DOI: 10.1002/ejic.201000593

Ditopic 8-Hydroxyquinoline-2-carboxamides as Ligands for the Formation of Dinuclear Lanthanide(III) Helicates

Markus Albrecht*[a] and Olga Osetska[a]

Keywords: Lanthanides / Self-assembly / Helicates

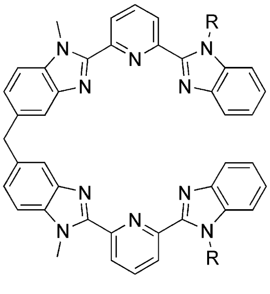
Ditopic ligands (**1**–**4**)-H_2 are easily obtained by coupling 8-hydroxyquinoline-2-carboxylic acid with diamines. Dinuclear helicate-type complexes [La_2(**L**)$_3$] (**L** = ligand) are easily obtained with alkyl-bridged ligands **2** and **3**. Short hydrazine as a linkage (**1**) seems to lead to polymerization, whereas with **4** only [Yb_2(**4**)$_3$] could be characterized by ESIMS. Comparison of the alkyl-bridged derivatives reveals that, in the case of short spacers, alkali cations can be incorporated into the interior of the helicate, whereas this is not observed with the butyl-bridged coordination compounds.

Introduction

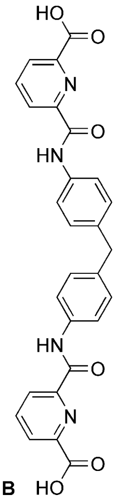
The chemistry of lanthanide ions is a topic that is currently under intense study. Due to their unique photophysical, magnetic, catalytic or redox properties, they are in the focus of attention for different applications. This special class of metal ions reveals a fascinating and highly versatile structural chemistry, which is due to the preference of high coordination numbers and coordination geometries that are not well-defined.[1] However, to control the properties of molecular derivatives of the lanthanides, we have to prepare structurally defined compounds. Especially interesting are oligonuclear derivatives that can exhibit cooperative behaviour or communication between several metal ions. Helicates are a representative class of simple coordination compounds in which metal ions are located at specific positions with a well-defined relative position to each other.[2]

As pioneering work in this field, the studies of Piguet and Bünzli have to be mentioned. They developed ligand systems based on compound **A** and related derivatives. Simple mixing of the ligand with the metal ions in a 3:2 ratio affords the dinuclear triple-stranded helicates. It was possible to obtain multinuclear arrays (up to four rare-earth metal ions) and to investigate their fascinating photophysical properties.[3] Other examples of lanthanide helicates are described by Lessman and Horrocks based on the dipicolinate ligand **B**[4] and by Pikramenou based on the β-diketonate **C**[5].

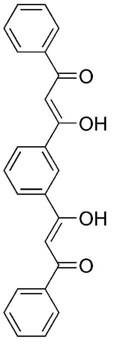
We studied the self-assembly and the photophysics of lanthanide(III) compounds of **D** with various f-element ions [e.g., europium(III)][6] and of hydroxyquinolines **E** with the near infrared (NIR)-emitting lanthanide ions neodymium(III), erbium(III) and ytterbium(III).[7]



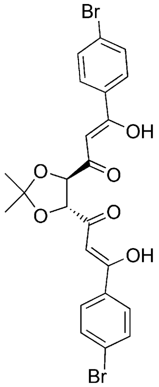
A



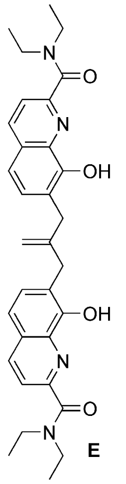
B



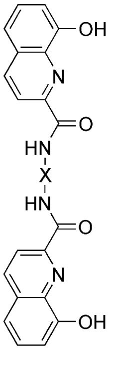
C



D



E



(**1**–**4**)-H_2

Recently we introduced the 8-hydroxyquinoline-2-carboxamide unit as an effective tridentate chelator for lanthanide(III) ions.[8] In **E** two such moieties are connected

