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[28] Synthetic **2** was obtained as an amorphous white solid after purification by preparative TLC:[29] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.17 (br s, 1H), 5.67 (dd, J = 15.5, 9.0 Hz, 1H), 5.46 (dd, J = 15.5, 8.5 Hz, 1H), 5.43 (s, 1H), 5.26 (s, 1H), 5.04 (s, 1H), 4.52 (q, J = 8.0 Hz, 1H), 4.07 (m, 3H), 3.93 (d, J = 9.0 Hz, 1H), 3.38 (t, J = 10.0 Hz, 1H), 3.27 (br d, J = 10.0 Hz, 2H), 2.22–2.00 (m, 4H), 2.00–0.82 (m, 29H), 1.69 (s, 3H), 1.34 (s, 3H), 1.03 (d, J = 6.5 Hz, 3H), 0.97 (d, J = 6.5 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H); HR-FAB-MS: calcd for $C_{45}H_{68}O_{12}$ $[M+H]^+$ 789.4789, found 789.4751; HPLC/MS[7] (C_{18} 3.5 μm, 2.1 × 150 mm, CH_3CN/H_2O/acetic acid, 70:30:0.05, 0.2 mL min^{-1}, 40 °C; ES$^-$ (Micromass Quattro, 70 eV): m/z: 787.5 $[M-H]^-$) t_R = 14.55 min, co-eluted with naturally occurring **2**. For HPLC traces and ^{1}H NMR spectra of synthetic (partial spectrum is shown in Figure 2) and naturally occurring **2** see Supporting Information.

[29] TLC (E. Merck Silica gel 60 F_{254}s, 0.2 mm, Art. 115696, hexanes/ethyl acetate/acetic acid, 1:1:0.05): R_f data for compounds **2**, 0.47; **23**, 0.58; **1**, 0.27; 7,24,27-tri-*O*-benzyl-**1**,[21] 0.69.

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Synthesis and Structure of the First Lanthanide Complex with the Bridging, Antiaromatic 2,2′-Bipyridine Dianion: $[\{Yb(\mu_2\text{-}N_2C_{10}H_8)(thf)_2\}_3]$**

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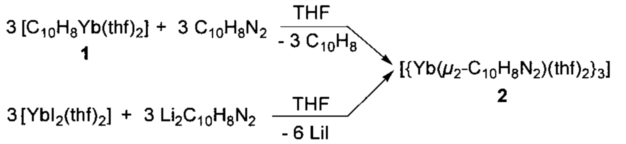
Neutral 2,2′-bipyridine (bipy) has been used for decades in coordination chemistry as a chelating N-donor ligand. In the last few years, a number of interesting reactions of bipy complexes of d-transition metals has been reported involving electron and proton transfer processes. In these reactions the bipy ligand is suggested to act as a kind of an electron reservoir.[1] The formation of bipy$^{\bullet-}$ radical anions and also of bipy^{2-} dianions from bipy and one or more equivalents of lithium was briefly described in 1968.[2] Some lanthanide complexes with bipy$^{\bullet-}$ radical anions as ligands have been well characterized by spectroscopic methods and by structure determination.[3] During the refereeing of our paper the first sodium complexes of the 2.2′-bipyridine dianion were described by Bock and Lehn.[4]

Here, we report the first lanthanide complex containing the antiaromatic bipy^{2-} as a ligand. Trimeric $[\{Yb(\mu_2\text{-}N_2C_{10}H_8)(thf)_2\}_3]$ (**2**) is formed by reduction of 2,2′-bipyridine with ytterbium naphthalene $[C_{10}H_8Yb(thf)_2]$ (**1**),[5] as well as by the reaction of $[YbI_2(thf)_2]$ with $[Li_2(bipy)]$ in THF at room temperature (Scheme 1). Complex **2** crystallized from the concentrated dark green solutions as large, almost black crystals (70 to 80 % yield), which are extremely sensitive to air and moisture and decompose without melting at 160 °C. The solubility of **2** in THF is low at room temperature, but increases significantly upon heating. The complex is insoluble in toluene and diethyl ether. As expected the complex is diamagnetic and does not display ESR signals.



Scheme 1. Synthesis of **2**.

