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Hydroxyquinoline-Calix[4]arene-Conjugates as Ligands for Polynuclear Lanthanide Complexes: Preparation, Characterization, and Properties of a Dinuclear Eu(III) complex

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Abstract: The synthesis of a calixarene-based N_4O_4 donor ligand H_6L, in which two *8*-hydroxyquinoline-2-carbaldehyde units are appended via hydrazone-carbonylmethoxy linkages in a 1,3-arrangement to the lower rim of *tert*-butyl-calix[4]arene, and its coordination properties towards Eu(III) are described. The reaction of H_6L with $Eu(NO_3)_3{\cdot}6H_2O$ produces a dinuclear complex $[Eu_2(H_3L)_2(MeCN)_2]$ (**4**). The Eu(III) ions in **4** are well-separated from each other (d > 8 Å) each being coordinated by two tetradentate hydroxyquinoline-2-carbaldehyde-hydrazone substituents from two triply deprotonated molecules $(H_3L)^{3-}$ in a dodecahedral geometry. As a consequence there are no exchange interactions between the Eu(III) ions, and the magnetic properties are solely associated with thermal population of excited ($^7F_1$-$^7F_6$) terms. The spin-orbit coupling constant λ is 325.2(4) cm^{-1}. Moreover, the ligand H_6L was found to extract Eu(III) and Tb(III) at pH 7-8 from aqueous solution, as established by radiotracing using the short-lived radio nuclide ^{160}Tb and ^{152}Eu.

Keywords: Polynuclear Complex / *8*-Hydroxyquinoline / Calix[4]arene / Europium / Extraction

Introduction

The *8*-hydroxyquinoline ligand (HOQ) is one of the most popular gravimetric reagents for trivalent metal ions because of the low solubility of the resulting complexes.[1] *8*-hydroxyquinolinolato complexes of the rare earth elements have also been studied as extraction agents,[2] infrared-emitting molecular materials,[3–5] and as therapeutic agents for metal chelation,[6] while some derivatives of *8*-hydroxyquinoline were employed in the construction of self-assembled lanthanide helicates[7] and heterobimetallic lanthanide/alkaline earth complexes.[8] However, only a few rare earth quinolinolato complexes have been obtained as single-crystals suitable for X-ray diffraction analysis due to their low solubility. So far four types of structures were encountered: mononuclear $Ln(OQ)_3$ or $Ln(OQ)_4$ complexes,[3] trinuclear $Ln_3(OQ)_8(L')$ compounds (e.g. Ln = Yb, L' = NO_3^-;[4] Ln = Yb, L' = $CH_3CO_2^-$)[9] and trinuclear $Ln_3(OQ)_9$ species (Ln = Er,[10] Ho,[11] Yb,[12] Dy[13]). Given the unusual magnetic properties of polynuclear lanthanide complexes,[14-16] it is remarkable that the magnetic properties of only a few hydroxyquinolinolato complexes have been studied.[13,17]

A few derivatives of the parent *8*-hydroxyquinolinolato ligand were designed to increase the solubility and to extend the coordination properties of this versatile ligand system.[18] Bünzli has introduced carbamide units in the 2-position to generate a tridentate ligand.[19] Albrecht has reported a semicarbazone derivative of *8*-hydroxyquinoline-*2*-carbaldehyde,[20] which was found to be an effective tetradentate ligand for rare earth metals. The structures of mononuclear (Y, Er, Ho) and dinuclear complexes (La, Eu) were reported. The same group also reported a ditopic hydroxquinolinolato ligand designed for dinuclear lanthanide helicates.[21]

As part of a program aimed at producing and characterizing discrete polynuclear lanthanide complexes, we became interested in the coordination chemistry of a *tert*-butyl-calix[4]arene-based *8*-hydroxyquinolinolato ligand H_6L (see scheme 1).

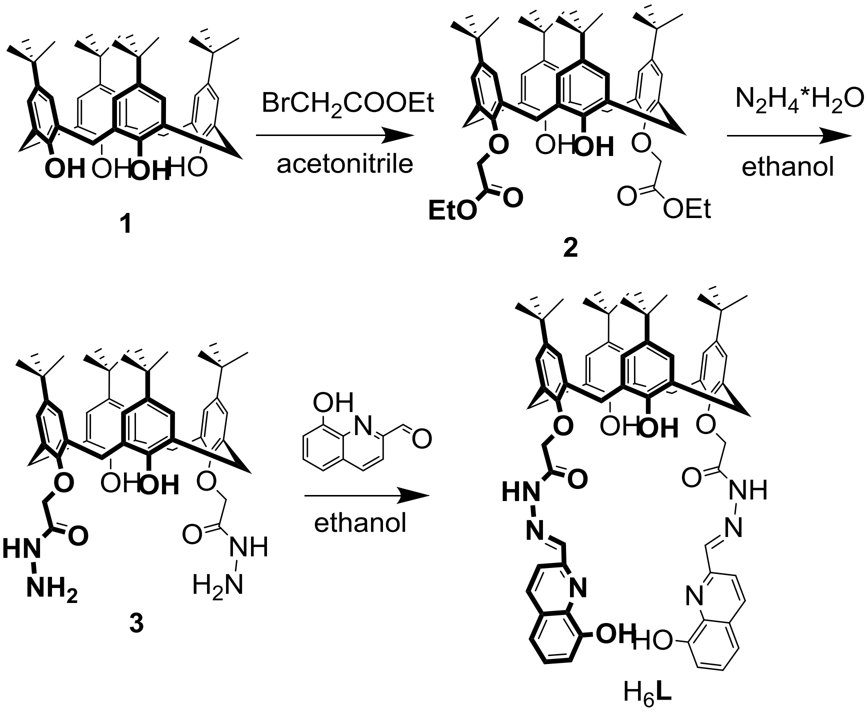
Our motivation for appending the hydroxyquinolinolato units to a calix[4]arene backbone were as follows: 1) The calixarenes are easily accessible and can be tailored synthetically by altering the moieties grafted on the lower rim.[22] 2) Several ligand systems utilizing calix[4]arene backbones have been reported and their complexation properties were investigated.[23–26] 3) The calix[4]arenes often confer solubility on the compounds,[27] and their coordination chemistries are more specific (and controllable) than their unmodified parents.[28–30] 4) There are only a few examples in the literature in which quinoline or *8*-hydroxyquinoline units are tethered on a calix[4]arene backbone,[31,32] and none of these have been structurally characterized.[33] 5) The macrocyclic platform can be used for preorganization of multicoordinate and chelating groups in two-phase solvent extractions for the separation of rare earth elements.[34–38]