---

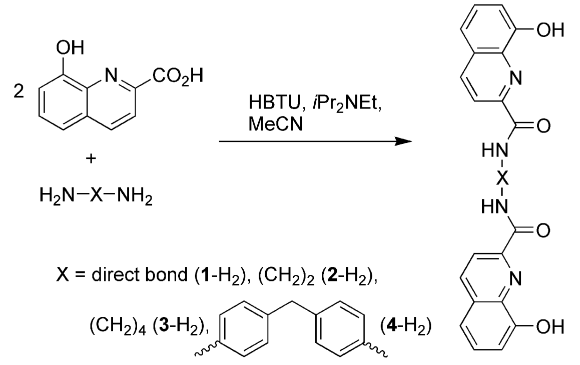
[a] Institut für Organische Chemie, RWTH Aachen University,
Landoltweg 1, 52074 Aachen, Germany
E-mail: markus.albrecht@oc.rwth-aachen.de

by an isobutynylidene linker that is easily introduced by applying the Hiratani–Tandem–Claisen rearrangement.[9] Due to the interesting photophysical properties of complexes with **E** and related ligands, we wondered if we could turn the hydroxyquinoline amide "around" and connect two such units at the amides by using appropriate diamines as spacers.

Therefore we prepared four bisamide ligands (**1**–**4**)-H_2 and studied their coordination chemistry with lanthanide ions. In this context it was of special interest to see if a templating ion is needed to obtain specific self-assembly of triple-stranded dinuclear helicates. Such behaviour was observed in case of the compounds with ligands **E**.

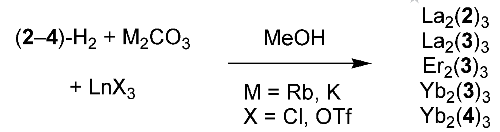
Results and Discussion

Ligands (**1**–**4**)-H_2 are easily prepared from 8-hydroxyquinoline-2-carboxylic acid (2 equiv.) with diamines by using 2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) as coupling reagent and diisopropylethylamine as the base (Scheme 1).[10] Hereby the hydrazide **1**-H_2 was obtained in 48% yield and the alkyl-bridged ligands **2**-H_2 in 53% and **3**-H_2 in 66% yield. The longest ligand system, **4**-H_2, with an 4,4′-diamindiphenylmethane spacer, was isolated in 59% yield.



Scheme 1. Preparation of the bis-amide-bridged (**1**–**4**)-H_2 ligands.

All ligands (**1**–**4**)-H_2 were treated with lanthanide(III) salts (either chloride or triflate) in the ratio 3:2 to obtain the corresponding helicate-type complexes (Scheme 2). Ligand **1**-H_2 afforded only insoluble material, which probably consists of polymeric or oligomeric and molecular species that are not well-defined. The direct bond between the amides might be too short and inflexible to allow the formation of the dinuclear complexes. All other ligands (**2**–**4**)-H_2 resulted in the formation of compounds that possess some solubility in highly polar solvents like DMSO. For analytical reasons (NMR spectroscopy) we focussed on the lanthanum(III) complexes. However, with ligand **4** it was only possible to characterize the ytterbium(III) complex unambiguously. Despite its low solubility, it was characterized by positive ESIMS that showed the peak of $[Yb_2(\mathbf{4})_3 + Na]^+$ at *m*/*z* = 1984.0. With other lanthanide(III) ions and **4**, coordination compounds were obtained with a solubility that was too low for sufficient characterization.



Scheme 2. Preparation of dinuclear triple-stranded helicates with selected lanthanide(III) ions.