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The ^1H NMR spectrum of **2** shows four well-resolved resonances of equal intensity in the $\delta = 6.6$ to 4.0 region. The significant upfield shift of these signals compared to the positions of the resonances of free 2,2′-bipyridine ($\delta = 8.8$ to 7.3) confirms the dianionic nature of the ligand.

The single-crystal X-ray structure determination of **2**[6] reveals that the unit cell contains three cyclic molecules, each consisting of three chemically equivalent subunits (Figure 1).

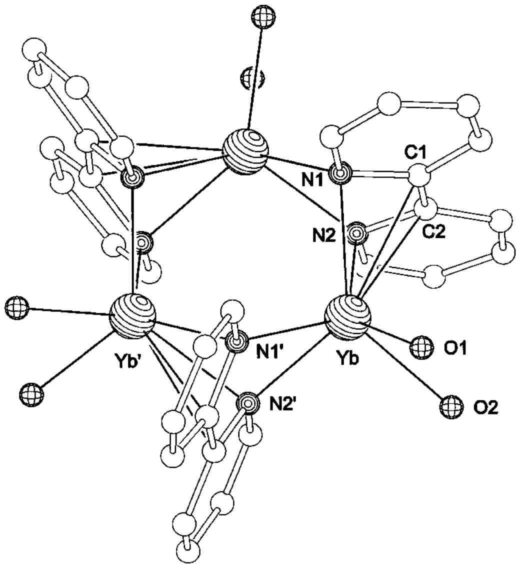
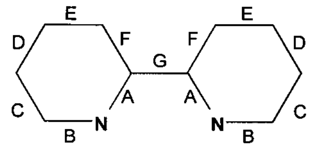


Figure 1. Molecular structure of **2** with a simplified labeling scheme. The hydrogen atoms, as well as the carbon atoms of the THF ligands, are omitted for clarity. Selected average distances [Å] and angles [°]: Yb–O(1) 2.46, Yb–O(2) 2.45, Yb–N(1)′ 2.47, Yb–N(2)′ 2.47, Yb–N(1) 2.54, Yb–N(2) 2.57, Yb–C(1) 2.76, Yb–C(2) 2.77, Yb ··· Yb′ 3.69; O(1)-Yb-N(1′) 82, O(2)-Yb-N(2′) 91, O(1)-Yb-N(2′) 123, O(2)-Yb-N(1′) 130, O(1)-Yb-N(1) 97, O(2)-Yb-N(2) 94, O(1)-Yb-N(2) 142, O(2)-Yb-N(1) 133, O(1)-Yb-C(1) 92, O(2)-Yb-C(2) 85, O(1)-Yb-C(2) 111, O(2)-Yb-C(1) 102, N(1′)-Yb-N(1) 94, N(2′)-Yb-N(2) 94, N(1′)-Yb-N(2) 129, N(2′)-Yb-N(1) 130, N(1′)-Yb-C(1) 123, N(2′)-Yb-C(2) 123, N(1′)-Yb-C(2) 145, N(2′)-Yb-C(1) 145, N(1)-Yb-C(1) 31, N(2)-Yb-C(2) 31, N(1)-Yb-C(2) 54, N(2)-Yb-C(1) 54, O(1)-Yb-O(2) 74, N(1′)-Yb-N(2′) 66, N(1)-Yb-N(2) 63, C(1)-Yb-C(2) 29.

