Activator-Controlled High Temperature In-Situ Ligand Synthesis for the Formation of Rare Earth Thiolate Amide Coordination Polymers

Alexander Zurawski,[a] Eva Wirnhier,[a] and Klaus Müller-Buschbaum*[a]

Dedicated to Prof. Ingo-Peter Lorenz on the occasion of his 65th birthday

1D rare earth thiolate amide coordination polymers can be obtained by an activator-controlled in situ ligand synthesis in reactions of molten 2-mercaptobenzimidazole with lanthanide metals. Catalytic amounts of mercury activate the metals and induce a C–S bond cleavage that in situ forms 2,2′-bibenzimidazole. The latter then reacts as a linker ligand to give $\frac{1}{\infty}[Ln_2(Mbim)_4(Bbim)]$, $Mbim^- = C_7H_5SN_2^-$, $Bbim^{2-}$, $C_{14}N_4H_8^{2-}$. In addition cinnabar is formed. Stoichiometric amounts of mercury cause the complete transformation of 2-mercaptobenzimidazole to 2,2′-bibenzimidazole. Instead of thiolate coordination polymers the reaction then yields sulfur-free monomeric bibenzimidazolate complexes $(BimH_2)^+$-$[Ln(BbimH)_4]^-$, $(BimH_2)^+ = C_7H_6N_2^+$, $BbimH^- = C_{14}N_4H_9^-$. Thus the amount of Hg also controls the dimensionality of the products by defining the reaction path.

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Introduction

Coordination polymers of different dimensionality are in the focus of interest as they exhibit various properties relevant for materials science such as catalysis, conductivity, luminescence, magnetism, and porosity.[1] Chemical constitution as well as hierarchy and structure of the solid material mainly determine its properties. Therefore a rational synthesis planning in form of crystal engineering attracts a lot of attention.[2] Rare earth chemistry places some new emphasis as it introduces a large bandwidth of coordination modes and numbers (between 3 and 16) with regard to the relatively low oxidation states.[3] This renders a large variety of different linkage types and topologies accessible for coordination polymers, that mainly consist of oxygen-containing ligands because of the high oxophilicity of the rare earth elements.[4] We invented a solvent free synthesis strategy for coordination polymers as an alternate option to solvent treatments. Self consuming ligand melts of suitable amines can oxidize lanthanide metals to give corresponding amides.[5] It is essential for the formation of coordination polymers that the ligands are sterically less demanding to avoid small molecular complexes.[6] Especially multi-N aromatic heterocycles give Ln–N coordination polymers and first Ln–N MOFs.[5,7] In order to introduce further functional groups we have now transferred our expertise in amine melts to mercapto amine melts to elaborate the solvent free syntheses for thiolate coordination polymers and to enrich the chemistry of rare earth thiolates.[8]

Results and Discussion

The reaction of lanthanide metals with melts of 2-mercaptobenzimidazole (MbimH) at temperatures above 300 °C results in the formation of one-dimensional thiolate amide coordination polymers of the formula $\frac{1}{\infty}[Ln_2(Mbim)_4$-$(Bbim)]$, $Mbim^- = C_7H_5SN_2^-$, $Bbim^{2-}$, $C_{14}N_4H_8^{2-}$. The products contain mono-anionic 2-mercaptobenzimidazolate and di-anionic bibenzimidazolate ligands (see Schemes 1 and 2) and could be isolated as single-crystalline material for Ln = Ho (**1**) and Yb (**2**). The bibenzimidazolate ligand derives from an in situ ligand synthesis by C–S bond cleavage and subsequent recombination as well as redox reaction with the metals (see Figure 1).[9] MbimH is also reduced by the rare earth metals with formation of H_2 and Ln^{III} ions. The C–S bond cleavage is promoted by the amount of mercury that is added as an activator for the rare earth metals. Hg is quantitatively transformed to α-HgS (cinnabar, **4**, see Figure 2), which is formed as dark red crystals in the cooler parts of the reaction ampoule.[10] We believe that the high affinity of mercury to sulfur together with the Ln/Hg amalgam formation is responsible for this double activator property. Formation of Hg-Mbim complexes[11a,11b] or heterometallic Ln/Hg thiolate complexes[11c] was not observed.

