyanate complex $[Eu(NCS)_2(Dme)_3]$ (2.598 Å) [21] and is 0.2 Å longer than that in the Eu(III) complex $[Eu(NCS)_3(OPPh_3)]$ (2.396 Å) [40], which is consistent with the difference between the di- and trivalent europium ionic radii [19]. The N(3)–C(37) distances (1.154(9) Å) and C(37)–S(1) (1.641(7) Å) in the isothiocyanate group of complex **VI** are close to the corresponding distances in the Eu(II) complex $[Eu(NCS)_2(Dme)_3]$, N–C (average 1.1535 Å) and C–S (average 1.6315 Å) [21], which confirms the isothiocyanate group structure.

Thus, we synthesized mono- and bimetallic europium and ytterbium complexes containing anionic groups (iodide, dithiocarbamate, or isothiocyanate) apart from the redox active acenaphthene-1,2-diimine ligand. The composition and structure of the complexes were investigated. The redox state of the redox active ligand and the metal oxidation state were determined for each complex. A divalent europium com-

Table 2. Selected bond lengths (Å) and bond angles (deg.) in compounds **II**, **III**, **V**, and **VI**

Bond	**II**	**III**	**V**	**VI**
		d, Å		
M*–N(1)	2.565(3)	2.6047(18)	2.1765(35)	2.602(6)
M–N(2)	2.585(3)	2.5819(18)	2.1863(35)	2.601(6)
M–N(3)		2.545(7)		2.545(7)
M–S(1)		3.0570(6)	2.7758(13)	
M–S(2)		3.1248(6)	2.6933(13)	
M–I(1)	3.2509(3)			
N(1)–C(1)	1.331(4)	1.330(3)	1.3867(58)	1.340(9)
N(2)–C(2)	1.325(4)	1.335(3)	1.4073(52)	1.331(9)
N(3)–C(37)		1.343(3)	1.315(6)	1.154(9)
C(1)–C(2)	1.449(5)	1.446(3)	1.4003(59)	1.443(9)
C(37)–S(1)		1.727(3)	1.7194(59)	1.641(7)
C(37) –S(2)		1.718(3)	1.7289(49)	
Angle		ω, deg		
N(1)MN(2)	67.53(8)	66.37(6)	83.647(138)	66.42(18)
N(1)MS(1)		89.87(4)	162.073(99)	
N(1)MS(2)		133.99(4)	103.633(103)	
MN(3)C(37)				169.683(5)
N(3)C(37)S(1)		120.151(2)	120.431(413)	179.4(7)
N(3)C(37)S(2)		120.951(2)	119.788(395)	

* M = Eu for **II**, **III**, and **VI**; M = Yb for **V**.

pound with dithiocarbamate bridges was obtained for the first time. The thiocyanate group was found to isomerize to the isothiocyanate group upon coordination to europium.

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