Since the nine subunits are not related to each other by crystallographic symmetry elements, the overall structure is rather expansive. Therefore, only averaged values for bond lengths and bond angles are used in the structure discussion. Within each molecular unit, three ytterbium atoms are bridged by three bipy^{2-} moieties in a novel μ_2-η^2:η^4 fashion forming a cyclic trimer. The three bipy^{2-} units are arranged perpendicular to the plane formed by the three Yb atoms and are orientated in a clockwise manner with their flat side towards one of the two neighboring Yb atoms. Additionally, each metal atom is coordinated by two thf molecules. The mean distances of each ytterbium atom to the nitrogen atoms of the two neighboring bipy units differ significantly due to the formation of two chelating σ bonds (Yb–N1′ and Yb–N2′ 2.47 Å) and longer π bonds (Yb–N1 2.54 Å and Yb–N2 2.57 Å). The mean Yb–C1 (2.76 Å) and Yb–C2 distances (2.77 Å) are somewhat shorter than the mean Yb–$C_{(HC\equiv CH)}$ distance in [$(Me_5C_5)_2Yb(HC\equiv CH)$] (2.85 Å)[7] and similar to the Yb–$C_{(H_2C=CH_2)}$ distances in [$(Me_5C_5)_2Yb(\mu\text{-}H_2C=CH_2)Pt(PPh_3)_3$] (2.77 and 2.79 Å).[8] Probably as a result of crystal packing forces, the two thf molecules coordinated to the ytterbium atoms are slightly twisted towards each other, thus lowering the symmetry of the molecule from C_{3h} to C_3 and thereby causing chirality. In two of the three molecules of the unit cell, the THF ligands situated above the Yb_3 plane are displaced in a clockwise manner relative to their counterparts below this plane. In the third molecule, the clockwise displacement of the THF ligands occurs below the Yb_3 plane. As a consequence, one of the three molecules has an absolute configuration opposite to those of the other two. If the bipy^{2-} ligand in its η^4-π-bonding state is regarded as a six-electron donor occupying three positions in the metal coordination sphere, a coordination number of seven may be assigned to the ytterbium atoms. In this connection it should be noted that the average Yb–Yb distance in **2** (3.69 Å) is significantly shorter than in ytterbium metal (3.88 Å). However, geometrical restraints in cyclic molecules often produce short contacts that are not necessarily of bonding nature.

A comparison of the bond lengths A to G in free bipyridine (Figure 2, a),[9] in the neutral chelating bipy ligand in the complex [Sm(bipy)(dad)$^-$(dad)$^{2-}$] (dad = *t*BuN=CHCH=N-*t*Bu)[3d] (b), and in the radical anionic bipy$^{\bullet-}$ in the complex [$(Me_5C_5)_2Sm(bipy)$][3a] (c) with the averaged bond lengths of the bipy^{2-} ligand in complex **2** (d) reveals that there are no significant differences between (a) and (b), and that the changes within the sequence (b) → (c) → (d) correspond to a successive filling of the LUMO of neutral bipy (the LUMO of bipy^0 is antibonding for the bonds A and D and nonbonding for bond B).[1] As expected there is a shortening of bond G going from (b) to (d) (the LUMO of bipy^0 is bonding for G); however, the shortening is not as pronounced as in the sodium complex [$Na_2(bipy)(dme)_2$]$_\infty$ (0.11 Å; dme = 1,2-dimethoxyethane).[4]



	A	B	C	D	E	F	G
a)	1.35	1.34	1.38	1.38	1.39	1.39	1.49
b)	1.36	1.33	1.38	1.36	1.37	1.39	1.46
c)	1.38	1.35	1.37	1.41	1.34	1.42	1.43
d)	1.44	1.39	1.36	1.43	1.36	1.46	1.41

Figure 2. Comparison of averaged C–C bond lengths [Å] in differently charged species of 2,2′-bipyridine: a) bipy^0 (transoid), b) bipy^0 (chelating), c) bipy$^{\bullet-}$, d) bipy^{2-}. See text for references.

Experimental Section

All manipulations were conducted in an inert gas atmosphere using Schlenk techniques. Compound **1** was prepared according to reference [5]. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O 2400 Analyzer. IR spectra were recorded on a Specord M-80 spectrometer, NMR spectra on a Bruker ARX 200 instrument.

2: Method A. A solution of 2,2′-bipyridine (0.843 g, 5.4 mmol) in THF (20 mL) was added to a suspension of **1** (2.4 g, 5.39 mmol) in THF (25 mL) to yield a dirty-brown mixture. After the mixture had been stirred for a few minutes, **1** dissolved gradually and the solution changed color to dark green. Complex **2** separated from the concentrated solution (10 mL) in form of large black crystals. Yield 2.1 g (82 %).