Recently, we have reported on the synthesis and coordination properties of some 1,3-functionalized calix[4]arene carboxylate ligands.[39] Herein we report on the synthesis, preparation and molecular structure of the ligand H_6L and demonstrate its ability to support a discrete dinuclear europium complex. Thus, the syntheses, crystal structures and magnetic properties of the homoleptic complex $[Eu_2(H_3L)_2(MeCN)_2]$ (**4**) are described. The properties of H_6L in the extraction of Eu(III) and Tb(III) from aqueous solution are also described.

Results and Discussion

Synthesis and characterization of the ligand H_6L

The new ligand H_6L was prepared in three steps, starting from para-*tert*-butylcalix[4]arene, [22] as depicted in Scheme 1.



Scheme 1. Synthesis of H_6L.

The reaction of **1** with ethyl bromoacetate in acetonitrile gave calix[4]arene **2**, with the two ethyl acetate groups appended in 1,3-position of the calix[4]arene backbone. [40] Treatment of **2** with hydrazine monohydrate gave the corresponding hydrazide **3** in nearly quantitative yield. [41] In the last step, *8*-hydroxyquinoline-*2*-carbaldehyde was subjected to a condensation reaction with the hydrazide **3** to give the target compound, which was isolated in the neutral H_6L form. The yield was 73 % (based on **3**). H_6L is readily soluble in chloroform and dichloromethane, less soluble in acetonitrile, and practically insoluble in ethanol and methanol. All compounds gave satisfactory elemental analysis and their formulation was

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confirmed by ESI-MS, ^1H, ^{13}C NMR, IR, and UV/vis spectroscopy. H_6L was also characterized by X-ray crystallography. Table 1 lists selected spectroscopic data.

The cone conformation of the macrocyle H_6L was confirmed by ^1H NMR spectroscopy (see Figure S1, Supporting Information), by the characteristic doublets at 4.3 and 3.6 ppm for the diastereotopic methylene protons.[42] The regioselective distal 1,3-substitution lowers the symmetry of the calix[4]arene to C_2, to cause a splitting of the individual NMR signals. Thus, two singlets of equal intensity are observed for the *tert*-butyl groups and the aromatic protons of the calix[4]arene unit. The signal at 11.96 ppm is most-likely associated with the hydroxyl group of the 8-hydroxyquinoline unit. This OH group resonates at a quite low field, indicating that it is involved in a hydrogen bonding interaction. For comparison, the hydroxyl H atoms of the calix[4]arene skeleton are observed at 8.38 ppm. The ^{13}C NMR spectrum of H_6L shows one signal for the methylene carbon atoms at 32.8 ppm which is also in agreement with the cone conformation.[43] One signal for the imine linkages (152.6 ppm) and one signal for the carbonyl group (163.8 ppm) agree with a C_2 symmetric structure.

Table 1: Selected spectroscopic data for H_6L and the dinuclear complex **4**.

	H_6L	**4**
IR, ν[cm^{-1}]$^{a)}$	1697 (C=O) 1597 (C=N) 1192 (C–O	1601 (C=O) 1588 (C=N) 1106 (C–O)
UV/vis, λ_{max} [nm] (ε, M^{-1}cm^{-1})$^{b)}$	200 (12892) 283 (7935) 320 (2678)	203 (13710) 290 (4325) 350 (2047)
ESI-MS, *m/z* $^{c)}$	$[M+H]^+$ 1103.6	$[EuH_4L(H_2O)_5]^+$ 1343.5

$^{a)}$ ATR spectra (ZnSe crystal). $^{b)}$ UV/vis spectra were recorded in MeCN solution at ambient temperature; $^{c)}$ ESI(+) in CH_3CN.

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Description of the crystal structure of $H_6L{\cdot}(CD_2Cl_2)_4{\cdot}H_2O$

Single crystals of $H_6L{\cdot}(CD_2Cl_2)_4{\cdot}H_2O$ suitable for X-ray diffraction analysis could be obtained from CD_2Cl_2. The asymmetric unit comprises one molecule of the neutral ligand H_6L and dichloromethane and water solvate molecules. Figure 1 shows the molecular structure of H_6L. Selected bond lengths and angles are given in the figure caption. The calix[4]arene unit adopts a flattened cone conformation, which is stabilized by intramolecular OH···O hydrogen bonds between the phenol H and the ether O atoms. The distortion from the ideal cone conformation is clearly evident from the different folding angles between the best plane fitted to the four methylene carbon atoms and the planes through the four aromatic rings of the calix[4]arene skeleton (ring A: 69.5°, ring B: 45.0°, ring C: 70.3°, ring D: 45.6°). One dichloromethane molecule is included in the cavity held in place by CH···π interactions with the aromatic rings (d(C···centroid) = 3.823(1) Å and 3.628(1) Å), as observed in other calixarene host-guest complexes.[44] The remaining CD_2Cl_2 molecules fill up the interstitial space between molecules. There are several intramolecular and intermolecular OH···O and NH···O hydrogen bonding interactions between the lower rim of the calix[4]arene and the dangling hydrazone units as illustrated in Figure 1. Note that the amide group of one substituent adopts the rare *cis* configuration, presumably stabilized by the bifurcated O2H···O5 hydrogen bond. The other amide group, on the other hand, adopts the *trans* configuration, with a weaker N4H···O2 hydrogen bond of length 3.247 Å.

