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Mono- and dichlorido terbium(III) and erbium(III) complexes coordinated by diazabutadiene ligands in different redox states

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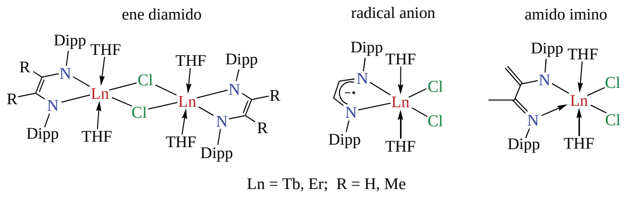
Treatment of 1,4-diazabutadienes (DADs) of formula DippN=C(R)C(R)=NDipp (Dipp = 2,6-$Pr^i_2C_6H_3$, R = H or Me) with 2 or 1 equiv. of potassium metal in THF leads to the corresponding dianions (DAD^{2-}) or radical anions ($DAD^{\bullet-}$), respectively. The subsequent salt metathesis between $LnCl_3$ (Ln = Tb or Er) and the above dianions affords dimeric monochlorido complexes $[(DAD^{2-})Ln(THF)_2(\mu\text{-}Cl)]_2$ with bridging chlorine atoms between the lanthanides. The reaction of the radical anion species with $LnCl_3$, if R = H, gives monomeric dichlorido complexes $(DAD^{\bullet-})Ln(THF)_2Cl_2$; however, if R = Me, the activation of one methyl group occurs, which in the reaction with $TbCl_3$ leads to the formation of a product with shifted double bonds $[DippN{=}C(Me)C({=}CH_2)N(Dipp)]Tb(THF)_2Cl_2$.

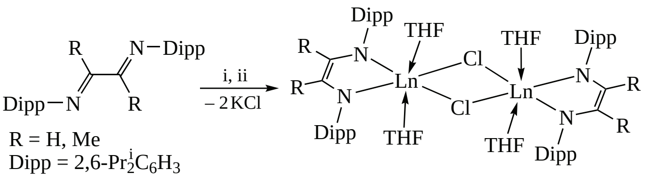


Keywords: lanthanides, terbium complexes, erbium complexes, diimino ligands, diazabutadienes, salt metathesis, structure.

1,4-Disubstituted diazabuta-1,3-dienes (DADs) and related diimino ligands have found wide applications in lanthanide chemistry.[1–7] The principal advantages of DAD ligands are variety of their coordination modes and redox active nature, as well as the ease of modification of their steric and electronic properties.[8] The presence in the DAD molecule of electron pairs on N atoms, as well as π-electrons of multiple C=N bonds, allows it to act as both a σ- and π-donor coordinating to a metal atom in the form of a neutral ligand.[9] The reduction of DADs by one or two electrons makes it possible to obtain radical anions[10] $[RNC(R')C(R')NR]^{\bullet-}$ and ene diamide[11–13] $[RN{-}C(R'){=}C(R'){-}NR]^{2-}$ ligands, respectively. For DADs containing methyl groups at imine carbon atoms there is an additional possibility of the ligand transformation due to the activation of one or two CH bonds of the Me-substituents, which allows one to obtain monoanionic amido imine[14–17] $[RN{=}C(Me){-}C({=}CH_2){-}NR]^-$ or diene diamide[18,19] $[RN{-}C({=}CH_2){-}C({=}CH_2){-}NR]^{2-}$ ligands. Moreover, the systematic studies of the possible transformations of redox active ligands in coordination sphere of rare-earth metals can provide a deeper insight to the understanding of relationship between redox-reactions and CH bond activation.[1] Lanthanide derivatives bearing DAD ligands in various reduction states proved to be efficient catalysts for ring-opening polymerization of lactide and β-butyrolactone,[20] polymerization of 2-vinylpyridine,[21] stereoselective polymerization of isoprene,[15,22] intermolecular hydroamination, hydrophosphination,[23] and hydrosilylation[24,25] of alkenes and acetylenes. Moreover, combination of Dy^{3+} ion with DAD ligands in different reduction states allowed obtaining a series of complexes exhibiting single ion magnet behavior.[26–30]

