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f-Block-Element–f-Block-Element NMR Spin–Spin Coupling

Anna M. Dietel,[a] Oleg Tok,[a] and Rhett Kempe*[a]

Dedicated to Professor Bernd Wrackmeyer on the occasion of his 60th birthday

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This is a report on the synthesis and structure of novel dinuclear Yb^{II} complexes. In one of the described compounds, the two Yb^{II} centres are in close proximity and chemically different. Thus, an f-block-element–f-block-element coupling pattern was observed. The low-field ^{171}Yb signal consists of a central singlet and two satellites with integral intensities of about 7 % each. This 14 % approximately corresponds to the natural abundance of the ^{171}Yb isotope and was assigned as a doublet arising from $^{1}J(^{171}\text{Yb}, ^{171}\text{Yb})$ spin–spin coupling with a magnitude of 76.1 Hz. Furthermore, the relevance of such studies in understanding dimer equilibria and the rearrangement chemistry of rather bulky structural ensembles is discussed.

Introduction

The last decade has seen a dramatic increase in the importance of the organometallic chemistry of lanthanide elements. Solution-state NMR, one of the organometallic chemist's most informative tools, has been applied infrequently to the direct observation of compounds of f-block elements. This omission is probably because the majority of the complexes (except those of La^{III}, Yb^{II} and Lu^{III}) are paramagnetic, and many of the NMR-active f-block nuclei have large quadrupole moments. ^{171}Yb is a spin-1/2 nucleus, with a natural abundance of 14.31 % and a moderately sized, positive gyromagnetic ratio (4.735×10^{7} rad T^{-1} s^{-1}); these features combine to give a receptivity about 4.5 times greater than that of ^{13}C.[1] The first direct high-resolution NMR observation of an f-block element was reported by Lawless, Lappert, et al.[2] In principle, ^{171}Yb–^{171}Yb coupling should be observable as well. Dinuclear and polynuclear Yb complexes are a well-documented class of compounds. The metal centres in many of these complexes are close enough (3.5 Å was used as the upper limit)[3] to observe f-block-element–f-block-element spin–spin coupling. Complexes that meet this requirement can consist of Yb^{III},[4] exhibit mixed oxidation states (II/III)[5] or might be diamagnetic due to the presence of Yb^{II}[6,7] ions only. Nonsymmetrical polynuclear Yb^{II} complexes are rare,[6] and metal centres in different chemical environments are a prerequisite to observe $^{1}J(^{171}\text{Yb},^{171}\text{Yb})$ coupling. Furthermore, in systems undergoing dynamic processes such as bridge–terminal exchange or monomer–dimer equilibria, coupling constants will be time-averaged and thus may be unobservable.[1] On the other hand, $^{1}J(^{171}\text{Yb},^{171}\text{Yb})$ coupling patterns, if observed, could be a highly sensitive probe on the dynamic aspect of f-block-element–f-block-element interactions in solution, an area of chemistry difficult to access by other methods. We started recently a research program in which we used very bulky aminopyridinato ligands[8] in order to avoid ligand redistribution in low-valent and organolanthanide chemistry.[9] We report here on the synthesis and structure of a novel dinuclear Yb^{II} complex in which the two Yb^{II} centres are in close proximity and chemically different within the NMR time scale, as well as the ^{171}Yb NMR spectroscopy of this species.

Results and Discussion

Bimetallic Yb^{II} complexes should be accessible by the introduction of a sterically encumbered extension at an aminopyridinato ligand, which leads to bipyridylamide ligands, and the nonsymmetrical bulk could lead to homobimetallic complexes having Yb^{II} in different chemical environments. The "simple" bipyridylamide ligand was already used successfully by Müller-Buschbaum to stabilise, for instance, multinuclear Yb^{III} complexes.[10] The sterically demanding dipyridylamide ligand precursor **1** was synthesised by Pd-catalysed aryl amination (Scheme 1) in good yield.