The alkyl-bridged ligands **2**-H_2 and **3**-H_2 resulted in the formation of the dinuclear lanthanum(III) compounds $[La_2(\mathbf{2})_3]$ and $[La_2(\mathbf{3})_3]$. The former $[La_2(\mathbf{2})_3]$ was obtained in 90% yield and could be observed by positive FAB-MS at *m*/*z* = 1481.4 $[HLa_2(\mathbf{2})_3]^+$. Figure 1 shows a comparison of the ^1H NMR spectra of ligand **2**-H_2 as well as of complex $[La_2(\mathbf{2})_3]$ in [D$_6$]DMSO. Upon complexation, the signal of OH disappears, whereas the NH signal is shifted from δ = 9.91 (ligand) to 10.85 ppm (complex). In contrast to this, the aromatic protons appear at higher field in the coordination compound. Most indicative of the formation of the helicate-type structure is the signal of the ethylene spacer. In the ligand it is observed as a signal at δ = 3.65 ppm, and in $[La_2(\mathbf{2})_3]$ it is highfield shifted and split (δ = 2.73 and 2.27 ppm). Splitting of the signals is due to the diastereotopicity of the methylene units in the coordination compound that possess chiral metal complex units.[11] However, from these data it cannot be concluded if a homo- (helicate) or heterochiral (*meso*-helicate) structure is adopted.[12]

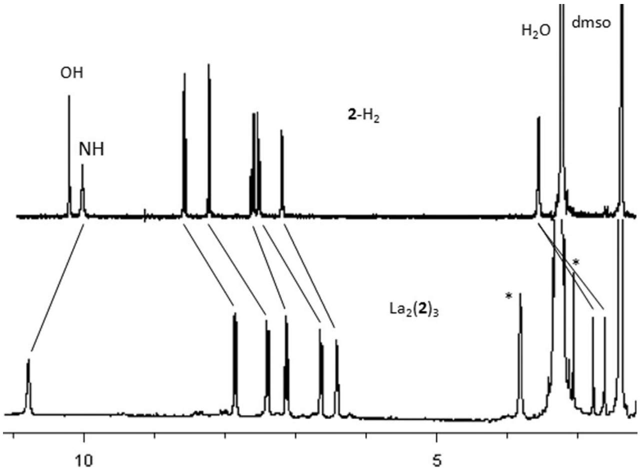


Figure 1. ^1H NMR spectrum of ligand **2**-H_2 (top) and its lanthanum(III) complex $[La_2(\mathbf{2})_3]$ (bottom) recorded in [D$_6$]DMSO (* denotes traces of methanol).

Similar NMR spectroscopic results are observed for $[La_2(\mathbf{3})_3]$ (Figure 2). However, the NH signal is only slightly shifted (vide infra), whereas the aromatic protons show a less pronounced shifting upon complexation compared to the analogous findings with ligand **2**. The methylene units close to the amides again show diastereotopic behaviour that leads to two signals at δ = 3.04 and 2.85 ppm for complex $[La_2(\mathbf{3})_3]$. The central methylene units are too far away from the chiral units; no splitting but some broadening is observed for the signal at δ = 1.40 ppm. In addition, [La_2(**2**)$_3$] was characterized by positive as well as negative ESIMS.

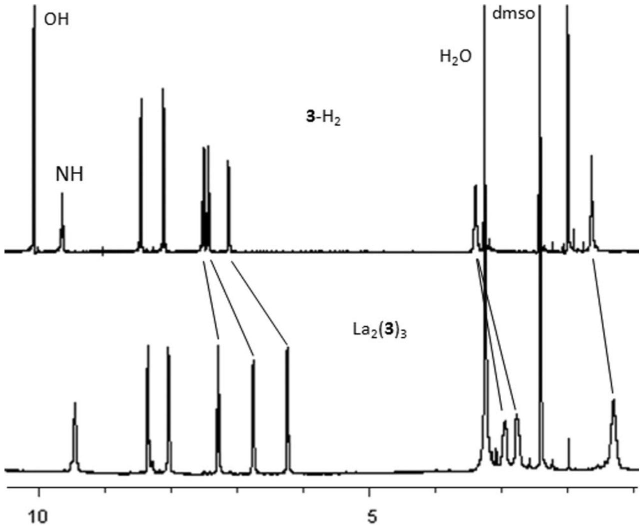
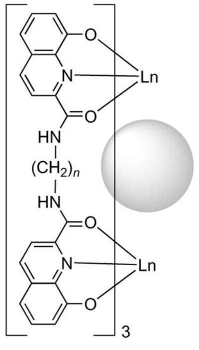