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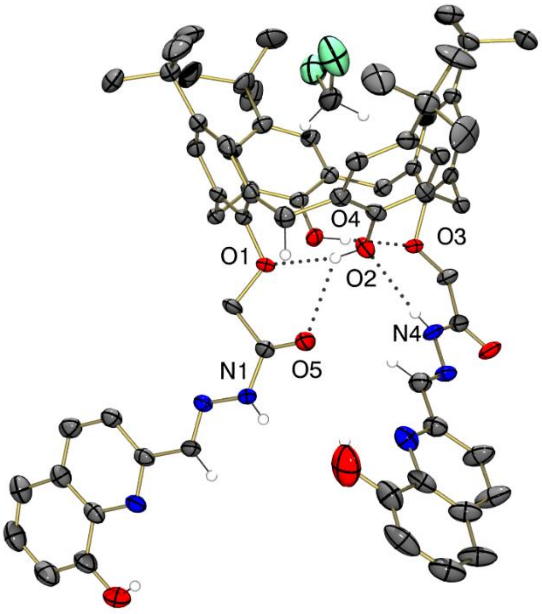


Figure 1. Molecular structure of $H_6L·(CD_2Cl_2)_4·H_2O$. Thermal ellipsoids are drawn at 50% probability level. Solvate molecules and H atoms, expect for those bonded to N and O, omitted for clarity. Only one orientation of a disordered *tert*-butyl group is displayed. Selected bond lengths / Å and angles / °: O1···O2 2.729(4), O3···O4 2.753(1), O5···O2 3.047(2), O2···N4 3.247(2), N1···O7' 2.963(3); O2-H2···O1 153.2(8), O4-H4···O3 163.4(2), O2-H2···O5 128.8(2), N4-H70···O2 171.7(2), N1-H71···O7' 166.5(8). Symmetry code: 1–*x*, 1–*y*, 1–*z* (').

The stacking interactions between the hydroxyquinolinecarbaldehyde-carbonylhydrazone units are also worth mentioning. Two different arrangements can be distinguished (Figure 2). Thus, the hydrazone unit bonded to O1, which has the amide group in the *cis* configuration, is involved in charge transfer interactions with the e^--rich hydroxyquinoline heterocycle of an adjacent molecule, as manifested in the short centroid(X1')···N1 and centroid(X2') ···C47 distances of 3.313(2) and 3.160(1) Å, respectively. As a consequence the hydroxyquinoline N and OH atoms engage in intra- rather than in intermolecular hydrogen bonding interactions.

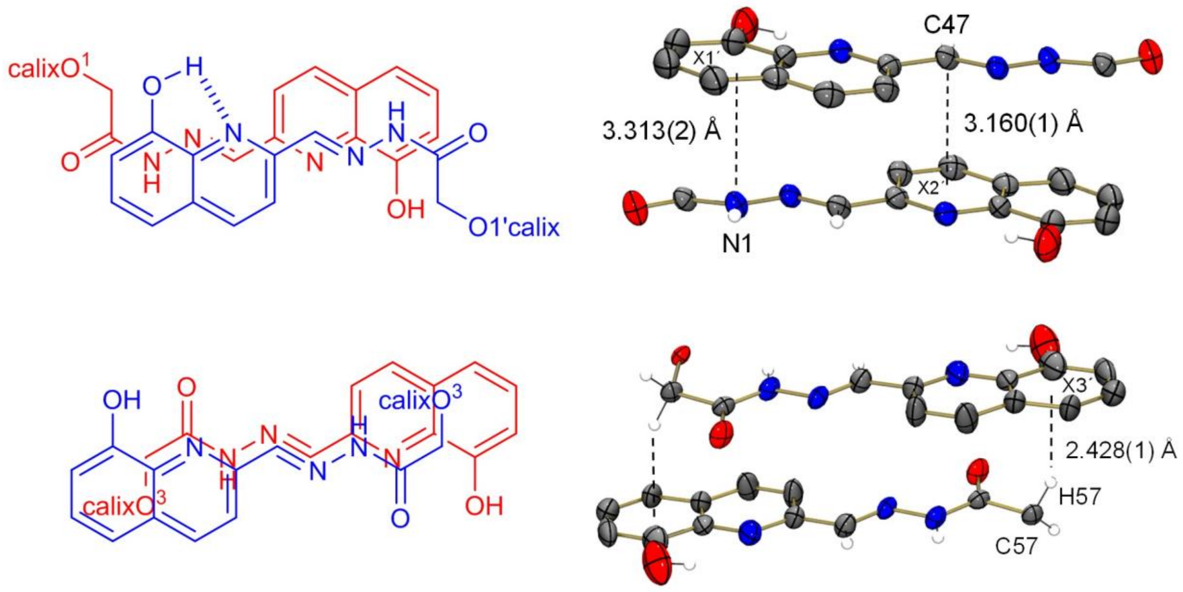
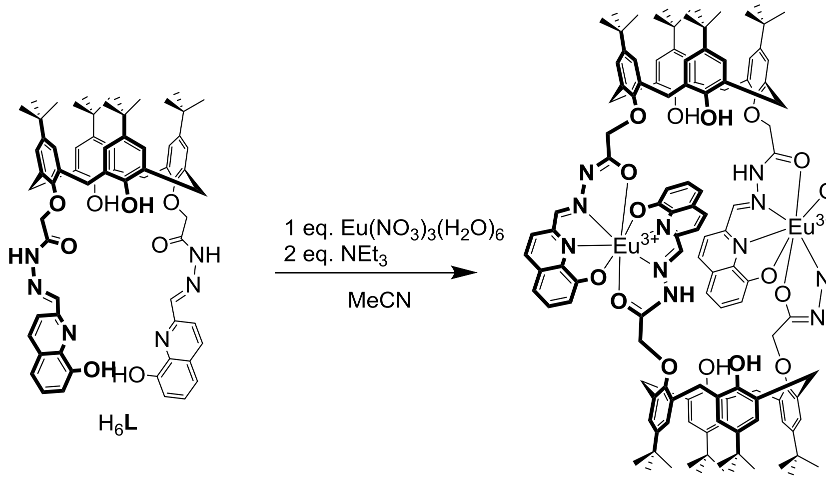


Figure 2. Stacking interactions between the substituents in crystals of $H_6L{\cdot}(CD_2Cl_2)_4{\cdot}H_2O$. Thermal ellipsoids are drawn at 50% probability level. Calix[4]arene units omitted for clarity.

