Inorganic Chemistry

Communication

pubs.acs.org/IC

Synthesis of Inert Homo- and Heterodinuclear Rare-Earth Cryptates

Jessica Wahsner[†] and Michael Seitz*[,†,‡]

[‡]Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

[†]Inorganic Chemistry I, Department of Chemistry and Biochemistry, Ruhr-University Bochum, 44780 Bochum, Germany

Supporting Information

ABSTRACT: A new ditopic cryptand based on two tris(biaryl)-based binding pockets bridged by a 2,2′-bipyrimidine unit enables the selective synthesis of homo- and heterodinuclear rare-earth cryptates, which are kinetically inert under challenging conditions and can even be purified by preparative high-performance liquid chromatography.

Trivalent rare-earth cations exhibit unique physical properties because of their special electronic structure. In molecular mononuclear rare-earth complexes, the utilization of these features has already matured to a relatively sophisticated level, especially in the areas of luminescence and molecular magnetism.[1,2] The most interesting phenomena, however, can only be accessed in assemblies with multiple and/or different rare-earth centers, e.g., most prominently in solid-state materials such as ytterbium/erbium-doped upconversion nanoparticles.[3] In the field of molecular rare-earth chemistry, the great chemical similarity of the trivalent rare-earth cations combined with their high kinetic lability makes it very difficult to obtain defined heterometallic complexes with enough stability to avoid scrambling of the different metal centers under challenging conditions. Only very few molecular architectures have been developed for this purpose, despite the enormous value that such systems could have for the elucidation of fundamental processes responsible for electronic and magnetic interaction between metal ions.[4] The most successful approach so far is the one pioneered by Faulkner and co-workers based on the covalent connection of macrocyclic, DO3A-derived lanthanoid complexes.[4a,b] In this report, we show that another common ligand family for rare-earth complexation, the tris(biaryl)-based cryptands introduced by Lehn and co-workers and later shown by others to be universally versatile for rare-earth complexation,[5] can also be expanded into ditopic chelators (Figure 1). In addition, we provide proof-of-concept that these dicryptates can be selectively prepared with either the same or different rare-earth cations and

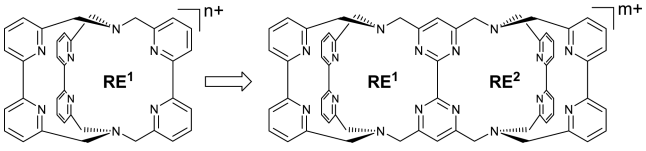
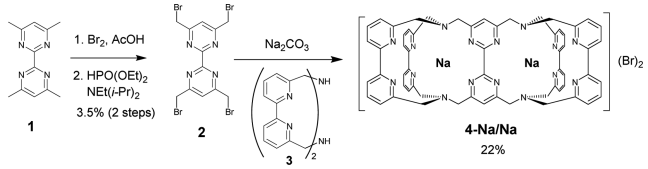


Figure 1. Expansion of the concept of the known mononuclear tris(2,2′-bipyridine) cryptates (left) into the related dinuclear cryptate reported here (right).

that they exhibit extraordinary kinetic stability, making even chromatographic purification available, which is usually not possible for rare-earth complexes.

For the design of the new ditopic chelators, we chose 2,2′-bipyrimidine as the bridging unit between the two macrobicyclic binding pockets because of its proven utility for the construction of homodinuclear lanthanoid complexes and because of its great potential for enabling electronic and magnetic communication between the metal centers.[6] The synthesis (Scheme 1) of the

Scheme 1. Synthesis of the Dinuclear Sodium Cryptate 4-Na/Na



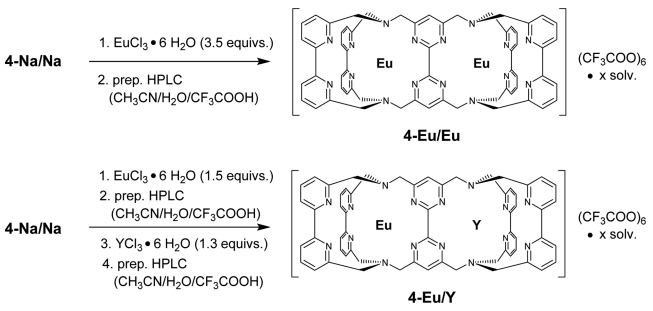
dicryptates started from known 4,4′,6,6′-tetramethyl-2,2′-bipyrimidine (**1**).[7] With the usual reaction sequence (formation of the *N*-oxides, Boekelheide rearrangement, nucleophilic substitution with bromide) not being applicable for preparation of the desired bipyrimidine **2**,[8] we opted for unselective benzylic halogenation using dibromine, giving a mixture of highly brominated compounds,[9] followed by the relatively straightforward isolation of the symmetric tetrakis(dibromomethyl) species.[10] This intermediate could then be selectively reduced to the desired tetrabromide **2** using diethyl phosphite.[11] 2-fold macrocyclization of building block **2** with the known azacrown ether **3**[12] under standard sodium-templated conditions gave the disodium cryptate **4-Na/Na** in reasonable yield (Scheme 1).