Figure 2. ^{1}H NMR spectrum of ligand **3**-H_2 (top) and its lanthanum(III) complex [La_2(**3**)$_3$] (bottom) recorded in [D_6]DMSO.

8-Hydroxyquinoline complexes are especially interesting with NIR-emitting lanthanide(III) ions. Therefore erbium(III) as well as ytterbium(III) complexes of ligand **3**-H_2 were also prepared. However, due to the presence of the NH quencher, no photophysical studies were performed with the obtained complexes (Scheme 3).



Scheme 3. Schematic representation of the internal cavity formed by three ligands, which bridge two metal ions.

In the case of the helicates of ligand **E**, a strong templating effect by cations was observed.[13] They are encapsulated in the interior of the dinuclear complex and bind to the phenolate oxygen atoms. They are thus stabilizing the compounds. Therefore it was checked to see if the new compounds bind cations using the amide oxygen atom. An indication for this is found in case of [La_2(**2**)$_3$] by elemental analysis, which reveals that an adduct of the dinuclear helicate with rubidium chloride is present. Positive FAB-MS shows the corresponding peak at m/z = 1781.6 for [La_2(**2**)$_3$ + Rb + H_2O]$^+$ in addition to the signal of the monoprotonated triple-stranded helicate. The cavity of the ethyldiamide-linked compounds seems to be appropriate for the encapsulation of the cation. However, with longer spacers (ligand **3** and **4**) no alkali metal salts are observed by elemental analysis. In this case, the cavity seems to be too big for effective binding of the cation. A further indication for the inclusion of cations in the smaller helicates is found by proton NMR spectroscopy. A lowfield shift is observed for the NH proton of ligand **2** upon complexation, whereas no significant change of the signal is observed with **3**.

Conclusion

In this manuscript, new bis(2-amido-8-hydroxyquinoline) ligands for the complexation of lanthanide(III) ions are introduced. In self-assembly processes, triple-stranded dinuclear helicate-type coordination compounds are obtained. The complexation works best if short ethylene or butanediyl spacers link the amide units of the two tridentate chelating units. In the case of the ethylene linker, alkali metal cations are bound to the complex and probably act as a template in its formation. With butanediyl, the complex formation still works although no strong interaction with templating cations can be observed.

The presented coordination compounds are model systems that show that this kind of bisamide-bridged ligand can be used for the formation of homoditopic lanthanide(III) helicates. This will be used to obtain related complexes that are of interest for photophysical studies in the future.

Experimental Section

General: NMR spectra were recorded with a Varian Mercury 300 or Inova 400 spectrometer. FTIR spectra were recorded with a Bruker IFS spectrometer. Mass spectra were taken with a Thermo Deca XP mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer.

General Procedure for the Preparation of the Bisamides: 8-Hydroxyquinoline-2-carboxylic acid (**30a**) (1.0 g, 5.29 mmol), HBTU (2.41 g, 6.35 mmol) and *N*,*N*-diisopropylethylamine (DIPEA; 0.75 g, 1.0 mL, 5.80 mmol) were stirred in MeCN (50 mL), and hydrazine hydrate (**1**, 0.132 g, 0.128 mL, 2.64 mmol), 1,2-diaminoethane (**2**, 0.159 g, 0.179 mL, 2.64 mmol), 1,4-diaminobutane (**3**, 0.233 g, 0.266 mL, 2.64 mmol) or 4,4′-diaminodiphenylmethane (**4**, 0.524 g, 2.64 mmol) in MeCN (2 mL) were added. The mixture was stirred for two days at room temperature. The precipitate was filtered off, washed with MeCN and then was recrystallized from methanol.