The other hydrazone unit bonded to O3 is not involved in π–π stacking interactions with quinoline units. The parallel arrangement is in this case brought about by CH–π interactions,[45] with a corresponding centroid(X3')···C57 distance at 3.325(3) Å. The presence of orientation b may be traced to the *trans* configuration of the amide bond, which brings the methylene group into the vicinity of the hydroxyquinolines' phenyl ring.

Synthesis and characterization of the dinuclear Eu(III) complex [$Eu_2(H_3L)_2(MeCN)_2$] (4)

When the macrocycle H_6L is treated with 1 eq. of $Eu(NO_3)_3{\cdot}6H_2O$ in acetonitrile in the presence of NEt_3 a red solution forms, from which a dark red product of composition [$Eu_2(H_3L)_2(MeCN)_2$] (**4**) can be isolated in 38 % yield (Scheme 2). Interestingly, the nitrate ions are not incorporated as coligands, suggesting that the coordination sites of the Eu(III) ions are saturated by the donor atoms of H_6L alone. This is in contrast to the behavior of related lanthanide hydroxyquinolinolate complexes, in which additional coligands are bound to the lanthanide(III) ions.[18] A typical example is [$LnL'(NO_3)(DMF)_2$] (where L' is a Schiff base derived from *8*-hydroxyquinoline carbaldehyde and aroylhydrazides), which binds additional NO_3^- and DMF molecules.[18c]



4

Scheme 2. Synthesis of [$Eu_2(H_3L)_2(MeCN)_2$] (**4**).

Complex **4** gave satisfactory elemental analyses and was fully characterized by spectroscopic methods (MS, UV/Vis, IR) and X-ray crystallography. The electrospray ionization mass spectrum (ESI(+)-MS) did not reveal a molecular ion peak for a [$Eu_2(H_3L)_2$] species, only a peak for a [$Eu(H_4L)(H_2O)_5$]$^+$ cation at m/z = 1343.5 was detected (Table 1). A comparison of the ATR infrared spectrum showed clear evidence for coordination of H_6L (Figure S3 and S4). Marked shifts for the ν(C=O), ν (C=N) and ν(C–O) bands from 1697, 1597 and 1192 cm^{-1} in H_6L to 1601, 1588 and 1106 cm^{-1} in **4**, indicate the involvement of the carbonyl group, the aromatic N atom as well as the hydroxy group of the quinoline unit in the binding process. The coordination of the quinoline unit could also be inferred by UV/vis spectroscopy. The UV/vis spectrum of H_6L in acetonitrile (Figure S7) displays three absorption bands at 203 nm, 290 nm, and 350 nm, attributable to *n*→π* and π→π* transitions (Table 1). Upon coordination of Eu(III), the π→π* transition at 350 nm is red-shifted by 30

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nm relative to the corresponding transition in H_6L. Further conclusions regarding the exact binding mode of $(H_3L)^{3-}$ could not be drawn from the spectroscopic data. On these grounds an X-ray crystallographic study of $[Eu_2(H_3L)_2]$ was undertaken.

Description of the crystal structure of $[Eu_2(H_3L)_2(MeCN)_2](MeCN)_x$ (**4**·$(MeCN)_x$) (x ~ 21)

Red crystals of **4**·$(MeCN)_x$ suitable for X-ray crystallographic analysis were obtained by slow evaporation of an acetonitrile solution containing H_6L and $Eu(NO_3)_3{\cdot}6H_2O$ in a 1:1 molar ratio. Crystals of **4**·$(MeCN)_x$ are monoclinic, space group $P2_1/n$. The asymmetric unit comprises one molecule of the neutral $[Eu_2(H_3L)_2(MeCN)_2]$ complex **4** and approximately 21 MeCN solvate molecules. Two MeCN are situated in the calixarene cages, as observed in many other calix[4]arene structures,[46] the other MeCN molecules (which are readily lost upon standing in air) fill the interstitial space between the molecules and were found to be heavily disordered. Figure 3 shows ORTEP and van der Waals diagrams of the neutral complex. Table S2 lists selected bond lengths and angles. The two Eu(III) ions are well-separated from each other (Eu1–Eu2 8.343(2) Å) being coordinated by two tetradentate *8*-hydroxyquinoline-2-carbaldehyde-hydrazone substituents from two calix[4]arene units.

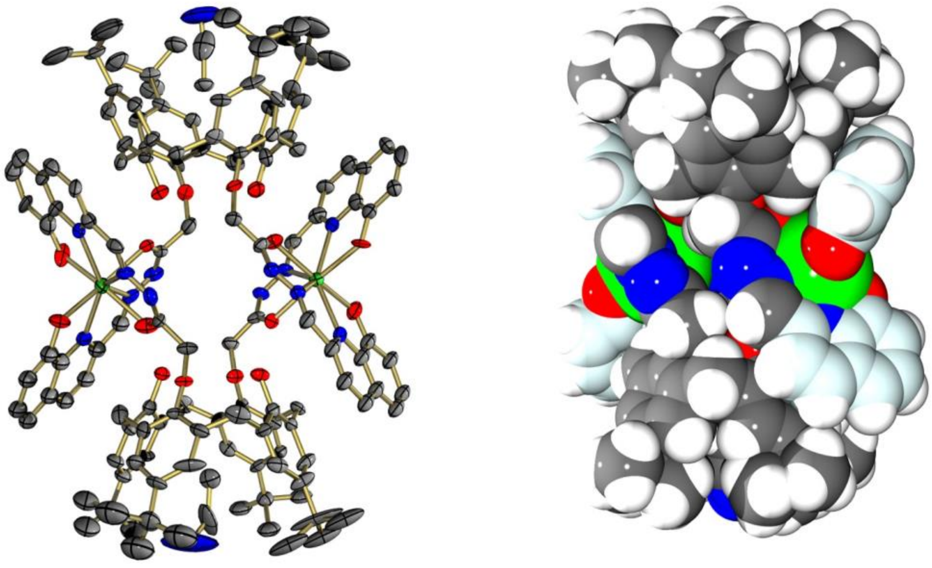

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Figure 3. ORTEP (left) and space filling (right) representation of the molecular structure of the neutral complex [$Eu_2(H_3L)_2(MeCN)_2$] in crystals of **4**·$(MeCN)_x$. Thermal ellipsoids are drawn at the 30% probability level. Color code: C grey, N blue, O red, Eu green. In the ORTEP representation, all hydrogen atoms are omitted for clarity. Default values for van der Waals radii as implemented in ORTEP 3 for Windows were used for the space filling representation.