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[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth,
95440 Bayreuth, Germany
E-mail: kempe@uni-bayreuth.de

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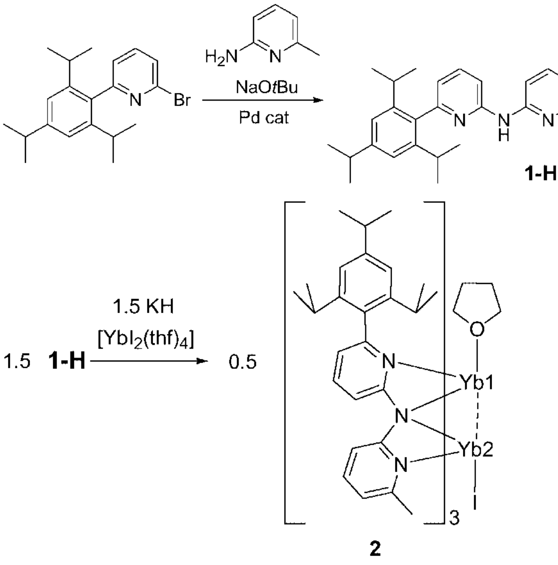


Scheme 1. Synthesis of **1** and **2**.

The reaction of **1-H** with KH and subsequent treatment with [YbI$_2$(thf)$_4$][11] leads to the bimetallic complex **2** with a residual iodido ligand to guarantee asymmetry. The molecular structure of complex **2** (Figure 1) was investigated by X-ray crystal structure analysis[12] and NMR spectroscopy.

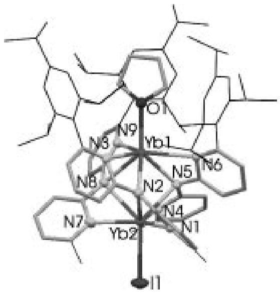


Figure 1. Molecular structure of **2** (ORTEP plot for all non-C,H-atoms). Substituents at the pyridine rings are plotted in wire frame style for clarity. Selected bond lengths [Å] and angles [°]: Yb1–Yb2 3.4200(3), N1–Yb2 2.469(3), N2–Yb1 2.538(3), N2–Yb2 2.640(3), N3–Yb1 2.611(3), N4–Yb2 2.476(3), N5–Yb1 2.568(3), N5–Yb2 2.578(3), N6–Yb1 2.681(3), N7–Yb2 2.451(4), N8–Yb1 2.604(3), N8–Yb2 2.622(3), N9–Yb1 2.613(3), O1–Yb1 2.431(3), I1–Yb2 3.0714(4); N5–Yb1–N6 52.19(10), N2–Yb1–N3 53.32(10), N8–Yb1–N9 52.55(10), N4–Yb2–N5 53.61(10), N7–Yb2–N8 53.58(10), N1–Yb2–N2 53.28(10).

The two Yb^{II} ions in complex **2** are triply bridged by the amido N atoms of **1**, which results in a short metal–metal distance [3.4200(3) Å]. Shorter Yb^{II}–Yb^{II} distances have been observed for carbon- and oxygen-bridged dimers.[5,6] The Yb–N$_{amido}$ bond lengths are indicative of two symmetric bridges (N5 and N8) and one nonsymmetrical (via N2) bridge. N2 seems to provide the anionic function of the amido ligand dominantly to Yb1, which is perfectly in accordance with the facts that the additional neutral ligand (thf) coordinates Yb1 and the anionic iodido ligand binds Yb2.