Starting from the dicryptate **4-Na/Na**, we attempted the synthesis of the envisaged rare-earth dicryptates, both homo- and heterodinuclear (Scheme 2). On the one hand, we chose europium as one metal for our proof-of-concept studies because of the well-established luminescence properties of this element[5a] and the structural information that the analysis of the emission spectra can provide (vide infra). On the other hand, we selected the photoinactive yttrium as the second metal because of its very similar ionic radius compared to europium. The synthesis of the homodinuclear cryptate **4-Eu/Eu** was straightforward using an excess of $EuCl_3 \cdot 6H_2O$ under standard metal-exchange conditions.[5] Crucially, the crude material could be purified by preparative high-performance liquid chromatography (HPLC)

Received: August 20, 2015
Published: October 5, 2015

DOI: 10.1021/acs.inorgchem.5b01922
Inorg. Chem. 2015, 54, 9681−9683

Scheme 2. Synthesis of the Dinuclear Rare-Earth Cryptates 4-Eu/Eu and 4-Eu/Y



without any decomplexation or loss of structural integrity (Figure 2).

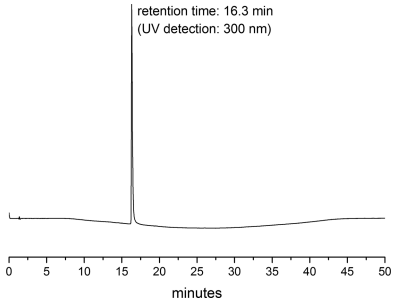


Figure 2. Analytical HPLC trace (Lichrospher RP-18e 125 mm × 4 mm−5 μm; eluents H_2O + 1% TFA/CH_3CN) of **4-Eu/Eu** after the preparative HPLC purification.[10]

Synthesis of the heterodinuclear europium/yttrium cryptate started similarly with the metal exchange of europium for sodium in **4-Na/Na** with 1.5 equiv of the europium salt. The obtained mixture (mainly complexes with one or two europiums in the dicryptate) could conveniently be purified again by HPLC to very cleanly yield the mono-Eu/H^+ cryptate (**4-Eu**),[10] which could then be subjected to a second complexation reaction with $YCl_3 \cdot 6H_2O$. For reasons not entirely clear to us yet, this conversion of **4-Eu** to the dinuclear **4-Eu/Y** proceeded rather sluggishly and only showed incomplete conversions, leaving the starting material **4-Eu** as the major component after the reaction (see Figure S9 in the Supporting Information). Because of the exceptional stability of the new dicryptates, however, **4-Eu/Y** could be isolated by preparative HPLC, albeit with **4-Eu** as a minor impurity (ca. 5−10%). Importantly, in addition to the apparent chemical stability under HPLC conditions, we did not observe any scrambling of the metals in **4-Eu/Y** [as evidenced by repeated luminescence, matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), and HPLC measurements after prolonged standing in solution at ambient temperature], which testifies to the high degree of kinetic stabilty of the cryptates.

With the inert dicryptates **4-Eu/Eu** and **4-Eu/Y** in hand, we performed luminescence measurements in order to see the effects of the close proximity of the two metal centers on the photophysical properties. The steady-state emission spectra of the two dicryptates in CD_3OD show very similar features overall (Figure 3).

In **4-Eu/Eu**, the emission band for the transition $^5D_0 \rightarrow {}^7F_0$ is split into two clearly distinguishable components around 572 and 575 nm, whereas in **4-Eu/Y**, this band is mainly composed of the

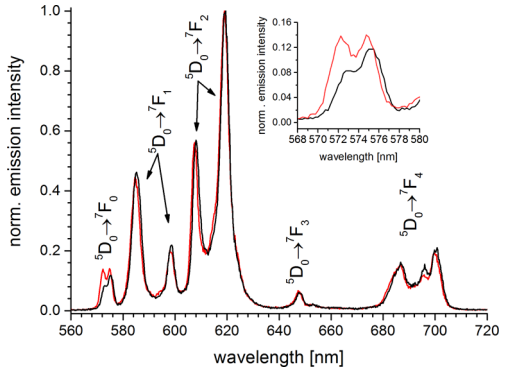


Figure 3. Steady-state emission spectra of **4-Eu/Y** (black) and **4-Eu/Eu** (red) (λ_{exc} = 305 nm; $c \approx 10$ μM in CD_3OD; 2.0 nm slit widths). Inset: Magnification of the $^5D_0 \rightarrow {}^7F_0$ transition.