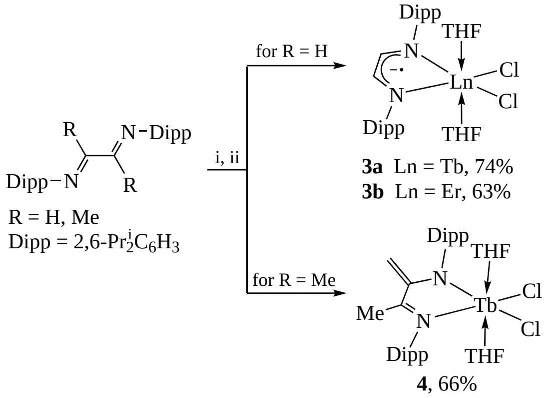
Herein, we report on the synthesis and structural studies of mono- and dichlorido Tb^{III} and Er^{III} complexes coordinated by DAD ligands in dianionic and radical-anionic state. Treatment of the DADs with 2 equiv. of potassium metal in THF (Scheme 1)[31] generates *in situ* the dianion species of type $[DippNC(R){=}C(R)NDipp]^{2-}K_2(THF)_n$. The subsequent salt metathesis with $LnCl_3$ (Tb, Er) affords dimeric monochlorido complexes **1a**,**b** or **2**. After separation of KCl, extraction with toluene and further recrystallization from THF/hexane mixtures, their yields approached 69, 74 and 72%, respectively.

On the other hand, treatment of the DADs with 1 equiv. of potassium metal in THF (Scheme 2) would generate radical anion species, one mesomeric form of which may be depicted as $[DippNC(R){=}C(R)NDipp]^{\bullet-}K(THF)_n$. The outcome of their reactions with $LnCl_3$ was found to be dependent on the nature of R substituent. For the cases with R = H, the reactions gave the expected monomeric dichlorido complexes **3a**,**b** or **4** with radical-anion ligand (see Scheme 2).



1a R = H, Ln = Tb, 69%
1b R = H, Ln = Er, 74%
2 R = Me, Ln = Tb, 72%

Scheme 1 *Reagents and conditions*: i, K (2 equiv.), THF, room temperature, 48 h; ii, $LnCl_3$, THF, room temperature, 12 h.



Scheme 2 *Reagents and conditions*: i, K (1 equiv.), THF, room temperature, 24 h; ii, $LnCl_3$, THF, room temperature, 12 h.

The similar synthetic procedure in the case of methyl substituted radical-anionic derivative $(DAD^{2Me})^{\bullet-}K(THF)_n$ and $TbCl_3$ is accompanied by activation of one of the sp^3-hybridized CH bond of the methyl group at imino carbon, the abstraction of one H atom and the formation of amido imino ligand $[RN{=}C(Me){-}C({=}CH_2){-}NR]^-$. This reaction affords monomeric Tb^{III} dichlorido complex $[DAD^{Me,CH_2}]TbCl_2(THF)_2$ **4** (see Scheme 2) in 66% yield. The analogous transformation of DAD^{Me_2} ligands was previously documented in the salt metathesis reaction of $(DAD^{2Me})^{\bullet-}K(THF)_n$ with $DyCl_3$, which resulted in the dichlorido complex coordinated by amido imino ligand $[DAD^{Me,CH_2}]DyCl_2(THF)_2$.[29] Yttrium and lutetium analogues were synthesized by the reactions of $LnCl_3$ and amido imino lithium salt $(DAD^{Me,CH_2})Li(OEt_2)$.[15] Also the activation of sp^3-CH bond of DAD^{2Me} ligand was earlier[32] observed in the reaction of Yb^{II} bis(fluorenyl) complex $(C_{13}H_9)_2Yb(THF)_2$ with DAD^{2Me}.

Molecular structures of monochlorido complexes **1b** and **2** as well as dichlorido complexes **3a**,**b** and **4** were established by single crystal X-ray analysis. Unfortunately, the single-crystal samples of **1a** cracked during the XRD experiment, what did not allow us to obtain data of sufficient quality. Monochlorido complexes **1b** and **2** adopt dimeric structures where two $(DAD^{2R})Ln$ moieties are linked by two μ^2-chlorido ligands (Figure 1).[†] Along with two bridging chlorido ligands each Ln^{3+} ion in dimers **1b** and **2** is bonded with chelating dianionic $(DAD^{2R})^{2-}$ ligands and additionally by two THF molecules. The Ln^{3+} ions feature coordination number of six and distorted octahedral geometry. The Ln−μ-Cl distances in **1b** [2.681(3) and 2.739(3) Å] and **2** [2.740(2) and 2.842(2) Å] slightly differ from each other but are comparable with related distances in six-coordinated dimeric Tb^{III} and Er^{III} complexes with μ^2-chlorido ligands: Er−(μ-Cl), 2.668(5)–2.789(3) Å;[33–37] Tb−(μ-Cl), 2.727(4)–2.749(3) Å.[36,38] The Ln···Ln distance in **1b** [4.236(3) Å] is comparable with related distance in six-coordinated dimeric chlorides [Er···Er, 4.105(2)–4.414(2) Å],[33–37] while for **2** this distance [4.457(2) Å] proved to be longer compared to the previously reported complexes [Tb···Tb, 4.154(3)–4.194(3) Å].[36,38] The metal–nitrogen bond lengths in **1b** [Er−N, 2.225(3) and 2.235(3) Å] and **2** [Tb−N, 2.243(2) and 2.262(2) Å] are very close to related distances in Er and Tb ionic complexes $[(DAD^{2H})_2^{2-}Ln][Li(DME)_3]$ [Er−N, 2.211(4)–2.245(4) Å; Tb−N, 2.204(5)–2.256(5) Å].[26] The geometry of the NCCN fragments in **1b** and **2** gives an evidence of dianionic state of DAD^{2R}