Charge considerations imply the presence of a triply deprotonated form $(H_3L)^{3-}$ of H_6L (2 × RO^- (quinolinolate), 1 × $=N–N=CR–O^-$), because counterions are absent and the +3 oxidation state of the europium atoms is unambiguous in this case. The presence of one deprotonated ligand arm with a $=N–N=CR–O^-$ valence structure as opposed to that of the protonated =N–NH–CR=O arm is also implied by the different N=C and C–O bond distances (1.295(4) Å (C58A=N4A) and 1.345(4) Å (C58A–O7) for the $N=CR–O^-$ versus 1.334(1) Å (C46–N1) and 1.285(3) Å (C46=O5) for the NH–CR=O moiety (Figure 4). The bond distances for the protonated ligand arm compare quite well with the corresponding distances in [$Ce(PBH)_2(NO_3)(NCS)(H_2O)$] (PBH = 2-pyridinecarboxaldehyde-benzoylhydrazone), where the benzoylhydrazone unit is bound in its protonated form.[47] The presence of a protonated and a deprotonated hydrazone unit is also reflected in the Eu–N and Eu–O distances. For example, the Eu–N2 and Eu–O5 distances involving the deprotonated ligand arm are significantly shorter than the corresponding Eu1–N5A and Eu1–O7A distances with the protonated arm, and the same holds for the other Eu site (Table S2). Unlike in H_6L, all amide functions adopt a *trans* configuration.

The quinoline units coordinate the Eu(III) ions in a nearly perfect dodecahedral fashion (Figure 4), the angle between the planes through the trapezoids spanned by the donor atoms being 88.9° (O6N3N2O5/O8AN6AN5AO7A) and 88.5°, respectively

(O8N6N5O7/O5AN2AN3AO6A, not shown in Figure 5).[48] The average Eu–O and Eu–N distances amount to 2.353(4) Å and 2.523(5) Å, respectively. These bond lengths are much smaller than the Eu–O (2.487(3) Å) and Eu–N (2.717(4) Å) average distances reported for the complex [LEu(NO$_3$)$_{2.5}$(DMF)] (L = 2-[(8-hydroxyquinolinyl)methylene]hydrazine-carboxamide,[19] with a coordination number of 11, but compare well with those of other 8-coordinate {EuN$_4$O$_4$} complexes.[49]

Upon coordination of the europium ions the calix[4]arene backbone changes its conformation from a *flattened* cone (free ligand H$_6$L) to a cone conformation as indicated by the angles between the best fitted plane through the bridging methylene groups (C2, C8, C14, C20) and the phenol units of the calix[4]arene (59.3, 63.7, 57.1, 64.4). Intramolecular hydrogen bonds between the phenols and the oxygen atoms of adjacent ether groups on the lower rim stabilize again the cone conformation. Additionally, weak hydrogen bonds were formed between the phenols of the first calix[4]arene and the nitrogen atoms of the quinoline unit of the second calix[4]arene. Interestingly, π–π stacking interactions between the phenol units of the macrocycle and the quinoline unit stabilize the closed packing of the structure (see Figure 3). The centroid···centroid distances between these aromatic units range from 3.30 to 3.41 Å.

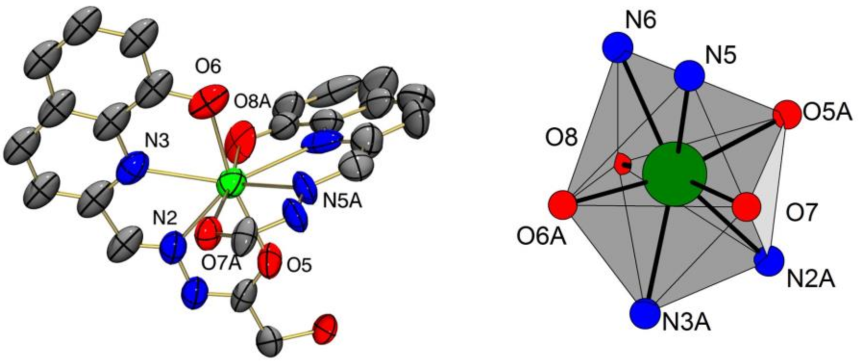

Figure 4. Perspective view of the coordination unit in **4** showing the dodecahedral coordination geometry of the Eu(III) ion. Color code: C grey, N blue, O red, Eu green. Bond lengths and angles are collected in Table S2.

Magnetic Properties

A desolvated sample of complex **4** was further studied by temperature-dependent magnetic susceptibility measurements using a SQUID-Magnetometer (MPMS Quantum Design) in applied magnetic fields of 1, 0.5 and 0.1 T in the temperature range 2-300 K (see Figure S8). Figure 5 displays the temperature dependence of the magnetic susceptibility in the form of a χ_mT versus T plot in applied magnetic field of 1 T. The χ_mT value at room temperature is found to be 2.77 cm^3 K mol^{-1}, a value which is close to that expected for two non-interacting Eu(III) ions (2.65 cm^3 K mol^{-1}), whose magnetic properties are associated with thermal population of the excited terms ($^7F_1$ – $^7F_6$). Upon cooling, the χ_mT values decrease steadily, reaching 0.03 cm^3 K mol^{-1} at 2 K. The residual magnetism is due principally to the second order Zeeman effect[50] in the ground $^7F_0$ multiplet.[51]