575 nm feature, with only a small shoulder at smaller wavelength (presumably due to the small impurities of **4-Eu** left after HPLC purification, vide supra). This transition only involves nondegenerate states and should consequently not show any crystal-field splitting, and therefore only one peak is expected for different europium sites.[13] The presence of two peaks in the emission spectrum of **4-Eu/Eu** is a clear indication that on the time scale of the measurement two nonequivalent europium sites are present in this dicryptate with small but clear energetic differences in their electronic structure. Luminescence lifetime measurements for **4-Eu/Eu** (λ_{exc} = 300 nm; λ_{em} = 619 nm) in a methanolic solution gave results also completely consistent with this interpretation (Table 1): In CD_3OD, **4-Eu/Eu** shows

Table 1. Luminescence Lifetimes for 4-Eu/Eu[a]

	solvent	τ_1 [ms][b]	τ_2 [ms][b]
4-Eu	CD_3OD	0.94 (100%)	
4-Eu/Y	CD_3OD	0.96 (100%)	
4-Eu/Eu	CD_3OD	1.54 (53%)	0.127 (47%)
4-Eu/Eu	CH_3OH	1.02 (50%)	0.096 (50%)
q_{MeOH}[c]		≈0.5	≈2.9

[a]Estimated uncertainties: $\tau \pm 10\%$; $c \approx 10$ μM; λ_{exc} = 300 nm; λ_{em} = 619 nm ($^5D_0 \rightarrow {}^7F_2$). [b]The relative contribution to the decay is in parentheses. [c]Estimated using the modified empirical equation $q_{MeOH} = 2.4(1/\tau_H - 1/\tau_D - 0.125\ ms^{-1})$ based on the corresponding equation in water.[14]

biexponential decay kinetics with two very different, almost equally contributing lifetimes τ_1 = 1.54 ms (53%) and τ_2 = 0.127 ms (47%), which expectedly shorten in CH_3OH to τ_1 = 1.01 ms (50%) and τ_2 = 0.096 ms (50%). These lifetime data allow the very crude approximation of the number of inner-sphere methanol molecules (q_{MeOH}) by modifying the usual empirical equation for water ($A_{MeOH} = 2A_{water}$ and $B_{MeOH} = 0.5B_{water}$).[14] This analysis gives two apparently very different solvation states at europium for the two sets of lifetimes: $q_{MeOH} \approx 0.5$ for the long-lived and $q_{MeOH} \approx 2.9$ for the short-lived component. The latter number is very similar to the hydration number (q_{water} = 2.5) found for the corresponding mononuclear europium cryptate.[5c] While the qualitative difference is quite apparent, the obtained values for q_{MeOH} must be considered with caution because, in our system, we cannot rule out directed Eu → Eu energy transfer affecting the lifetimes, which has recently attracted attention and the existence of which has been called into doubt for molecular europium complexes.[15] The reason for

DOI: 10.1021/acs.inorgchem.5b01922
Inorg. Chem. 2015, 54, 9681−9683

the very different environments around the europium centers in **4-Eu/Eu** is not entirely clear at this moment, but it is likely due to the very strong mechanical coupling of the conformational dynamics in the two binding pockets. Further investigations into the details of this effect are currently underway. The fact that the metal centers in the new homodinuclear cryptates are clearly distinguishable is a rarely encountered feature in similar systems and is quite significant because it implies that any interaction between the two metal sites could have a high degree of directionality, which, in turn, would prove very helpful for future studies concerning intermetallic electronic or magnetic interactions.

In conclusion, we have developed a synthetic route for the selective preparation of homo- and heterodinuclear rare-earth cryptates. These complexes are very inert and can be purified by chromatographic methods without the loss of structural integrity and/or scrambling of the metal centers in the case of **4-Eu/Y**. These new cryptates will open up new, exciting avenues for addressing fundamentally important basic questions related to intermetallic communication pathways in rare-earth materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01922.

Synthetic procedures, HPLC traces, MALDI-MS spectra, and experimental details for the photophysical measurements (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.seitz@uni-tuebingen.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from DFG (Emmy Noether, Heisenberg Fellowships for M.S.; Research Grant SE 1448/6-1) and International Isotope Society, Central European Division (predoctoral fellowship for J.W.), is gratefully acknowledged.

■ REFERENCES

(1) Bünzli, J.-C. G.; Eliseeva, S. V. In *Comprehensive Inorganic Chemistry II*; Reedijk, J., Poeppelmeier, K., Eds.; Elsevier: Amsterdam, The Netherlands, 2013; Vol. 8, p 339.

(2) (a) Habib, F.; Murugesu, M. *Chem. Soc. Rev.* **2013**, *42*, 3278. (b) Woodruff, D. N.; Winpenny, R. E. P.; Layfield, R. A. *Chem. Rev.* **2013**, *113*, 5110. (c) Liddle, S. T.; van Slageren, J. *Chem. Soc. Rev.* **2015**, *44*, 6655.

