SUPPORTING INFORMATION

Synthesis and structural characterization of lanthanide complexes with the di- or tri-anionic diguanidinate ligand: New insight into the flexibility and distinct reactivity of the linked diguanidinate ligand

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EXPERIMENTAL SECTION

General procedures

All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified nitrogen gas using standard Schlenk techniques. The solvents THF, and n-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen gas prior to use. Elemental analyses for C, H, and N were carried out by using a Rapid CHN-O analyzer. Infrared spectra were obtained on a NICOLET FTIR 360 spectrometer with samples prepared as Nujol mulls. The complex Cp_3Yb[1] was prepared according to the modified procedures described in the literature. The 2,6–diaminopyridine and *N*,*N*'-diisopropylcarbodiimide were purchased from commercial sources and were used without further purification.

Preparation of $[Cp_2Yb(THF)]_2[\mu\text{-}\eta^1\text{:}\eta^2\text{-}(C_5H_3N\text{-}2,6)(NH)_2]$ (1)

To a 30 mL THF solution of Cp_3Yb (1.656 g, 4.50 mmol) was added 2,6–diaminopyridine [$C_5H_3N(NH_2)_2$-2,6] (0.246 g, 2.25 mmol) at room temperature and stirred for another 15 hours. The solution was concentrated and cooled at −15 °C for several days to give **1** as black-red crystals. Yield: 1.293 g (67%). Anal. Calc. for $C_{33}H_{41}N_3O_2Yb_2$: C, 46.21; H, 4.90; N, 4.82. Found: C, 46.10; H, 4.51; N, 4.61. IR (Nujol, cm^{-1}): 3561 (m), 3507 (m), 3388 (m), 3333 (m), 3071 (m), 1612 (m), 1578 (vs), 1344 (w), 1285 (m), 1243 (s), 1177 (m), 1121 (w), 1069 (m), 1010 (s), 920 (m), 861(s), 773 (s), 724 (s), 699 (w), 670 (w).

Preparation of $Cp_2Yb[\mu\text{-}\eta^2\text{:}\eta^2\text{-}^i PrN(^i PrNH)CN(C_5H_3N\text{-}2,6)NC(NH^i Pr)N^i Pr]YbCp_2$ (2)

To a 30 mL THF solution of **1** (0.350g, 0.41 mmol) was added *N*,*N*'-diisopropylcarbodiimide (0.116g, 0.82 mmol) at −30°C. After stirred for 30 min, the mixture solution was warmed to ca 5 ^oC and stirred for another 8 h. Then, the solution was concentrated and subsequently cooled to −15 °C for several days to give **2** (0.205 g, 52%) as orange crystals. Anal. Calc. For $C_{39}H_{54}N_7Yb_2$: C, 48.44; H, 5.63; N, 10.14. Found: C, 48.39; H, 5.59; N, 10.11. IR (Nujol, cm^{-1}): 3209 (m), 3078 (m), 1622 (m), 1572 (vs), 1543 (vs), 1490 (m), 1339 (s), 1262 (m), 1194 (w), 1153 (m), 1013 (s), 886 (m), 861(s), 775 (s), 724 (m), 664 (w).

Preparation of $(Cp_2Yb)_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(^i PrNH)_2C{=}N(2,6\text{-}C_5H_3N)NC(N^i Pr)_2](THF)$ (3)

To the 30 mL THF solution of **1** (0.515 g, 0.60 mmol) was added *N*,*N*'-diisopropylcarbodiimide (0.151 g, 1.20 mmol) at −30 °C. After stirred for 30 min, the mixture solution was slowly warmed to room temperature. After stirring for 48 h, the solution was concentrated under vacuum and several drops of *n*-hexane were added to it. Cooling at −15 °C for two weeks gave **3**·0.5*n*-hexane as red crystals. Yield: 0.500 g (77%). Anal. Calc. for $C_{46}H_{69}N_7OYb_2$: C, 51.10; H, 6.34; N, 9.07. Found: C, 50.72; H, 6.38; N, 8.99. IR (Nujol, cm^{-1}): 3561 (m), 3507 (m), 3388 (m), 3333 (m), 3071 (m), 1612 (m), 1578 (vs), 1344 (w), 1285 (m), 1243 (s), 1177 (m), 1121 (w), 1069 (m), 1010 (s), 920 (m), 861(s), 773 (s), 724 (s), 699 (w), 670 (w).