1-H_2: Yield 0.52 g (48%); m.p. 327 °C. ^{1}H NMR (300 MHz, [D_6]-DMSO): δ = 11.60 (s, 2 H, NH), 10.22 (s, 2 H, OH), 8.60 (d, J = 8.5 Hz, 2 H, H_{ar}), 8.20 (d, J = 8.5 Hz, 2 H, H_{ar}), 7.63 (dd, J = 8.4, 7.4 Hz, 2 H, H_{ar}), 7.55 (dd, J = 8.4, 1.2 Hz, 2 H, H_{ar}), 7.23 (dd, J = 7.4, 1.2 Hz, 2 H, H_{ar}) ppm. MS (ESI+): m/z (%) = 375.2 (100) [M + H^+]. IR (KBr): $\tilde{\nu}$ = 3494, 3426, 1677, 1628, 1500, 1466, 1238, 1189, 1157, 1088, 841, 735, 627 cm^{-1}. $C_{20}H_{14}N_4O_4 \cdot 2H_2O$ (410.4): calcd. C 58.54, H 4.42, N 13.65; found C 58.03, H 4.95, N 13.59.

2-H_2: Yield 0.58 g (53%); m.p. 305 °C. ^{1}H NMR (300 MHz, [D_6]-DMSO): δ = 10.09 (s, 2 H, NH), 9.91 (br. s, 2 H, OH), 8.52 (d, J

= 8.5 Hz, 2 H, H_{ar}), 8.17 (d, J = 8.5 Hz, 2 H, H_{ar}), 7.57 (dd, J = 8.2, 7.4 Hz, 2 H, H_{ar}), 7.49 (dd, J = 8.2, 1.2 Hz, 2 H, H_{ar}), 7.16 (dd, J = 7.4, 1.2 Hz, 2 H, H_{ar}), 3.65 (d, J = 2.6 Hz, 4 H, CH_2) ppm. MS (ESI+): m/z (%) = 403.3 (100) [M + H^+]. IR (KBr): $\tilde{\nu}$ = 3370, 3426, 1661, 1502, 1461, 1237, 1189, 852, 760, 715 cm^{-1}. $C_{22}H_{18}N_4O_4\cdot\frac{3}{4}H_2O$ (415.5): calcd. C 63.53, H 4.73, N 13.47; found C 63.66, H 5.12, N 13.38.

3-H_2: Yield 0.80 g (66%); m.p. 276–277 °C. ^1H NMR (300 MHz, [D_6]DMSO): δ = 10.09 (s, 2 H, NH), 9.66 (t, J = 6.0 Hz, 2 H, OH), 8.48 (d, J = 8.4 Hz, 2 H, H_{ar}), 8.14 (d, J = 8.4 Hz, 2 H, H_{ar}), 7.55 (dd, J = 8.2, 7.7 Hz, 2 H, H_{ar}), 7.47 (dd, J = 8.2, 1.2 Hz, 2 H, H_{ar}), 7.16 (dd, J = 7.7, 1.2 Hz, 2 H, H_{ar}), 3.46 (m, 4 H, CH_2N), 1.72 (m, 4 H, CH_2) ppm. MS (ESI+): m/z (%) = 431.3 (100) [M + H^+]. IR (KBr): $\tilde{\nu}$ = 3135, 3052, 1613, 1481, 1389, 1321, 1292, 1160, 1081, 865, 785, 748 cm^{-1}. $C_{24}H_{22}N_4O_4\cdot1.5H_2O$ (457.5): calcd. C 63.01, H 5.51, N 12.25; found C 62.92, H 5.55, N 11.94.

