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

Dmitry M. Lyubov, Anton V. Cherkasov and Alexander A. Trifonov

Experimental section

All operations were carried out under an argon atmosphere using Schlenk techniques or in nitrogen filled glovebox. THF and toluene were purified by distillation from sodium/benzophenone ketyl and degassed thoroughly. Hexane was dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. $LnCl_3$,[S1] and DAD^{2R} (2,6-$Pr^i_2C_6H_3$-NC(R)C(R)N$C_6H_3Pr^i_2$-2,6) (R = H, Me)[S2] were prepared according to literature procedures. Lanthanide metal analysis was carried out by complexonometric titration.[S3] IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of $[(DAD^{2H})Tb(THF)_2(\mu\text{-}Cl)]_2(THF)$ (1a). A solution of $(DAD^{2H})K_2(THF)_n$ generated *in situ* (THF, rt, 48 h) from DAD^{2H} (0.650 g, 1.73 mmol) and potassium metal (0.140 g, 3.46 mmol) was added slowly to a suspension of $TbCl_3$ (0.460 g, 1.73 mmol) in THF (10 mL). The resulted solution was stirred at ambient temperature for 12 h, then all volatiles were removed in vacuum, and the solid residue was extracted from KCl with toluene (30 mL). The toluene extract was filtered, toluene was evaporated in vacuum. Recrystallization of the resulting solid from THF/hexane mixture at 20 °C afforded orange crystals of **1a** in 69% yield (0.895 g, 0.59 mmol). Elemental analysis calcd (%) for: $C_{68}H_{104}Cl_2N_4O_4Tb_2 \cdot (C_4H_8O)$ (1502.44 g mol^{-1}): C, 57.56; H, 7.51; N, 3.73; Tb, 21.16; Found: C, 57.70; H, 7.73; N, 3.59; Tb, 20.98. IR (Nujol, KBr) υ/cm^{-1}: 1590 (m), 1310 (s), 1260 (s), 1240 (m), 1200 (s), 1100 (m), 1075 (m), 1020 (s), 935 (m), 880 (m), 860 (s), 800 (s), 755 (s), 670 (m), 590 (w), 535 (w), 485 (w).

S1 M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, 1962, **24**, 387.
S2 M. Svoboda and H. T. Dieck, *J. Organomet. Chem.*, 1980, **191**, 321.
S3 S. J. Lyle and M. M. Rahman, *Talanta*, 1963, **10**, 1177.

Synthesis of [(DAD^{2H})Er(THF)$_2$(μ-Cl)]$_2$ (1b). A solution of (DAD^{2H})K$_2$(THF)$_n$ generated *in situ* (THF, rt, 48 h) from DAD^{2H} (0.210 g, 0.56 mmol) and potassium metal (0.045 g, 1.12 mmol) was added slowly to a suspension of $ErCl_3$ (0.152 g, 0.56 mmol) in THF (10 mL). The resulted solution was stirred at ambient temperature for 12 h, then all volatiles were removed in vacuum, and the solid residue was extracted from KCl with toluene (30 mL). The toluene extract was filtered, toluene was evaporated in vacuum. Recrystallization of the resulting solid from THF/hexane mixture at 20 °C afforded orange yellow crystals of **1b** in 74% yield (0.30 g). Elemental analysis calcd. (%) for: $C_{68}H_{104}Cl_2Er_2N_4O_4$ (1446.97 g mol^{-1}): C, 56.44; H, 7.24; N, 3.87; Er, 23.12. Found: C, 56.15; H, 7.19; N, 4.11; Er, 22.90. IR (Nujol, KBr) υ/cm^{-1}: 1585 (s), 1570 (s), 1430 (s), 1355 (s), 1310 (s), 1245 (s), 1205 (s), 1110 (s), 1075 (s), 1020 (s), 925 (s), 860 (s), 800 (s), 755 (s), 680 (s), 580 (s), 535 (m), 485 (m) cm^{-1}.

Synthesis of [(DAD^{2Me})Tb(THF)$_2$(μ-Cl)]$_2$(THF) (2). Complex **2** was synthesized and isolated analogously to **1a** starting form *in situ* generated (DAD^{2Me})K$_2$(THF)$_n$ (DAD^{2Me}: 0.345 g, 0.85 mmol; potassium metal: 0.070 g, 1.71 mmol; THF, rt, 48 h) and $TbCl_3$ (0.225 g, 0.85 mmol). Complex **2** was isolated as yellow crystals in 72% yield (0.30 g). Elemental analysis calcd (%) for: $C_{72}H_{112}Cl_2N_4O_4Tb_2\cdot(C_4H_8O)$ (1558.55 g/mol): C, 58.57; H, 7.76; N, 3.59; Tb, 20.39. Found: C, 58.70; H, 7.72; N, 3.45; Tb, 20.11. IR (Nujol, KBr) υ/cm^{-1}: 1640 (m), 1585 (s0, 1425 (s0, 1305 (s), 1250 (s), 1200 (m), 1155 (s), 1115 (m), 1105 (m), 1055 (w), 1030 (m), 1020 (s), 1005 (m), 990 (m), 935 (s), 885 (s), 870 (m), 850 (m), 795 (w), 785 (s), 765 (m), 665 (s), 635 (m), 600 (s), 540 (s), 500 (m).