Preparation of $[CpYb\{\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}^i PrN(^i PrNH)CN(2,6\text{-}C_5H_3N)NC(N^i Pr)_2\}YbCp_2]_2$ (4)

The solution of **3**·0.5*n*-hexane (0.420 g, 0.39 mmol) in THF (30 mL) was stirred at 70 °C for 5 hours. Then the reaction mixture was allowed to be cooled to room temperature. The solution was concentrated and layered with *n*-hexane for a few days to give **4** as orange-red crystals. Yield: 0.204 g (58% based on Yb). Anal. Calc. for $C_{68}H_{94}N_{14}Yb_4$: C, 45.38; H, 5.26; N, 10.90. Found: C, 45.21; H, 5.24; N, 10.89. IR (Nujol, cm^{-1}): 3442 (m), 3411 (m), 3098 (m), 3070 (m), 1610 (s), 1571(s), 1539(s), 1437 (vs), 1360(s), 1335 (s), 1313 (m), 1088 (m), 1271 (s), 1228 (m),1153 (m), 1120 (m), 1069 (m), 1013 (s), 965 (w), 926 (w), 867(m), 798 (w), 773 (m) 708 (m), 668 (m).

X-ray structure determinations

Suitable single crystals were sealed under N_2 in thin-walled glass capillaries. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo-*K*a radiation, φ-ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by means of the SAINT program.[2] SADABS[3] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package.[4] All non-hydrogen atoms were refined anisotropically.

The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker Smart program. Crystallographic parameters for compounds **1**, **3**, and **4** along with details of the data collection and refinement, are collected in Table 1.

Table 1. Crystal and Data Collection Parameters of Complexes 1, 3 and 4.

	1	**3**·0.5*n*-hexane	**4**
Formula	$C_{33}H_{41}N_3O_2Yb_2$	$C_{46}H_{68}N_7OYb_2$	$C_{68}H_{94}N_{14}Yb_4$
Molecular weight	857.77	1081.15	1799.73
Crystal color	black-red	Orange-red	orange-red
Crystal dimens (mm)	0.20 × 0.15 × 0.15	0.40 × 0.20 × 0.10	0.15 × 0.12 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/c
Unit cell dimensions			
a (Å)	15.286(5)	18.734(7)	13.906(5)
b (Å)	13.357(4)	9.805(4)	16.461(5)
c (Å)	15.847(5)	26.843(10)	15.924(5)
β (deg)	100.134(4)	108.652(5)	98.049(5)
V (Å^3)	3185.2(16)	4672(3)	3609(2)
Z	4	4	2
Dc (g.cm^{-3})	1.789	1.537	1.656
μ (mm^{-1})	5.868	4.019	5.182
F (000)	1664	2164	1760
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α	Mo-K_α
Temperature (*K*)	293.2	293.2	293.2
Scan type	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.35 to 25.01	1.60 to 25.01	1.48 to 26.01
h,k,l range	-13 ≤ *h* ≤ 18 -15 ≤ *k* ≤ 15 -18 ≤ *l* ≤ 18	-22 ≤ *h* ≤ 21, -11≤ *k* ≤ 5 -31≤ *l* ≤30	-12 ≤ *h* ≤ 17 -20 ≤ *k* ≤17 -19 ≤ *l* ≤ 19
No. of reflections measured	13125	18894	16386
No. of unique reflections	5604 [R_{int} = 0.0710]	8232 [R_{int} = 0.0456]	7080 [R_{int} = 0.0434]
Completeness to θ	99.8% [θ=25.01]	99.9 % [θ=25.01]	99.6% [θ=26.01]
Max. and min. Transmission	0.4731 and 0.3865	0.6893 and 0.2962	0.6253 and 0.5103
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5604 / 0 / 361	8232 / 0 / 505	7080 / 0 / 388
Goodness-of-fit on F^2	0.889	0.980	0.955
Final R indices [*I*>2σ (*I*)]	R_1 = 0.0374, wR_2 = 0.0732	R_1 = 0.0383, wR_2 = 0.0780	R_1 = 0.0344, wR_2 = 0.0757
R indices (all data)	R_1 = 0.0599, wR2 = 0.0797	R_1 = 0.0582, wR_2 = 0.0842	R_1 = 0.0549 wR_2 = 0.0829
Largest diff. peak and hole (e·Å^{-3})	1.355 and -0.931	1.194 and -0.929	1.737 and -0.829