4-H_2: Yield 0.86 g (59%); m.p. 301 °C. ^1H NMR (300 MHz, [D_6]DMSO): δ = 11.15 (s, 2 H, NH), 10.40 (s, 2 H, OH), 8.57 (d, J = 8.7 Hz, 2 H, H_{ar}), 8.26 (d, J = 8.7 Hz, 2 H, H_{ar}), 7.84 (d, J = 8.4 Hz, 4 H, H_{ar}), 7.60 (dd, J = 8.2, 7.7 Hz, 2 H, H_{ar}), 7.52 (dd, J = 8.2, 1.2 Hz, 2 H, H_{ar}), 7.34 (d, J = 8.4 Hz, 4 H, H_{ar}), 7.23 (dd, J = 7.4, 1.2 Hz, 2 H, H_{ar}), 3.99 (s, 2 H, CH_2) ppm. MS (ESI–): m/z (%) = 539.8 (100) [M – H^-]. IR (KBr): $\tilde{\nu}$ = 3340, 1681, 1592, 1524, 1463, 1405, 1318, 1237, 1189, 849, 762 cm^{-1}. $C_{33}H_{24}N_4O_4\cdot0.5H_2O$ (549.6): calcd. C 72.12, H 4.59, N 10.59; found C 72.57, H 5.07, N 10.29.

General Procedure for the Preparation of Helicate-Type Complexes: M_2CO_3 (M = Rb, K) was added as base to the corresponding ligand **1**–**4**-H_2 (3.0 equiv.) in MeOH (15 mL), thereby resulting in a transparent yellowish solution, to which a $Ln(OTf)_3$ or a hydrated $LnCl_3$ (2.0 equiv.) was successively added. The reaction mixture was gently heated at reflux for 15 h and then cooled to room temp. The precipitate was filtered off, washed with chilled water, MeOH and Et_2O to afford the product.

[Rb(2)$_3$La$_2$]Cl: Yield 0.049 g (90%). ^1H NMR (300 MHz, [D_6]DMSO): δ = 10.85 (br. s, 6 H, NH), 7.94 (d, J = 8.4 Hz, 6 H, H_{ar}), 7.49 (d, J = 8.4 Hz, 6 H, H_{ar}), 7.12 (dd, J = 7.7, 7.9 Hz, 6 H, H_{ar}), 6.73 (d, J = 7.9 Hz, 6 H, H_{ar}), 6.50 (d, J = 7.7 Hz, 6 H, H_{ar}), 2.73 (s, 6 H, $CH_{methylene}$), 2.27 (s, 6 H, $CH_{methylene}$) ppm. MS (FAB+; 3-NBA): m/z = 1781.6 [La_2(**2**)$_3$ + Rb + H_2O]$^+$, 1481.4 [La_2(**2**)$_3$ + H]$^+$. IR (KBr): $\tilde{\nu}$ = 1635, 1590, 1556, 1499, 1451, 1344, 1306, 1105, 846, 742 cm^{-1}. $C_{66}H_{48}ClLa_2N_{12}O_{12}Rb\cdot3H_2O$ (1653.9): calcd. C 47.93, H 3.29, N 10.16; found C 47.85, H 3.61, N 9.69.