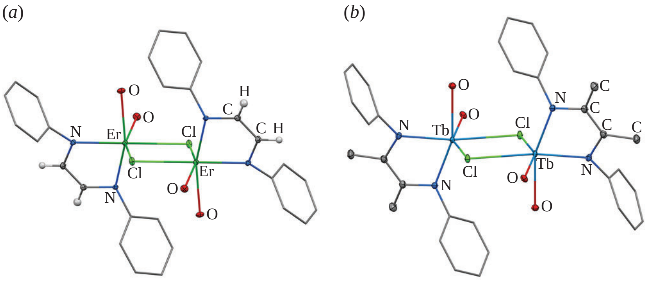


Figure 1 Molecular structures of (*a*) complex **1b** and (*b*) complex **2**. Thermal ellipsoids are given with 30% probability. Hydrogen atoms (except of NC(H)C(H)N fragments in **1b**) and carbon atoms of coordinated THF and Pr^i groups of the DAD ligands are omitted for clarity.

[†] *Crystal data for* **1b**. $C_{68}H_{104}Cl_2Er_2N_4O_4$, $F_w = 1446.97$, orthorhombic, $a = 19.1720(5)$, $b = 15.3350(4)$ and $c = 23.2547(6)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 6836.9(3)$ Å^3, space group *Pbca*, $Z = 4$, $d_{calc} = 1.406$ g cm^{-3}, $F(000) = 2968$, $\mu(MoK\alpha) = 2.563$ mm^{-1}, yellow prism with dimensions *ca*. 0.19×0.10×0.05 mm. Total of 85075 reflections (9965 unique, $R_{int} = 0.0587$). The final residuals were: $R_1 = 0.0381$ for 8103 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0772$ for all data and 384 parameters. GoF = 1.076.

Crystal data for **2**. $C_{72}H_{112}Cl_2N_4O_4Tb_2 \cdot C_4H_8O$, $F_w = 1558.49$, monoclinic, $a = 15.3491(4)$, $b = 16.0935(4)$ and $c = 15.7508(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 108.4270(10)°$, $V = 3691.3(2)$ Å^3, space group $P2_1/n$, $Z = 2$, $d_{calc} = 1.402$ g cm^{-3}, $F(000) = 1616$, $\mu(MoK\alpha) = 2.023$ mm^{-1}, yellow prism with dimensions *ca*. 0.25×0.21×0.11 mm. Total of 51481 reflections (10892 unique, $R_{int} = 0.0227$). The final residuals were: $R_1 = 0.0219$ for 9840 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0552$ for all data and 434 parameters. GoF = 1.043.

Crystal data for **3a**. $C_{34}H_{52}Cl_2N_2O_2Tb$, $F_w = 750.59$, monoclinic, $a = 10.1207(5)$, $b = 19.7298(10)$ and $c = 18.5792(10)$ Å, $\alpha = \gamma = 90°$, $\beta = 105.3200(10)°$, $V = 3578.1(3)$ Å^3, space group $P2_1/n$, $Z = 4$, $d_{calc} = 1.393$ g cm^{-3}, $F(000) = 1540$, $\mu(MoK\alpha) = 2.156$ mm^{-1}, red prism with dimensions *ca*. 0.32×0.18×0.14 mm. Total of 46230 reflections (10463 unique, $R_{int} = 0.0335$). The final residuals were: $R_1 = 0.0200$ for 9287 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0444$ for all data and 386 parameters. GoF = 1.019.