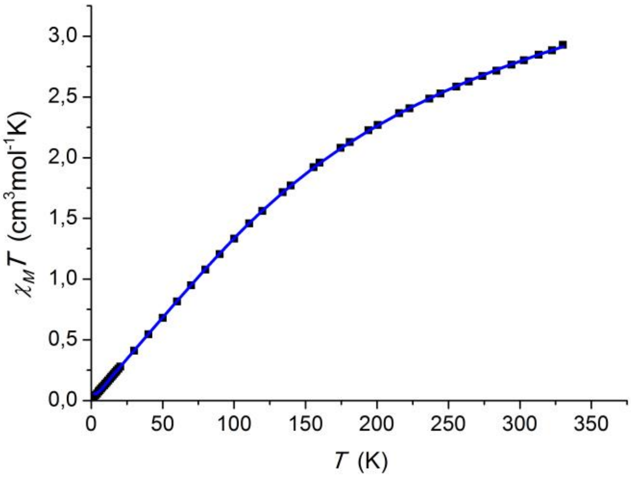

Figure 5. χ_mT versus temperature for $[Eu_2(H_3L)_2(MeCN)_2]$ (**4**) in an applied magnetic field of 1.0 T. The solid line is a fit of the experimental data to eq. 1 using the parameter given in the text.

The 4f electrons of Eu(III) ions are generally shielded by the outer sphere s and p electrons, and superexchange interactions between the spins of the 4f electrons are usually very weak. In **4**, the Eu(III) ions are well-separated, and the magnetic susceptibility of the $[Eu_2(H_3L)_2(MeCN)_2]$ complex can be fitted with a single-ion Eu(III) model, which only considers the spin-orbital coupling of Eu(III) ions. The magnetic susceptibility of an Eu(III) ion for the two-level system ($^7F_1$, $^7F_0$) is given by eq. 1, where λ is the multiplet spacing, N_a Avogadros number, μ_B the Bohr magneton and k_B the Boltzmann constant.

$$\chi_m = \frac{N_a \mu_B^2}{3k_B T} \cdot \left(\frac{\frac{24k_B T}{\lambda} + 3\left(\frac{9}{2} - \frac{k_B T}{2\lambda}\right)\exp\left(\frac{-\lambda}{k_B T}\right)}{1 + 3\exp\left(\frac{-\lambda}{k_B T}\right)} \right) \qquad (1)$$

As can be seen from Figure 5, a good fit was possible over the whole temperature range, yielding $\lambda = 325.2(4)\ \mathrm{cm}^{-1}$. Since the multiplet spacing is on the order of kT, the first excited state is thermally populated at 300 K, and the magnetic properties deviate significantly from the Curie law. The λ parameter agrees with literature values.[52]

Liquid-liquid extractions

In orienting experiments, we studied the ability of H_6L to act as an extraction agent for lanthanide ions, in view of literature reports that functionalized calixarene ligands exhibit good extraction efficiency.[35,53–57] The two-phase solvent extraction studies were performed in chloroform/water mixtures and were monitored by radiotracing utilizing ^{160}Tb as well as ^{152}Eu. Figure 6 shows the extraction yields (%E) of H_6L towards Tb(III) and Eu(III) as a function of pH. As can be seen, the extraction yields depend markedly upon pH value, showing a sigmoidal profile with the lanthanide extraction (%E ~(95–98)%) being essentially nearly quantitative above pH ~7 at a metal to ligand ratio of 1:10. The strong pH dependence is in good agreement with the acid-base behavior of H_6L, which is considered to be present in

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its triply deprotonated form based on the pK_a values of the hydroxyquinoline and hydrazone units, as also implied by the crystal structure of **4** described above. Deprotonation of H_6L was also implied by a shift of the pH value of the aqueous phase that accompanied the extraction of the Ln(III) ions.

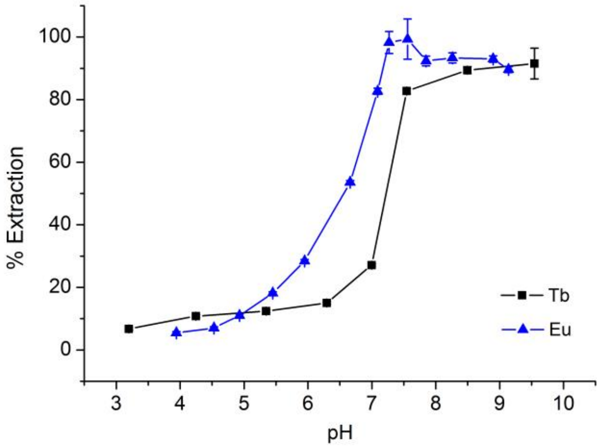

Figure 6. Extraction yields obtained for H_6L at different pH values. Conditions: chloroform/water (1/1, v/v), [Tb^{III} / Eu^{III}]: 1×10^{-4} mol/L, [H_6L]: 10^{-3} mol/l, 25 °C, equilibration time: 60 min.

Finally, the addition of H_2SO_4 lead to 92 % back-extraction of the lanthanide ion at a pH value of 4. Overall, the calix[4]arene-based hydroxyquinoline-ligand H_6L described in this study exhibits good extraction ability for Tb(III) and Eu(III) ions which, due to its solubility properties, may be of use as an alternative extraction agent for lanthanide ions.

Conclusion

A short and efficient synthesis of the calixarene based ligand H_6L with two appended hydroxyquinoline-2-carbaldehyde-hydrazone groups has been achieved. The ligand was found to be an effective supporting ligand for polynuclear lanthanide complexes. The reaction of H_6L with $Eu(NO_3)_3{\cdot}6H_2O$ produces a discrete, homoleptic $[Eu_2(H_3L)_2(MeCN)_2]$ complex (**4**), where H_6L is in a triply deprotonated $(H_3L)^{3-}$ form with one singly and one doubly deprotonated ligand arm. The Eu(III) ions in **4** are well-separated from each other (d > 8 Å) each being coordinated by two tetradentate hydroxyquinoline-2-carbaldehyde-hydrazone substituents from two triply deprotonated molecules $(H_3L)^{3-}$ in a dodecahedral geometry. The structures of H_6L as well as **4** appear to be also governed by inter- and intramolecular CH_2–π and π–π interactions involving the heterocyclic 8-hydroxyquinoline ring. The ligand H_6L was found to extract Tb(III) and Eu(III) at pH 7–8 from aqueous solution, as established by radiotracing. In addition back-extraction of the lanthanide ions at a pH value of 4 was also successfully carried out.