The bimetallic nature of complex **2** in solution was confirmed by ^{171}Yb NMR spectroscopy. In C_6D_6 there are two signals at 585.6 (broad, $\nu_{1/2}$ = 92.0 Hz) and 646.6 (sharp, $\nu_{1/2}$ = 8.5 Hz) ppm. The broad signal belongs to the Yb atom bonded directly to iodine, and the broadening arises from unresolved ^{171}Yb–^{127}I scalar coupling. The low-field signal consists of a central singlet and two satellites with an integral intensity of about 7% each. This 14% approximately corresponds to the natural abundance of the ^{171}Yb isotope and was assigned as a doublet arising from $^{1}J(^{171}\mathrm{Yb}, {}^{171}\mathrm{Yb})$ spin–spin coupling with a magnitude of 76.1 Hz. The chemical shift for Yb^{II} amides ranges from $\delta(^{171}\mathrm{Yb})$ = 614 ppm to $\delta(^{171}\mathrm{Yb})$ = 1228 ppm, and the line width associated with ^{171}Yb resonances of these compounds ranges from $\Delta\nu_{1/2}$ = 70 Hz to $\Delta\nu_{1/2}$ = 550 Hz.[2] $^{n}J(^{171}\mathrm{Yb},\mathrm{X})$ couplings have been observed for a variety of nuclei. Coupling constants usually cover a large range, for instance from 8627–9479 Hz (X = ^{119}Sn) and 8254–9058 Hz (X = ^{117}Sn),[13] 758 Hz (X = ^{125}Te),[14] 233–265 Hz (X = ^{13}C; resulting from alkyl carbon atoms)[15] up to 73 Hz (X = ^{31}P).[16] Well-resolved $^{3}J(^{171}\mathrm{Yb},{}^{19}\mathrm{F})$ and $^{4}J(^{171}\mathrm{Yb},{}^{19}\mathrm{F})$ couplings have been recorded for perfluorophenyl ytterbium complexes. Coupling constants range from 13 to 48 Hz.[17]

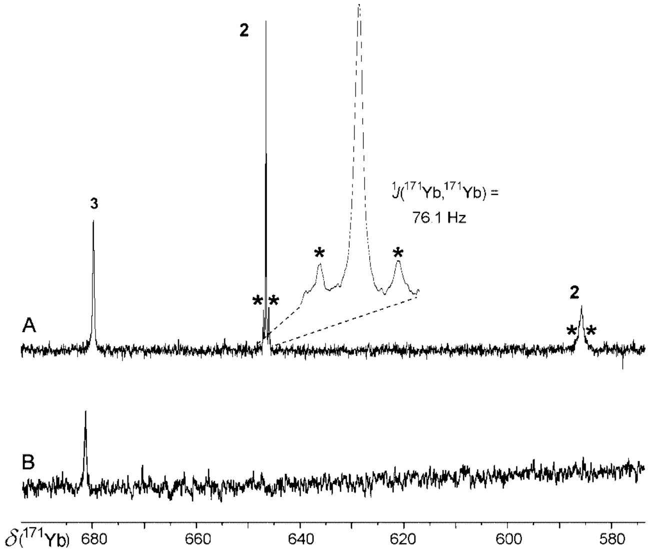


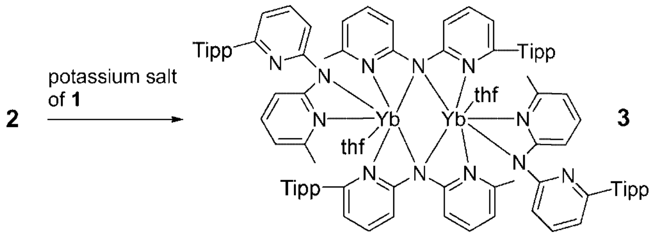
Figure 2. ^{171}Yb{^{1}H} NMR spectra (69.96 MHz, [D$_8$]thf) of complex **2** (A) and complex **3** (B).

$$\underset{\textbf{2}}{[\mathrm{Yb_2L_3(thf)I}]} \xrightarrow{+\mathrm{thf}} \underset{\textbf{2(thf)}}{[\{\mathrm{Yb_2L_3(thf)_2}\}^+\ \mathrm{I}^-]} \rightleftharpoons \underset{\textbf{3}}{[\mathrm{Yb_2L_4(thf)_2}]} + \underset{\textbf{4}}{[\{\mathrm{Yb_2L_2(thf)}_n\}^{2+}\ 2\mathrm{I}^-]}$$

Scheme 2. Observed rearrangement reactions of **2** in thf (L = **1**).