Method B: A solution of $[Li_2(bipy)]$ in THF (20 mL), freshly prepared from 2,2′-bipyridine (0.5 g, 3.0 mmol) and excess lithium, was added to a suspension of $[YbI_2(thf)_2]$ (1.7 g, 2.98 mmol) in THF (25 mL). The reaction proceeded immediately and black colored, crystalline **2** separated from the concentrated solution (15 mL). Yield 1.03 g (73 %). Decomposition: 160 °C; ^{1}H NMR (200 MHz, $[D_8]$THF, 20 °C, TMS): $\delta = 6.54$ (d, $^3J(H,H) = 6.2$ Hz, 2H; CH), 5.28 (d, $^3J(H,H) = 9.7$ Hz, 2H; CH), 5.02 (dd, $^3J(H,H) = 9.7$, 5.3 Hz, 2H; CH), 4.01 (dd, $^3J(H,H) = 6.2$, 5.3 Hz, 2H; CH); IR(Nujol): $\tilde{\nu} = 1590$, 1520, 1480, 1445, 1380, 1345, 1320, 1275, 1265, 1255, 1185, 1150, 1115, 1045, 980, 955, 890, 760, 710, 640, 625, 575, 495 and 425 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{24}N_2O_2Yb$ (473.44): C 45.67, H 5.11, N 5.92, Yb 36.55; found: C 44.42, H 4.05, N 6.17, Yb 36.58.

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[6] X-ray structure data: Siemens SMART CCD diffractometer, ω scans, $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), graphite-monochromator, $T = 173$ K, SADABS[10] for absorption correction, structure solution with direct methods (SHELXS-97[11]), refinement against F^2 (SHELXL-97[12]) with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positions with fixed isotropic thermal parameters ($U_{iso} = 0.08 \times 10^4$ pm^2) on calculated positions. Data collection for **2**: crystal dimensions $0.46 \times 0.42 \times 0.19$ mm, triclinic, $P1$, $a = 1031.60(1)$, $b = 2116.64(2)$, $c = 2138.61(1)$ pm, $\alpha = 118.088(1)$, $\beta = 93.653(1)$, $\gamma = 101.500(1)°$, $V = 3969.40(4) \times 10^6$ pm^3, $Z = 3$, $\rho_{calcd} = 1.782 \times 10^3$ kg m^{-3}, $\mu = 5.312$ mm^{-1}, $F(000) = 2088$, $2.20° \leq 2\theta \leq 55.0°$, $-13 \leq h \leq 13$, $-27 \leq k \leq 27$, $-27 \leq l \leq 16$, 30947 data collected, 23263 unique data ($R_{int} = 0.0266$), 21953 data with $I > 2\sigma(I)$, 1864 refined parameters, three floating origin restraints, GOF (F^2) = 1.050, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$), $R_1 = 0.0411$, $wR_2 = 0.1103$, max./min. residual electron density $2.908/-2.593 \times 10^{-6}$ e pm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116026. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Tuning of Magnetic Anisotropy in Hexairon(III) Rings by Host – Guest Interactions: An Investigation by High-Field Torque Magnetometry**

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Magnetic anisotropy plays a central role in understanding the properties of molecular magnetic clusters, which are often characterized by large ground spin states. The zero field splitting (ZFS) of the multiplets in fact gives rise to important effects, which are now under investigation for many different systems ranging from models for biological clusters to single-molecule magnets.[1–4] In single-molecule magnets the interest is associated with the fact that the magnetic anisotropy drives the spin dynamics of magnetic clusters and leads to slow magnetic relaxation which allows the observation of quantum tunneling of the magnetization at very low temperature.[4]

From an experimental point of view it is necessary to perform measurements on magnetic anisotropy, which so far have been largely based on EPR spectroscopy[5] and inelastic neutron scattering.[6] Direct measurement of the anisotropic magnetization has been hampered by the need for relatively large single crystals. Recently a new technique, cantilever torque magnetometry, has become available, which allows the use of microgram single crystals.[7] Applications of this very sensitive technique in the field of molecular magnetism are quite recent, but they certainly appear to be very promising.[8] Torque magnetometry exploits the mechanical couple acting on a single crystal of a magnetically anisotropic substance in a uniform magnetic field. The couple can be precisely measured by simply anchoring the sample to a tiny metal cantilever and measuring the deflection by a capacitive method.[8a]

We report here on the magnetic anisotropy of the antiferromagnetic iron(III) rings $[LiFe_6(OMe)_{12}(dbm)_6]^+$ (**1**) and $[NaFe_6(OMe)_{12}(pmdbm)_6]^+$ (**2**), where Hdbm = 1,3-diphenyl-1,3-propanedione and Hpmdbm = 1,3-di(4-methoxyphenyl)-1,3-propanedione (Figure 1). The strong tendency of the $Fe_6(OMe)_{12}$ skeleton to encapsulate alkali metal ions[9] can be exploited to drive the self-assembly of cyclic nanostruc-

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