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Experimental Section

Materials and Methods. All preparations were carried out in air without specific precautions. Reagent grade solvents were used throughout. Compounds **1-3** were synthesized according to known procedures.[21,32,33] All other reagents were obtained from standard commercial sources and were used without further purifications. Elemental analyses were carried out with a VARIO EL elemental analyzer. Infrared spectra were recorded on a Bruker VECTOR 22 FT-IR spectrophotometer. The UV/vis absorption spectra were recorded on a Jasco V-570 UV/vis/NIR spectrometer. NMR experiments were conducted on a BRUKER AVANCE DRX

400. ESI-mass-spectra were recorded on a APEX II FT-ICR device (BRUKER). Temperature-dependent (350 K - 2 K) magnetic susceptibility measurements were conducted on polycrystalline samples on a MPMS 7XL SQUID (QUANTUM DESIGN) in external magnetic fields of 0.1, 0.5 and 1T. Diamagnetic corrections were applied for the sample holder (gelatine capsule) and the core diamagnetism from the sample (estimated with Pascals constants).

5,11,17,23-Tetra-*p*-*tert*-butyl-25,27-bis[(*8*-hydroxyquinolinecarbaldehyde-hydrazone-carbonylmethoxy)]-26,28-dihydroxycalix[4]arene (H_6L). Hydrazide **3** (0.5 g; 631 µmol) was dissolved in 30 mL ethanol. A solution of 8-hydroxyquinoline-2-carbaldehyde (219 mg; 1.26 mmol) in 5 mL ethanol was added dropwise. The yellow solution was refluxed over night. The obtained pale yellow precipitate was filtrated and washed with ethanol and acetonitrile. Yield: 521 mg (75 %). ^{1}H NMR (400 MHz, CD_2Cl_2) cone conformation δ [ppm] = 11.96 (s, 2H, OH), 8.61 (s, 2H, N=CH), 8.38 (s, 2H, OH), 8.18 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 8.04 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.50 (d, $^3J_{HH}$ = 7.9, 2H), 7.39 (dd, $^3J_{HH}$ = 8.2, 1.3, 2H), 7.22 (d, $^3J_{HH}$ = 8.0 Hz, 2H) (all ArH substituent), 7.2 (s, 4H), 6.99 (s, 4H) (all ArH calixarene), 4.84 (s, 4H, OCH_2); 4.31 (d, $^2J_{HH}$ = 13.5 Hz, 4H, $ArCH_2Ar$), 3.65 (d, $^2J_{HH}$ = 13.5 Hz, 4H, $ArCH_2Ar$), 1.31 (s, 18H, ^{t}Bu), 1.06 (s, 18H, ^{t}Bu). ^{13}C{1H} NMR (101 MHz, CD_2Cl_2) cone conformation δ [ppm] = 164.36 (C=O); 152.78 (N=CH), 149.75, 149.66, 149.09, 148.14, 144.28, 136.48, 128.91, 118.87, 117.94, 110.75 (ArC substituents), 150.81, 149.75, 132.03, 129.65, 128.65, 126.94, 126.80, 126.28 (all ArC calixarene), 74.69 (OCH_2), 33.84, 33,81 (2 × $C(CH_3)_3$), 32.80 ($ArCH_2Ar$), 31.20, 30.80 (2 × $C(CH_3)_3$). *m/z* (ESI+, CH_3CN): $C_{68}H_{75}N_6O_8$ (1103.37) $[M+H^+]^+$ calc: $[M+H^+]^+$: 1103.6, found: 1103.6. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3246 ν(NH), 2958 ν(CH), 1697 ν(CO), 1597 ν(CN), 1192 ν (CO). UV/Vis (MeCN): λ_{max} [nm] (ε[L·mol^{-1}·cm^{-1}]) = 200 (12892), 283 (7935), 320 (2678). $C_{68}H_{74}N_6O_8$ (1102.4): calcd. C 74.02, H 6.76, N 7.62, found C 74.10, H 6.81, N 7.61.

$[Eu_2(H_3L)_2(MeCN)_2](MeCN)_x$ (4(MeCN)$_x$, x~21). H_6L (75 mg; 68 µmol) was dissolved in 20 mL acetonitrile and NEt_3 (19 µL, 136 µmol). A solution of $Eu(NO_3)_3{\cdot}6H_2O$ (30 mg, 68 µmol) in acetonitrile was added. After 2 days red crystals were obtained, which were filtered, washed with acetonitrile, and dried in air. Crystals of **4**(MeCN)$_x$ (x ~ 21) quickly lose the ~ 21 MeCN solvate molecules upon standing in air and turn dull. Yield: 65 mg (38 %). *m/z* (ESI+, CH_3CN): $C_{68}H_{81}N_6O_{13}Eu$ (1343.51) $[Eu(H_3L)(H_2O)_5]^+$ calcd: 1343.51, found: 1343.5. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3358 ν(NH), 2954 ν(CH), 1601 ν(CO), 1588 ν(CN). UV/Vis (MeCN): λ_{max} [nm] (ε[L·mol^{-1}·cm^{-1}]) = 203 (13710), 290 (4325), 344 (2047). $C_{136}H_{142}Eu_2N_{12}O_{16}$ + 2MeCN (2504.4 + 82.1): calc. C 65.01, H 5.77, N 7.85, found C 65.10; H 5.82; N 7.91.