(3) (a) Dong, H.; Du, S.-R.; Zheng, X.-Y.; Lyu, G.-M.; Sun, L.-D.; Li, L.-D.; Zhang, P.-Z.; Zhang, C.; Yan, C.-H. *Chem. Rev.* **2015**, DOI: 10.1021/acs.chemrev.5b00091. (b) Chen, G.; Qiu, H.; Prasad, P. N.; Chen, X. *Chem. Rev.* **2014**, *114*, 5161. (c) Gai, S.; Li, C.; Yang, P.; Lin, J. *Chem. Rev.* **2014**, *114*, 2343. (d) Bünzli, J.-C. G.; Chauvin, A.-S.; In *Handbook on the Physics and Chemistry of Rare Earths (Vol. 44)*, Gschneidner, K. A. Jr; Bünzli, J.-C. G.; Pecharsky, V. K.; Eds.; Elsevier: Amsterdam, 2014; pp 169.

(4) Selected examples: (a) Sørensen, T. J.; Kenwright, A. M.; Faulkner, S. *Chem. Sci.* **2015**, *6*, 2054 and references cited therein. (b) Faulkner, S.; Pope, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 10526. (c) Andre, N.; Scopelliti, R.; Hopfgartner, G.; Piguet, C.; Bünzli, J.-C. G *Chem. Commun.* **2002**, 214.

(5) (a) Alpha, B.; Lehn, J.-M.; Mathis, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 266. (b) Faulkner, S.; Beeby, A.; Carrie, M.-C.; Dadabhoy, A.; Kenwright, A. M.; Sammes, P. G. *Inorg. Chem. Commun.* **2001**, *4*, 187. (c) Alzakhem, N.; Bischof, C.; Seitz, M. *Inorg. Chem.* **2012**, *51*, 9343. (d) Scholten, J.; Rosser, G. A.; Wahsner, J.; Alzakhem, N.; Bischof, C.; Stog, F.; Beeby, A.; Seitz, M. *J. Am. Chem. Soc.* **2012**, *134*, 13915. (e) Doffek, C.; Alzakhem, N.; Molon, M.; Seitz, M. *Inorg. Chem.* **2012**, *51*, 4539.

(6) Selected examples: (a) Demir, S.; Zadrozny, J. M.; Nippe, M.; Long, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 18546. (b) Zucchi, G.; Le Goff, X. F. *Polyhedron* **2013**, *52*, 1262. (c) Swavey, S.; Swavey, R. *Coord. Chem. Rev.* **2009**, *253*, 2627. (d) Romanova, K. A.; Freidzon, A. Ya.; Bagaturyants, A. A.; Galyametdinov, Y. G. *J. Phys. Chem. A* **2014**, *118*, 11244.

(7) (a) Liu, Q.-D.; Wang, R.; Wang, S. *Dalton Trans.* **2004**, 2073. (b) Inagaki, A.; Yatsuda, S.; Edure, S.; Suzuki, A.; Takahashi, T.; Akita, M. *Inorg. Chem.* **2007**, *46*, 2432.

(8) Lehn, J.-M.; de Vains, J.-B. R. *Helv. Chim. Acta* **1992**, *75*, 1221.

(9) In analogy to: Strekowski, L.; Wydra, R. L.; Janda, L.; Harden, D. B. *J. Org. Chem.* **1991**, *56*, 5610.

(10) For details, see the Supporting Information.

(11) In analogy to: Liu, P.; Chen, Y.; Deng, J.; Tu, Y. *Synthesis* **2001**, *2001*, 2078.

(12) Newkome, G. R.; Pappalardo, S.; Gupta, V. K.; Fronczek, F. R. *J. Org. Chem.* **1983**, *48*, 4848.

(13) Binnemans, K. *Coord. Chem. Rev.* **2015**, *295*, 1.

(14) Beeby, A.; Clarkson, I. M.; Dickins, R. S.; Faulkner, S.; Parker, D.; Royle, L.; de Sousa, A. S.; Williams, J. A. G.; Woods, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 493.

(15) (a) Nonat, A.; Regueiro-Figueroa, M.; Esteban-Gomez, D.; de Blas, A.; Rodriguez-Blas, T.; Platas-Iglesias, C.; Charbonniere, L. J. *Chem. - Eur. J.* **2012**, *18*, 8163. (b) Zaim, A.; Eliseeva, S. V.; Guenee, L.; Nozary, H.; Petoud, S.; Piguet, C. *Chem. - Eur. J.* **2014**, *20*, 12172.

DOI: 10.1021/acs.inorgchem.5b01922
Inorg. Chem. 2015, 54, 9681−9683