[La$_2$(3)$_3$]: Yield 0.049 g (94%). ^1H NMR (300 MHz, [D_6]DMSO): δ = 9.44 (br. s, 6 H, NH), 8.39 (d, J = 8.8 Hz, 6 H, H_{ar}), 8.06 (d, J = 8.8 Hz, 6 H, H_{ar}), 7.33 (t, J = 8.0 Hz, 6 H, H_{ar}), 6.81 (d, J = 8.0 Hz, 6 H, H_{ar}), 6.30 (d, J = 8.0 Hz, 6 H, H_{ar}), 3.04 (br. s, 6 H, $CH_{methylene}$), 2.85 (br. s, 6 H, $CH_{methylene}$), 1.40 (br. s, 12 H, CH_2) ppm. MS (ESI+): m/z (%) = 1585.9 [La_2(**3**)$_3$ + Na^+], 1019.1 (100) [La(**3**)$_2$ + Na^+]. MS (ESI–): m/z (%) = 1597.8 (8.0) [La(**3**)$_3$ + Cl^-], 1561.1 (86.0) [La_2(**3**)$_3$ – H^-], 995.4 (69.0) [La(**3**)$_2^-$]. IR (KBr): $\tilde{\nu}$ = 1629, 1591, 1552, 1499, 1449, 1374, 1343, 1307, 1104, 845, 741 cm^{-1}. $C_{72}H_{60}La_2N_{12}O_{12}\cdot7H_2O$ (1688.7): calcd. C 51.19, H 4.42, N 9.95; found C 51.25, H 4.57, N 9.79.

[Er$_2$(3)$_3$]: Yield 0.050 g (93%). MS (ESI+): m/z = 1657.2 [K(**3**)$_3$-Er_2]$^+$. IR (KBr): $\tilde{\nu}$ = 1633, 1592, 1556, 1500, 1454, 1378, 1350, 1312, 1107, 845, 746 cm^{-1}. $C_{72}H_{60}Er_2N_{12}O_{12}\cdot7H_2O$ (1744.5): calcd. C 49.53, H 4.27, N 9.63; found C 49.11, H 4.25, N 9.53.

[Yb$_2$(3)$_3$]: Yield 0.050 g (96%). MS (ESI+): m/z = 1176.0 [Yb(**3**)$_2$$Na_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 3389, 3272, 3076, 1633, 1593, 1558, 1500, 1455, 1379, 1351, 1313, 1108, 845, 747 cm^{-1}. $C_{72}H_{60}N_{12}O_{12}Yb_2\cdot3H_2O$ (1685.4): calcd. C 51.31, H 3.95, N 9.97; found C 51.23, H 4.48, N 9.90.

[Yb$_2$(3)$_3$]: Yield 0.072 g (95%). MS (ESI+): m/z = 1984.0 [Yb_2(**3**)$_3$ + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 3375, 1635, 1600, 1543, 1510, 1455, 1416, 1379, 1349, 1314, 1107, 843, 747 cm^{-1}. $C_{99}H_{66}N_{12}O_{12}Yb_2\cdot5H_2O$ (2050.8): calcd. C 57.95, H 3.73, N 8.19; found C 57.91, H 3.98, N 8.07.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) (SPP 1166) and the Fonds der Chemischen Industrie.

---

[1] a) T. Gunnlaugsson, F. Stomeo, *Org. Biomol. Chem.* **2007**, *5*, 1999; b) S. Comby, J.-C. G. Bünzli, in: *Handbook on the Physics and Chemistry of Rare Earths* (Eds.: K. A. Gschneidner Jr., J.-C. G. Bünzli, V. K. Pecharsky), Elsevier, Amsterdam, **2007**, Vol. 37, Ch. 235; c) V. Alexander, *Chem. Rev.* **1995**, *95*, 273; d) G. Mathis, *Clin. Chem.* **1995**, *41*, 1391; e) D. Parker, J. A. G. Williams, *J. Chem. Soc., Dalton Trans.* **1996**, 3613.

[2] a) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; b) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457.