[a] Department of Chemistry and Biochemistry, Ludwig-Maximilians-Universität München,
Butenandtstr. 5–13 (D), 81377 München, Germany
Fax: +49-89-2180-77851
E-mail: Klaus.Mueller-Buschbaum@cup.uni-muenchen.de
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.
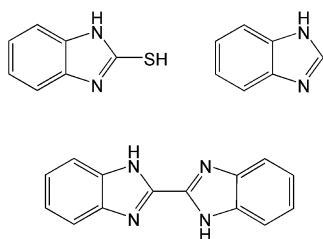
Scheme 1. 2-Mercapto-1H-benzimidazole, 1H-benzimidazole, 2,2′-bibenzimidazole.

To the best of our knowledge this is the first example of an activator-controlled in situ ligand synthesis by C–S bond cleavage in the field of coordination polymers; C–S bond cleavage leads to oxygen-free products. This kind of bond cleavage was only rarely used for the synthesis of coordination polymers before.[12] For none of the two ligands were rare earth compounds previously described.[13]

We also proved that the in-situ-formed ligand 2,2′-bibenzimidazole cannot successfully be utilized in a melt synthesis itself as it decomposes around its melting point (395–400 °C). Syntheses of comparable transition metal complexes show that the solubility enforces strongly coordinating and mainly oxygen-containing solvents.[13] Considering the oxo philicity of the lanthanides this would lead to unwanted solvent co-coordination and hence is not useful for our purpose. The in situ synthesis prevents both problems.

In addition, 1 and 2 can also not be obtained from 1H-benzimidazole as the in situ synthesis cannot take place in the absence of a C–S bond. 1H-Benzimidazole is instead transformed into a new high-temperature β-form 5 of the molecule.[14]