Although complex **2** is stable in C_6D_6 for days, the ^{171}Yb NMR spectrum in [D_8]thf solution consists of two already noted resonances (δ = 585.6 and 646.6 ppm) together with a third signal at δ = 679.8 ppm ($\nu_{1/2}$ = 25.5 Hz). In the ^{1}H NMR spectrum at room temperature there is an additional set of broad signals. At low temperature (from 0 °C and lower), the signal set which belongs to the monoiodido complex **2** did not change, but the broad lines were more narrow and gave two sets (in a ratio of ca. 1:3) where the chemical shifts of the major set were completely identical to the ^{1}H NMR spectrum of binuclear complex **3** (Scheme 2). In the ^{171}Yb NMR spectrum of **3** in [D_8]thf, the signal at δ = 681.9 ppm was observed (Figure 2B). This value is very close to the chemical shift of the third signal in the spectrum presented in Figure 2A. Both ^{1}H and ^{171}Yb NMR spectroscopic data suggest that in thf solution complex **2** can dissociate to give cationic compound **2**(thf), where one coordination position is occupied by thf instead of iodine (Scheme 2). Complex **2**(thf) seems not to be stable and rearranges with the formation of neutral compound **3** and (most likely) dicationic **4**. The signal for complex **4** was not observed because of the low solubility of the complex (precipitation was observed).

In order to confirm the identity of complex **3**, it was independently synthesised by the reaction of **2** with the potassium salt of **1-H**, generated by treatment of **1-H** with KH (Scheme 3).



Scheme 3. Synthesis of **3** [Tipp = tri(isopropyl)phenyl].

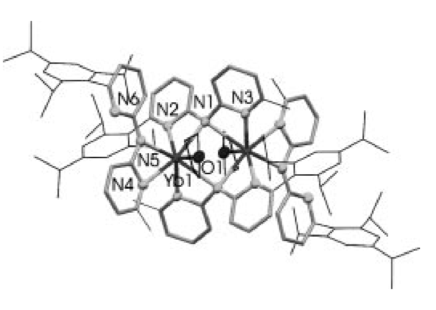


Figure 3. Molecular structure of **3** (ORTEP plot for all non-C,H-atoms). Substituents at the pyridine rings are plotted in wire frame style for clarity. Selected bond lengths [Å] and angles [°]: Yb1–O1 2.457(6); Yb1–N3 2.462(7), Yb1–N5 2.488(7), Yb1–N1 2.517(8), Yb1–N4 2.586(8), Yb1–N2 2.607(8), Yb1–N1′ 2.681(7), Yb1–Yb1′ 3.8685(11); N1–Yb1–N2 53.6(2), N3–Yb1–N1 53.0(2), N5–Yb1–N4 52.7(2).

The X-ray crystal structure analysis of **3** revealed[11] it to be a bimetallic complex in which two deprotonated bipyridylamide ligands act as tridentate bridging ligands and two of them as terminal bidentate aminopyridinates (Figure 3).

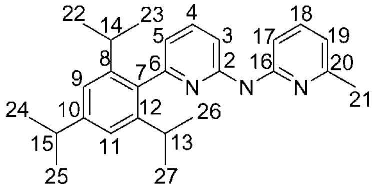
Conclusion

We observed the first f-block-element–f-block-element coupling pattern in solution and have shown the relevance of such investigations in understanding dimer equilibria and rearrangement chemistry of rather bulky structural ensembles. Chemical transformations of low-valent lanthanide species has hitherto been difficult to follow.

Experimental Section

NMR Investigations: The ^{171}Yb NMR spectra were recorded by using a single-pulse sequence with pulse: approx. 30°, relaxation delay: 1 s, digital FID resolution: 0.3–0.5 Hz before zero filling and with proton decoupling during acquisition. The suitable signal-to-noise ratio was reached after 2–4 h. The chemical shifts are given relative to 0.171 M [Yb(η^5-C_5Me_5)(thf)$_2$] in thf [δ (^{171}Yb) = 0 ppm for Ξ (^{171}Yb) = 17.499306 MHz].