Crystal structure determinations. The intensity data were collected on a STOE-IPDS-2T-diffractometer. Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The data were processed with X-AREA and corrected for absorption using STOE X-Red32.[58] The structures were solved by direct methods (SHELXS-2013)[59] and refined by full-matrix least-squares on F^2. Hydrogen atoms were included on idealized positions; nonhydrogen atom positions were refined with anisotropic thermal parameters, except some disordered tert-butyl groups. Figures were generated with Diamond 3.2i, Ortep-III and POV-Ray v3.7.[60-62] In the crystal structure of $H_6L{\cdot}(CD_2Cl_2)_4(H_2O)$, no hydrogen atoms were calculated for the H_2O solvate, which is located in the vicinity of an inversion center. Most solvate molecules in the structure of **4** were found to be severely disordered and/or partially occupied. Electron density attributed to heavily disordered acetonitrile molecules was removed from the structures (and the corresponding F_0) with the SQUEEZE algorithm implemented in the PLATON program suite.[63] The SQUEEZE routine revealed total potential

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solvent area of 5111.9 Å^3 (16569.0 Å^3 per unit cell, 30.9%) in **4** corresponding to approximately 21 MeCN molecules per formula unit.[64]

Liquid-liquid extractions. ^{160}Tb ($T_{1/2}$ = 72.3 d, E_γ = 879.4 keV, I_γ = 30.1%) and ^{152}Eu ($T_{1/2}$ = 13.5 a, E_γ = 344.3 keV, I_γ = 26.6%) were purchased from POLATOM (Poland) with a specific activity of 979.4 MBq/mg ^{160}Tb and 586.9 MBq/mg ^{152}Eu and were dissolved in 1 mL 10 mmol/L nitric acid to give the stock solution. All radiometric measurements (γ-counting) were performed by using a Wizard Gamma-Counter 1480 (PerkinElmer) which was calibrated with an ^{152}Eu-standard (PTB 443-88, PTB, Germany) in the energy range from 50 to 1500 keV. The ligand H_6L was dissolved in chloroform to give solutions with a concentration range from (0.5 to 1000) µmol/L. The radionuclide stock solutions were diluted to give a radioactivity of ~10 kBq/mL. Additionally, non-radioactive terbium nitrate was added as carrier to give aqueous solutions from (0.1 to 100) µmol/L. The pH was adjusted to the desired value with 0.1 M nitric acid or ammonia. 3 mL of the organic solution was shaken with 3 mL of the aqueous solution in a stoppered vial on a horizontal shaker at 300 min^{-1}. The phases were allowed to equilibrate for 60 min. After separation of the phases for 1 min, an aliquot of 2 mL of the aqueous phase were measured by γ-counting in comparison to 2 mL of the aqueous solution before extraction. The percentage extraction (%E) was calculated by means of the two activities ($A_{initial}$ = radionuclide in aqueous solution before extraction, A_{final} = radionuclide in aqueous solution after extraction) using equation 2. All activities were decay–corrected to the first measured sample.

$$\%E = 100 \cdot \frac{[A_{initial} - A_{final}]}{[A_{initial}]} \qquad (2)$$

Supporting Information

Supporting Information contain the X-ray crystallographic format in CIF format, NMR, ATR-IR, ESI-MS, and UV/Vis spectra for all new compounds. CCDC-1474404 (for H_6L) and -1409111 (for **4**·(MeCN)$_x$) 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/data_request/dif.

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[64] A comparison of the experimental and simulated powder diffraction diagrams for **4**·$(MeCN)_{21}$ and the desolvated sample 4 (Fig. S9) is indicative of severe structural changes (which one might expect in view of the de-occupation of ca. 30% of the original cell volume). The corresponding IR spectra, however, reveal only minor shifts for the ν(C=O), ν (C=N) and ν(C–O) bands. This indicates the involvement of the carbonyl group, the aromatic N atom as well as the hydroxy group of the ligands quinoline units in the coordination of the Eu^{III} ions, and suggests that the integrity of the $[Eu_2(H_3L)_2(MeCN)_2]$ complex is maintained upon desolvation.

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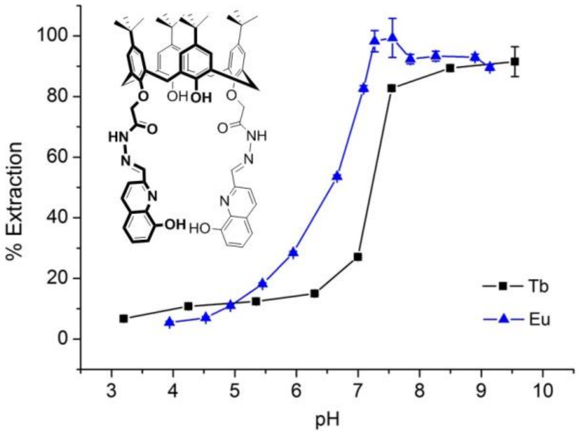

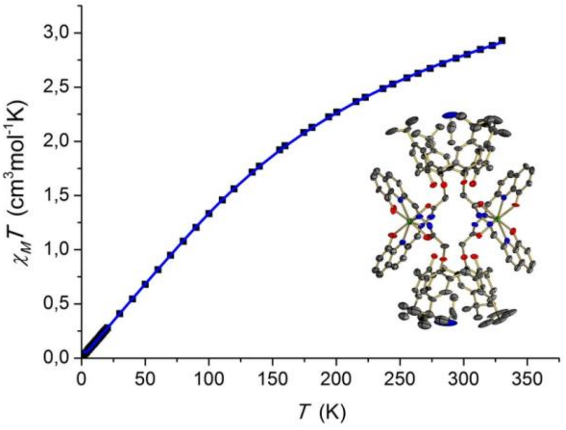

The synthesis of a new hybrid hydroxyquinoline-calixarene ligand (H_6L) has been achieved. H_6L is an effective supporting ligand for polynuclear lanthanide complexes. The neutral, homoleptic $[Eu_2L_2]$ complex features two well-separated Eu(III) ions (d > 8 Å) each being coordinated by two tetradentate hydroxyquinoline-2-carbaldehyde-hydrazone substituents in a dodecahedral geometry. H_6L extracts Eu(III) and Tb(III) from aqueous solution, as established by radiotracing.

Keywords: Polynuclear Complex / *8*-Hydroxyquinoline / Calix[4]arene / Europium / Extraction