For existence and formation of the coordination polymers 1 and 2 the presence of both sorts of ligands (Mbim⁻ und Bbim²⁻) is essential as completion of the in situ syntheses of 2,2′-bibenzimidazole by larger amounts of mercury does not lead to coordination polymers anymore. Homoleptic monomeric ate complexes of the formula (BimH₂)⁺[Ln(BbimH)₄]⁻ are formed instead [single crystalline: Ln = La (3)].[15] The rare earth cations are surrounded by four mono-anionic 1,4-chelating bibenzimidazolate ligands (BbimH⁻) to give a square antiprismatic coordination of nitrogen atoms (see Figure 3).[16] Constitution and structure of 3 correspond to other 1,4-chelating ligands in amides of the lanthanides like 2,2′-pyridylbenzimidazolates.[6b,c,17] In contrast to the coordination polymers $^1_\infty$[Ln₂(Mbim)₄-(Bbim)] (1, 2) double deprotonation and back-side coordination of BbimH⁻ are missing in 3. For the first time S-coordination of 2-mercaptobenzimidazolate to rare earth ions is observed in $^1_\infty$[Ln₂(Mbim)₄(Bbim)] (1, 2).[19] The Ln ions are coordinated by a distorted pentagonal bipyramid of S and N atoms with short Ln–N and longer Ln–S distances (Table 1). The bipyramids are linked via μ₂-coordinating S atoms.[8] The di-anionic character of the Bbim²⁻ ligands essentially adds to the polymeric character enabling front and backside coordination through all N atoms.
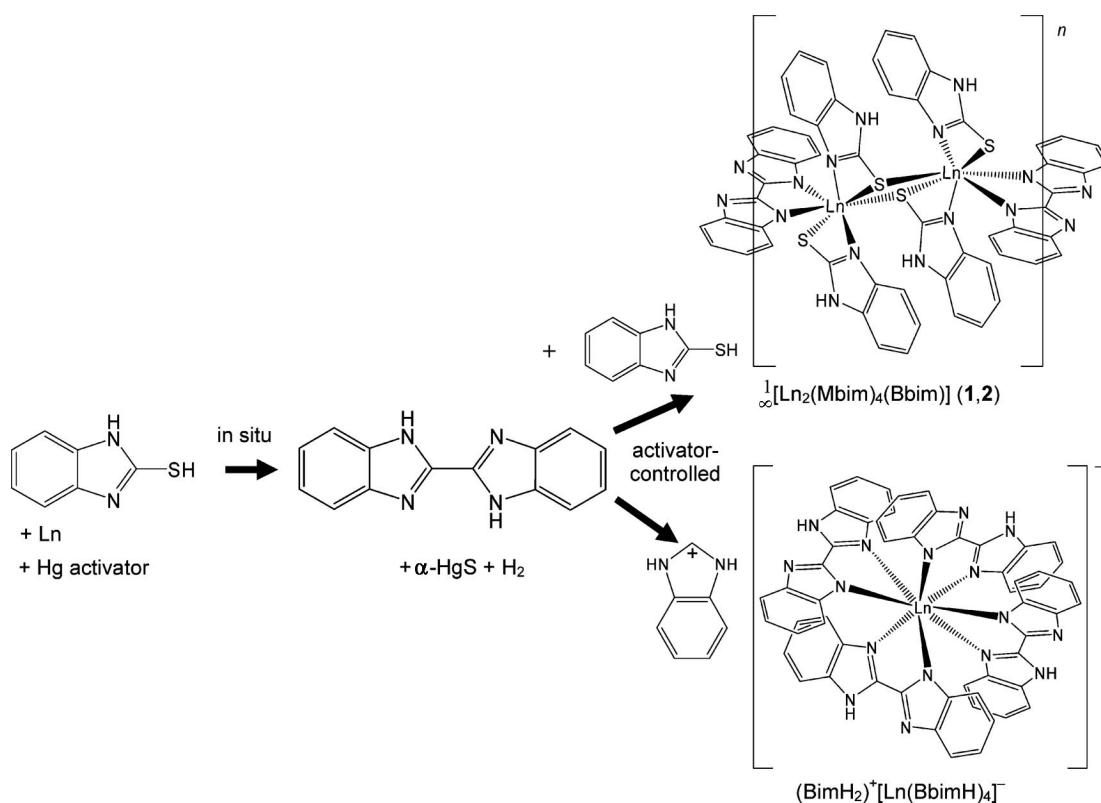
Scheme 2. Reaction paths of the in situ syntheses. The activator Hg controls if thiolate containing coordination polymers or homoleptic monomeric anions of the referring Ln^III ions are formed.
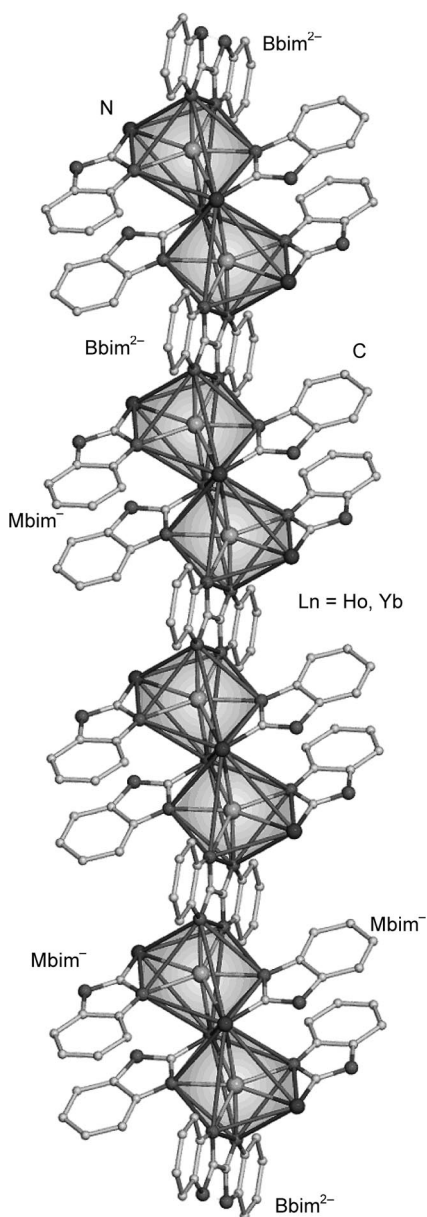
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Figure 1. The chain structure of $^1_\infty$[Ln$_2$(Mbim)$_4$(Bbim)] (**1**,**2**) shown for Yb in **2**. Coordination polyedra of S and N atoms are depicted, H atoms omitted for clarity.