[3] a) C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347; b) J.-C. G. Bünzli, C. Piguet, *Chem. Rev.* **2002**, *102*, 1897; c) J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048; d) B. Bocquet, G. Bernardinelli, N. Ouali, F. Floquet, F. Renaud, G. Hopfgartner, C. Piguet, *Chem. Commun.* **2002**, 930; e) M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli, C. Piguet, *J. Am. Chem. Soc.* **1999**, *121*, 10747; f) N. André, T. B. Jensen, R. Scopelliti, D. Imbert, M. Elhabiri, G. Hopfgartner, C. Piguet, J.-C. G. Bünzli, *Inorg. Chem.* **2004**, *43*, 515; g) S. Torelli, D. Imbert, M. Cantuel, G. Bernardinelli, S. Delahaye, A. Hauser, J.-C. G. Bünzli, C. Piguet, *Chem. Eur. J.* **2005**, *11*, 3228; h) C. Piguet, C. Edder, S. Rigault, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* **2000**, 3999; i) D. Imbert, M. Cantuel, J.-C. G. Bünzli, G. Bernardinelli, C. Piguet, *J. Am. Chem. Soc.* **2003**, *125*, 15698; j) T. B. Jensen, R. Scopelliti, J.-C. G. Bünzli, *Chem. Eur. J.* **2007**, *13*, 8404; k) K. Zeckert, J. Hamacek, J.-M. Senegas, N. Dalla-Favera, S. Floquet, G. Bernardinelli, C. Piguet, *Angew. Chem. Int. Ed.* **2005**, *44*, 7954; l) for related chemistry involving quinolinates, see: E. Terazzi, L. Guénée, B. Bocquet, J.-F. Lemonnier, N. D. Favera, C. Piguet, *Chem. Eur. J.* **2009**, *15*, 12719.

[4] J. J. Lessmann, W. D. Horrocks, *Inorg. Chem.* **2000**, *39*, 3114.

[5] A. P. Bassett, S. W. Magennis, P. B. Glover, D. J. Lewis, N. Spencer, S. Parsons, R. M. Williams, L. De Cola, Z. Pikramenou, *J. Am. Chem. Soc.* **2004**, *126*, 9413.

[6] M. Albrecht, S. Schmid, S. Dehn, C. Wickleder, S. Zhang, A. P. Bassett, Z. Pikramenou, R. Fröhlich, *New J. Chem.* **2007**, *31*, 1755.

[7] a) M. Albrecht, O. Osetska, R. Fröhlich, J.-C. G. Bünzli, A. Aebischer, F. Gumy, J. Hamacek, *J. Am. Chem. Soc.* **2007**, *129*, 14178; b) M. Albrecht, O. Osetska, J.-C. G. Bünzli, F. Gumy, R. Fröhlich, *Chem. Eur. J.* **2009**, *15*, 8791; c) for lanthanide quinolinate chemistry, see: R. van Deun, P. Fias, P. Nockemann, A. Schepers, T. N. Parac-Vogt, K. van Hecke, L. van Meervelt, K. Binnemans, *Inorg. Chem.* **2004**, *43*, 8461.

[8] a) M. Albrecht, O. Osetska, R. Fröhlich, *Eur. J. Org. Chem.* **2007**, 4902; b) M. Albrecht, O. Osetska, J. Klankermayer, R. Fröhlich, F. Gumy, J.-C. G. Bünzli, *Chem. Commun.* **2007**, 1834; c) M. Albrecht, O. Osetska, T. Abel, G. Haberhauer, E. Ziegler, *Beilstein J. Org. Chem.* **2009**, *5*, No. 78; d) for comparison, see: N. M. Shavaleev, R. Scopelliti, F. Gumy, J.-C. G. Bünzli, *Inorg. Chem.* **2008**, *47*, 9055.

[9] K. Hiratani, M. Albrecht, *Chem. Soc. Rev.* **2008**, *37*, 2413.

[10] M. Bodanszky, A. Bodanszky, *The Practice of Peptide Synthesis*, Springer, Berlin, **1984**.

[11] M. Albrecht, M. Schneider, H. Röttele, *Chem. Ber./Recueil* **1997**, *130*, 615.

[12] M. Albrecht, *Chem. Eur. J.* **2000**, *6*, 3485.

[13] M. Albrecht, in: *Topics in Current Chemistry - Templates in Chem.* (Eds.: C. A. Schalley, F. Vögtle, K.-H. Dötz), **2004**, vol. 248, p. 105.

Received: May 28, 2010