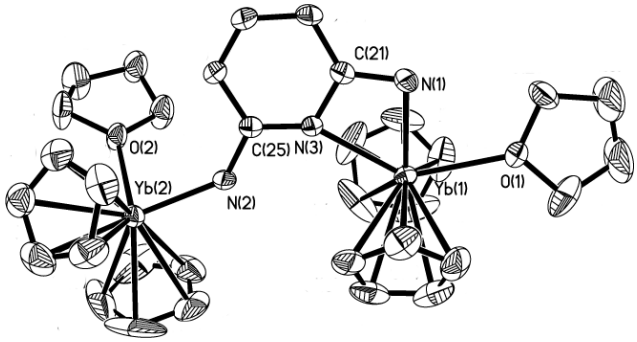

Fig. 1. Thermal ellipsoid (30%) plot of complex **1**. Hydrogen atoms are omitted for clarity. Key Selected Bond Lengths (Å) and Angles (deg): Yb(1)–N(1) 2.291(6), Yb(1)–N(3) 2.392(5), Yb(1)–O(1) 2.454(5), Yb(2)–N(2) 2.194(6), Yb(2)–O(2) 2.272(5), N(2)–C(25) 1.362(9), N(1)–C(21) 1.360(8), N(3)–C(25) 1.334(8), N(3)–C(21) 1.354(9), N(1)–Yb(1)–N(3) 57.7(2), N(3)–C(21)–N(1) 112.8(6), N(3)–C(25)–N(2) 119.0(6).