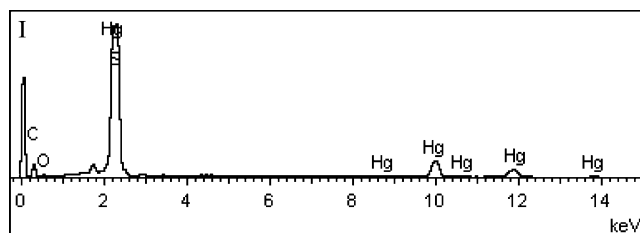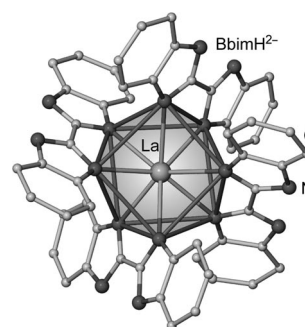Figure 3. Structure and coordination polyedron of the monomeric homoleptic anion [La(BbimH)$_4$]$^-$ in **3**. La exhibits a square anti-prismatic coordination of N atoms.

Table 1. Selected interatomic distances/pm between atoms of $^1_\infty$[Ln$_2$(Mbim)$_4$(Bbim)], Ho (**1**), Yb (**2**) and (BimH$_2$)$^+$[La(BbimH)$_4$]$^-$ (**3**). Deviations are given in brackets.

1	Distances	**2**	Distances	**3**	Distances
Ho–N5	236.1(5)	Yb–N5	232.3(6)	La–N1	258.9(7)
Ho–N1	237.3(5)	Yb–N1	233.8(6)	La–N5	260.7(7)
Ho–N3	238.1(4)	Yb–N3	236.1(5)	La–N8	261.3(6)
Ho–N6[a]	238.7(5)	Yb–N6[a]	236.4(6)	La–N4	268.0(6)
Ho–S1	278.6(1)	Yb–S1	277.7(2)		
Ho–S2	289.0(1)	Yb–S2	288.0(2)		
Ho–S2[b]	283.3(2)	Yb–S2[b]	280.8(2)		

[a] Symmetry operation: $1 - x$, $1 - y$, $-z$. [b] $2 - x$, $1 - y$, $-z$.

Conclusions

In this work we present the successful transformation of our solvent-free synthesis strategy to thiolate coordination polymers of the rare earth elements. The synthesis is accompanied by an activator-controlled in situ ligand synthesis of 2,2′-bibenzimidazole that is essential for the formation of the coordination polymers which are *S*-linked and O-free. Large amounts of the activator mercury lead the reaction path away from strand-like thiolates to homoleptic bibenzimidazolate complexes. The in situ synthesis can thus be controlled by the amount of mercury (see Scheme 2) and used for crystal engineering. It can thus be of interest for other multifunctional thioles, too.

Experimental Section

$^1_\infty$**[Ln$_2$(Mbim)$_4$(Bbim)] 1 (Ln = Ho), 2 (Ln = Yb), and α-HgS (cinnabar, 4):** 2-Mercaptobenzimidazole (MBimH, C$_7$H$_6$N$_2$S; 1 mmol, 150 mg, ACROS 98%), the lanthanide metals (ChemPur 99.9%, 0.33 mmol, Ho: 54 mg, Yb: 57 mg), and Hg (0.05 mmol, 10 mg) were sealed in a Duran glass ampoule under vacuum and heated to 305 °C in 29 h. After annealing for 336 h it was cooled to 290 °C in 150 h, in another 200 h to 250 °C and in 44 h to room temperature. Colourless/yellow platelet crystals of **1/2** result. In cooler parts of the ampoules deep red crystals of **4** are observed. Analysis (EDX) **1**: C$_{21}$H$_{14}$HoN$_6$S$_2$ (579.4): calcd. Ho 28.47, S 11.07; found Ho 27.0, S 11.8. Analysis (EDX) **2**: C$_{21}$H$_{14}$N$_6$S$_2$Yb (587.5): calcd. Yb 29.45, S 10.92; found Yb 28.5, S 11.7. Elemental analysis (EDX) for **4**: Hg$_1$S$_1$ (233.7): calcd. Hg 86.21, S 13.78; found Hg 84.4, S 14.2.

Figure 2. EDX analysis of **4** (C sputtered).

(BimH₂)⁺[La(BbimH)₄]⁻ (3) and α-HgS (cinnabar, 4): 2-Mercapto-benzimidazole (MBimH, $C_7H_6N_2S$; 1.5 mmol, 225 mg, ACROS 98%), La metal (0.5 mmol, 69 mg, ChemPur 99.9%), and Hg (2 mmol, 401 mg, Riedel-de Haën 100%) were sealed in a Duran glass ampoule under vacuum and heated to 305 °C in 29 h. After annealing for 336 h it was cooled to 290 °C in 150 h, in another 200 h to 250 °C and in 26 h to room temperature. Surrounded by dark S- and C-containing decomposition products (by EDX analyses) colourless platelet crystals of **3** are formed. In cooler parts of the ampoules deep red crystals of **4** are observed. Elemental analysis for **3**: $C_{63}H_{43}LaN_{18}$ (1191.1): calcd. C 63.52, H 3.61, N 21.16, La 11.76; found C 64.0, H 4.4, N 20.6, La (EDX) 10.7.