Synthesis of Complex 2:



In a glove box, [YbI$_2$(thf)$_4$][18] (2.13 g, 2.98 mmol) and 1.90 g (3.82 mmol) of **1-K** were combined in a flask and thf (100 mL) was added at 0 °C. The resulting dark red reaction mixture was stirred at room temperature for 16 h. After separation of the solution from the precipitated potassium iodide by filtration, the solvent was removed under reduced pressure. The resulting solid was dissolved in toluene (100 mL) and filtered. The filtrate was reduced to dryness, and a dark red-black product was obtained. Crystals of **2** were grown from a concentrated toluene solution. Yield 2.06 g (72%). M.p. 190 °C. $C_{82}H_{104}IN_9OYb_2\cdot 3C_4H_8O$ (1921.06): calcd. C 58.77, H 6.72, N 6.56; found C 58.77, H 6.67, N 6.93. ^{1}H NMR (250 MHz, C_6D_6, 323 K): δ = 0.67–1.24 (m, ^{3}J = 6.7 Hz, 54 H, 22-H, 23-H, 24-H, 25-H, 26-H, 27-H), 1.43 (br., 4 H, β-CH_2, thf), 2.38 (sept, ^{3}J = 6.9 Hz, 3 H, 15-H), 2.60 (sept, ^{3}J = 7.0 Hz, 3 H, 14-H), 2.66 (s, 9 H, 21-H), 2.78 (sept, ^{3}J = 6.7 Hz, 3 H, 13-H), 3.53 (br., 4 H, α-CH_2, thf), 6.00 (d, ^{3}J = 6.7 Hz, 3 H, 19-H), 6.16 (d, ^{3}J = 6.6 Hz, 3 H, H^5), 6.83–7.16 (m, 18 H, 3-H, 4-H, 9-H, 11-H, 17-H, 18-H) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, 298 K): δ = 24.0 (s, C-22, C-23, C-26, C-27), 24.1 (s, C-22, C-23, C-26, C-27), 24.2 (s, C-22, C-23, C-26, C-27), 24.3 (s, C-22, C-23, C-26, C-27), 26.1 (s, β-CH_2, thf), 26.8 (s, C-24, C-25), 27.1 (s, C-24, C-25), 29.8 (s, C-13, C-14), 30.0 (s, C-13, C-14), 34.6 (s, C-15), 67.7 (s, α-CH_2, thf), 109.5 (s, C-19), 113.4 (s, C-17), 114.5 (s, C-5), 116.2 (s, C-3), 121.0 (s, C-9, C-11), 135.8 (s, C-4), 137.5 (s, C-7, C-18), 137.6 (s, C-7, C-18), 146.9 (s, C-8, C-12), 147.1 (s, C-8, C-12), 148.5 (s, C-10), 156.8 (s, C-2, C-16), 157.4 (s, C-2, C-16), 164.2 (s, C-20), 169.1 (s, C-6) ppm. ^{171}Yb NMR (70 MHz, C_4H_8O, 298 K): δ = 646.6 [s, ^{1}J(^{171}Yb, ^{171}Yb) = 76.1 Hz, *Yb*-thf], 585.6 (br., *Yb*-I) ppm.

Supporting Information (see footnote on the first page of this article): Details of the synthesis of the other compounds (ligand and complexes) reported for the first time within this publication can be found in the supporting information.

Acknowledgments

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[12] Selected details of the X-ray crystal structure analyses: **2**·2thf/C_6D_6: space group: $P\bar{1}$, a = 13.3350(5) Å, b = 15.8580(6) Å, c = 22.9500(9) Å, α = 102.371(3) °, β = 91.499(3) °, γ = 107.584(3) °, V = 4497.4(3) Å^3, z = 2, reflections collected/unique/observed [$I > 2\sigma(I)$] = 58816/16943/13427, parameters = 933, R (obs.) = 0.0336, wR^2 (all data) = 0.0825, wR^2 (obs.) = 0.0785; **3**·2C_6D_6 space group: $P\bar{1}$, a = 14.2870(12) Å, b = 14.3730(10) Å, c = 16.8380(14) Å, α = 114.563(6) °, β = 93.070(6) °, γ = 109.525(6) °, V = 2888.2(4) Å^3, z = 1, reflections collected/unique/observed [$I > 2\sigma(I)$] = 37338/10918/5889, parameters = 672, R (obs.) = 0.0654, wR^2 (all data) = 0.1385, wR^2 (obs.) = 0.1201; X-ray crystal structure analysis was carried out with a STOE IPDS II diffractometer equipped with an Oxford Cryostream low-temperature unit. CCDC-642879 (**2**) and CCDC-642880 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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