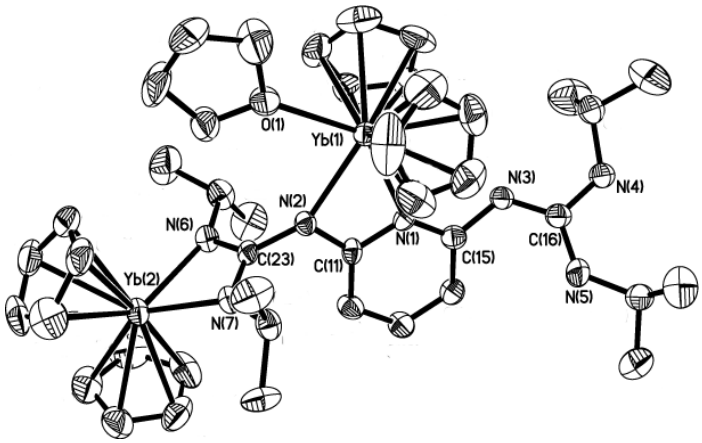

Fig. 2. Thermal ellipsoid (30%) plot of complex **3**. Hydrogen atoms are omitted for clarity. Selected Bond Lengths (Å) and Angles (deg): Yb(1)–N(1) 2.374(4), Yb(1)–N(2) 2.395(4), Yb(1)–O(1) 2.419(4), Yb(2)–N(7) 2.281(4), Yb(2)–N(6) 2.282(5), N(2)–C(23) 1.409(6), N(6)–C(23) 1.345(6), N(7)–C(23) 1.321(7), N(1)–C(11) 1.378(6), N(2)–C(11) 1.363(7), N(3)–C(15) 1.384(7), N(3)–C(16) 1.307(8), N(4)–C(16) 1.350(7), N(5)–C(16) 1.347(8), N(1)–Yb(1)–N(2) 56.61(14), N(2)–C(11)–N(1) 111.1(5), N(7)–C(23)–N(6) 113.9(5), N(7)–C(23)–N(2) 124.6(5), N(6)–C(23)–N(2) 121.5(5), N(3)–C(16)–N(5) 125.5(6), N(3)–C(16)–N(4) 118.0(6), N(5)–C(16)–N(4) 116.4(6), N(1)–C(15)–N(3) 114.5(5) C(16)–N(3)–C(15) 121.6(5).

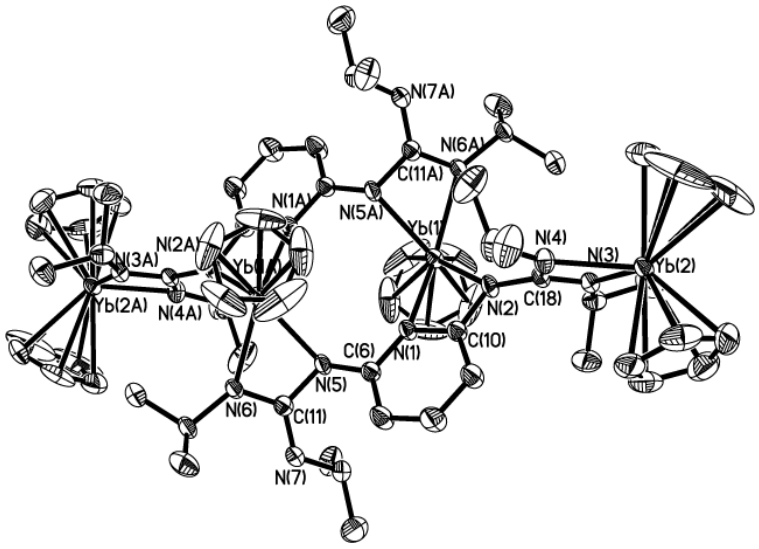

Fig. 3. Thermal ellipsoid (30%) plot of complex **4**. Hydrogen atoms are omitted for clarity. Selected Bond Lengths (Å) and Angles (deg): Yb(1)–N(2) 2.272(5), Yb(1)–N(6A) 2.309(4), Yb(1)–N(5A) 2.315(5), Yb(1)–N(1) 2.355(5), Yb(2)–N(4) 2.264(5), Yb(2)–N(3) 2.276(5), N(5)–C(11) 1.393(7), N(6)–C(11) 1.310(8), N(7)–C(11) 1.350(8), N(2)–C(18) 1.405(7), N(3)–C(18) 1.316(7), N(4)–C(18) 1.353(7), N(6A)–Yb(1)–N(5A) 58.37(17), N(2)–Yb(1)–N(1) 58.47(17), N(6)–C(11)–N(7) 124.2(6), N(6)–C(11)–N(5) 113.0(5), N(7)–C(11)–N(5) 122.7(6), N(3)–C(18)–N(4) 113.7(6), N(3)–C(18)–N(2) 123.2(5), N(4)–C(18)–N(2) 123.1(6), C(10)–N(2)–C(18) 117.3(5), N(1)–C(6)–N(5) 115.3(5). Letter A indicates the following symmetry transformation: 1-*x*, 2-*y*, 1-*z*.

References

1 J. M. Birmingham, G. Wilkinson, *J. Am. Chem. Soc.* 1956, **78**, 42.

2 Bruker (**2000**) SAINTPlus Data Reduction and Correction Program v. 6.02 a, Bruker AXS, Madison, Wisconsin, USA.

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