Synthesis of (DAD^{2H})TbCl$_2$(THF)$_2$ (3a). A solution of (DAD^{2H})K(THF)$_n$ generated *in situ* (THF, rt, 48 h) from DAD^{2H} (0.760 g, 2.02 mmol) and potassium metal (0.080 g, 2.02 mmol) was added slowly to a suspension of $TbCl_3$ (0.520 g, 2.02 mmol) in THF (10 mL). The resulted solution was stirred at ambient temperature for 12 h, then all volatiles were removed in vacuum, and the solid residue was extracted from KCl with toluene (30 mL). The toluene extract was filtered, toluene was evaporated in vacuum. Recrystallization of the resulting solid from THF/hexane mixture at 20 °C afforded red crystals of **3a** in 73% yield (1.120 g, 1.49 mmol). Elemental analysis calcd (%) for $C_{34}H_{52}Cl_2N_2O_2Tb$ (750.62 g mol^{-1}): C, 54.40; H, 6.98; N, 3.73; Tb, 21.17. Found: C, 54.52; H, 6.90; N, 3.70; Tb, 21.03. IR (Nujol, KBr): 1580 (s), 1540 (s), 1430 (s), 1365 (s), 1320 (s), 1260 (s), 1235 (s), 1200 (s), 1100 (s), 1055 (s), 1040 (s), 1010 (s), 920 (s), 840 (s), 800 (s), 760 (s), 675 (s), 590 (m), 530 (s), 435 (m) cm^{-1}.

Synthesis of (DAD^{2H})ErCl$_2$(THF)$_2$ (3b). Complex **3b** was synthesized and isolated analogously to **3a** starting form *in situ* generated (DAD^{2H})K(THF)$_n$ (DAD^{2H}: 0.406 g, 1.08 mmol; potassium metal: 0.042 g, 1.08 mmol; THF, rt, 48 h) and $ErCl_3$ (0.295 g, 1.08 mmol). Complex **3b** was isolated as red crystals in 63% yield (0.523 g, 0.69 mmol). Elemental analysis calcd (%) for $C_{34}H_{52}Cl_2ErN_2O_2$ (758.95 g/mol): C, 53.81; H, 6.91; N, 3.69; Er, 22.04. Found: C, 53.52; H, 7.13; N, 3.87; Er, 22.19. IR (Nujol, KBr): 1585 (s), 1540 (s), 1430 (s), 1360 (s), 1325 (s), 1260 (s), 1230 (s), 1195 (s), 1105 (s), 1055 (s), 1040 (s), 1015 (s), 915 (s), 845 (s), 800 (s), 765 (s), 675 (s), 590 (m), 530 (s), 430 (m) cm^{-1}.

Synthesis of (DAD^{CH3,CH2})TbCl$_2$(THF)$_2$ (4). Complex **4** was synthesized and isolated analogously to **3a** starting form *in situ* generated (DAD^{2Me})K(THF)$_n$ (DAD^{2Me}: 0.520 g, 1.28 mmol; potassium metal: 0.052 g, 1.28 mmol; THF, rt, 48 h) and $TbCl_3$ (0.341 g, 1.28 mmol). Complex **4** was isolated as orange red-orange crystals in 66% yield (0.660 g, 0.85 mmol). Elemental analysis calcd (%) for $C_{36}H_{55}Cl_2N_2O_2Tb$ (777.67 g/mol): C, 55.60; H, 7.13; N, 3.60; Tb, 20.44. Found: C, 55.68; H, 7.37; N, 3.52; Tb, 20.27. IR (Nujol, KBr): 1575 (s), 1540 (s), 1365 (s), 1350 (s), 1315 (s), 1240 (s), 1205 (s), 1180 (s), 1150 (s), 1105 (s), 1055 (s), 1015 (s), 985 (s), 960 (s), 940 (s), 920 (s), 890 (s), 865 (s), 850 (s), 825 (m), 805 (s), 790 (s), 745 (s), 700 (s), 665 (s), 590 (m), 525 (m), 435 (m) cm^{-1}.