Crystal data for **3b**. $C_{34}H_{52}Cl_2ErN_2O_2$, $F_w = 758.93$, monoclinic, $a = 10.1072(3)$, $b = 19.6768(5)$ and $c = 18.4890(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 105.5000(10)°$, $V = 3543.3(2)$ Å^3, space group $P2_1/n$, $Z = 4$, $d_{calc} = 1.423$ g cm^{-3}, $F(000) = 1552$, $\mu(MoK\alpha) = 2.549$ mm^{-1}, brown prism with dimensions *ca*. 0.29×0.18×0.17 mm. Total of 34472 reflections (10398 unique, $R_{int} = 0.0205$). The final residuals were: $R_1 = 0.0175$ for 9726 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0413$ for all data and 387 parameters. GoF = 1.068.

Crystal data for **4**. $C_{36}H_{55}Cl_2N_2O_2Tb$, $F_w = 777.64$, monoclinic, $a = 13.7236(16)$, $b = 17.421(2)$ and $c = 15.5119(18)$ Å, $\alpha = \gamma = 90°$, $\beta = 90.233(2)°$, $V = 3708.5(7)$ Å, space group $P2_1$, $Z = 4$, $d_{calc} = 1.393$ g cm^{-3}, $F(000) = 1600$, $\mu(MoK\alpha) = 2.083$ mm^{-1}, yellow prism with dimensions *ca*. 0.32×0.21×0.18 mm. Total of 51077 reflections (51077 unique). The final residuals were: $R_1 = 0.0341$ for 46582 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0891$ for all data and 806 parameters. GoF = 0.988.

The single crystal X-ray diffraction data were collected with Bruker D8 Quest (**1b**, **2**, **3b**) and Bruker Smart APEX II (**3a**, **4**) diffractometers (MoK_α-radiation, ω-scans technique, $\lambda = 0.71073$ Å) using APEX3[46] software package. The structures were solved *via* intrinsic phasing algorithm and refined by full-matrix least squares against F^2 using SHELX.[47,48] Program SADABS[49] was used to perform absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and refined anisotropically. Hydrogen atoms H(1), H(2) in **1b** and **3a**,**b** were also found from Fourier syntheses of electron density. All other hydrogen atoms in all complexes were placed in calculated positions and refined isotropically in the ‘riding’ model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms $[U(H)_{iso} = 1.5U_{eq}$ for methyl groups]. The structure of **4** was solved and refined as four component pseudo-merohedral inversion twin. The crystallographic data and structures refinement details for **1b**, **2** and **3b** are given in Table S1 (see Online Supplementary Materials).

CCDC 2291546 (**1b**), 2291547 (**2**), 2291548 (**3b**), 2294708 (**3a**), and 2294709 (**4**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge by The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

ligands. Thus, the C−N distances [1.406(4) and 1.419(4) Å, **1b**; 1.412(3) and 1.423(3) Å, **2**] are noticeably longer compared to those in the parent ligand [1.279(3) and 1.280(3) Å][39] and are indicative of their single character. The C−C bonds [1.344(4) Å for **1b**; 1.388(3) Å for **2**] became shorter compare to parent ligand [1.498(3) Å][39] and correspond to double bond.[40] Thus, the distribution of bond lengths in the NCCN fragment is similar to that in previously known lanthanide complexes with a dianionic ligand $(DAD^{2Me})^{2-}$.[20,24–29,41] It is noteworthy, that in contrast to the ionic compounds $[(DAD^{2H})_2Ln][Li(DME)_3]$, featuring κ^2-N,N:η^2-CC coordination mode of the dianionic $(DAD^{2H})^{2-}$ ligands due to the π-interaction of the metal centres with double C=C bond of the NCCN-moiety, in **1b** and **2** no interactions with NCCN carbons were detected. This is proved by long distances between Ln ions and carbons of NCCN moiety [Er···C, 3.023(3) Å; Tb···C, 3.124(3) and 3.134(3) Å] and nearly planar geometry of the five-membered metallacycles. The dihedral angles between the NCCN and NLnN planes are 168.8 and 165.5°. So, the coordination mode of $(DAD^{2R})^{2-}$ ligands in **1b** and **2** is κ^2-N,N similar to that in Dy^{3+} analogues $[(DAD^{2R})Dy(THF)_2(\mu\text{-}Cl)]_2$ (R = H, Me).[29]

Dichlorido complexes **3b** and **4** coordinated by radical-anionic $(DAD^{2H})^{\bullet-}$ or amido imino $(DAD^{Me,CH_2})^{-}$ ligands adopt monomeric structures. The coordination environment of Ln^{3+} ions is composed of two N atoms of a DAD ligand, two terminal chloride ligands and two O atoms of coordinated THF molecules, thus resulting in a coordination number of six (Figure 2; for the structure of **3a**, see Online Supplementary Materials, Figure S1).