β-1H-Benzimidazole (5): α-1H-Benzimidazole (BimH, $C_7H_6N_2$; 2 mmol, 335 mg, Aldrich 98%), various lanthanide metals (investigated La–Yb except Pm) (0.5 mmol, ChemPur 99.9%), and Hg (0.1 mmol, 20 mg) were sealed in a Duran glass ampoule under vacuum and heated to 300 °C in 100 h. Subsequently the reaction was cooled in 168 to 300 h to 90 °C and in 12 h to room temperature. For Ln = La, Ce, Nd, Pr, Sm, Tb and Yb large amounts of colourless crystals of **5** were obtained; yield 210–244 mg (62–73%); elemental analysis (reaction on Tb metal): $C_7H_6N_2$ (118.1): calcd. C 71.19, H 5.08, N 23.71; found C 71.1, H 5.3, N 23.6.

Supporting Information (see also the footnote on the first page of this article): Additional information on the crystallographic, structural and experimental details for **1–5** can be downloaded as Supporting Information including four figures.

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[9] In the crystal structure of $\frac{1}{\infty}$[Ln₂(Mbim)₄(Bbim)] (**1,2**) each Ln atom (Ln = Ho, Yb) is coordinated by an end-on and a μ₂-bridging S atom of 1,3-chelating 2-mercaptobenzimidazolate anions, as well as a 1,4-chelating 2,2'-bibenzimidazolate dianion. Pairs of the resulting pentagonal bipyramidal LnS₃N₄ coordination polyedra are edge sharing via common S atoms. These dimeric units are linked to strands via the 2,2'-bibenzimidazolate dianions. For detailed data on the single-crystal X-ray investigations and presentations of the crystal structure of isotypic **1** and **2**: see Supporting Information. Further information was deposited at the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223336033 or E-mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposition numbers CCDC-716039 (for **1**), -716041 (for **2**), the names of the authors and the literature citation. Single crystal X-ray data of **1** and **2**: $C_{21}H_{14}HoN_6S_2$, $M = 579.4$ gmol⁻¹ (**1**): crystal dimensions $0.1 \times 0.1 \times 0.05$ mm; triclinic, space group $P\bar{1}$ (No. 2), $a = 998.0(2)$ pm, $b = 1023.0(2)$ pm, $c = 1050.6(2)$ pm, $\alpha = 88.6(1)$, $\beta = 84.7(1)$, $\gamma = 67.3(1)$, $T = 140$ K, $Z = 2$, $V = 985.3(3) \times 10^6$ pm³, $\rho_{calcd.} = 1.953$ g cm⁻³, $2\theta_{max.} = 61.00°$, diffractometer STOE IPDS I, φ-scan with $\Delta\phi = 1.5°$, radiation Mo-K_α, wave length $\lambda = 0.71073$ Å, 11718 measured reflections, 5435 independent reflections, 3101 reflections with

$I > 2\sigma(I)$, refined parameters 271. $R_1 = 0.0368$ for 3101 with $I > 2\sigma(I)$, $wR_2 = 0.0855$ for all 5435 independent reflections; remaining electron density: $+1.10/–1.57$ e (pm 10^6). $C_{21}H_{14}N_6S_2Yb$, $M = 587.5$ gmol^{-1} (**2**): crystal dimensions $0.1 \times 0.1 \times 0.05$ mm triclinic, space group $P\bar{1}$ (No.2), $a = 991.4(2)$ pm, $b = 1023.4(2)$ pm, $c = 1062.2(2)$ pm, $\alpha = 88.3(3)$, $\beta = 84.7(3)$, $\gamma = 67.2(3)$, $T = 170$ K, $Z = 2$, $V = 989,4(3) \times 10^6$ pm^3, $\rho_{calcd.} = 1.972$ gcm^{-3}, $2\theta_{max.} = 59.34°$, diffractometer STOE IPDS II, Ω-scan with $\Delta\Omega = 2.0°$ and $\phi = 0$, 90°, radiation Mo-K_α, wave length $\lambda = 0.71073$ Å, 16364 measured reflections, 5513 independent reflections, 2717 reflections with $I > 2\sigma(I)$, refined parameters 271. $R_1 = 0.0385$ for 2717 with $I > 2\sigma(I)$, $wR_2 = 0.0650$ for all 5513 independent reflections; remaining electron density: $+1.74/–2.49$ e (pm 10^6).