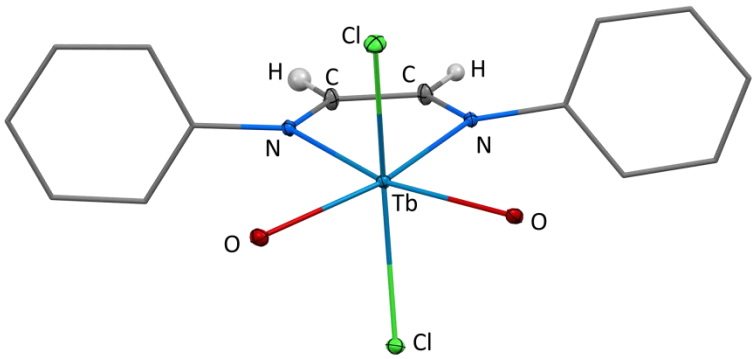

Figure S1. Molecular structure of complex **3a**. Thermal ellipsoids are given with 30% probability Hydrogen atoms (except of NC(H)C(H)N fragments) and carbon atoms of coordinated THF and Pr^i groups of DAD-ligands are omitted for clarity.

Table S1. Crystal Data and Structure Refinement Details for Complexes **1b**, **2**, **3a,b** and **4**.

	1b	**2**	**3b**	**3a**	**4**
CCDC	2291546	2291547	2291548	2294708	2294709
Empirical formula	$C_{68}H_{104}Cl_2Er_2N_4O_4$	$C_{72}H_{112}Cl_2N_4O_4Tb_2$, C_4H_8O	$C_{34}H_{52}Cl_2ErN_2O_2$	$C_{34}H_{52}Cl_2N_2O_2Tb$	$C_{36}H_{55}Cl_2N_2O_2Tb$
Formula weight	1446.97	1558.49	758.93	750.59	777.64
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1$
Unit cell dimensions	a = 19.1720(5) Å b = 15.3350(4) Å c = 23.2547(6) Å α = 90° β = 90° γ = 90°	a = 15.3491(4) Å b = 16.0935(4) Å c = 15.7508(4) Å α = 90° β = 108.4270(10)° γ = 90°	a = 10.1072(3) Å b = 19.6768(5) Å c = 18.4890(5) Å α = 90° β = 105.5000(10)° γ = 90°	a = 10.1207(5) Å b = 19.7298(10) Å c = 18.5792(10) Å α = 90° β = 105.3200(10)° γ = 90°	a = 13.7236(16) Å b = 17.421(2) Å c = 15.5119(18) Å α = 90° β = 90.233(2)° γ = 90°
V, Å^3	6836.9(3)	3691.28(16)	3543.31(17)	3578.1(3)	3708.5(7)
Z	4	2	4	4	4
d_{calc}, g/cm^3	1.406	1.402	1.423	1.393	1.393
μ, mm^{-1}	2.563	2.023	2.549	2.156	2.083
F_{000}	2968	1616	1552	1540	1600
Crystal dimensions, mm	0.19×0.10×0.05	0.25×0.21×0.11	0.29×0.18×0.17	0.32×0.18×0.14	0.32×0.21×0.18
θ range for data collection, °	2.44–30.07	2.57–30.17	2.07–30.10	1.54–30.03	1.31–27.10
HKL indicies	$-27 \le h \le 27$ $-21 \le k \le 21$ $-32 \le l \le 32$	$-21 \le h \le 21$ $-22 \le k \le 22$ $-22 \le l \le 22$	$-14 \le h \le 12$ $-27 \le k \le 27$ $-26 \le l \le 23$	$-14 \le h \le 14$ $-27 \le k \le 27$ $-26 \le l \le 26$	$-17 \le h \le 17$ $-22 \le k \le 22$ $-19 \le l \le 19$
Reflns collected	85075	51481	34472	46230	51077
Independent reflns (R_{int})	9965 (0.0587)	10892 (0.0227)	10398 (0.0205)	10463 (0.0335)	51077 (-)
Parameters (restraints)	384 (90)	434 (64)	387 (0)	386 (0)	806 (1)
Completeness to θ, %	99.2	99.7	99.7	100.0	99.4
$S(F^2)$	1.076	1.043	1.068	1.019	0.988
Final R Indices ($I > 2\sigma(I)$)	R_1 = 0.0381 wR_2 = 0.0666	R_1 = 0.0219 wR_2 = 0.0632	R_1 = 0.0175 wR_2 = 0.0406	R_1 = 0.0200 wR_2 = 0.0426	R_1 = 0.0341 wR_2 = 0.0858
R Indices (all data)	R_1 = 0.0536 wR_2 = 0.0722	R_1 = 0.0262 wR_2 = 0.0552	R_1 = 0.0198 wR_2 = 0.0413	R_1 = 0.0251 wR_2 = 0.0444	R_1 = 0.0395 wR_2 = 0.0891
Largest diff. peak and hole, e/Å^3	1.13 / –1.32	1.04 / –0.95	0.93 / –0.80	0.58 / –0.42	1.05 / –1.00