The geometric parameters of the $(DAD^{2H})^{\bullet-}$ ligands in **3a**,**b** are indicative of their radical-anionic state. The C−N [1.334(4) Å, **3b**; 1.329(2) and 1.331(2) Å, **3a**] and C−C [1.403(4) Å, **3b**; 1.402(2) Å, **3a**] bond lengths within the NCCN moieties demonstrate intermediate values between those expected for single and double bonds[39] and are comparable with those in lanthanide complexes with the radical-anion ligand $(DAD^{2H})^{\bullet-}$ [C−N, 1.319(5)–1.338(2) Å; C−C, 1.395(2)–1.399(3) Å].[29,42,43] The Ln−N bond distances measured in **3a**,**b** [2.354(3) Å for **3b**; 2.395(2) and 2.396(2) Å for **3a**] are significantly longer compared to the covalent Ln−N bonds in **1b** and **2** coordinated by ene diamido DAD^{2R} ligands.

Complex **4** displays a significant difference in the Tb−N and C−N bond lengths. Thus, the length of one Tb−N bond, 2.291(8) Å, is typical for a covalent bond and only slightly exceeds the related bond lengths in **2** [2.243(2) and 2.262(2) Å]. The second Tb−N bond is significantly longer [2.480(8) Å], which indicates its coordination character. The length of one C−N bond [1.376(13) Å] is closer to a single, while the second one [1.302(13) Å] corresponds to a double C=N bond.[40] The C−C bond length [1.484(13) Å] is in good agreement with those measured in the related dichlorido Y and Dy complexes $(DAD^{Me,CH_2})LnCl_2(THF)_2$ in which these values were 1.494(6) and 1.48(2) Å, respectively.[15,29] The $C{-}CH_3$ bond length [1.487(14) Å] corresponds to a single bond,[40] while the $C{=}CH_2$ distance [1.370(16) Å] indicates its double character.

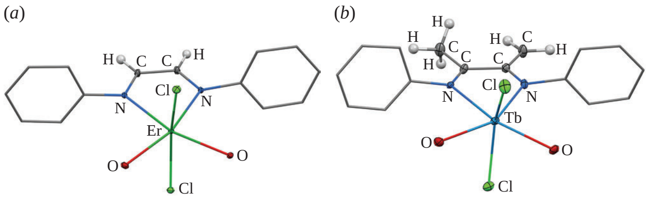


Figure 2 Molecular structure of (*a*) complex **3b** and (*b*) complex **4**. Thermal ellipsoids are given with 30% probability. Hydrogen atoms (except for NC(R)C(R)N fragments) and carbon atoms of coordinated THF and Pr^i groups of the DAD ligands are omitted for clarity.

The Er−Cl bond lengths found in **3b** [2.554(3) and 2.562(3) Å] are very close to related distances in six-coordinated erbium dichlorido with β-diketiminato ligand [2.547(4) and 2.579(3) Å].[44] Despite the different structures of the DAD ligands (radical anionic *vs.* amido imino monoanionic) Tb−Cl distances in **3a** and **4** are very close to each other [2.591(2) and 2.597(2) Å for **3a**; 2.589(3) and 2.620(3) Å for **4**] and comparable with six-coordinated Tb β-diketiminato analogue [2.594(5) and 2.605(5) Å].[45] On the other hand, the passage from radical-anionic ligand in **3a** to amido imino in **4** resulted in some elongation of Tb−O distances: 2.387(3) and 2.389(3) Å (for **3a**) *vs.* 2.423(3) and 2.437(3) Å (for **4**).

A study of the luminescent properties of lanthanide complexes **1–3** in solid state showed the absence of metal-centred luminescence in the cases of both Tb and Er. In contrast to the previously reported related Dy^{3+} complexes, slow relaxation of magnetization in a zero field turned out to be uncharacteristic for **1–3**.

In conclusion, it was demonstrated that dimeric Tb and Er monochlorido complexes coordinated by dianionic ene diamido ligands $(DAD^{2R})^{2-}$ can be obtained by salt metathesis between $LnCl_3$ and dipotassium derivatives $(DAD^{2R})K_2(THF)_n$. In the case of radical-anionic potassium species, the outcome of the reactions with $LnCl_3$ depends on the nature of the substituents at the imino carbons (H *vs.* Me). While DAD^{2H} dichlorido complexes $(DAD^{2H})LnCl_2(THF)_2$ are rather stable and isolable, the radical anion of Me-substituted DAD^{2Me} in the coordination sphere of Tb^{3+} undergoes the activation of one of CH-bonds of methyl group transforming into amido imino ligand.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.01.013.

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