[10] a) We also determined the structure of α-HgS (**4**). It corresponds with the determination of the spiral structure by Buckley and Vernon.[10b] The atom distances match with the determination by Schleid et al.;[10c] b) H. E. Buckley, W. S. Vernon, *Mineral. Mag.* **1925**, *20*, 382–392; c) T. Schleid, P. Lauxmann, C. Schneck, *Z. Kristallogr. Suppl.* **1999**, *16*, 95.

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[14] Referring experiments carried out directly from benzimidazole melts together with Ln elements gave no in situ formation of 2,2′-bibenzimidazole but a previously unknown high-temperature form of benzimidazole itself. It forms on the surface of the lanthanide metals. We also determined the crystal structure of this *β*-1-*H*-benzimidazole (**5**). It can be distinguished from the room temperature α-form by a closer overall packing (see Supporting Information and CCDC-716038).

[15] CCDC-716040 and the Supporting Information contain detailed crystallographic data for **3**: $C_{63}H_{43}LaN_{18}$, $M = 1191.1$ gmol^{-1}, crystal dimensions $0.1 \times 0.08 \times 0.03$ mm; orthorhombic, space group $C222_1$ (No. 20), $a = 1673.6(3)$ pm, $b = 1513.5(3)$ pm, $c = 2243.9(4)$ pm, $T = 200$ K, $Z = 4$, $V = 5683,8(2) \times 10^6$ pm^3, $\rho_{calcd.} = 1.392$ gcm^{-3}, $2\theta_{max.} = 47.12°$, diffractometer Nonius Kappa CCD, Ω-Scan with $\Delta\Omega = 0,9°$, radiation Mo-K_α, wave length $\lambda = 0.71073$ Å, Flack-X Parameter $0,00(6)$, 21191 measured reflections, 4192 independent reflections, 3614 reflections with $I > 2\sigma(I)$, refined parameters 372. $R_1 = 0.0541$ for 3614 with $I > 2\sigma(I)$, $wR_2 = 0.0953$ for all 4192 independent reflections; remaining electron density: $+1.45/–0.68$ e (pm 10^6).

[16] The negative charges of the square antiprismatic ions of **3** are compensated by benzimidazolium cations in a ratio of 1:1 resulting in the overall formula $(BimH_2)^+$ $[La(BbimH)_4]^-$ for this salt like compound. As no benzimidazole was added to the reaction, the cations also derive from the C–S bond cleavage but with subsequent protonation instead of recombination to bibenzimidazole. The benzimidazolium cations are non-coordinating. Anionic benzimidazolates are not known for lanthanides today. The cationic character is evident in a reduction of the aromatic character of the ring system by elongating C–N distances in the imidazole part. This behaviour resembles pyridylbenzimidazolium cations that also compensate the charges of corresponding square antiprismatic Ln-pyridylbenzimidazolate anions.[6c] Further information on the crystal structure of **3** can be deduced from the Supporting Information.

[17] K. Müller-Buschbaum, C. C. Quitmann, *Z. Anorg. Allg. Chem.* **2004**, *630*, 131–136.

[18] On the steric demand of N-heterocycles such as substituted aminopyridinato ligands in complexes see Kempe et al. for the example of 1,3-chelation: a) R. Kempe, *Eur. J. Inorg. Chem.* **2003**, 791–803; b) A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem.* **2008**, *120*, 7356–7359; *Angew. Chem. Int. Ed.* **2008**, *47*, 7246–7259; c) N. M. Scott, R. Kempe, *Eur. J. Inorg. Chem.* **2005**, 1319–1324.

[19] Known are complexes of the Ln elements that are acetylbenzopyranone substituted on the S atom of 2-mercaptobenzimidazole. Because of the oxophilicity of the lanthanides they are coordinated via O and not S atoms, accordingly: K. B. Gudasi, T. R. Goudar, *J. Indian Chem. Soc.* **1997**, *74*, 786–788.